

On the formation of crystalline and non-crystalline solid states and their thermal transport properties: A topological perspective via a quaternion orientational order parameter

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“The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade. The solution of the problem of spin glass in the late 1970s had broad implications in unexpected fields like neural networks, computer algorithms, evolution and computational complexity. The solution of the more important and puzzling glass problem may also have a substantial intellectual spin-off. Whether it will help make better glass is questionable.”

~ P. W. Anderson (Science 1995, Ref. [1])

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Abstract

The work presented in this thesis is a topological approach for understanding the formation of structures from the liquid state. The strong difference in the thermal transport properties of non-crystalline solid states as compared to crystalline counterparts is considered within this topological framework. Herein, orientational order in undercooled atomic liquids, and derivative solid states, is identified with a quaternion order parameter.

In light of the four-dimensional nature of quaternion numbers, spontaneous symmetry breaking from a symmetric high-temperature phase to a low-temperature phase that is globally orientationally ordered by a quaternion order parameter is forbidden in three- and four-dimensions. This is a higher-dimensional realization of the Mermin-Wagner theorem, which states that continuous symmetries cannot be spontaneously broken at finite temperatures in two- and one-dimensions.

Understanding the possible low-temperature ordered states that may exist in these scenarios (of restricted dimensions) has remained an important problem in condensed matter physics. In approaching a topological description of solidification in three-dimensions, as characterized by a quaternion orientational order parameter, it is instructive to first consider the process of quaternion orientational ordering in four-dimensions. This 4D system is a direct higher-dimensional analogue to planar models of complex n -vector ($n = 2$) ordered systems, known as Josephson junction arrays.

Just as Josephson junction arrays may be described mathematically using a lattice quantum rotor model with $O(2)$ symmetry, so too can 4D quaternion n -vector ($n = 4$) ordered systems be modeled using a lattice quantum rotor model with $O(4)$ symmetry. $O(n)$ quantum rotor models (that apply to n -vector ordered systems that exist in restricted dimensions) include kinetic and potential energy terms. It is the inclusion of the kinetic energy term that leads to the possible realization of two distinct ground states, because the potential and kinetic energy terms cannot be minimized simultaneously.

The potential energy term is minimized by the total alignment of $O(n)$ rotors in the ground state, such that it is perfectly orientationally ordered and free of topological defects. On the other hand,

minimization of the kinetic energy term favors a low-temperature state in which rotors throughout the system are maximally orientationally disordered.

In four-dimensions, the $O(4)$ quantum rotor model may be used to describe a 4D plastic crystal that forms below the melting temperature. A plastic crystal is a mesomorphic state of matter between the liquid and solid states. The realization of distinct low-temperature states in four-dimensions, that are orientationally-ordered and orientationally-disordered, is compared with the realization of phase-coherent and phase-incoherent low-temperature states of $O(2)$ Josephson junction arrays. Such planar arrays have been studied extensively as systems that demonstrate a topological ordering transition, of the Berezinskii-Kosterlitz-Thouless (BKT) type, that allows for the development of a low-temperature phase-coherent state.

In $O(2)$ Josephson junction arrays, this topological ordering transition occurs within a gas of misorientational fluctuations in the form of topological point defects that belong to the fundamental homotopy group of the complex order parameter manifold (S^1). In this thesis, the role that an analogous topological ordering transition of third homotopy group point defects in a four-dimensional $O(4)$ quantum rotor model plays in solidification is investigated. Numerical Monte-Carlo simulations, of the four-dimensional $O(4)$ quantum rotor model, provide evidence for the existence of this novel topological ordering transition of third homotopy group point defects.

A non-thermal transition between crystalline and non-crystalline solid ground states is considered to exist as the ratio of importance of kinetic and potential energy terms of the $O(4)$ Hamiltonian is varied. In the range of dominant potential energy, with finite kinetic energy effects, topologically close-packed crystalline phases develop for which geometrical frustration forces a periodic arrangement of topological defects into the ground state (major skeleton network). In contrast, in the range of dominant kinetic energy, orientational disorder is frozen in at the glass transition temperature such that frustration induced topological defects are not well-ordered in the solid state.

Ultimately, the inverse temperature dependence of the thermal conductivity of crystalline and non-crystalline solid states that form from the undercooled atomic liquid is considered to be a consequence of the existence of a singularity at the point at which the potential and kinetic energy terms become comparable. This material transport property is viewed in analogue to the electrical transport properties of charged $O(2)$ Josephson junction arrays, which likewise exhibit a singularity at a non-thermal phase transition between phase-coherent and phase-incoherent ground states.

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List of Abbreviations

BKT Berezinskii-Kosterlitz-Thouless

$\mathbb{C}$ Complex numbers

DAS Developable approximation surface

D_{low} lower critical restricted dimension

E_C charging energy

E_J Josephson coupling energy

FCC Face-centered cubic close-packed

G symmetry group of a symmetric high-temperature phase

g non-thermal tuning parameter that enters the $O(n)$ Hamiltonian

g_C critical value of g at the point where potential and kinetic energies are comparable

$\mathbb{H}$ Quaternion numbers (H stands for Hamilton who discovered quaternion algebra)

H isotropy subgroup $H \in G$ that applies to the ordered state

H' the binary representation of $H \in G$

$\hat{\mathcal{H}}$ Hamiltonian is the combination of kinetic and potential energy of the model system

HCP Hexagonal close-packed

IFM Iterative Flattening Method

JJAs Josephson junction arrays

LRO Long-range order

$\mathcal{M}$ Topological order parameter manifold ($\mathcal{M} = G/H$)

MC Monte-Carlo

NGB Nambu-Goldstone boson

$\hat{\mathbf{n}}$ director order parameter field

O(n) The orthogonal group in dimension n

$\mathbb{R}^4$ Real coordinate space in four-dimensions

SSB Spontaneous symmetry breaking

S^m the m -sphere (the surface of constant positive curvature in m -dimensions)

QPT quantum phase transition

TCP Topologically close-packed

T_M Melting temperature

T_{BCS} Bardeen-Cooper-Schrieffer temperature

T^m a torus in m -dimensions (the Cartesian product of m circles)

$\hat{T}$ kinetic energy

$\hat{V}$ potential energy

$\mathbb{Z}$ A one-dimensional lattice of integers ($\mathbb{Z} = 0, \pm 1, \pm 2, \dots$)

$\pi_i(\mathcal{M})$ The i^{th} homotopy group of $\mathcal{M}$

χ susceptibility

ζ correlation length

Chapter 1

Introduction

1.1 Motivation

The primary motivation of this thesis is the development of a unified topological framework, based on symmetry breaking, within which to characterize the formation of crystalline and non-crystalline structures from undercooled atomic liquids. Furthermore, this topological framework is to be employed in the development of an understanding of the origins of the thermal conductivity of non-crystalline solids that are markedly distinct from crystalline counterparts [2, 3, 4, 5], at temperatures above approximately 50 K (see Figure 1.1). The anomalous features of the thermal conductivity of non-crystalline matter, as compared with crystalline counterparts, have been of interest to the heat transfer community for over a century [2, 6, 3, 7, 8, 4, 5, 9].

In crystalline solid states, i.e., structures that exhibit the translational periodicity of a lattice, heat conduction is due to the motion of lattice vibrational modes (known as phonons) which are collective excitations [10, 11] that are associated with the vibration of all atoms within the lattice. Lattice vibrational modes (plane waves) exhibit well-defined group and phase velocities. At high-temperatures, these modes are scattered predominantly by resistive phonon-phonon interactions (Umklapp scattering) [11]. The crystalline thermal conductivity increases with decreasing temperatures, as resistive phonon-phonon interactions become less frequent. Eventually, at sufficiently low temperatures, the phonon mean free path becomes comparable to the dimensions of the sample and the thermal conductivity reaches a maximum before decreasing due to the temperature dependence of the specific heat.

On the other hand, the thermal conductivity of non-crystalline solid states decreases with decreasing temperatures over the same temperature range. In non-crystalline solids, above approximately 50 K, the magnitude and temperature dependence of the thermal conductivity agrees with the model originally proposed by Einstein [6]. Einstein assumed that thermal energy transport between neighboring groups of atoms, vibrating with random phases [8, 4, 12, 5], was by a random walk the mechanism. The assumption of a random phase critically distinguishes Einstein's model of heat

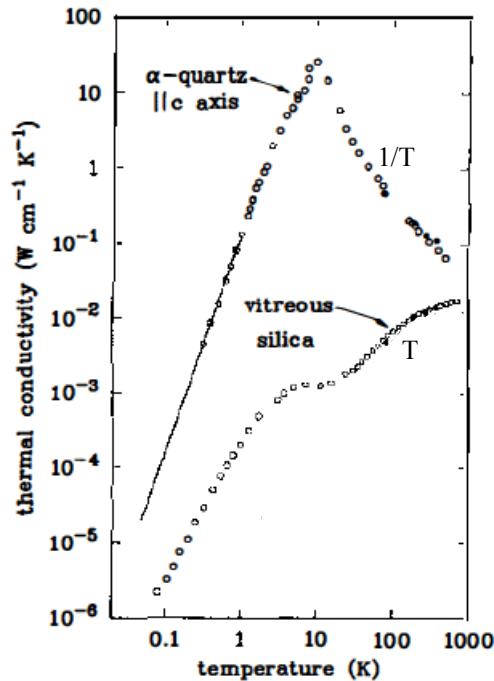


Figure 1.1: Eucken's measurements (Ref. [2]) of the thermal conductivity of crystalline and amorphous SiO_2 . [Image reproduced from Ref. [4]]

transport from the phonon gas picture. The work presented in this thesis pursues answers to the question of the origin of the random phase of vibration between neighboring groups of atoms, which has been left open in the thermal transport literature concerning non-crystalline solids [5, 13]. For a more in depth discussion on the history of thermophysical models of the thermal properties of the solid state in three-dimensions, see Appendix A.

In this thesis, the thermal transport properties of crystalline and non-crystalline solid states are viewed within the context of a duality of low-temperature states that can be realized for ordered systems that exist in restricted dimensions. In particular, the notion that structure (on which the thermal conductivity depends) can be controlled by the ratio of competing energies in the Hamiltonian that applies to the system is explored. In general, the realization of distinct phase-coherent and phase-incoherent low-temperature states is a consequence of orientational ordering in restricted dimensions.

Orientational order in solidifying atomic systems (and derivative solid states) is related to the tessellation of the three-dimensional sphere by the preferred orientational symmetry of atomic clustering in three-dimensions [14, 15]. In this thesis, this tessellation is identified with a quaternion orientational order parameter, which is four-dimensional. As a consequence of the dimensionality of this orientational order parameter, conventional global orientational order is prevented at finite temperatures in four- and three-dimensions. This suggests that solidifying systems that exist in four- or three-dimensions must undercool below the melting temperature. These undercooled atomic

systems are mesomorphic states of matter, that exists between the liquid and the solid states. Such systems are able to solidify into low-temperature states that are either orientationally-ordered or orientationally-disordered, and the relevant material transport property (here, thermal conductivity) should vary dramatically across a (non-thermal) transition between these distinct low-temperature states [16, 17].

Historically, charged Josephson junction arrays (JJAs) of complex n -vector order parameters have provided the prototypical example of such a material transport property (electrical conductivity) that can be controlled in such a manner (across the superconductor-to-superinsulator transition [16, 18]). Such arrays are naturally occurring in two- and one-dimensions, which are restricted dimensions for the complex n -vector order parameter. In light of this, an analogy between solidification and the formation of distinct low-temperature ordered states of charged JJAs (in the vicinity of a superconductor-to-superinsulator transition [18]) is pursued. This analogy forces one to compare the thermal transport properties of the solid state (crystalline and non-crystalline) with the electrical conductivity of charged JJAs, across the superconductor-to-superinsulator transition.

The topological framework for solidification that is developed herein relies on the presence of topologically stable defect elements, that exist as a consequence of symmetry breaking. Homotopy theory [19, 20] is a powerful tool to use in these scenarios where ordered phases coexist with topologically stable defects^a that arise during symmetry breaking transitions, as it enables a characterization of the available topological defect elements and their combination rules [19, 20, 21]. A particular emphasis on geometrically frustrated [22] systems, that possess a finite density of topological defects as structural components of the ground state [23, 15], is explored in this thesis.

The remainder of this introduction (Section 1) is organized as follows. In Section 1.2, the orientational order parameter that applies to undercooled atomic liquid systems in three-dimensions is introduced as the group of unit quaternion numbers. This orientational order parameter is four-dimensional and, hence, undercooling of solidifying atomic fluids in three-dimensions can be viewed as a topological consequence of orientational ordering in restricted dimensions (wherein spontaneous symmetry breaking (SSB) is prevented at finite temperatures). Topological defects, which play a critical role in suppressing global orientational order at finite temperatures in restricted dimensions, are introduced in Section 1.3. Having introduced the concept of topological defects, geometrical frustration in undercooled atomic liquids and the solid state is discussed in Section 1.4. In Section 1.5, characteristics of topological ordering phase transitions (Berezinskii-Kosterlitz-Thouless type [24, 25]) that allow for the existence of low-temperature orientationally-ordered states in restricted dimensions are introduced. Planar complex n -vector ordered systems represent the prototypical example of a such an ordered system for which the phase-coherent low-temperature state is obtained by a defect-driven Berezinskii-Kosterlitz-Thouless type [25] topological ordering transition. The realization of

^aTopologically stable defects are those that cannot be made to disappear with any continuous deformation of the order parameter throughout the system.

distinct low-temperature states of $O(n)$ quantum rotor models, that mathematically model n -vector ordered systems that exist in restricted dimensions, is discussed in Section 1.6. Finally, the anticipated inverse material transport properties of the distinct low-temperature states of systems that are described using quantum rotor models with $O(n)$ symmetry, are discussed in Section 1.7.

1.2 Undercooling of solidifying atomic fluids:

The fact that all solidifying atomic liquids must undercool is readily given by thermodynamics, because there is no thermodynamic driving force (i.e., change in free energy) for the formation of a solid at the melting temperature T_M . However, thermodynamics simply shows that undercooling is necessary for solidification to occur and does not allow further elucidate the nature of undercooling. In this work, a framework for undercooling and solidification that is based on the notions of topology and symmetry breaking is pursued. Using this framework, a more complete understanding of the formation of solid states from the undercooled atomic liquid can be developed in terms of the topologically stable defects that are spontaneously generated below the melting temperature T_M .

Below the melting temperature, orientational order in three-dimensional undercooled atomic liquids is characterized by the preferred orientational symmetry of atomic clustering [26] $H \in G$ where the symmetry group^b G of the high-temperature liquid is the group of proper rotations in three-dimensions $SO(3)$. The $SO(3)$ group is a non-Abelian group, which is related to the group of unit quaternion numbers via a 2-to-1 homomorphism [19, 20]. This homomorphism maps from the three-sphere (S^3) onto $SO(3)$, by identifying the antipodal points of S^3 . By this mapping, the orientational order in undercooled atomic liquids (and derivative solid state systems) is related to the regular tessellation of the three-sphere [15] by the binary representation^c of $H \in SO(3)$ in $SU(2)$.

The unitary group of degree two, i.e., $SU(2)$, is the group of all unit quaternion elements. Therefore, the quaternion orientational order parameter $\hat{\mathbf{n}}$ is a four-dimensional number:

$$\mathbb{H} : \hat{\mathbf{n}} = x_0 + x_1\hat{i} + x_2\hat{j} + x_3\hat{k}, \quad (1.1)$$

where $\hat{i}^2 = \hat{j}^2 = \hat{k}^2 = -1$ ($\mathbb{H}$ stands for Hamilton, who discovered quaternion algebra [28] in 1843). A quaternion orientational order parameter is defined on the three-dimensional curved manifold, that is embedded in 4D Euclidean space, for which:

$$x_0^2 + x_1^2 + x_2^2 + x_3^2 = R^2, \quad (1.2)$$

^bFor the definition of a group, and for additional information on the unitary groups $U(1)$ (Abelian) and $SU(2)$ (non-Abelian), and orthogonal groups $SO(2)$ (Abelian) and $SO(3)$ (non-Abelian), see Appendix B.

^cA binary representation H' is the “lift” of $H \in SO(3)$ into its universal covering group $G' = SU(2)$. The lifted group, $H' \in SU(2)$, is called a binary group because it is twice the size of $H \in SO(3)$ since two quaternions correspond to each rotation in three-dimensions [19, 20, 23, 27] (see Appendix C).

where R is the radius of the three-sphere. Thus, only three of four coordinates are independent, which are the three scalar phase angles that parameterize the unit three-sphere:

$$\hat{\mathbf{n}} = (\cos \theta_0, \sin \theta_0 \cos \theta_1, \sin \theta_0 \sin \theta_1 \cos \theta_2, \sin \theta_0 \sin \theta_1 \sin \theta_2), \quad (1.3)$$

where $\theta_0 \in [0, \pi]$, $\theta_1 \in [0, \pi]$, and $\theta_2 \in [0, 2\pi]$.

When considering orientational ordering by an n -vector order parameter, of dimensionality n , it is important to consider the effect that the geometric space dimension of the sample (D) has on the orientational ordering process [29, 30, 31]. The foundation of this concept is described by the universality hypothesis [32, 33], which classifies the long-range order (LRO) properties of model systems based on these two important dimensions (D, n). The critical properties of all systems within the same (D, n) class will be the same, since they belong to the same “universality class.” The geometric space dimension known as the lower critical restricted dimension, D_{low} , is the value of the largest geometric space dimension in which conventional global orientational order (by spontaneous symmetry breaking) is no longer possible at finite temperatures [33]. In general, the phenomena of undercooling below a bulk critical transition temperature is a topological consequence that applies to ordered systems that exist in restricted dimensions, $D \leq D_{low}$, such that SSB [34] is prevented [29].

The prevention of spontaneous symmetry breaking at finite temperatures, for ordered systems that exist in restricted dimensions, is a consequence of the existence of a gas of misorientational fluctuations in the orientational order parameter throughout the system. For complex n -vector order parameters, i.e., that are two-dimensional ($n = 2$) and are characterized by a single scalar phase angle parameter (θ), spontaneous symmetry breaking is prevented by misorientational fluctuations (in θ) in two-dimensions [33, 35]. Thus, for complex n -vectored ordered systems $D_{low} = 2$. This concept was originally discussed by Mermin and Wagner [29], who showed that there is no conventional long-range ordering in two- or one-dimensions. Similarly, for quaternion n -vector ordered systems, i.e., that are four-dimensional ($n = 4$) and are characterized by a set of three scalar phase angles, the lower critical restricted dimension in which conventional orientational order by spontaneous symmetry breaking is prevented due to the presence of misorientational fluctuations is $D_{low} = 4$.

These misorientational fluctuations take the form of topological defects that are available to n -vector ordered systems [36], which have locally broken the full symmetry group of the high-temperature phase to the isotropy subgroup $H \in G$ that leaves the system invariant [20]. One can gain physical insight into the types of available topological defect elements, that act as elementary excitations in the condensed matter system [19, 20, 21], by considering the topological properties of the topological ground state manifold $\mathcal{M}$. $\mathcal{M}$ defines the order parameter space and, is taken to be the quotient group [20, 34, 37] of H in G :

$$\mathcal{M} = G/H. \quad (1.4)$$

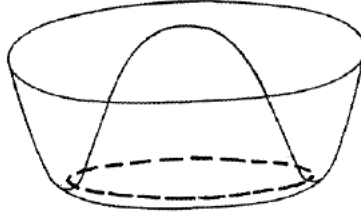


Figure 1.2: Below a bulk critical transition temperature, the free energy of a system with $U(1)$ symmetry is minimum along a circle $\mathcal{M} = S^1$; the traditional Landau free energy functional now looks like a ‘Mexican hat.’ For systems that exist in three-dimensions (bulk), a spontaneous symmetry breaking event occurs at a finite critical temperature as condensed particles adopt a particular ground-state along $\mathcal{M}$ by selecting a particular real scalar phase angle parameter $\theta \in [0, 2\pi]$.

In n -vector ordered systems, the order parameter manifold is $\mathcal{M} = S^m$ where $m = (n - 1)$. For example, in the case of complex ordered systems ($n = 2$), the free energy is minimized in the complex plane (i.e., $\mathcal{M} = U(1) \cong S^1$); below T_C , this free energy function looks like a ‘Mexican hat’ (Fig. 1.2). A bulk complex ordered system exists in three-dimensions, and is characterized globally by a particular ground state $\theta \in [0, 2\pi]$. Similarly, in the case of quaternion ordered systems ($n = 4$), the free energy is minimized in the quaternion plane ((i.e., $\mathcal{M} = SU(2) \cong S^3$). The main type of topological defect available to n -vector ordered systems [36] are $\pi_m(\mathcal{M})$ where $m = (n - 1)$. For n -vector ordered systems that exist in the lower critical restricted dimension D_{low} , these available topological defects are points [36] that are spontaneously generated and that behave as misorientational fluctuations in the order parameter field just below the bulk transition temperature. The phase-destabilizing effect of these misorientational fluctuations becomes even stronger for ordered systems that exist in a dimension less than D_{low} .

For ordered systems that exist in a restricted dimension D , a D -dimensional network of n -vector ordered region forms such that each region is weakly-coupled to its nearest-neighbors [17]. Such systems are well-described by $O(n)$ quantum rotor models in D -dimensions [17]. Despite the development of an order parameter amplitude within separate n -dimensional regions, the entire system remains disordered at finite temperatures due to the effect of misorientational fluctuations throughout the system in the form of topological defects [35] of $\mathcal{M}$. Such ordered systems, that exist in restricted dimensions, are forced to undercool below the bulk critical transition temperature T_C as a topological consequence of the existence of these misorientational fluctuations.

A prototypical example of an ordered system that exists in a restricted dimension is that of complex n -vector ($n = 2$) ordered systems in thin-film configurations (i.e., $D_{low} = 2$). In two-dimensions, below the bulk critical transition temperature, a network of complex ordered regions forms that generates a naturally occurring Josephson junction array [38] (JJA). Josephson junction arrays are well-described by $O(2)$ quantum rotor models [39, 17] (see Fig. 1.3). In approaching a topological framework for solidification of undercooled atomic liquids in three-dimensions, as characterized by a

quaternion n -vector ($n = 4$) order parameter, a direct comparison can be made with the processes of orientational ordering in complex ordered systems that exist in restricted dimensions [25]. In particular, a quaternion ordered system that exists in the lower critical restricted dimension $D_{low} = 4$ may be well-described using an $O(4)$ quantum rotor model in four-dimensions. Such a system, that is forced to undercool below the melting temperature, is a direct higher-dimensional analogue to thin-film complex n -vector ordered systems.

1.3 Topological defects

The question of understanding the possible ordered phases that are able to exist at low-temperatures, for ordered systems that exist in restricted dimensions, has remained an important problem in condensed matter physics over the past century [40, 29, 38, 41]. Such a description requires that the misorientational fluctuations that prevent global orientational ordering may be discretized as topological defect elements that are available to the system [25, 42]. Such topological defect elements describe configurations of the order parameter for which order vanishes (i.e., becomes ill-defined) at the core of the topological defect [21]. The available topological defect elements of n -vector ordered systems [36], for which $\mathcal{M} = S^m$ where $m = n - 1$, belong to the homotopy groups [36, 21]:

$$\pi_r(S^m) = 0 \text{ for } r < m, \quad (1.5)$$

$$\pi_m(S^m) = \mathbb{Z}. \quad (1.6)$$

That is, the non-trivial topological defects that are available to an ordered system that is characterized by a continuous n -vector belong to the homotopy group $\pi_m(S^m) = \mathbb{Z}$, where $\mathbb{Z} = 0, \pm 1, \pm 2, \dots$ is a lattice of integers. This homotopy group describes the possible mappings from an m -sphere (S^m) to an m -sphere, which are identified with the lattice of integers $\mathbb{Z}$. Hence, these topological defects are necessarily Abelian [21]. These non-trivial topological defects exist as points that are

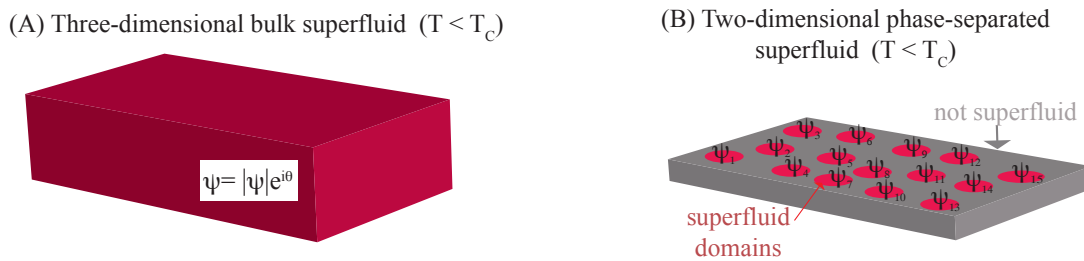


Figure 1.3: (A) A bulk superconductor forms in three-dimensions at the bulk critical transition temperature T_{BCS} . (B) In two-dimensions, a network of superfluid islands forms below T_{BCS} . Each island exhibits its own complex n -vector order parameter, and is weakly coupled to its nearest-neighbors, creating an array of Josephson junctions.

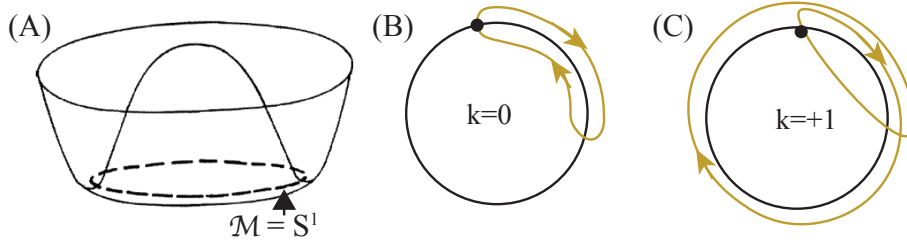


Figure 1.4: (A) The ground state manifold $\mathcal{M} = S^1$ that applies to complex n -vector ordered systems. $\pi_1(S^1) = \mathbb{Z}$ topological defects are available. (B) A partial winding around the manifold $\mathcal{M}$ can be contracted to its base point, and is homotopic to the uniform state. (C) A configuration of the order parameter that wraps once around $\mathcal{M}$ cannot be contracted to its base point [21].

spontaneously generated in the lower critical restricted dimension^d and prevent the development of global orientational order at finite temperatures.

It is by the specification of the order parameter in the coordinate space $\mathcal{D}$ of the ordered system, that defines a mapping from $\mathcal{D}$ to $\mathcal{M}$ which enables the determination of the existence of topological defects within the ordered system [21]. As an introduction to topological defects, consider the simplest type of topological defect which is an element of the fundamental homotopy group of $\mathcal{M} = S^1$ (i.e., $\pi_1(S^1) = \mathbb{Z}$). This simple example allows for topological defect singularities by mapping a closed loop in the relevant coordinate space $\mathcal{D}$ to $\mathcal{M}$ (Fig. 1.4). This topological ground state manifold is representative of complex n -vector ordered parameters ($n = 2$), that are characterized by a single scalar phase angle parameter $\theta \in [0, 2\pi]$. Specification of θ on some closed loop Γ (in $\mathcal{D}$) defines a mapping to $\mathcal{M}$. If, on taking a closed loop in space, θ undergoes a change by $2\pi k$ (for any arbitrary non-zero integer value of k) then a topological defect core exists within the circuit. If a defect core is enclosed within the loop, such that the value of θ is undefined at the core of the loop [21], a singularity exists that ensures that the loop Γ is topologically stable around $\mathcal{M}$ (cannot be contracted to a point).

These topological defect elements, known as vortices, exist as points in two-dimensional complex n -vector ordered systems that are spontaneously generated at temperatures just below T_C . Similarly, a quaternion ordered system admits third homotopy group defects of $\mathcal{M} = S^3$, i.e., $\pi_3(\mathcal{M}) = \mathbb{Z}$. These third homotopy group defects exist as points in four-dimensions and are therefore spontaneously generated just below the bulk critical transition temperature. Thus, undercooling is a topological necessity in four- and three-dimensions, which are therefore restricted dimensions for the quaternion n -vector order parameter.

A full characterization of the topological defects that are available to solidifying undercooled atomic liquids, that express some orientational order, is developed by considering the algorithms of

^dThe dimensionality of a topological defect (that belongs to the group π_m) is determined using the topological charge equation [36, 37]:

$$d = D - m - 1 \quad (1.7)$$

where D is the geometric space dimension. In the case of n -vector ordered systems, where $m = n - 1$, Eqn. 1.7 become $n = D - d$. Thus, topological defect elements available to n -vector ordered systems are points [36] in n -dimensions.

homotopy theory that have been prescribed by Mermin [19, 20]. Owing to the discrete symmetry of atomic clustering ($H \in SO(3)$), topological defects classified by closed paths are also available to solidifying undercooled atomic liquids [43, 23, 15]. In solidifying atomic systems, the topology of closed paths of $\mathcal{M}$ (i.e., that belong to the fundamental (first) homotopy group [21]) identify disclination defect elements. The topology of paths in $SO(3)$ is best identified by making use of the 2-to-1 homomorphism [20, 23] that exists between the group of proper rotations in three-dimensions $G = SO(3)$ and $SU(2)$, which is a simply-connected group [19, 20] (universal covering group).

The topological order parameter manifold, whose topological properties allow for the identification of topological defect elements [20, 44] is therefore given by the tessellation of S^3 by the preferred orientational order of atomic clustering, i.e., $\mathcal{M} = S^3/H'$. By applying the important algorithms of homotopy [19, 20], the topologically stable defect elements that are available to the undercooled atomic liquid are then:

$$\pi_3(\mathcal{M}) = \mathbb{Z} \quad \text{and} \quad \pi_1(\mathcal{M}) = H'. \quad (1.8)$$

In four-dimensions, π_3 defects are points and π_1 defects are planar wedge disclinations. In three-dimensions, topologically stable π_1 elements are wedge disclination line defects and π_3 defects are instantons [45, 43], which have not yet been identified in models of solidification or the low-temperature thermal transport properties of the solid state.

To reiterate, topological defects that are available to undercooled atomic liquids and that are characterized by closed-paths are considered to be wedge disclinations [46, 15, 47]. Wedge disclination topological defects are identified by an angular deficit (Frank vector), on taking a closed loop (measuring circuit) in the sample. A measuring circuit surrounds a point in the plane, wherein orientational order is lost; a three-dimensional line defect is constructed as a contiguous line of such points. Wedge disclinations are the angular ‘cousin’ of dislocation topological defects which, carry no angular deficit and, are characterized by translational imperfections (Burger’s vector). Both disclinations and dislocations belong to the fundamental group of a particular topological order parameter manifold $\mathcal{M}$, and are thus characterized by a measuring circuit. Just as loss of translational order in the core region of a dislocation is a consequence of the topology of the translational order parameter manifold (i.e., the torus $\mathcal{M} = T^m$), the loss of orientational order in the core region of a wedge disclination is owing to the topology of the orientational order parameter manifold ($\mathcal{M} = S^m$). Historically, in the field of materials science, the discussion of topological defects in three-dimensions is reduced to dislocation line defects in systems that are translationally ordered [47].

Wedge disclination defects can be introduced by a standard Volterra process [22], by cutting the material and adding or removing a wedge (of material) between the lips of the cut. As a two-dimensional example of the Volterra process to introduce a wedge disclination, consider Fig. 1.5 (A); one starts with a flat piece of paper, removes (or adds) a wedge, and tapes the paper back together [49, 47, 50]. By gluing the material back together, one obtains a conical shape that is

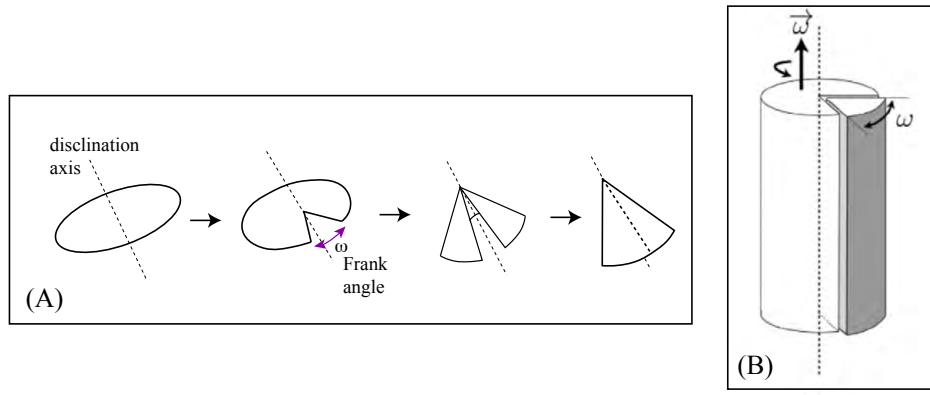


Figure 1.5: (A) Volterra process to introduce a positive wedge disclination in two-dimensions, characterized by an angular deficit ω that is magnitude of the Frank vector (topological invariant). Starting from a perfect system, an angular wedge is removed; gluing the openings together leads to a cone-like topological defect (positive curvature). (B) Volterra process to generate a wedge disclination in three-dimensions.

curved. Thus, the angular deficit that is introduced by the Volterra process concentrates curvature at the core of a wedge disclination topological defect [49, 22, 50]. Depending of the sign of the angular deficit, negative or positive curvature is attributed to the topological defect that is concentrated at its core. Such wedge disclinations are the basic topological line defect elements in three-dimensional structures that express continuous symmetries, like: mesomorphic phases (i.e., liquid crystals [51, 52] and plastic crystals [53]), undercooled atomic liquids [23, 15] and glassy solids [46, 43]. A three-dimensional Volterra process is depicted in Fig. 1.5(B). For a summary of the types of fundamental group defects that are available in atomic systems, i.e., dislocations and disclinations, see Fig. 1.6

Fundamental homotopy group defects ($\pi_1(\mathcal{M})$) in solids and atomic liquids

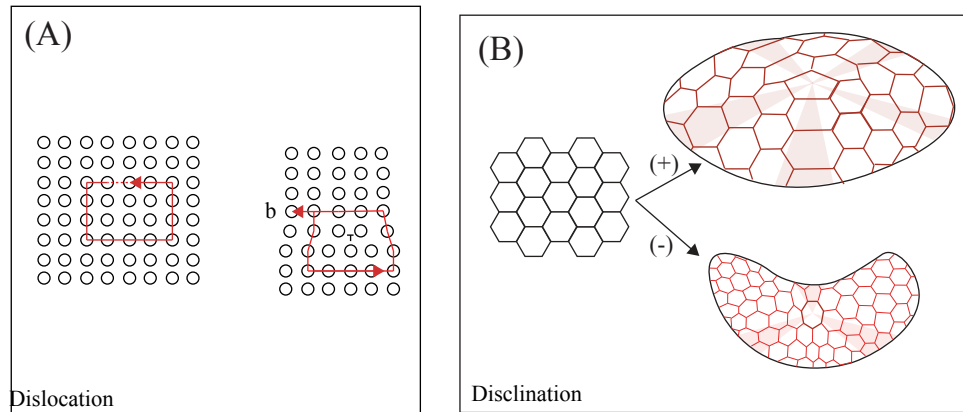


Figure 1.6: Fundamental homotopy group defects in atomic systems (i.e., $\pi_1(\mathcal{M})$). (A) An edge dislocation is a crystallographic defect that identifies a singularity which is characterized by a Burger's vector topological invariant. (B) Disclinations (positive and negative) in a two-dimensional hexagonal structure. A wedge disclination is characterized by an angular deficit [48] (Frank vector).

(A) and (B).

1.4 Geometrical frustration

Geometrically frustrated systems [22], for which a finite density of topological defects persist in the solid ground state, may be understood within the topological framework for solidification that is developed herein. In three-dimensions, such geometrically frustrated solid states derive from undercooled atomic liquids that present preferred orientational order of atomic clustering ($H \in SO(3)$) that is incompatible with a space-filling crystal. Three-dimensional geometrically frustrated crystalline solid states are those that are built solely by tetrahedral interstices (i.e., topologically close packed (TCP) phases [54]). Packings of tetrahedra are incompatible with space-filling arrangements in three-dimensional Euclidean space. This is because regular tetrahedra exhibit dihedral angles that are not commensurable with 2π . As a consequence, when regular tetrahedra are packed into space, gaps remain between certain faces as not all atoms are able to sit in the potential energy minima of all of their nearest-neighbors. This is geometrical frustration, which introduces (group specific) angular disclination topological defects that are necessary constituents of geometrically frustrated condensed matter systems.

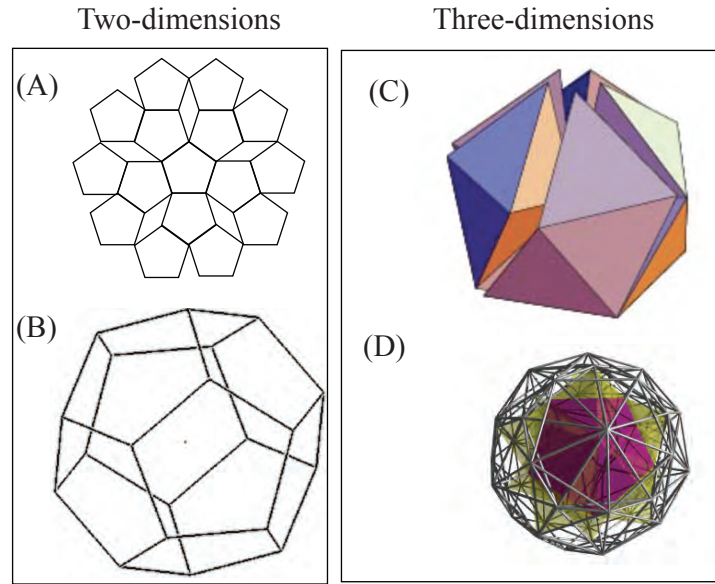


Figure 1.7: (A) There is no regular pentagonal tiling of the Euclidean plane. (B) A regular tessellation of two-sphere by pentagonal faces is possible as the $\{3, 5\}$ Platonic solid. (C) Geometrical frustration occurs in systems that exhibit dihedral angles that are not commensurable with 2π . As a consequence, gaps remains between certain faces when regular tetrahedra are packed into space. (D) On the surface of the three-dimensional space of constant positive curvature, i.e., $S^3 \in \mathbb{R}^4$, the angular deficit of packing regular tetrahedra is avoided. In particular, the $\{3, 3, 5\}$ regular polytope [55] relieves the geometrical frustration [14] of icosahedral packing in Euclidean space.

Geometrical frustration, evident in n -dimensional flat (Euclidean) space, may be relieved by allowing for curvature into each atomic cluster, such that particles with geometrically frustrated coordination shells tessellate a positively-curved surface in $(n + 1)$ dimensions [55, 15]. For example, in two-dimensional Euclidean space, there is no regular pentagonal tiling of the plane (Fig. 1.7(A)); however, if curvature is added into each of the pentagonal tiles, geometrical frustration may be relieved on the finite surface of positive curvature in three-dimensions (Fig. 1.7(B)). A most common example of geometrical frustration in three-dimensions occurs in icosahedrally-coordinated media [15, 23]. While geometrical frustration prevents long-range icosahedral packing (Fig. 1.7(C)), geometrical frustration may be relieved by considering [14] the regular icosahedral tessellation that is inscribed on the surface of the three-sphere [15] in $\mathbb{R}^4$ and consists of 120 particles (see Fig. 1.7(D)). It is the curvature mismatch between the tessellation of the positively curved space, i.e., $\mathcal{M}$, and Euclidean (flat) space that quantifies the geometrical frustration of the atomic structure in flat space.

In contrast to geometrically frustrated systems, atomic clusters that are able to generate three-dimensional space-filling arrangements are 13-atom crystallographic FCC and HCP clusters. While undercooling below the melting temperature remains a topologically necessity for such solidifying atomic systems, that are compatible with space-filling crystals, the ground state obtained in these scenarios is free of topological defects. In contrast to FCC and HCP atomic clusters, in considering geometrically frustrated undercooled atomic liquid systems one is drawn to the fact that there is an energetic preference for icosahedral coordination of atoms in dense liquids [15, 23] (Sir Charles Frank [56] (1952)). The incompatibility of the preferred local orientational order with a space-filling “crystal” is the key to understanding the structure and thermal transport properties of geometrically frustrated systems [15].

In geometrically frustrated icosahedrally-clustered undercooled atomic fluids, the relevant topological manifold is $\mathcal{M} = S^3/Y'$, where Y' is the 120-element binary icosahedral group [23] $Y \in SO(3)$. The elements of the binary icosahedral group give the 120-vertices of the $\{3, 3, 5\}$ regular polytope, which is (in fact) the Poincaré homology sphere ($\mathbb{P}$). This manifold ($\mathbb{P}$) is unique from the traditional three-sphere, despite resembling it, because it contains non-trivial loops that cannot be contracted to a point. The algebra of topologically stable disclination defects in such an icosahedral medium is given by the first homotopy group [23, 15] of $\mathbb{P}$: $\pi_1(\mathbb{P}) = Y'$. Frank-Kasper crystalline structures [57, 58] are a particular family of topologically close-packed (TCP) crystalline solids, which express local icosahedral orientational order, that present an ordered array of such wedge disclinations induced by geometrical frustration [15]. As a consequence of the curvature mismatch between the $\{3, 3, 5\}$ regular polytope and flat three-dimensional (Euclidean) space, there is a finite positive Gaussian curvature attributed to each icosahedrally-coordinated atom in three-dimensions. The finite positive curvature that is associated with each geometrically frustrated atomic cluster biases the plasma of disclinations that exists just below the melting temperature towards the concentration that carries negative curvature, so that the Euclidean space is flat on average. These excess negatively signed

topological defects persist to the ground state [57, 58, 23], forming the characteristic “major skeleton network.”

1.4.1 Mapping from curved space ($S^n \in \mathbb{R}^{n+1}$) into flat space ($\mathbb{R}^n$)

The concept of geometrical frustration in the solid state, which applies to systems with well-defined local order that is unable to fill all of space without distortions [59], has been a rich field in condensed matter physics for many decades. A general approach to treat geometrically frustrated solid state structures [15, 23] was originally introduced by Sadoc [60, 59, 22]. This method is achieved in two steps. First, in order to relieve the geometrical frustration in flat space [22], the space-filling constraint (in flat space) is relaxed by imparting finite positive curvature to each atomic cluster [50]. During this step, one obtains a polytope arrangement of vertices on the three-dimensional space of constant positive curvature (S^3) that is embedded in four-dimensions (e.g., the $\{3, 3, 5\}$ regular polytope).

After defining the curved space structure, in a second step, one transforms the curved space structure back into Euclidean (flat) three-dimensional space [61, 62, 22, 50]. It is in the second step of the procedure that disclination defects are incorporated. In three-dimensional geometrically frustrated solid states, the free propagation of local configurations is interrupted by these misoriented regions, which are wedge disclination topological defects that are characterized by the topological properties of $\mathcal{M}$. These wedge disclination defects carry curvature within their core [50, 22], and ensure that the Euclidean space is flat on average despite the positive curvature that is associated with geometrically frustrated atomic clusters. That is, the geometrically frustrated solid state structure in flat (Euclidean) space contains positively curved regions where the orientational order approaches that of ideal curved space structure [63, 64, 22, 50] and defective (misoriented) regions of negative curvature.

While many ways of mapping from curved space to flat space exist [59] (e.g. conformal mapping and geodesic mapping) the method that produces only a minimal amount of distortions of bond lengths is an extension of the standard Volterra process [47] known as [62, 50] the “Iterative Flattening Method” (IFM). The iterative flattening method introduces only small bond-length distortions [65], and produces alterations in the coordination number of atomic components. The IFM method introduces negative disclinations into the solid state structure, in order to nullify the intrinsic positive curvature that is associated with the ideal curved space structure [65]. The IFM method can proceed either randomly or in a single step (ordered) [65], the resulting structure is geometrically frustrated (i.e., it contains topologically stable disclination defects) and is either non-crystalline or crystalline.

Disclinated crystalline solids, i.e., topologically close-packed (TCP) solids, may be obtained via the single-step IFM procedure [61, 66]. This procedure approximates the ideal curved space structure,

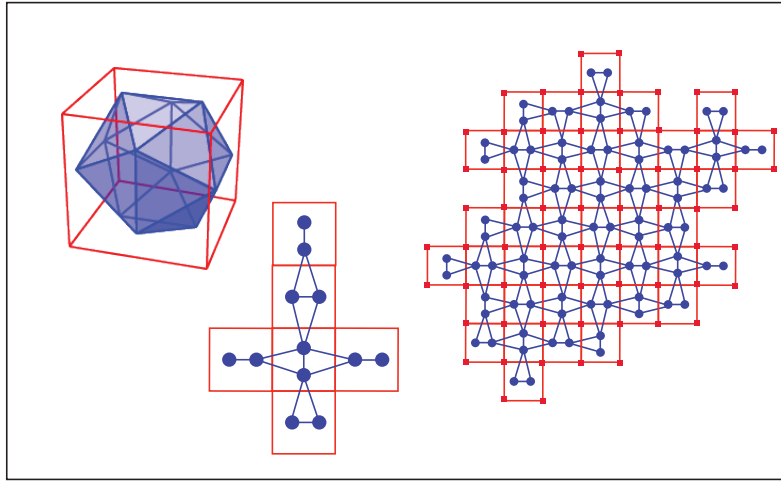


Figure 1.8: A two-dimensional example of the “iterative flattening procedure,” performed in a single step. The vertices of the ideal curved space structure (here $\{3, 5\}$ on S^2) are approximated using a developable approximation surface (DAS) (here $\{4, 3\}$). The DAS is unwrapped, and a space-filling structure is generated by tiling the unwrapped DAS in flat space.

which is a tessellation of the spherical space that is not a developable surface^e, such that it can be made to lay flat and fill Euclidean space. The single-step IFM procedure is performed by mapping the vertices of ideal curved space structure to an approximation surface that is developable, and is called the developable approximation surface [61, 65] (DAS).

As a two-dimensional example, consider the vertices of the curved space icosahedron ($\{3, 5\}$) that are approximated onto the faces of a cube ($\{4, 3\}$) which is a developable approximation surface. The faces of the cube are then unwrapped onto the plane, as shown in Fig. 1.8. By this method, a periodic array of negative wedge disclinations are introduced at the vertices of the unwrapped DAS. These disclinations appear where originally 3-sided faces of the icosahedron have become 4-sided faces in flat space [61, 66]. The angular defects that have been introduced concentrate negative curvature, which balances the positive curvature that is associated with the coordination of vertices on the curved space structure. A similar procedure in three-dimensions results in the ordered major skeleton network [57, 58] of angular disclination lines in topologically close-packed crystalline phases.

In cases of icosahedrally-coordinated media, at temperatures just below the melting temperature, the dominant topological disclinations carry an angular deficit of $+72^\circ$ and -72° [23, 15]. These disclinations correspond to rotations about a fivefold symmetry axis, upon traversing a closed path around a defect core [23] and are elements of the Y' binary icosahedral group. The 120 elements of the binary icosahedral group identify the vertices of the $\{3, 3, 5\}$ polytope [55]. This Schläfli notation [55] implies that the polytope is composed of tetrahedral cells ($\{3, 3\}$) with 5 tetrahedra per near-neighbor bond [15]. Microscopically, the $+72^\circ$ and -72° disclination lines correspond to chains of nearest-neighbor bonds surrounded by four and six tetrahedra, respectively [15].

^eDevelopable surfaces express zero Gaussian curvature, and can be flattened into Euclidean space without distortion.

In such geometrically frustrated systems, the curvature mismatch between Euclidean three-dimensional space and the $\{3, 3, 5\}$ polytope forces an asymmetry in the density of $+72^\circ$ and -72° wedge disclinations [15]. As the temperature is lowered below the melting temperature, simulation results suggest that there is a gradual pairing of angular disclination lines of opposite sign into low-energy configurations [67, 23]. However, excess -72° disclinations cannot form low-energy configurations and persist to the ground state [23, 15]. In Frank-Kasper TCP structures [23, 15], these frustration induced negative disclinations form the ordered major skeleton network.

It has been suggested by many authors that a tangled up network of these defects is an appealing model for non-crystalline solid state structures [68, 15, 23, 65]. The IFM method has been used in this context, in order to model glass formation, by implementing a series of random flattening iterations [69, 70]. In this case, on each IFM iteration, disclinations are added to the surface of the structure in curved space which becomes more flat as a result [65]. This procedure is similar to the $\langle$ inflation $\rangle$ procedure that is used for generating Penrose tilings in flat space [69, 70]. At the glass formation temperature, as the system falls out of metastable equilibrium, it has been suggested that the inflation procedure stops and the Euclidean space is filled by arranging the iteratively flattened (inflated) curved space structures as grains within Euclidean space [65].

The current work builds upon the discussion of the formation of geometrically-frustrated condensed matter by characterizing the orientational order that develops below the melting temperature using a quaternion orientational order parameter. In this way, this work goes beyond the “Iterative Flattening Method” as a model of solidification by giving a more complete topological framework within which to understand the formation of low-temperature geometrically frustrated solid states. Ultimately, this enables the development of a deeper perspective (from a topological point of view) on the thermal transport properties of solid state systems that derive from undercooled atomic liquids.

1.5 Defect-driven topological phase transitions (Berezinskii-Kosterlitz-Thouless type)

For ordered systems that exist in restricted dimensions, a topological ordering transition within the gas of misorientational fluctuations that would otherwise prevent conventional orientational order necessarily allows for the existence of an orientationally-ordered low-temperature state at finite temperatures. In a recent review on the early work on defect-driven phase transitions, Kosterlitz and Thouless [41] noted that “the idea that certain phase transitions might be driven by the occurrence of an equilibrium concentration of [topological] defects, such as dislocations in solids or quantized vortices in superfluids is almost as old as the recognition that such defects have an important role in the mechanical or electrical properties of such materials.” A prototypical example of such a transition towards the orientationally phase-coherent state, that is driven as a result of topological defects,

was first given by Berezinskii [24] and Kosterlitz and Thouless [25, 71] for planar complex ordered systems (i.e., the XY model).

In the classical 2D XY model [25], it is a gas of misorientational fluctuations in the single scalar phase angle parameter throughout the system that prevents long-range order at finite temperatures [72, 33]. Such misorientational fluctuations are aptly discretized as point defects known as vortices (i.e., of the fundamental homotopy group $\pi_1(S^1) = \mathbb{Z}$) that are spontaneously generated at temperatures below the bulk critical transition temperature. The novel phase towards the phase-coherent low-temperature state at finite temperatures was explained [24, 25] by the introduction of such vortices (+) and anti-vortices (−) as elementary excitations. Figure 1.9(A) depicts a closed loop Γ that surrounds a pair of topological point defect cores in two-dimensions with equal and opposite winding number. Topological defects that belong to the homotopy group $\pi_m(S^m)$ are identified with the lattice of integers $\mathbb{Z}$ and are hence necessarily Abelian. As a result, the closed measuring circuit that surrounds a pair of point defects (Fig. 1.9(A)) is homotopic to the two paths enclosing the point defects individually [21]. For ordered systems that exist in restricted dimensions, below a critical finite temperature, it is the formation of such low-energy bound pairs of point defects (i.e., of opposite sign – a vortex and antivortex) at a Berezinskii-Kosterlitz-Thouless (BKT) type transition that enables the development of a phase-coherent state [72, 38].

Just below the critical transition temperature, i.e., at temperatures above the Berezinskii-Kosterlitz-Thouless transition temperature, spontaneously generated isolated point defects are stabilized by a large configurational entropy. It is the low-energy of pairs of point defects with equal and opposite topological number, i.e., sum-0 pairs, that makes them favorable over isolated defects below a critical temperature (the defect-driven BKT transition temperature). It is the isolated nature of point defects above the BKT transition which destroys the global phase coherence of the low-temperature phase-coherent state. This traditional BKT transition of point defects in two-dimensions provides the simplest example of a topological phase transition. A summary of the series of transitions followed towards the low-temperature phase-coherent state in two-dimensions is given in Fig. 1.9(B). As is evident from the nature of topological ordering transitions [25], topological numbers (integer quantities) play an important role in condensed matter physics [42]. In this two-dimensional example, it is the low-energy of vortex point defects with equal and opposite topological numbers that allows for the existence of a phase-coherent superfluid state at finite temperatures.

This type of defect-driven topological ordering phase-transition is not exclusive to complex ordered systems in two-dimensions, for which spontaneously generated $\pi_1(\mathcal{M} = S^1)$ defects are points [36]. One also expects an analogous defect-driven topological phase transition to exist in a four-dimensional quaternion n –vector ordered system, for which misorientational fluctuations take the form of spontaneously generated $\pi_3(\mathcal{M} = S^3)$ topological point defects. In this thesis, this type of defect-driven topological phase transition is considered as it applies to the crystallization of undercooled atomic liquids. The concept that an equilibrium density of topological defects (wedge disclination lines) that

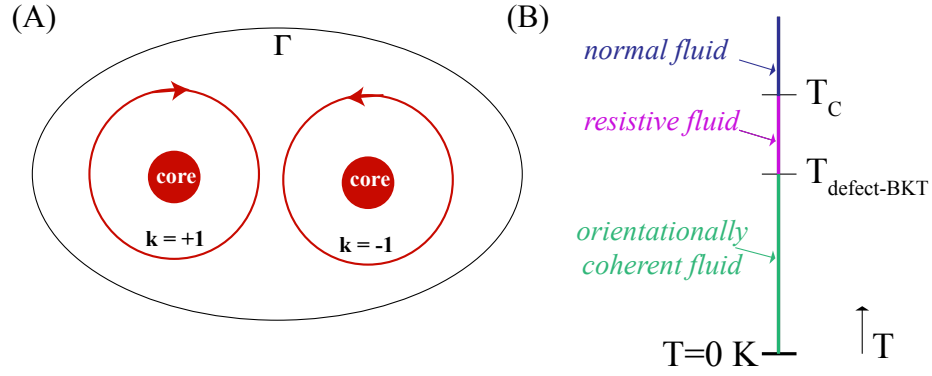


Figure 1.9: (A) A loop Γ enclosing a pair of point defect cores with equal and opposite winding number is topologically equivalent of the ground state. That is, since point defects are necessarily Abelian they combine by addition [21]. (B) For ordered systems that exist in restricted dimensions, as the temperature is lowered below the bulk critical transition temperature (T_c), global orientational ordering is prevented due to the existence of spontaneously generated topological defects. A low-temperature phase-coherent state of matter is achieved, at a subsequently lower temperature $T_{\text{defect-BKT}}$, by the binding of these defects into low-energy pairs.

exist in three-dimensional undercooled atomic liquids could lead to the transition from liquid with viscous flow properties to a rigid solid has been discussed by many authors [46, 23, 41].

Just like in planar XY models [25], the development of a theory of defect-driven topological ordering in quaternion n -vector ordered systems (i.e., $n = 4$) in four-dimensions is made comprehensible by the discretization of the system as a ‘lattice gas’ model. This is facilitated by considering the formation of a plastic crystal phase in four-dimensions, that is comprised of polytope, at temperatures just below the melting temperature T_M . A quaternion orientational order parameter characterizes the internal orientational degrees of freedom of each component of the 4D plastic crystal, such that a magnitude and set of three scalar phase angle parameters are associated with each site in the four-dimensional array. It is by the discretization of the internal orientational degrees of freedom of each component of the system at the sites of a lattice that topological defect elements belonging to the third homotopy group of $\mathcal{M} = S^3$, i.e., $\pi_3(S^3) = \mathbb{Z}$, naturally arise. At low enough temperatures, it is anticipated that such point defects (Abelian) will form low-energy paired configurations that are topologically equivalent to the defect-free state. Such a topological ordering transition belongs to the Berezinskii-Kosterlitz-Thouless universality class and is hypothesized to enable the development of the orientationally-ordered (crystalline) solid states in this scenario.

1.6 $O(n)$ quantum rotor model: Duality and frustration of low-temperature states

Below a bulk critical transition temperature, n -vector ordered systems that exist in a restricted dimension D are well-modeled by $O(n)$ quantum rotor models [33] in D -dimensions. $O(n)$ quantum rotor models mathematically describe systems that can be visualized as D -dimensional arrays of rotating condensed particles (rigid rotors), characterized by n -vector order parameters, that are weakly-linked to their nearest-neighbors [17]. Complex n -vector ($n = 2$) ordered systems that exist in the lower critical restricted dimension $D_{low} = 2$, are well-studied examples that are described by $O(2)$ quantum rotor models [39, 38] in two-dimensions. Quaternion n -vector ($n = 4$) ordered systems that exist in the lower critical restricted dimension $D_{low} = 4$ are higher-dimensional analogues to complex ordered systems that exist in two-dimensions, and may be described mathematically by four-dimensional $O(4)$ quantum rotor models [73].

Notably, $O(n)$ quantum rotor model Hamiltonians include a kinetic energy term ($\hat{T}$). While the potential energy term ($\hat{V}$) depends only on the configurations of $O(n)$ rotor orientations throughout the system ($\hat{\mathbf{n}}$), the kinetic energy term depends on the momentum of each $O(n)$ rotor ($\hat{\mathbf{p}}$). These operators are related by commutation relations [17] for the components $\alpha, \beta = 0, \dots, n$:

$$[n_\alpha, p_\beta] = i\delta_{\alpha\beta}. \quad (1.9)$$

However, it is more convenient to work with [17] the rotor angular momentum operators ($\hat{\mathbf{L}}$, where $\hat{L}_{\alpha\beta} = \hat{n}_\alpha p_\beta - \hat{n}_\beta p_\alpha$). There are $n(n-1)/2$ angular momentum operators for each $O(n)$ rotor [17]; these operators generate the group of rotations in n dimensions, denoted $O(n)$.

In studying the development of low-temperature states, it is important to consider full Hamiltonian ($\hat{\mathcal{H}}$) of the $O(n)$ quantum rotor model, developed by placing a single $O(n)$ quantum rotor on the sites i of a D -dimensional lattice. In general, such a Hamiltonian takes the form [17]:

$$\hat{\mathcal{H}} = \hat{T}(g) + \hat{V} = \frac{gJ}{2} \sum_i \hat{\mathbf{L}}_i^2 - J \sum_{\langle ij \rangle} \hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j, \quad (1.10)$$

where $1/gJ$ is the rotor moment of inertia, $J > 0$ is a coupling energy between nearest-neighbors, and the interactions are summed over nearest-neighbors $\langle ij \rangle$. Such an $O(n)$ quantum rotor model allows for the realization of ‘dual’ low-temperature states, that are anticipated as a function of the (non-thermal) tuning parameter g that enters the Hamiltonian [17]. This is because the potential and kinetic energy terms cannot be minimized simultaneously, as a consequence of the commutation relations that exist between the momentum and orientation operators [74].

The potential energy term is minimized by the simple state of perfectly aligned rotors, and there-

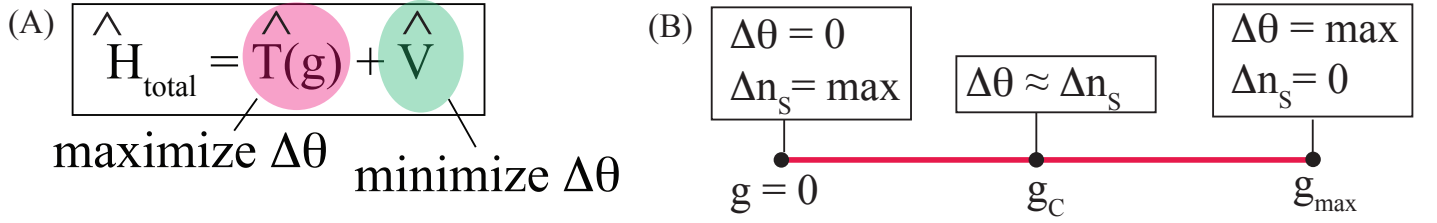


Figure 1.10: (A) The kinetic and potential energy terms that describe the $O(n)$ quantum rotor model cannot be minimized simultaneously [17, 75]. The non-thermal tuning parameter g , that enters the Hamiltonian, mediates the ratio of importance of these competing energy terms. (B) The value of g determines the structure and transport properties of the low-temperature system. In the limit of dominant potential energy, the alignment of rotor orientations in the ground state is favored; on the other hand, the kinetic energy is minimized where the orientation of each rotor is maximally uncertain and favors the localization of condensed particles [16] (by the uncertainty principle).

fore establishes global orientational order. In contrast, the kinetic energy term is minimized when the orientation of each rotor is maximally uncertain favors the localization of condensed particles [75] (by the uncertainty principle [17]). That is, for small or large g , on either side of a critical value $g_C \approx 1$, the rotor model with $O(n)$ symmetry predicts distinct ground states that are either aligned (“magnetic”) or disordered rotors (“paramagnetic”). see Fig. 1.10(A). These distinct low-temperature configurations are dual to one another, as a consequence of symmetric uncertainty relations that apply to the $O(n)$ quantum rotor model [16] which can be recast as a duality between topological point defects and condensed particles [18] (Fig. 1.10(B)).

Furthermore, for n -vector ordered systems that exist in restricted dimensions, there is the possibility of frustration of the dual low-temperature states [76], that can be realized in the limit of finite g . That is, the realization of frustration in restricted dimensions is an effect of a combination of kinetic and potential energy. For example, in the extreme limit that $g = 0$, the potential energy term is minimized independently and gives rise to perfectly aligned rotor orientations in the ground state [17]; this ground state is unfrustrated. On the other hand, for small g less than a critical value, the ground state now exhibits frustration in the scalar phase angle field [77]. With the incorporation of frustration into the phase-coherent ground state, it is no longer one of perfectly aligned rotors but instead the scalar phase angle parameter(s) will vary from site to site so as to try and minimize the potential energy term in the presence of kinetic energy effects [17]. Such a ground state now consists of a periodic configuration of unpaired/signed topological defects in the scalar phase angle field throughout the system, similar to the Abrikosov vortex flux lattice of defects in a type-II superconductor.

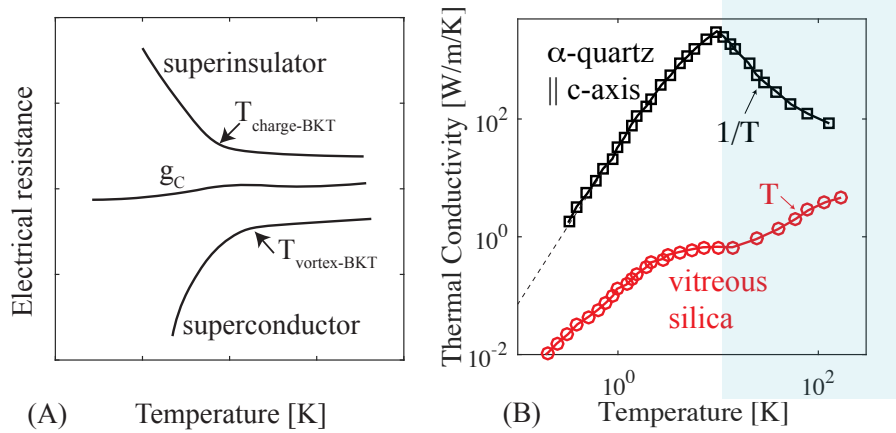


Figure 1.11: (A) Sketch of the electrical resistance of charged JJA systems across the superconductor-to-superinsulator transition [75, 78]. The electrical resistance goes sharply to zero on the formation of a low-temperature superconductor (i.e., $g < g_c$); inverse electrical transport properties are anticipated in the superinsulator (i.e., $g > g_c$). (B) Measured thermal conductivity (κ) of crystalline α -quartz and vitreous silica (Ref. [79]). The thermal conductivity of crystalline and amorphous systems exhibit an inverse dependence on temperature above approximately 50 K (shaded region).

1.7 Duality of low-temperature transport properties

Historically, charged Josephson junction arrays (JJA) of complex n -vector order parameters have provided the prototypical example of a material transport property (electrical resistance) that can be controlled by a non-thermal tuning parameter (g) that enters the Hamiltonian. Such systems are modeled by $O(2)$ quantum rotor models, and exhibit a superconductor-to-superinsulator [16, 18] transition between distinct ground states as a function of a tuning parameter g . The existence of this transition leads to inverse behavior of the electrical resistance as a function of temperature on either side of the superconductor-to-superinsulator transition [16, 18, 78]. In charged planar JJAs, in the absence of kinetic energy, a perfect 2D superconducting ground state is obtained that has zero electrical resistance in the finite temperature range [18]. On the other hand, in the absence of potential energy, a perfect 2D superinsulator is obtained that has a large electrical resistance at finite temperatures (that increases with decreasing temperatures). Recent comprehensive measurements of the electrical resistance of a series of thin-film charged JJAs have been made by Poran et al. [78], across the superconductor-to-superinsulator transition. Sketches of the temperature dependence of the electrical resistance of charged JJA systems [78, 75], that are realized on either side of the superconductor-to-superinsulator transition, are shown in Fig. 1.11(A).

In general, the distinct orientationally-ordered (phase-coherent) and orientationally-disordered (phase-incoherent) low-temperature states of the $O(n)$ quantum rotor model are anticipated to

present material transport properties that are inverse to one another [18, 78]. A motivation of this thesis is to apply the topological framework for solidification in order to understand the quite different material transport properties of crystalline and non-crystalline solid states [3, 2]. The origin of the inverse temperature dependence of the thermal conductivity of crystalline and non-crystalline solids, above approximately 50 K , has remained of interest to the heat transfer community for over a century [3, 2, 5]. While the thermal conductivity of crystalline materials increases sharply with decreasing temperatures, the thermal conductivity of non-crystalline solids decreases with decreasing temperature over the same temperature range [3] (see Fig. 1.11(B)). The inverse behavior of the thermal conductivity of crystalline and non-crystalline materials is reminiscent of the electrical transport properties of charged JJAs, across the superconductor-to-superinsulator transition that belongs to the $O(2)$ quantum rotor model. In light of this, in this work, the thermal transport properties of crystalline and non-crystalline solids are viewed as duals across a non-thermal transition (i.e., of ground states) that belongs to an $O(4)$ quantum rotor model.

Structurally, the thermal transport properties of the solid state may be a consequence of the development of a lattice of lack thereof. Crystalline systems possess a well-defined first Brillouin zone [10] such that resistive Umklapp scattering [11] is the dominant process for thermal resistivity at high temperatures; as the temperature of the system is decreased, resistive Umklapp scattering becomes less frequent [79] and as a result the thermal conductivity increases proportional to T . On the other hand, the opposite dependence of the thermal conductivity as a function of temperature is evident for non-crystalline materials. Non-crystalline materials, which lack translational order, lack a well-defined reciprocal lattice and thereby do not exhibit resistive Umklapp scattering processes. Above approximately 50 K , the thermal conductivity of non-crystalline materials agrees with the model of a minimum limit to thermal conductivity [5, 7, 6], which predicts that heat exchange takes place within a distance that is approximately equal to the interatomic spacing.

1.8 Hypotheses

1. Order parameter: The hypothesis that drives the current work is the identification of a quaternion number as the orientational order parameter in solidifying undercooled atomic fluids.
2. Restricted dimensions: Just as complex n -vector ($n=2$) ordered systems that exist in restricted dimensions (two- or one-), that form Josephson junction arrays below a bulk critical transition temperature, may be modeled mathematically using a lattice quantum rotor model with $O(2)$ symmetry, so too can quaternion n -vector ($n=4$) ordered systems that exist in restricted dimensions (four- or three-) be modeled using a lattice quantum rotor model with $O(4)$ symmetry.
3. Ground states: The formation of crystalline and non-crystalline solid states from undercooled

atomic liquids can be drawn in analogy to the realization of dual superconducting and superinsulating low-temperature states of charged $O(2)$ Josephson junction arrays.

4. Topological ordering: Orientationally-ordered solid states that exist in the restricted dimension $\mathbb{R}^4$ are realized by a topological ordering transition of point defects, i.e., a defect-driven Berezinskii-Kosterlitz-Thouless (BKT) transition in four-dimensions, and not by spontaneous symmetry breaking at the melting temperature.
5. Scaling behavior: The thermodynamic response functions, susceptibility and heat capacity, of a four-dimensional $O(4)$ quantum rotor model (simulated using numerical Monte-Carlo) should show scaling behavior that is similar to what is observed in the vicinity of the defect-driven BKT transition in planar $O(2)$ models.
6. Structure and frustration: Geometrical frustration acts as a tuning parameter that controls the structure of the crystalline ground state, in the range of dominant potential energy. Above a critical value of geometrical frustration, the ground state is no longer crystalline. In contrast, in the range of dominant kinetic energy, a glass forms from an undercooled atomic liquid whose orientational correlations can be tuned by the applied cooling rate.
7. Thermal transport properties: The inverse temperature dependence of the thermal conductivity of crystalline and non-crystalline solid states can be understood as a higher-dimensional analogue to the electrical transport properties of charged $O(2)$ Josephson junction arrays that exhibit a singularity at the characteristic superconductor-to-superinsulator transition.

1.9 Outline of Thesis

The two main sections of this thesis (Section 2 and Section 3) consider the phenomena of orientational ordering in complex ordered systems (i.e., superfluids) and in quaternion ordered systems (i.e., solid state). The focus of these separate sections is to develop an understanding of the possible ordered states that are able to exist at low-temperatures in restricted dimensions, by considering the relevant $O(n)$ quantum rotor model. The relevant material transport properties of the dual low-temperature states (orientationally-ordered and orientationally-disordered) that can be realized for $O(n)$ quantum rotor models in restricted dimensions are discussed.

Section 2 focuses on charged $O(2)$ Josephson junction arrays that are well-modeled by $O(2)$ quantum rotor models, and that exhibit a dramatic dependence of the electrical conductivity as a function of temperature across the superconductor-to-superinsulator transition. In Section 3, a natural extension is made to a four-dimensional plastic crystal that develops below the melting temperature. This hypothetical system proves useful in the interpretation of solidification of undercooled atomic liquids in three-dimensions, towards crystalline and non-crystalline low-temperature solid states.

Chapter 2

$U(1)$ orientational ordering

2.1 Ordering in bulk dimensions:

2.1.1 Free energy minimization

Both helium fluids and electron gases possess $U(1)$ symmetry, and can undergo Bose-Einstein condensation towards a superfluid phase as the temperature is lowered past a critical value. Exemplifying the connection between these two kinds of $U(1)$ superfluids (uncharged and charged) are the two volumes on the macroscopic theory of superfluidity published by Fritz London [80, 81] in the mid 20th century: “Superfluids, Vol. I: Macroscopic Theory of Superfluidity (1950)” and “Superfluids, Vol II: Macroscopic Theory of Superfluid Helium (1961).” In the case of uncharged atomic helium-4 (He^4) superfluids, each atom is bosonic independently and condenses (on its own) below a critical temperature. The simple arrangement of Helium-4 (He^4), two electrons, two protons and two neutrons, is consistent with $U(1)$ symmetry [82] (Fig. 2.1 (A)). Below a critical temperature, on Bose-Einstein-Condensation, the even number of nucleons (each having $1/2$ spin) form sets of oppositely aligned nucleon spins that sum to zero. The single scalar phase angle parameter θ describes the orientation of the ground state that the nucleons of each condensed He^4 atom lock into. On the other hand, charged $U(1)$ superfluidity (i.e., superconductivity) develops by pairing single electrons^a into composite bosons known as Cooper pairs which Bose-Einstein condense below the bulk Bardeen-Cooper-Schrieffer (BCS) critical transition temperature (T_{BCS}). A Feynman diagram of a Cooper pair composite boson is depicted in Fig. 2.1 (B); the scalar phase angle parameter in a Cooper pair condensate is the pairing phase [37] between electrons.

Bulk superfluidity is a low-temperature phase-coherent state of condensed matter that is obtained by the spontaneous symmetry breaking of the full $U(1)$ orientational symmetry group of a high-temperature fluid, at the bulk critical transition temperature. The bulk superfluid state exists in three spatial dimensions and is characterized by a complex order parameter $\psi = |\psi|e^{i\theta}$, where the

^aElectrons are fermions with spin $1/2$.

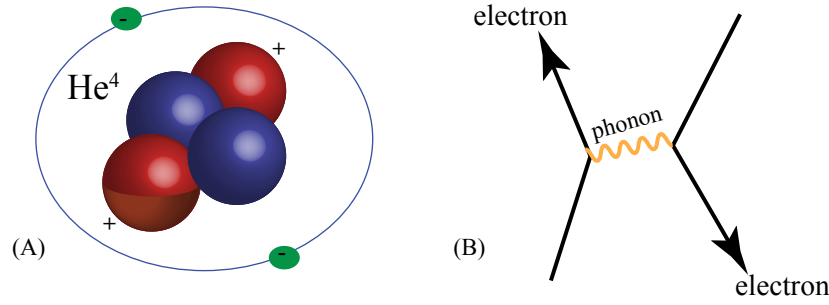


Figure 2.1: (A) Helium-4 (He^4) consists of two electrons, two protons and two neutrons. Below a critical temperature, on Bose-Einstein condensation, the even number of nucleons (each having $1/2$ spin) form sets of oppositely aligned nucleon spins that sum to zero. (B) Coupling between electrons in a lattice generates composite bosons known as Cooper pairs; this coupling can be depicted by the Feynman diagram shown here.

scalar phase angle θ is well-defined across the entire system and $n_S = |\psi|^2$ is the number density of condensed particles. The condensation of $U(1)$ superfluids is a second-order phase transition [83, 84], and is understood by the minimization of the traditional Landau (2-4) free energy:

$$f_{\text{Landau}} = \frac{\alpha}{2}|\psi|^2 + \frac{\beta}{4}|\psi|^4 \quad (2.1)$$

where $\alpha = a(T - T_C)$ changes sign on either side of the critical transition temperature T_C , and a and β are positive constants. On spontaneous symmetry breaking, the bulk superfluid adopts a particular ground state $\theta \in [0, 2\pi]$ from among an infinite number of degenerate ground states on $\mathcal{M} = S^1$. This free energy configuration, where $\mathcal{M} = S^1$, is colloquially known as the Mexican hat (Fig. 2.2). There is an energy cost to change $|\psi|$ from its ideal position that defines the radius of $\mathcal{M}$; at a given temperature, if $|\psi|$ is varied slightly away from its ideal value the energy of the superfluid (Eqn. 2.1) will increase quadratically [34]. In bulk systems (i.e., three-dimensional), as a consequence of spontaneous symmetry breaking at T_C , all condensed particles adopt a particular ground state along $\mathcal{M}$ such that the orientational order parameter is macroscopic [82, 85].

Because there is no energy cost associated with changing the ground state of the system, by rotating the single real scalar phase angle parameter θ to $\theta + \theta_0$, the scalar phase angle θ acts as the single Nambu-Goldstone boson [86] (NGB) that is anticipated in low-temperature states that exhibit spontaneous breakdown of the $U(1)$ symmetry of a high-temperature fluid. In uncharged Bose-Einstein condensate superfluids, these Nambu-Goldstone bosons remain ‘massless’ and in the long-wavelength limit behave as sound waves [87, 88]. On the other hand, in bulk charged superfluids (i.e., 3D superconductors), the Nambu-Goldstone bosons are oscillations of a Cooper pair condensate and acquire a gapped dispersion due to the long-range nature of the Coulomb interaction [89, 90, 91].

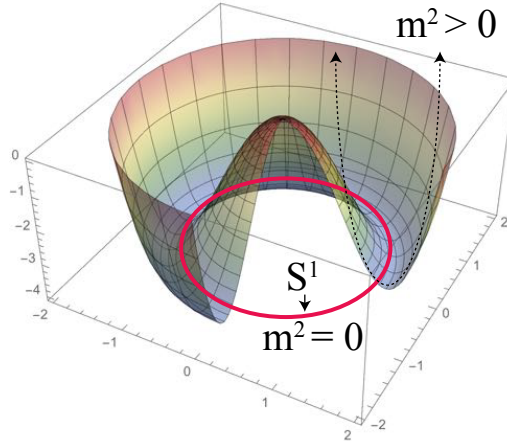


Figure 2.2: The free energy configuration of the $U(1)$ (i.e., complex) superfluid system, below the bulk critical transition temperature. At any given temperature free energy is minimized for radius $|\psi| = \sqrt{\frac{-\alpha}{\beta}}$ at any arbitrary angle $\theta \in [0, 2\pi]$ such that the basin of degenerate ground states that the topology of $\mathcal{M} = S^1$.

2.1.2 Meissner effect and topological defects

In addition to the scalar phase angle parameter (θ), the amplitude of the complex order parameter ($\rho = |\psi|$) is an important degree of freedom in $U(1)$ superfluid systems. There is always an energy cost associated with changing the amplitude of the order parameter slightly away from its ideal value, as the radius of $\mathcal{M} = S^1$ at any given temperature. The energy cost associated with variations in the amplitude of the order parameter within the bulk superfluid attributes mass to this degree of freedom. The massive nature of ρ establishes that any variation in ρ will rapidly be drawn to towards the minimum energy state along $\mathcal{M}$. This constraint excludes variations in ρ within the bulk of the system resulting in a rotational Meissner effect, in which applied complex rotational fields are constrained to decay exponentially over a finite region from a surface into the bulk.

The mass associated with ρ is owing to the non-linear terms in ρ in Eqn. 2.1. In particular, the energy increases quadratically if ρ is varied slightly away from the value along the potential energy minima, ρ_0 as [92]:

$$\frac{\alpha}{2}(\rho^2 - \rho_0^2) + \frac{\beta}{4}(\rho^4 - \rho_0^4) \approx \frac{1}{2}(\alpha + 3\beta\rho_0^2)(\rho - \rho_0)^2. \quad (2.2)$$

It follows that an effective free energy for ρ near ρ_0 can be written as [92]: $f = \frac{1}{2}m(\rho - \rho_0)^2$, where $m \approx \frac{1}{2}(\alpha + 3\beta\rho_0^2)$. The lowest energy state happens when ρ takes its mean value, which costs zero energy, and variations in ρ in space are constrained to zero.

In order to determine the configuration of $\rho(\mathbf{x})$ in the presence of an applied field, consider pulling on the ends of the fluid density at the surfaces of the system by applying direct boundary

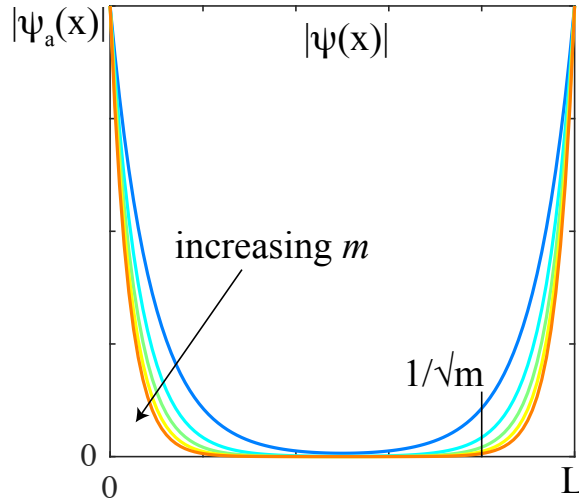


Figure 2.3: A massive field decays exponentially, with a decay constant $\sqrt{m}$.

conditions. The solution to this problem is given by using the method of calculus of variations, wherein one realizes that $\rho(\mathbf{x})$ is the minimum energy configuration and any change would have a higher energy [93]. In order for this to be true, $\rho(\mathbf{x})'' = m\rho(\mathbf{x})$. A one-dimensional example is a very simple instance of a second order linear homogeneous differential equation; the solution is any function of the form $\rho = A\exp(\sqrt{m}x) + B\exp(-\sqrt{m}x)$, provided that A and B coincide with the boundary conditions. A one-dimensional example of this condition, applying simple boundary conditions^b is shown in Fig. 2.3 for $L = 5$ and $5 < m < 25$. Because the system wants to quickly achieve its ideal value $\rho(x) = 0$, the solution decays exponentially to e^{-1} over a characteristic length $1/\sqrt{m}$. This phenomena of exponential decay of a massive field into a superfluid is known as the Meissner effect.

The energy cost to change the value of the amplitude of the superfluid order parameter causes the system to become “irrotational.” In uncharged superfluids, the irrotational condition implies that any rotational field ω is constrained to zero

$$\omega = \nabla \times \mathbf{v} = 0, \quad (2.4)$$

where $\mathbf{v}$ is the superfluid velocity; this irrotational condition leads to the expulsion of rotational fields. In charged superfluids, the analogous phenomenon is the Meissner effect in which magnetic fields are expelled so that: $\mathbf{B} = \nabla \times \mathbf{A} = 0$, where $\mathbf{A}$ is the magnetic vector potential [94, 82]. In uncharged superfluids, the irrotational condition ensures that the velocity distribution of condensed

^bThe direct boundary conditions are: $\rho(0) = \rho(L) = \rho_a$. Making use of these boundary conditions, the constants A and B solve as:

$$A = \rho_a - B, \quad \text{and} \quad B = \frac{\rho_a(1 - \exp(\sqrt{m}L))}{\exp(-\sqrt{m}L) - \exp(\sqrt{m}L)}. \quad (2.3)$$

particles corresponds to a potential flow [94], i.e., the velocity distribution depends only on the scalar phase angle parameter [82, 95]. This condition is satisfied provided that $\mathbf{v} \propto \nabla\theta$, where θ is the scalar phase angle parameter, because the curl of a gradient of a scalar function is zero [94] by definition. The particular velocity field configuration that satisfies the irrotational condition (Eqn. 2.4) that is characteristic of $U(1)$ superfluids, everywhere except for the core of a topological defect, is derived in Appendix D.1. This derivation is performed for bulk superfluids (i.e., three-dimensional) using a 3D curl; the definition of the curl in three-dimensions is derived using quaternion multiplication rules in Appendix E.1.

The irrotational condition that applies to $U(1)$ superfluids, characterized by a single scalar phase angle parameter, is satisfied everywhere except for the core of a $\pi_1(S^1)$ topological defect (known as a potential vortex). In uncharged superfluids, rotational deformations are kicked out of the bulk superfluid into the cores of such topological defect elements; in type-II superconductors (charged superfluids), applied magnetic fields are pushed into these $\pi_1(S^1)$ topological defects that are thin threads in three-dimensions. To reiterate, it is the irrotational nature of the superfluid that leads directly to the quantization of any rotational flow that enters the system into the core of topological defects. The available types of topological defects are determined by considering the topological properties of the ground state manifold $\mathcal{M}$, which (in this case) is the unit circle S^1 at the basin of the ‘Mexican hat’ (Fig. 2.2). This topological ground state manifold admits topologically stable defect elements that belong to the fundamental (first) homotopy group (of closed paths) that loop around $\mathcal{M} = S^1$, and cannot be contracted to a point [21, 82], i.e., $\pi_1(S^1) = \mathbb{Z}$. In bulk $U(1)$ superfluid ordered systems, a vortex line must pass through any closed loop around which the scalar

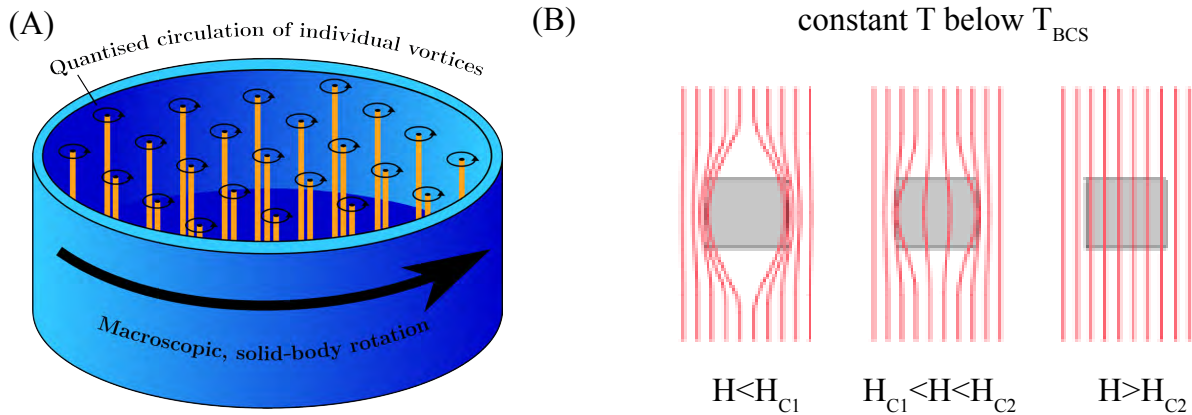


Figure 2.4: (A) If bulk helium superfluid is exposed to an applied macroscopic solid-body rotation, a regular array of linear $\pi_1(S^1)$ vortex topological defects that are aligned with the axis of rotation develops. [Image: Ref. [96]] (B) In type-II superconductors, if an applied magnetic field is greater than a critical value H_{C1} (and less than an upper critical value H_{C2}) the magnetic field is pushed into thin threads ($\pi_1(S^1)$ topological defects). For applied magnetic fields less H_{C1} , the bulk type-II superconductor behaves like a type-I superconductor, i.e., it expels the entire applied magnetic field.

phase angle parameter of the order parameter changes by 2π . At the position of the defect core, the orientational order parameter is not defined [82]. This allows for a rotational (or magnetic) flux quantum to penetrate the superfluid, and the expelled field decays exponentially from the defect core into the bulk.

In uncharged $U(1)$ superfluids (i.e. He^4), the realization of $\pi_1(S^1)$ vortex topological defects in the bulk phase is most easily considered by applying a macroscopic solid-body rotation (about a central axis) to a whole cylindrical container of liquid helium superfluid. If the whole cylinder is rotated, the irrotational condition (Eqn. 2.4) suggests that the superfluid component should not rotate along with the walls of the cylinder [82]. It follows that one would expect the free surface of the superfluid to remain perfectly flat. What actually happens is that the free surface of a rotating helium superfluid becomes curved due to centrifugal forces [82], as would be anticipated for a normal flow that is rotational. This is possible because the bulk superfluid is able to contain topological defects, that allow for the development of a velocity field configuration that satisfies the irrotational condition everywhere except at the core of the defect. The order parameter is zero at the defect core, and represents a normal rotating classical fluid [82].

Despite the $\mathbb{Z}$ topological invariant that characterizes the winding number (k) of $\pi_1(S^1)$ topological defects, in practice, only $k = \pm 1$ vortices are observed. A schematic of a lattice of quantized vortices that develops in uncharged superfluid systems, in the presence of an applied macroscopic solid-body rotation, is shown in Fig. 2.4(A). The development of rotational vortices in uncharged superfluids can be described in much the same way as the development of magnetic vortices in type-II bulk superconductors [82], as an Abrikosov vortex lattice [97]. Type-II bulk superconductors allow for the first topological defects to enter into the system for applied magnetic fields above a critical value (Fig. 2.4 (B)). With the introduction of its first topological defects, the system enters into a mixed state by allowing some of the applied field to be pushed into these topological defects in a quantized fashion [82].

Not only do single strength topological defects have the lowest energy [23, 82, 21], in the presence of applied fields, the surface area of superfluid states of matter is maximized by the development

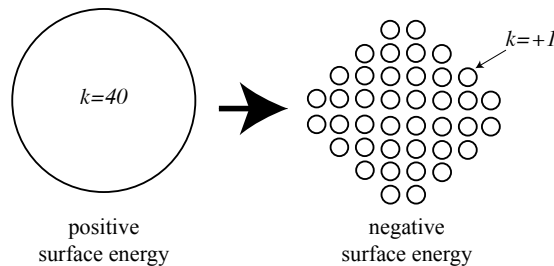


Figure 2.5: Negative surface energy forces the quantization of flux that enters into the system into topological defects of single strength.

of only single strength defects. Type-II superconductors, for example, exhibit negative surface energy [98, 97] (defined between the normal and superfluid phases) which suggests that the condensed matter system will lower its free energy by increasing its surface area. In superconductors, negative surface energy is due to the Ginzburg-Landau parameter being larger than a particular value [98, 97]. The Ginzburg-Landau parameter is defined as the ratio of the two important characteristic lengths in a superconductor: the coherence length (associated with the order parameter field) and the penetration depth (associated with the exponentially decaying applied magnetic field). The limiting value the Ginzburg-Landau parameter, that separates type-I superconductors (with positive surface energy) from type-II superconductors (with negative surface energy) is $1/\sqrt{2}$. In these ordered systems, in the presence of an applied field, flux enters within topological defect cores of a single strength $|k| = 1$ (Fig. 2.5) in order to maximize the surface area of the ordered system. In the presence of increasingly strong applied fields, superfluidity is suppressed as the distance between topological defects becomes smaller. At some critical applied field, the normal defect cores will overlap and suppress the order parameter everywhere within the ordered system, driving it into the normal state.

In bulk superfluids, the possible existence of a finite density of topological defects just below the bulk critical transition temperature does not prevent spontaneous symmetry breaking [85, 82, 99]. This is a consequence of the linear nature of $\pi_1(S^1)$ topological defects in three-dimensional (bulk) $U(1)$ superfluids, which are supported because the free energy cost to produce a topological defect line is too high to permit them in the absence of applied external fields [99]. A linear $\pi_1(S^1)$ topological defect in a bulk superfluid, where the orientational order parameter is not defined along a line, is shown schematically in Fig. 2.6(A). Topologically stable defects that belong to the homotopy group $\pi_i(\mathcal{M})$ have the dimensionality [36, 37]: $d = D - i - 1$ where D is the geometric spatial dimension of the ordered system. Thus, vortex topological defects are points in two-dimensions (Fig. 2.6(B)).

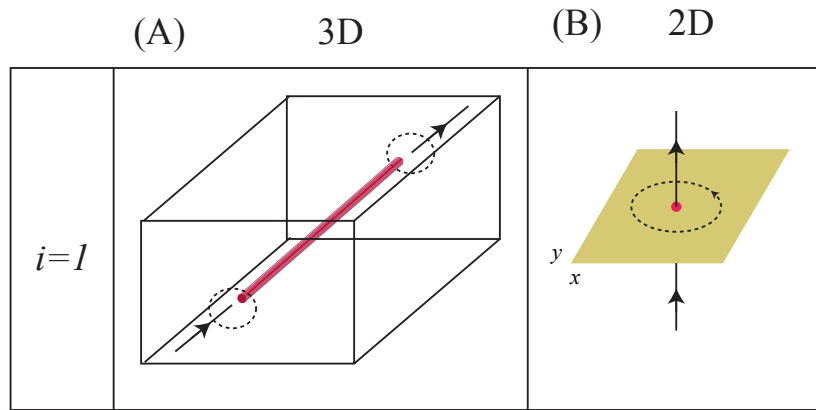


Figure 2.6: Topological defects that belong to the homotopy group $\pi_1(S^1) = \mathbb{Z}$ are: (A) linear in three-dimensional systems (bulk) and, (B) point defects in thin-films.

In two-dimensions, these point defects are of crucial importance in the prevention of spontaneously symmetry breaking [99], as will be discussed in Section 2.2.

2.1.3 $U(1)$ Josephson junctions

A Josephson junction is comprised of two macroscopically ordered $U(1)$ superfluid domains, separated by a weak-link. In the case of a Josephson junction between two superconductors, the weak link may be a thin insulating material that forms a tunnel barrier. A schematic of a charged Josephson junction is shown in Fig. 2.7(A). The Josephson effect has also been observed in superfluid helium [100, 101, 102, 103]; the first observation of the Josephson effect in superfluid helium was reported by Richards and Anderson [100] (1965), by immersing two reservoirs in He^4 superfluid such that the baths are weakly coupled through a small orifice (Fig. 2.7(B)). The Josephson relations that characterize transport across Josephson junctions apply to both charged and uncharged junctions.

The total wave function of the Josephson junction ($\Psi(t)$) is a time-dependent superposition of the individual macroscopic wave functions of the separate superfluids that comprise the junction [104]:

$$\Psi(t) = \psi_1 \Psi_1(0) + \psi_2 \Psi_2(0) \quad (2.5)$$

where ψ_1 and ψ_2 are complex numbers, i.e., $\psi_1, \psi_2 \in \mathbb{C}$, that represent the macroscopic order parameter on either side of the junction. It is owing to the superposition of ψ_1 and ψ_2 across the junction that the separate systems comprising the junction can exchange information in the form of tunneling of condensed particles or scalar phase angle information [105, 106]. The general theory of Josephson junctions is determined by characterizing the time-derivatives of the four degrees of freedom that

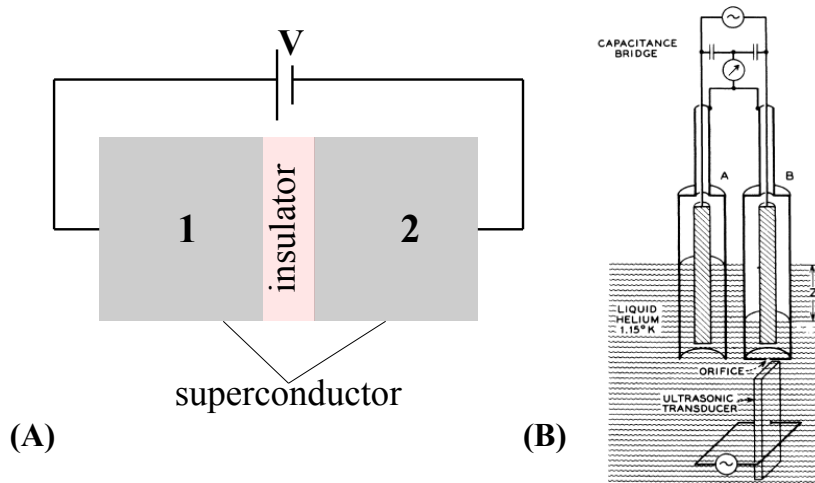


Figure 2.7: (A) Schematic diagram of a charged Josephson junction, comprised of two bulk superconducting grains, and an insulating tunnel barrier. (B) Schematic of an apparatus used to measure the Josephson effect in superfluid He^4 , driven by a helium head difference z . [Image: Ref. [100]]

characterize the junction [104], i.e., the amplitude and scalar phase angle parameters of each of the macroscopic wave functions that comprise the junction. For full derivations of these expressions, that provide a general theory of Josephson junctions [104], see Appendix F.

The general theory of Josephson junctions, between two macroscopically ordered $U(1)$ superfluids, may be summarized by two expressions [95]. Firstly, the current that can be transferred across the junction is:

$$I = I_C \sin \phi, \quad (2.6)$$

where I_C is the critical current of a junction (if you try to pass a larger current than I_C , the junction will turn normal), and ϕ is the relative scalar phase angle across the junction. Secondly, a potential can develop across the junction owing to the difference in the time-evolution of scalar phase angles on either side of the junction:

$$\dot{\phi} = \dot{\theta}_1 - \dot{\theta}_2 = \frac{\mu}{\hbar}, \quad (2.7)$$

where μ is a potential difference between the two sides of the junction. In the case of charged Josephson junctions, one can consider connecting the two superconducting regions on either side of the junction to the terminals of a battery so that the potential difference that develops across the junction is: $\mu = \mu_1 - \mu_2 = qV$ (where V is a voltage and $q = 2e$ is the charge of a Cooper pair). Similarly, a difference in head between two weakly-linked reservoirs of superfluid helium generates a potential difference ($\mu = \mu_1 - \mu_2 = mgz$, see Fig. 2.7 (B)).

A given Josephson junction, between two systems that are macroscopically ordered by complex order parameters, is conveniently characterized by a pair of characteristic energies: the Josephson coupling energy (E_J), and the charging energy (E_C). E_J is proportional to the critical current I_C , and E_C is proportional to the potential difference μ across the junction. In charged Josephson junctions [107], $E_J = \hbar I_C / q$ and $E_C = +qV/2 \equiv q^2/2C$ where $C = q/V$ is the capacitance of the junction. In the case of uncharged Josephson junctions (i.e., between baths of superfluid He^4), $E_J = \hbar I_C / (mg)$ and $E_C = +mgz/2 \equiv (mg)^2/2C$ where $C = (mg)/z$.

In three-dimensions, a Josephson junction can be formed by placing two bulk macroscopically ordered superfluids next to one another separated by a weak-link. On the other hand, for complex ordered systems that exist in restricted dimensions (i.e., two- and one-), a naturally occurring array of Josephson junctions forms below the bulk critical transition temperature as a consequence of the prevention of spontaneous symmetry breaking. Such Josephson junction arrays are comprised of weakly-linked complex n -vector order parameters, and are well-described by $O(2)$ quantum rotor models. The ratio of the pair of characteristic energies that parameterize a Josephson junction, i.e., $g = E_C/E_J$, plays an important role in determining the properties of low-temperature ordered states that can be obtained for such systems that exist in restricted dimensions.

2.2 Ordering in restricted dimensions (two- and one-): $O(2)$ quantum rotor model

In two- and one-dimensional systems, as a consequence of the Mermin-Wagner theorem [29], a Bose-Einstein condensate with $U(1)$ orientational symmetry cannot develop by spontaneous symmetry breaking at finite temperatures. In superconducting systems, below the bulk Bardeen-Cooper-Schrieffer (BCS) critical transition temperature (T_{BCS}), a naturally occurring array of charged Josephson junctions forms as superconducting order develops in 2D regions that are weakly-linked to their nearest-neighbors [74, 35] (see Fig. 1.3(B)). Each superconducting region expresses an amplitude and orientation of a complex n -vector order parameter, and the internal orientational degrees of freedom of each region i are well-represented by an $O(2)$ quantum rotor that is a complex unit vector $\hat{n}_i = (\cos \theta_i, \sin \theta_i)$ that satisfies [17]:

$$\hat{n}_i^2 = 1. \quad (2.8)$$

A lattice model of such $O(2)$ quantum rotors in two-dimensions enables a mathematical description of the Josephson junction array (JJA) that develops naturally below T_{BCS} . A schematic of a single ‘unit cell’ of a planar JJA of Josephson junctions is shown in Fig. 2.8(A). It is a consequence of the weak-linking between nearest-neighbors within the array that, despite the formation of superfluid order within separate regions, the whole array remains in a resistive state just below T_{BCS} owing to the possibility of the existence of a gas of misorientational fluctuations in θ across the system.

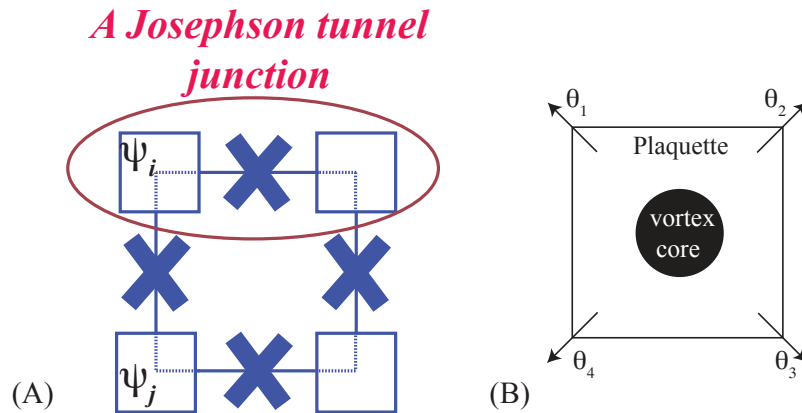


Figure 2.8: (A) Schematic of a single ‘unit cell’ (i.e., elementary plaquette) in a planar JJA. The squares depict superfluid regions, and the X ’s identify weak-links between nearest-neighbors that form Josephson junction tunnel barriers. (B) A possible phase field configuration in the vicinity of a topological point defect core, of strength $k = +1$. The defect core is located at the center of an elementary plaquette of nearest-neighbors.

In complex n -vector ordered systems ($\mathcal{M} = S^1$), these misorientational fluctuations in θ can be discretized as $\pi_1(\mathcal{M}) = \mathbb{Z}$ topological defects known as vortices. In two-dimensions (D_{low}), these topological defects are points [36] that play a crucial role in the prevention of the development of global phase coherence at finite temperatures [25, 99]. In thin-films, the free energy cost to introduce single topological point defects may be comparable to $k_B T$ in the absence of applied external fields [99]; as a result, these excitations are spontaneously generated at temperatures just below T_{BCS} [35].

The discretization of the system as a Josephson junction array assists in modeling the misorientational fluctuations as topological point defects, that appear naturally [108] around closed circuits of nearest-neighbors (i.e., an elementary plaquette). Figure 2.8(B) depicts a phase field configuration that can develop owing to the presence of a defect core. A topological point defect core, indicating a singularity in the order parameter field [21], is situated at the center of any closed loop around which the relative scalar phase angles ($\theta_{ij} = \theta_i - \theta_j$) between nearest-neighbors [108] sum to an integer multiple of 2π , i.e., $2\pi k$, where $k = \pm 1, \pm 2, \dots$ is the integer topological number (winding number) that characterizes the point defect. A non-zero value of k implies the existence of a singularity in the gradient of the scalar phase angle at the core of the topological defect.

Because topological point defects are spontaneously generated in two-dimensions, just below T_{BCS} , condensed particles and topological point defects coexist as the two types of “charges” (i.e., the electric charges and the topological charges) in the Josephson junction array [109, 18]. There is a duality between electric charges and topological point defects, that derives from the fact that the amplitude and phase angle parameters of Josephson junctions are quantum mechanical conjugate variables [95, 75]. As a consequence, these degrees of freedom can be modeled as a “coupled Coulomb-gas” that has the form of an $O(2)$ quantum rotor model in two-dimensions [74, 109].

Despite the prevention of conventional spontaneous symmetry breaking at T_{BCS} in restricted dimensions, low-temperature ordered states can develop by the minimization of the $O(2)$ quantum rotor model Hamiltonian energy. In restricted dimensions, in addition to a low-temperature state of superconductivity, a dual low-temperature state (of Cooper pairing) that is phase-incoherent can be obtained that is known as superinsulation [16, 35, 18]. In order to study the ordering process that is followed as the temperature of the JJA is lowered towards zero Kelvin, one must develop the full $O(2)$ quantum rotor Hamiltonian that models a Josephson junction array [39, 110]. The full Hamiltonian is developed by considering a system of $O(2)$ rotors that, reside on the sites of a two-dimensional lattice [17] and, interact across Josephson junctions.

The dynamics of each rotor are governed by its kinetic energy [17]. The kinetic energy of the system the form [17]:

$$\hat{T} = \frac{E_C}{2} \sum_i \hat{L}_i^2, \quad (2.9)$$

where E_C is the charging energy, $\hat{L}_i$ is the single rotor angular momentum component^c of the $O(2)$

^cIn general, an $O(n)$ quantum rotor possess $n(n-1)/2$ angular momentum components [17].

rotor (see Appendix G.1 for the derivation of $\hat{L}$) located at site i and the sum is over all rotors. Interesting effects arise by considering the potential energy that results due to coupling between nearest-neighbor order parameters [17]. The potential energy due to interactions between nearest-neighbors is:

$$\hat{V} = -E_J \sum_{\langle ij \rangle} \hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j, \quad (2.10)$$

where $\hat{\mathbf{n}}_j$ is the complex n -vector order parameter located at site j , E_J is the Josephson coupling energy between nearest-neighbor rotors, and the sum is over nearest-neighbors $\langle ij \rangle$. The full Hamiltonian can then be written as [74, 17] the sum of Eqn. 2.9 and Eqn. 2.10: $\hat{H} = \hat{T} + \hat{V}$.

In $O(n)$ quantum rotor models, the potential energy term is minimized by the establishment of global orientational phase-coherence; in contrast, the kinetic energy term favors localization of condensed particles and suppresses orientational phase-coherence [17, 75]. This is a consequence of the uncertainty relations that apply to the n -vector ordered system, which make the model a quantum model [111, 16, 75]. In charged JJAs (complex n -vector ordered systems), the uncertainty relation relates the uncertainty in the Josephson phase angle difference across a junction ($\Delta\phi$) and the uncertainty in the number of Cooper pairs transferred across a junction [95, 18, 16]:

$$\Delta\phi\Delta N \geq 1. \quad (2.11)$$

In the range of dominant potential energy, a phase-coherent ground state develops as $\Delta\phi$ takes on a minimized value (as a result of a defect-driven topological ordering transition). On the other hand, in the range of dominant kinetic energy, a phase-incoherent low-temperature state is realized in which $\Delta\phi$ is maximized such that ΔN is minimized by Eqn. 2.11.

The transition between the distinct low-temperature states, that can be realized for ordered systems that exist in restricted dimensions (for which $O(n)$ quantum rotor models apply), is driven by a non-thermal tuning parameter $g = E_C/E_J$ that enters the Hamiltonian. This tuning parameter describes the ability of condensed particles and topological defects (relative scalar phase angle differences) to move throughout the system via Josephson junctions [112]. This type of transition is known as a quantum phase transition (QPT) [17, 75], that occurs at a critical value of g and zero temperature (it is a transition between ground states). In charged $O(2)$ Josephson junction arrays, this QPT is the well-studied superconductor-to-superinsulator transition [17, 16, 18].

In the following sections (Section 2.2.1 and Section 2.2.2), the transitions to dual low-temperature states of planar $O(2)$ Josephson junction arrays are explored in the dual extreme (classical) limits: $E_C = 0$, and $E_J = 0$ (i.e., by the minimization of the potential energy term or the kinetic energy term). In Josephson junction arrays, a defect-driven topological ordering transition enables the development of a phase-coherent low-temperature state (superfluid) at finite temperatures that is of the Berezinskii-Kosterlitz-Thouless type [25]. By duality, in the limit that the parameters of

the Josephson junctions that comprise the array are tuned such that interactions between nearest-neighbor regions become negligible [18], the phase-incoherent low-temperature state (superinsulator) is obtained via a Berezinskii-Kosterlitz-Thouless topological transition in which Cooper pair charges bind with anticharges and become pinned within the system [113, 16]. By Eqn. 2.11, this implies that [18, 75, 17] the transport of condensed particles is eliminated such that $\Delta N = 0$. Frustration that can be induced into the ground state, on either side of g_C , is discussed in Section 2.2.1 and Section 2.2.2 for $g < g_C$ and $g > g_C$, respectively. A description of the phase diagram of charged $O(2)$ JJAs, in the proximity of the superconductor-to-superinsulator transition, is given in Section 2.2.3. Finally, the temperature dependence of the electronic transport properties are considered in Section 2.2.4.

2.2.1 Dominant potential energy:

(Classical) limit $g = 0$ (i.e., $E_C = 0$):

Classical Josephson junction arrays in the limit that $E_C = 0$, i.e., in the absence of kinetic energy, are physical realizations of the XY model and have been studied extensively as model systems that demonstrate a defect-driven Berezinskii-Kosterlitz-Thouless (BKT) topological phase transition towards an phase-coherent ground state. In this limit, although conventional orientational order is prevented below the bulk critical transition temperature, a ground state can nevertheless be obtained by the minimization of the potential energy term (Eqn. 2.10). To solve Eqn. 2.10, one must consider that the dot product of imaginary numbers (say, $\mathbf{A}$ and $\mathbf{B}$) generalizes to:

$$\langle \mathbf{A} | \mathbf{B} \rangle = \sum A_i B_i^\dagger \quad (2.12)$$

where the $\dagger$ over B_i represents the complex conjugate. This is an inner product, which is a generalization of the notion of the dot product between two imaginary vectors [114, 115]. By making use of the fact that $\hat{i}^2 = -1$, and using a standard cosine angle difference identity, the potential energy (Eqn. 2.10) can be written in its traditional form:

$$\hat{V} = -E_J \sum_{\langle ij \rangle} \cos(\theta_i - \theta_j), \quad (2.13)$$

where θ_i is the orientational of the complex order parameter located at site i .

In the limit of dominant potential energy, below the bulk critical transition temperature, a gas of misorientational fluctuations in θ throughout the system exists in the form of a plasma of spontaneously generated topological point defects [35]. These topologically stable defects, that belong to the fundamental homotopy group of $\mathcal{M}$, must undergo a topological ordering event [24, 25] in order to allow for the existence of a phase-coherent state at finite temperatures. In the phase-coherent state, not only do ordered regions within the two-dimensional array act as superconductors but their

separate phases will be strongly locked together by Josephson coupling [42, 38]. In the absence of frustration, i.e., for $g = 0$, the ground state is one of perfect phase-coherence (aligned $O(2)$ rotors) that develops by a topological ordering event within a balanced plasma [35] of topological point defects (i.e., the concentrations of point defects with opposite signs are equal).

These topologically stable point defect cores appear naturally within closed circuits of nearest-neighbors, and are spontaneously generated just below the bulk critical transition temperature (as the group $G = U(1)$ is broken locally). It is the large configurational entropy associated with isolated point defects that leads to their stability, at temperatures just below the bulk critical transition temperature, and thereby prevents global phase-coherence [35]. The critical BKT transition temperature, that marks the binding of topological point defects into low-energy (sum-0) pairs, may be determined by considering the competition between the configurational entropy and gradient potential energy of an isolated point defect (that is related to misorientations in θ throughout the system). This is facilitated within the context of the Helmholtz free energy:

$$F = V_{\text{gradient-isolated}} - TS_{\text{config}}. \quad (2.14)$$

The configurational degeneracy [41] is related to the possible placement of the isolated point defect core within the system of size L . In two-dimensions, an isolated point defect core can be located within any elementary closed circuit of nearest-neighbors. Thus, the configurational degeneracy may be approximated^d as $(L/a)^2$ where a is the radius of the point defect core; the configurational entropy of an isolated point defect in two-dimensions is therefore $S_{\text{config}} = 2k_B \ln \left(\frac{L}{a} \right)$. The gradient potential energy ($V_{\text{gradient-isolated}}$) may be determined by considering a continuum expression of Eqn. 2.13.

In order to develop a continuum expression of the potential energy (Eqn. 2.13), a spin-wave approximation [71] must be applied to Eqn. 2.13. This is facilitated by assuming that the orientation of the rotors varies smoothly from site to site. In order to apply the spin-wave approximation, one expands the cosine in the Hamiltonian (Eqn. 2.13) by the first two terms in its Taylor series expansion, i.e., $1 - \frac{1}{2}(\theta_i - \theta_j)^2$. Taking the sum over nearest-neighbors corresponds to the discrete Laplace operator [116], which can be expressed in terms of partial derivatives through: $\theta_i - \theta_j = \partial_x \theta$ for sites i and j which are nearest-neighbors. This leads to a continuum expression [71] of Eqn. 2.13:

$$V_{\text{gradient-isolated}} = \frac{E_J}{2} \int d^2\mathbf{r} (\nabla\theta)^2 \quad (2.15)$$

where $V_{\text{gradient-isolated}}$ is the potential energy that is related to misorientations in θ throughout the system (from the ground state of perfectly aligned rotors). The critical properties of this system have been shown to be dominated by the long-range effects associated with misorientational fluctuations, in the form of spin-wave excitations and topologically stable point defects [25, 71]. Although the

^dThe actual configurational degeneracy is $L^2/(\pi a^2)$, where πa^2 is the area of the $\pi_1(S^1)$ defect core in 2D.

ground state of this system is unstable against low-energy spin-wave excitations [29, 33], one may characterize a topological ordering transition by considering the existence of topological point defects in the order parameter field [25].

The far-field gradient potential energy due to the presence of a vortex point defect core is calculated using Eqn. 2.15. The field configuration that applies to a vortex point defect [21] is:

$$\theta = k\phi, \text{ where, } \phi = \tan(y/x) \quad (2.16)$$

and k is the winding number topological invariant of the vortex. It follows, using a cylindrical gradient^e, that $\nabla\theta = \frac{k}{r}e_\phi$ where $r = \sqrt{x^2 + y^2}$. The gradient potential energy of the point defect is then easily calculated as [21]:

$$V_{\text{gradient-isolated}} = \frac{E_J}{2} k^2 \int_0^{2\pi} \int_a^L \frac{r}{r^2} dr \equiv \pi E_J k^2 \ln\left(\frac{L}{a}\right). \quad (2.17)$$

By this expression, the energy of the isolated point defect increases logarithmically with the size of the system^f; at large distances from the isolated defect core, the gradient potential energy produced is inversely proportional to the distance [99]. As a consequence, the probability of isolated topological point defects appearing in large systems will be almost nonexistent at low-temperatures [25, 99, 21].

While isolated point defects cause energetically costly distortions far from their core, that diverge logarithmically with the size of the system (Eqn. 2.17), bound pairs of point defects with equal and opposite topological winding number (i.e., sum-0) do not. This is a consequence of the Abelian nature of point defects, such that a path Γ' that encloses two single point defects with winding numbers k_1 and k_2 is homotopic to the two paths enclosing the point defects individually. Sum-0 pairs are topologically equivalent to the uniform state [21], and are energetically preferred below a critical finite temperature [25]. These sum-0 bound pairs allow for a rigid phase-coherent low-temperature state to develop below a critical transition temperature, by minimizing the uncertainty in the real scalar phase angle parameter of the orientational order parameter throughout the system. In fact, topological point defects with equal and opposite sign have the potential to be confined logarithmically. This is because the gradient energy associated with the paired configuration decreases logarithmically as the defects that comprise the pair are brought together [21], as:

$$V_{\text{gradient-pair}} \propto -2\pi E_J \log\left(\frac{a}{r}\right), \quad (2.18)$$

^eThe cylindrical gradient is: $\nabla\theta = \frac{\partial\theta}{\partial r}e_r + \frac{1}{r}\frac{\partial\theta}{\partial\phi}e_\phi$.

^fSimilarly, strain energy owing to the distortion around a dislocation line in crystalline materials generates an elastic energy (per unit length) [47]: $V_{\text{gradient}} = \frac{1}{2} \int_0^{2\pi} \int_a^L (\sigma_{\theta z} e_{\theta z} + \sigma_{z\theta} e_{z\theta} r dr d\theta)$ where the factor 1/2 enters because the stress builds up from zero to the final values during the displacement process. The integration is performed from the dislocation core radius (a) to an outer radial limit (L). For a screw dislocation: $e_{\theta z} = e_{z\theta} = b/4\pi r$ and $\sigma_{\theta z} = \sigma_{z\theta} = Gb/2\pi r$ where b is the Burger's vector (analogous to the winding number k), G is the shear modulus and r is the distance from the central line of a straight dislocation [47]. Taking the integral, $V_{\text{gradient}} = \frac{Gb^2}{4\pi} \ln\left(\frac{L}{a}\right)$.

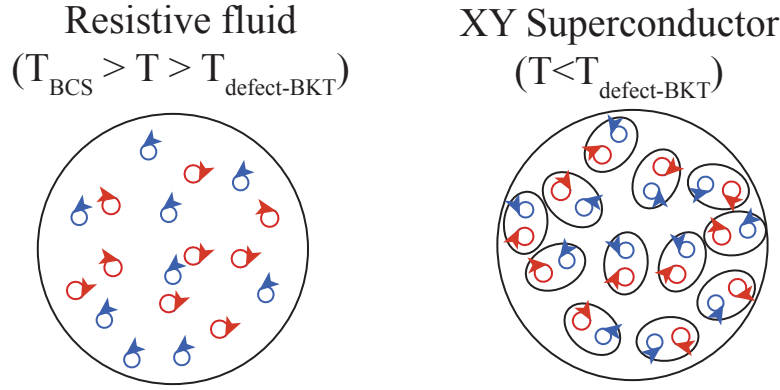


Figure 2.9: In planar complex n -vector ordered systems, below the bulk critical transition temperature, there is the possibility for the existence of a gas of misorientational fluctuations in the form of spontaneously generated point defects. These point defects cannot be made to disappear, but they can form low-energy sum-0 bound pairs below a critical BKT transition temperature that allow for the existence of a phase-coherent low-temperature state.

where the defects that comprise the pair are separated by a distance r . Therefore, topological point defects in two-dimensions can be thought of as behaving like $+1$ and -1 elementary charges in a 2D Coulomb gas [42, 117] of logarithmic interactions. This picture of logarithmically interacting point defects leads directly to the Berezinskii-Kosterlitz-Thouless picture [25] of a defect-driven transition.

Since both the energy and entropy depend on the system size logarithmically, the energy term will dominate the free energy at low-temperatures [25]. The finite temperature that marks the binding of isolated point defects into bound pairs is determined where the total free energy of an isolated point defect (of strength $|k| = 1$):

$$F = \ln \left(\frac{L}{a} \right) (\pi E_J - 2k_B T), \quad (2.19)$$

crosses a zero point. In Eqn. 2.19, the terms in $\ln \left(\frac{L}{a} \right)$ have been collected, and a constant core energy (associated with the destruction of the order parameter at the core of the defect) has been neglected because it becomes negligible in the thermodynamic limit ($L \rightarrow \infty$). Point defects should only occur in low-energy bound pairs of opposite signs for temperatures below:

$$T_{\text{defect-BKT}} = \frac{\pi}{2k_B} E_J. \quad (2.20)$$

This topological ordering event allows for the development of a phase-coherent low-temperature BKT state, for $T < T_{\text{defect-BKT}}$. This topological ordering event is depicted schematically in Fig. 2.9.

Monte-Carlo simulations of an $O(2)$ quantum rotor model in two-dimensions In this section, the thermodynamic response functions of the classical two-dimensional $O(2)$ rotor model are studied using numerical Monte-Carlo simulations. The two-dimensional simulations presented in this

section were performed in order to benchmark our code against previously reported results from the literature [118, 119, 120, 121]; this is important to do since we will extend this Monte-Carlo code into four-dimensions in Section 3. By the minimization of potential energy (Eqn. 2.13), a perfectly phase-coherent state is obtained at zero Kelvin. Square lattices with periodic boundary conditions are considered for system sizes $L \times L$, for: $L = 8, 10, 12, 14, 16$. Within the 2D array, initial order parameter field configurations (of complex n -vector order parameters) are constructed by generating randomized distributions of the scalar phase angle parameters (θ) throughout the system. At each temperature, 2000 Monte-Carlo steps are taken to achieve thermal equilibrium and 10000 subsequent steps are used to collect the statistical data that is required to compute physical observables.

On each MC step, $N = L \times L$ rotors are selected in turn (and at random) and an attempt is made to change its state. As the simulation proceeds, physical observables of interest are computed. In general, the nature of ordering transitions may be determined by considering the behavior of thermodynamic response functions such as heat capacity and susceptibility [33, 120, 71, 122]. The susceptibility is defined using fluctuations in the order parameter, and the heat capacity is defined as the fluctuations in the entropy per site. Importantly, the order parameter is the first derivative of the free energy with respect to an external field, and the entropy is the first derivative of the free energy with respect to temperature. The fluctuations of a quantity X can be determined by changing the free energy while keeping the thermodynamic conjugate variable of X , called Y , fixed [123]:

$$\langle X \rangle = -\frac{\partial F}{\partial Y} \quad (2.21)$$

$$\chi = \frac{\partial \langle X \rangle}{\partial Y} = -\frac{\partial^2 F}{\partial Y^2} = \beta[\langle X^2 \rangle - \langle X \rangle^2] \quad (2.22)$$

where $\beta = 1/k_B T$ is the thermodynamic *beta* (k_B is Boltzmann's constant).

Conventionally, in Monte-Carlo simulations, the susceptibility and order parameter are measured as the average susceptibility per site and the average order parameter per site, so that:

$$\langle \tilde{\mathbf{n}} \rangle = \frac{1}{N} \sum_i^N \hat{\mathbf{n}}_i, \quad (2.23)$$

where $\hat{\mathbf{n}}_i$ is the orientational order parameter, located at site i , in a system of N rotors. It follows that susceptibility, i.e., fluctuations in the order parameter, can be evaluated as:

$$\chi = N\beta[\langle \tilde{\mathbf{n}}^2 \rangle - \langle \tilde{\mathbf{n}} \rangle^2]. \quad (2.24)$$

Likewise, heat capacity (C_V) is proportional to the first derivative of the entropy (S) with respect to temperature, where the entropy is the (negative) first derivative of the free energy with respect to temperature. The heat capacity may also be defined as the fluctuations in the total energy of the

system (E), which is more convenient to calculate. This is owing to the relationship between energy and entropy:

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{N,V} \equiv \left(\frac{\partial E}{\partial T} \right)_{N,V}. \quad (2.25)$$

This relationship can be seen more clearly by a decomposition into partial derivatives:

$$\left(\frac{\partial E}{\partial T} \right)_{N,V} = \left(\frac{\partial E}{\partial S} \right)_{N,V} \cdot \left(\frac{\partial S}{\partial T} \right)_{N,V} = T \left(\frac{\partial S}{\partial T} \right)_{N,V} \quad (2.26)$$

where $\frac{\partial E}{\partial S} = T$. The proportionality between specific heat and energy fluctuations may then be written as:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \equiv k_B \beta^2 [\langle E^2 \rangle - \langle E \rangle^2]. \quad (2.27)$$

Topological ordering transitions have special properties [33] that make them distinct from first and second order phase transitions, which exhibit discontinuities in the first and second derivatives of the free energy (respectively). In first order transitions, there is a discontinuity in the order parameter (first derivative of the free energy) at the critical transition temperature. In second order transitions, the discontinuity is in the second derivative of the free energy and not in its first derivative. Thus, there is a major difference in the behavior of the specific heat around the transition temperature

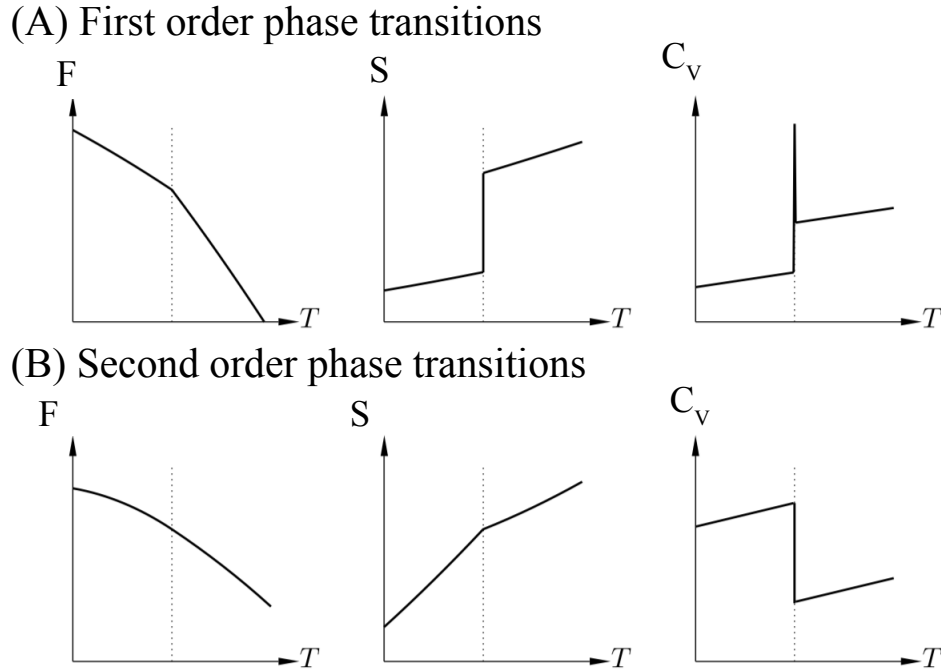


Figure 2.10: (A) First order (discontinuous) and, (B) second order (continuous) phase transition behavior of the free energy (F), entropy ($S = -(\partial F / \partial T)_V$) and heat capacity $C_V = -T(\partial^2 F / \partial T^2)$. [Image from Ref. [124]].

in first and second order transitions. In first order transitions, the specific heat diverges to infinity at the transition (latent heat) whereas in second order transitions there is a finite discontinuity at the transition. The first and second derivatives of the Helmholtz's free energy (F), with respect to temperature, are plotted schematically for first and second order phase transitions in Fig. 2.10.

In contrast to first and second order phase transitions, topological ordering transitions [71] are known as infinite-order phase transitions [125]. Infinite-order phase transitions show no *regular* singularity [33] in any finite derivative of the free energy (in an Ehrenfest sense). Therefore, despite being continuous, topological ordering transitions cannot be identified as second order phase transitions because the usual critical exponents that characterize second order continuous phase transitions cannot be defined [33]. For example, the correlation length in second order phase transitions follows a power law: $\zeta \sim \tau^{-\nu}$ where ν is a critical exponent and $\tau = (T - T_C)/T_C$ is a reduced temperature. This power law, which is responsible for the scaling behavior seen in second-order phase transitions, does not apply to topological ordering transitions [71]. Instead, in topological ordering transitions, the correlation length has an exponential dependence on the temperature on approaching the topological ordering transition from above [71, 33]: $\zeta \sim \exp^{\tau^{-1/2}}$. It is this exponential dependence of the correlation length, on reduced temperature, that leads to the interesting behavior of the thermodynamic response functions [71] in the vicinity of topological ordering transitions. The defect-driven Berezinskii-Kosterlitz-Thouless transition, in planar XY systems [24, 25], behaves in this way.

The observed heat capacity and susceptibility are plotted versus temperature in Figure. 2.11 (A) and (B), for the various lattice sizes considered here. The heat capacity (second derivative of the free energy w.r.t. temperature) and the susceptibility (second derivative of the free energy w.r.t. an external field) remain smooth and finite through the transition. This gives an indication that the transition is not a first or second order transition in the Ehrenfest sense [126]. The smooth maximum in the heat capacity, that occurs in the vicinity of the topological ordering transition in planar $O(2)$ rotor models [127, 33, 128], is associated with the entropy that is liberated by the unbinding of vortex pairs [127, 21].

Moreover, it is important to consider the role that size-effects play in the behavior of the thermodynamic response functions in the vicinity of the ordering transition. The observed heat capacity as a function of temperature does not depend on system size, for large enough systems. This is typical behavior in the vicinity of topological ordering transitions [120, 121]. In contrast, the susceptibility response function (χ) is proportional [71, 33] to the system size over all system sizes. This is due to the scaling relationship between χ and a correlation length (ζ) (Kosterlitz [71] 1974):

$$\chi \approx \zeta^{2-\eta} \quad (2.28)$$

where η is the critical exponent of the BKT transition in two-dimensions. The critical exponent η depends on temperature as [33]: $\eta(T) = \frac{k_B T}{(2\pi)E_J}$ (where (2π) is the circumference of the measuring

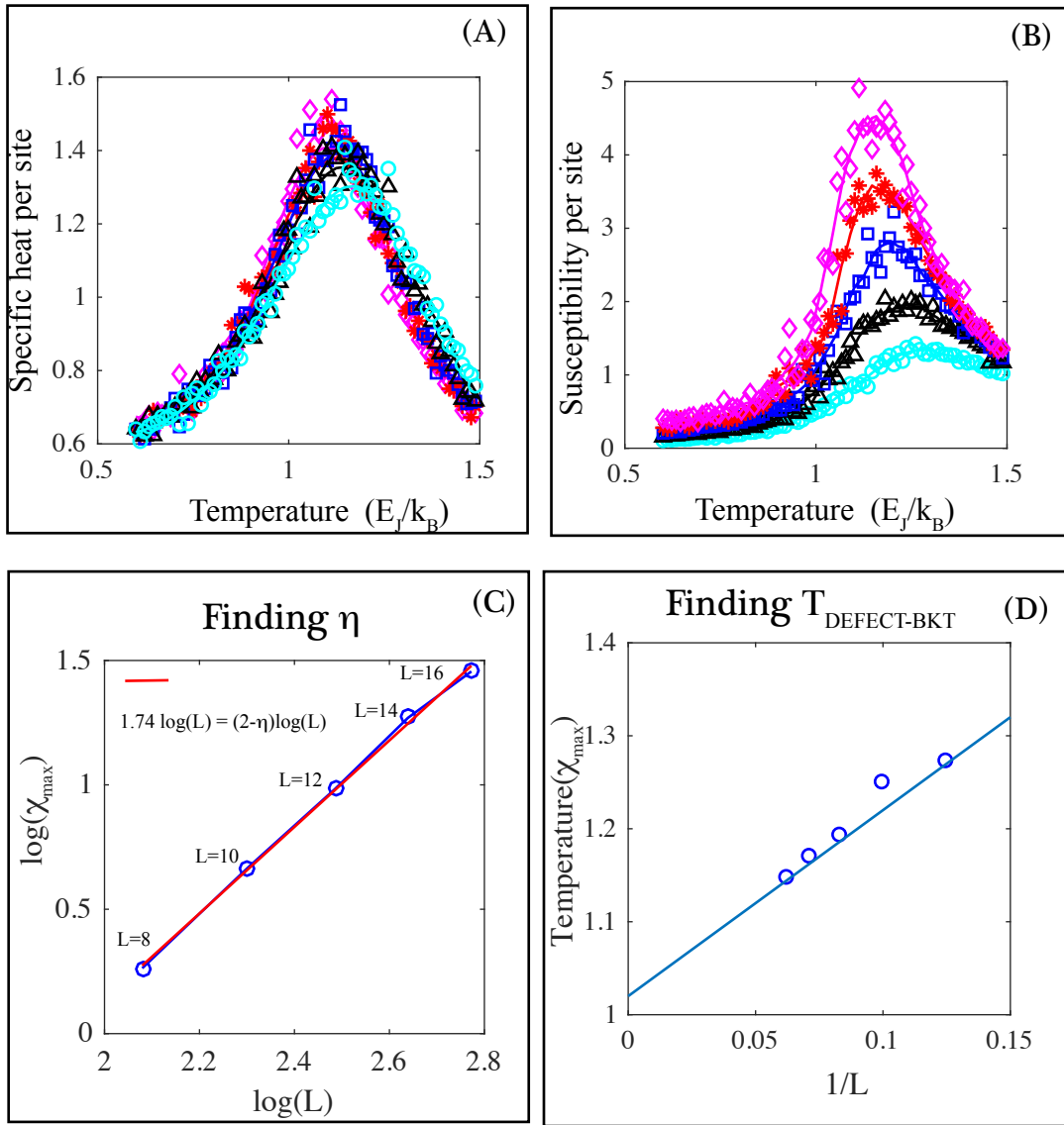


Figure 2.11: (A) Specific heat and, (B) susceptibility per site versus temperature for various lattice sizes ($L \times L$): $L = 8, 10, 12, 14, 16$ ($\circ, \triangle, \square, *, \diamond$). (C) Planar complex n -vector ordered system: $\chi_{\max}$ versus system length (L) on a log-log scale. The slope of a straight line through the data allows for the determination of the critical exponent η at the transition temperature. (D) Finite size effects on the location of the peak of susceptibility, in order to estimate $T_{\text{defect-BKT}}$ in the thermodynamic limit.

circuit that surrounds a vortex point defect). The value of $\eta = 1/4$ allows one to recover [71, 122, 129, 130, 33] the definition of the critical BKT transition temperature (Eqn. 2.20).

The necessary condition for the stability of the phase-coherent low-temperature state is that $\eta(T) \leq 1/4$, which indicates that point defects are only excited as bound pairs [99, 129]. As the topological ordering transition temperature is approached from above, the correlation length rapidly approaches the system size L . By Eqn. 2.28, the maximum of the susceptibility is proportional to

the system size as [120, 122]:

$$\chi_{\max} \approx L^{2-\eta}. \quad (2.29)$$

Due to the relationship between $\chi_{\max}$ and the system size L (Eqn. 2.29), size effect studies may be utilized in order to determine the critical exponent η at the defect-driven topological ordering transition. In particular, on a logarithmic scale, one obtains a linear fit [122, 120, 71]: $\log(\chi_{\max}) = (2 - \eta) \log(L)$. Such analyses have been performed previously by a number of authors [120, 122] and (as stated earlier) are implemented here as a benchmark.

The peak values of the susceptibility thermodynamic response function that have been observed using MC simulations (Fig. 2.11(B)) are plotted on a log-log scale in Figure 2.11(C). A linear fit to the slope of the data gives an estimation of the critical exponent at the transition temperature as $\eta = 0.26 \pm 0.04$. This is near to the anticipated value of $\eta = 1/4$. Furthermore, an estimation of the critical topological ordering transition temperature is made by considering the effect of size on the location of the maximum in susceptibility Fig. 2.11(D). With infinite system sizes, the peak location extrapolates to approximately $1.0 E_J/k_B$ where E_J is the coupling energy between nearest-neighbors [118]. This is near to the anticipated value [118, 131, 119] of $T_{\text{defect-BKT}} = 0.89 E_J/k_B$. This provides evidence that the heat capacity maximum is dislocated from the topological ordering transition temperature (the heat capacity peaks at a temperature that is larger than the transition temperature [121, 21, 122]), which is yet another characteristic of a topological ordering transition [21, 33, 122, 121]. These simulation results give an indication that the system of $O(2)$ rotors in two-dimensions has undergone a defect-driven BKT transition [25, 71] towards a ground state of perfectly aligned rotors.

Phase angle frustration (magnetic frustration, i.e., $g < g_C$)

In the limit of dominant potential energy (i.e., $g < g_C$), $O(2)$ Josephson junction arrays exhibit a spectrum of ground states as a function of phase angle frustration. In charged systems, this phase angle frustration can be introduced by the application of a uniform magnetic field [75, 75, 110] H_0 . An applied magnetic field biases the concentration of topological point defects [35], that exist below T_{BCS} . In such cases, signed topological point defects (through which a magnetic flux quantum penetrates) persist to the ground state [110]. That is, in the presence of an applied magnetic field, magnetic frustration will force that the ground state is no longer one of uniform orientation of the order parameter, but instead θ_i will vary from node to node [110]. Explicitly, in the presence of magnetic frustration, the Hamiltonian energy is minimized by the incorporation of a periodic configuration of topological point defects ($\pi_1(S^1)$) into the ground state. This non-trivial configuration is similar to the Abrikosov vortex lattice that develops in a type-II superconductor above a critical applied magnetic field [97, 77].

In the presence of an applied magnetic field, the classical expression of the potential energy

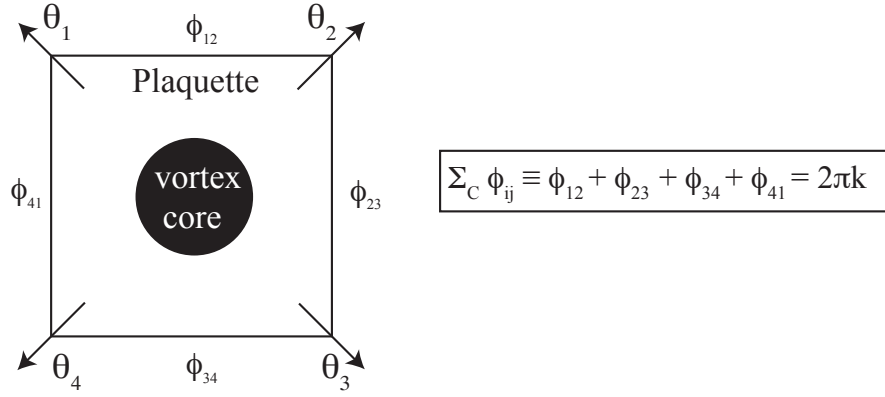


Figure 2.12: $\pi_1(S^1)$ vortex point defect configuration of single strength ($k = +1$) is shown here. A vortex point defect is characterized by the sum of relative scalar phase angles around an elementary plaquette, i.e., $\sum_C \phi_{ij} \equiv \phi_{12} + \phi_{23} + \phi_{34} + \phi_{41} = 2\pi k$ where $k = 0, \pm 1, \pm 2, \dots$ is the winding number of the point defect [76, 26]. The defect core, located at the plaquette center, is in the normal state.

(Eqn. 2.13) must be modified so that the difference between scalar phase angle parameters becomes gauge invariant between neighboring nodes [76, 110]. This is accomplished by including a link parameter [76, 77] Ψ_{ij} :

$$\hat{V}_{g < g_C} = -E_J \sum_{\langle ij \rangle} \cos(\theta_i - \theta_j - \Psi_{ij}), \quad (2.30)$$

where Ψ_{ij} is a bond angle (between nearest-neighbors $\langle ij \rangle$). The bond angle Ψ_{ij} is defined such that the sum around an elementary plaquette of nearest-neighbors [110, 76] equals $2\pi g$. In cases of uniform frustration, g is constant over the entire array. By way of illustration, Figure 2.12 depicts an isolated point defect configuration (of single strength, $k = +1$). The defect is discretized on a square lattice, for simplicity, and is characterized by the sum of relative scalar phase angles on taking a circuit around an elementary plaquette of nearest-neighbors (1-4):

$$\sum_C \Psi_{ij} = \Psi_{12} + \Psi_{23} + \Psi_{34} + \Psi_{41} = 2\pi g. \quad (2.31)$$

The number g is a constant, referred to as the uniform frustration of the model [76], is related to the uniform applied transverse magnetic field H_0 as [110, 76]: $g = H_0 a^2 / \Phi_0$, where Φ_0 is the magnetic flux quantum and a^2 is the area of an elementary plaquette within the array.

The vortex cores are constrained to sit at the centers of plaquettes, because the energy associated with the topological point defect is at a minimum when the defect core sits in the middle of the plaquette [75]. The parameter g describes the number of flux quanta per “unit cell” of the array, on average. In the limit that the frustration constant is unity, i.e., for $g = g_C = 1$, there is a single flux quanta within each unit cell on average. Ground state vortex configurations [110] for some simple rational fractions of g , between $g = 0$ and $g = g_C = 1$, are shown in Fig. 2.13. The classical case of

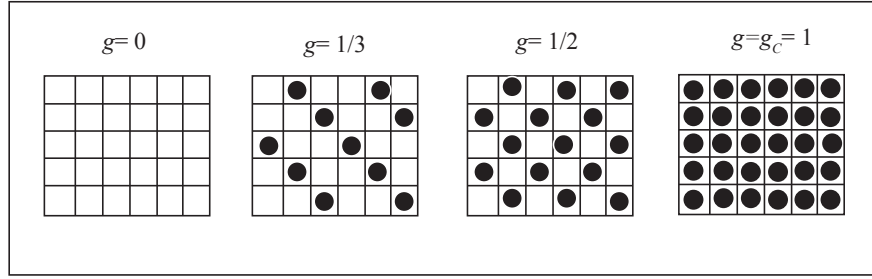


Figure 2.13: In the absence of magnetic frustration (i.e., $g = 0$) no topological defects persist to ground state of perfectly aligned rotors. In the limit of small g less than g_C , the phase-coherent ground state will contain a periodic configuration of signed point defects in the phase angle θ (solid dots), whose core is located at the center of a closed circuit of nearest-neighbors.

$g = 0$ corresponds to a ground state of perfectly aligned order parameters. In the limit of non-zero g , i.e., in an applied magnetic field^g, magnetic frustration is incorporated into the phase-coherent ground state [77, 110]. In these scenarios, the ground state will no longer be perfectly phase-coherent [76, 77] (i.e., with all $\theta_i(\mathbf{r})$ equal) and will now consist of a periodic configuration of vortex point defects.

2.2.2 Dominant kinetic energy:

(Classical) limit $1/g \rightarrow 0$ (i.e., $E_J = 0$):

If one tunes the parameters of the Josephson junction array towards the alternate extreme limit (i.e., $1/g \rightarrow 0$), a dual low-temperature ordered state is obtained by the minimization of the kinetic energy term in the absence of interaction effects. The kinetic energy is minimized in the limit that the orientation of each rotor is maximally uncertain [17]. By the uncertainty principle [95, 16] (Eqn. 2.11), this implies that condensed particles will become pinned within the system in order to remove uncertainty in the number of condensed particles transferred across junctions within the array [18]. In the range of dominant kinetic energy, at temperatures just below the bulk critical transition temperature, thermal fluctuations generate a gas of condensed particles [113, 16, 132, 18] (instead of topological point defect charges). In the absence of potential energy effects, in order to conserve overall charge neutrality, excessive Cooper pairs and an equal number of “anti-Cooper pairs” (that represent a local deficit of Cooper pairs [133, 18]) are generated by thermal fluctuations. This is a Coulomb gas with 2D interactions [113, 18].

^gAnd hence, with the addition of the link parameter Ψ_{ij} to the cosine argument.

In three-dimensions, Coulomb's law states that the force between electrically charged particles is:

$$F = \frac{1}{4\pi\epsilon} \cdot \frac{q_1 q_2}{r^2} \quad (2.32)$$

where the factor $4\pi r^2$ in the denominator expresses the surface of a virtual sphere of radius r . The potential interaction energy between charges in three-dimensions ($F = -\nabla V(r)$) is therefore:

$$V(r) = \frac{q_1 q_2}{4\pi\epsilon} \cdot \frac{1}{r}. \quad (2.33)$$

On the other hand, in two-dimensional systems, Eqn. 2.32 is modified:

$$F = \frac{1}{2\pi\epsilon} \cdot \frac{q_1 q_2}{r} \quad (2.34)$$

where $2\pi r$ is the area of a virtual circle. In this two-dimensional case, the potential interaction energy between charges is [134, 18]:

$$V(r) = -\frac{q_1 q_2}{2\pi\epsilon} \cdot \log\left(\frac{r}{r_0}\right), \quad (2.35)$$

where r_0 is an arbitrary scaling length that is commonly set to $r_0 = a$ (a is the lattice constant of the JJA). For charges of opposite sign, Eqn. 2.35 grows logarithmically with their separation distance as $V(r) \propto \log\left(\frac{r}{r_0}\right)$. Therefore, by the 2D Coulomb law, interactions between charges are logarithmic [113, 74] and one can expect that these charges will form bound pairs below a critical transition temperature. Thus, JJAs possess an intrinsic duality [18] between logarithmically interacting topological charges [42] ($g < g_C$) and logarithmically interacting electrical charges ($g > g_C$).

In the range of dominant kinetic energy (i.e., $g > g_C$), a phase-incoherent low-temperature state is obtained (on lowering the temperature below a critical value $T_{\text{dual-BKT}}$) as a result of a Berezinskii-Kosterlitz-Thouless type transition within the 2D Coulomb gas of condensed particles (Cooper pair electric charges) [113, 18, 135]. This transition is dual to the defect-driven BKT transition [25, 24], that allows for the realization of a low-temperature phase-coherent state in the range of dominant potential energy [75]. For temperatures below $T_{\text{dual-BKT}}$, only bound states (charge dipoles) are present [113]; for temperatures above $T_{\text{dual-BKT}}$, free Cooper pairs are generated by thermal fluctuations [113]. The dual BKT-transition in the 2D Coulomb gas of condensed particles occurs at a temperature that is proportional to the charging energy [75, 136, 113]: $T_{\text{dual-BKT}} \propto E_C/k_B$.

In the extreme limit that $1/g \rightarrow 0$, there is a complete localization of condensed particles within charge dipoles at temperatures below $T_{\text{dual-BKT}}$. This completely eliminates the uncertainty in the number of Cooper pairs that are transferred across junctions throughout the system (i.e., $\Delta N = 0$). By the uncertainty principle, this implies that the kinetic energy term is minimized in the low-temperature state for which each orientation θ_i is maximally uncertain [17, 18]. Localization of electric charges, within charge dipoles that are confined within separate sites of the array, causes the

phase-incoherent low-temperature state to exhibit electrical transport properties that are dual to the superconductor. This low-temperature state, known as superinsulation, has “zero electrical conductivity” at finite temperatures [16, 18]. The duality between low-temperature states of Cooper pairing (i.e., superconductivity and superinsulation), which breaks the traditional schema that the only result of Cooper pairing is the state that exhibits “zero electrical resistance” at finite temperatures, is a consequence of complex n -vector ordering in restricted dimensions [18].

Number frustration (charge frustration, i.e., $g > g_C$)

The duality between condensed particles and topological point defects (in the coupled 2D Coulomb gas representation [75, 75]) manifests itself in the manner that frustration effects can be incorporated into the low-temperature ordered states of $O(2)$ Josephson junction arrays. Distinct frustrated low-temperature states are achieved in the dual limits, i.e., $g > g_C$ and $g < g_C$, by introducing frustration into either the scalar phase angle field or into the number density field of condensed particles [74]. In the limit that $g < g_C$ (dominant potential energy), the application of a uniform transverse magnetic field [110] leads to scalar phase angle frustration that forces the development of a periodic configuration of $\pi_1(S^1)$ point defects (magnetic vortices) into the 2D superconductor ground state. On the other hand, for large g greater than g_C , it is the application of a uniform gate voltage that leads to charge frustration [75, 16]. The application of a voltage introduces charge frustration as a background of Cooper pair charges that are not bound into charge dipoles.

The presence of charge frustration (of the 2D superinsulator) is related to magnetic frustration (of the 2D superconductor), by the duality between topological charges and Cooper pair charges [137, 16, 18]. In the presence of uniform frustration, the relevant plasma that exists just below the bulk critical transition temperature (i.e., 2D vortex-antivortex, or 2D charge-anticharge) will become biased towards the concentration of a particular sign. With increasing frustration in either limit (i.e., as g_C is approached from $g = 0$ or $1/g \rightarrow 0$), the relevant plasma becomes increasingly biased towards a particular sign. The excess concentration of topological defects (of a single sign) are unable to form low-energy bound pairs (i.e., sum-0 point defect dipoles, or charge dipoles) at the relevant Berezinskii-Kosterlitz-Thouless transition temperature. These unpaired degrees of freedom persist to zero Kelvin. A large enough applied magnetic field will completely bias the plasma of topological defects, leading to the prevention of vortex pair formation and, suppressing the superconducting ground state. By duality, a large enough applied voltage completely liberates all charge dipoles into free Cooper pairs [132, 16, 117] driving the system towards the superconducting state.

2.2.3 $O(2)$ phase diagram: superconductor-to-superinsulator transition

A sketch of the phase diagram of charged $O(2)$ JJAs, across the superconductor-to-superinsulator transition [18], is shown in Figure 2.14. The diagram is plotted as temperature versus the non-

thermal tuning parameter that characterizes a Josephson junction: $g = E_C/E_J$, where E_C is the charging energy and E_J is the Josephson coupling energy between neighboring superconducting islands. A critical value of the tuning parameter ($g = g_C$ where $E_C \approx E_J$), identifies the point at which the kinetic and potential energy terms in the $O(2)$ quantum rotor model Hamiltonian are comparable. The fact that these two competing energy terms (kinetic and potential) cannot be minimized simultaneously [17, 75] makes the model a quantum model, by leading to the existence of a zero-temperature (quantum) phase transition between distinct ground states at g_C .

In considering the phase diagram of charged $O(2)$ JJAs (Fig. 2.14), it is useful to recast the uncertainty relation [95, 16] that applies to the complex order parameter (Eqn. 2.11) as a duality between topological point defect charges ($\pi_1(S^1)$) and Cooper pair electrical charges. In the limit of dominant potential energy ($g < g_C$), a gas of misorientational fluctuations prevents the existence of a conventional disorder-order phase transition at finite temperatures. A phase-coherent low-temperature state is obtained, below a critical finite temperature $T_{\text{defect-BKT}}$ (Eqn. 2.20), by a defect-driven Berezinskii-Kosterlitz-Thouless transition. The topological ordering transition in planar charged JJAs separates a resistive state from the low-temperature phase-coherent superconducting state [18]. On the other hand, in the limit of dominant kinetic energy ($g > g_C$), a phase-incoherent low-temperature state is obtained via a dual Berezinskii-Kosterlitz-Thouless transition within a 2D Coulomb gas of condensed particles [113, 75] that occurs at a temperature on the order of E_C .

With increasing frustration, i.e., as g tends to g_C from either extreme limit (i.e., $g = 0$ or $1/g \rightarrow 0$), the critical BKT transition temperatures become suppressed to zero at the superconductor-to-superinsulator transition (where $E_J \approx E_C$). Within this framework, for finite g less than g_C , the frustrated phase-coherent low-temperature state (i.e., superconducting) can be viewed as a Cooper pair condensate together with an array of frustration-induced magnetic vortex point defects [138, 18]. By duality, the frustrated phase-incoherent low-temperature state (i.e., superinsulating) consists of a condensate of magnetic vortices^h and background Cooper pair charges that do not belong to charge dipoles [133, 75, 138, 18]. Below, each important state of matter on the $O(2)$ phase diagram that applies to charged Josephson junction arrays (Fig. 2.14, *I, II, III, IV*) and its process of formation is discussed.

1. Region I [$T_{BCS} > T > T_{\text{defect-BKT}}$, $g < g_C$ (i.e., $E_C < E_J$)]. Just below the bulk critical transition temperature T_{BCS} , the system develops an amplitude of a complex order parameter within separate superconducting islands that are weakly-linked. However, in this temperature range, the whole array remains in a resistive state owing the existence of a gas of misorientational fluctuations that prevents the development of conventional orientational order at finite temperatures. This gas of misorientational fluctuations takes the form of a plasma of unbound

^hTopological defects are bosons, and any number can exist in the same state. At low energies, the vortices in the system exist in the same lowest energy state – creating a Bose-Einstein condensate.

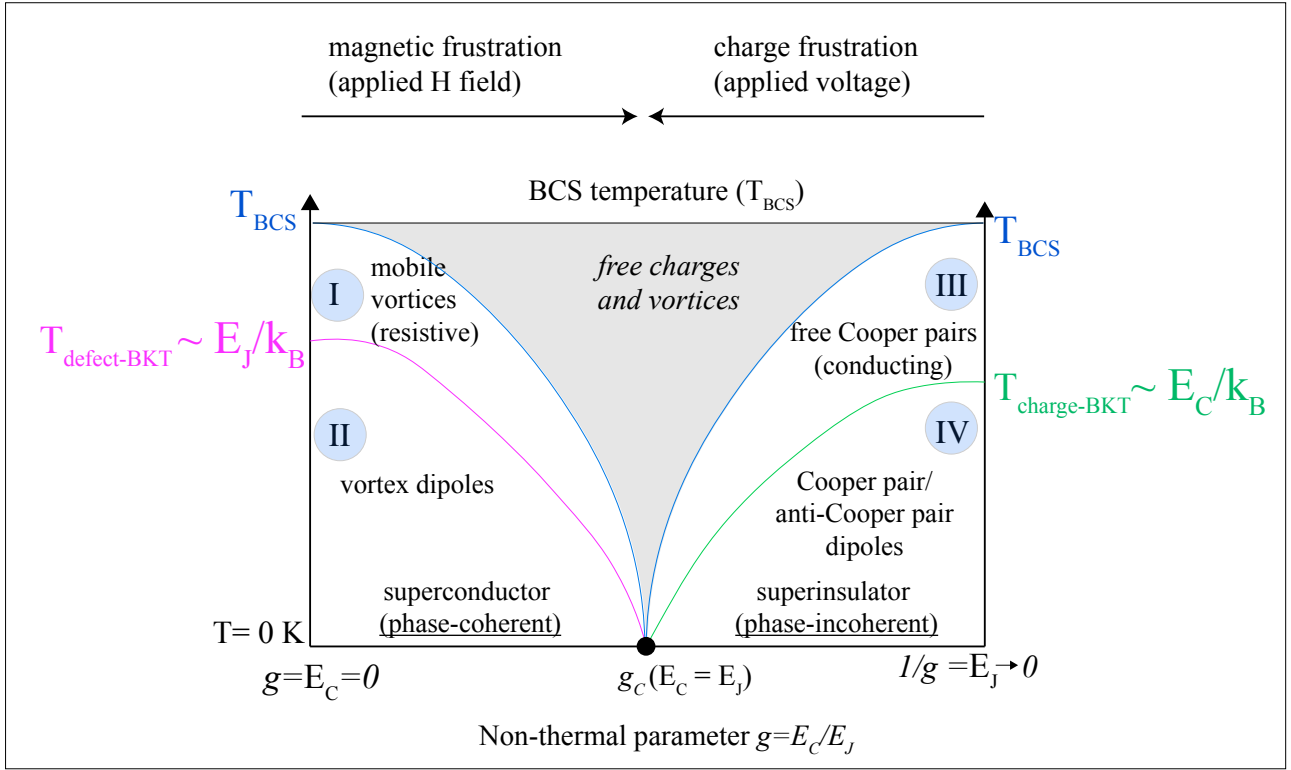


Figure 2.14: Schematic phase diagram that applies to $O(2)$ Josephson junction arrays, plotted as temperature (T) versus the non-thermal tuning parameter ($g = E_C/E_J$).

magnetic vortex point defects that can diffuse freely and thereby prevent global phase coherence. In the presence of magnetic frustration (i.e., an applied magnetic field), the plasma of topological point defects that characterize the system becomes biased towards those that carry a particular sign. In the limit of critical frustration, i.e., $g = g_C$, the temperature that marks the defect-driven Berezinskii-Kosterlitz-Thouless transition ($T_{\text{defect-BKT}}$) is suppressed to zero.

2. Region II [$T < T_{\text{defect-BKT}}$ and $g < g_C$ (i.e., $E_C < E_J$)]. For temperatures below $T_{\text{defect-BKT}}$, topological point defects ($\pi_1(S^1)$ magnetic vortices) should only appear in bound pairs of opposite sign. For any given g less than g_C , the ordered system that exists below $T_{\text{defect-BKT}}$ is a 2D phase-coherent superconductor. The bound pairs of topological point defects are elementary excitations from the 2D superconducting ground state. For finite g less than g_C , the 2D superconducting ground state is magnetically frustrated such that a vortex lattice of unpaired topological defects is a structural component at zero Kelvin (Fig. 2.13). The spacing between magnetic vortices is inversely proportional to the applied magnetic field. Above a critical value of magnetic frustration, the ground state is no longer phase-coherent and 2D superconductivity is entirely suppressed.
3. Region III [$T_{BCS} > T > T_{\text{dual-BKT}}$ and $g > g_C$ (i.e., $E_J < E_C$)]. The system is a conductor that

exhibits exponentially low electrical conductivity due to tunneling transfer of charges [18]. Condensed particles act as a 2D Coulomb gas with logarithmic interactions. With the introduction of charge frustration, (i.e., an applied voltage), the 2D Coulomb gas becomes biased.

4. Region IV [$T < T_{\text{dual-BKT}}$ and $g > g_C$, (i.e., $E_J < E_C$)]. At $T_{\text{dual-BKT}}$, a dual Berezinskii-Kosterlitz-Thouless transition occurs within the 2D Coulomb gas of Cooper pairs. Neutral Cooper pair dipoles are formed that do not carry any charge. This allows for the existence of a phase-incoherent low-temperature state that is known as superinsulation [16, 18] (dual to the 2D superconductor (Region II)). With sufficient charge frustration (i.e., with a sufficiently large applied voltage), Cooper pair dipoles are liberated into free Cooper pairs and the state of superinsulation is destroyed.

A similar phase diagram can be drawn for the $O(2)$ quantum rotor model in one-dimension, that applies to 1D chains of Josephson junctions [139, 140]. This is because the traditional Mermin-Wagner theorem not only applies universally to any system that is characterized by a continuous symmetry and exists in two-dimensions, spontaneous symmetry breaking is also prevented in one spatial dimensions [29]. Just as in the case of complex ordered systems that exist in two-dimensions, spontaneously generated topological defects prevent the development of conventional orientational order at finite temperatures in one-dimension. Critically, one-dimensional chains of Josephson junctions map to the 2D XY problem by the inclusion of a time direction [139, 140, 141] as a one space and one time dimension model. The relevant topological excitations in Josephson junction chains, can be viewed as $\pi_1(S^1)$ vortex point defects in the space-time manifold. For a brief comment on orientational ordering in Josephson junction chains, see Appendix H.

2.2.4 Electrical transport properties of charged $O(2)$ JJAs:

In charged Josephson junction arrays, the existence of a superconductor-to-superinsulator transition leads to a dramatic sensitivity of the temperature dependence of the electrical resistance on the value of g (i.e., for different ratios of importance of the kinetic and potential energies in the $O(2)$ quantum rotor model Hamiltonian). Historically, charged JJAs have provided the prototypical example of a material transport property (electrical conductivity) that can be controlled by such a ratio [78, 75]. The most distinctive feature of charged JJAs, that are realized in restricted dimensions and that allow for the realization of distinct ground states, is the anticipated singularity in the electrical transport properties at the superconductor-to-superinsulator transition [16, 18]. In particular, the inverse behavior of the electrical conductivity of charged JJAs across the superconductor-to-superinsulator transition is characteristic of dual low-temperature states that are ‘mirror images’ of one another, in the context that the superconducting state is a Bose-Einstein condensate of Cooper pairs while the superinsulating state is a condensate of topological point defects [138, 18]. A schematic of the electrical

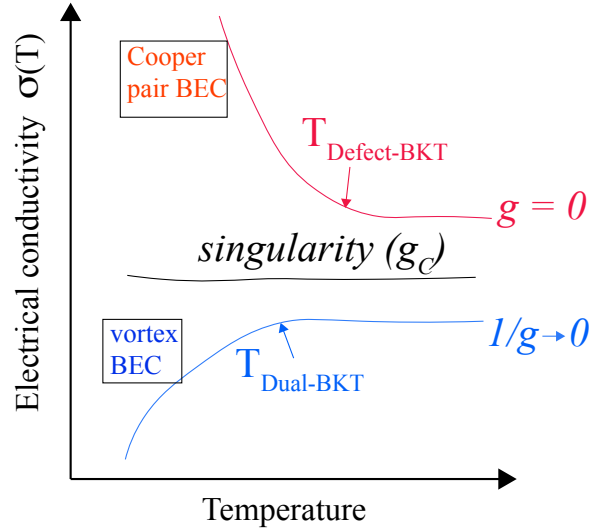


Figure 2.15: The existence of a superconductor-to-superinsulator transition in charged JJAs leads to a distinctive singularity in the temperature dependence of the electrical transport properties at the transition. A 2D superconductor ($T < T_{\text{defect-BKT}}$) has “zero electrical resistance” at finite temperatures. In contrast, the flow of current is blocked in the low-temperature state of superinsulation ($T < T_{\text{dual-BKT}}$), which exhibits “zero electrical conductivity” in the finite temperature range.

resistance of charged JJAs as a function of temperature, across the superconductor-to-superinsulator transition, is shown in Fig. 2.15.

A recent series of measurements of the electrical resistance across the critical point $g = g_c$ (superconductor-to-superinsulator transition) were taken by Poran et al. [Ref. [78]], and are reproduced in Figure 2.16 (for convenience). Poran et al. utilized the inverse thickness of thin-films as the non-thermal tuning parameter g . Driving g past a critical value brings about the superconductor-to-superinsulator transition [78, 17]. The measurements were collected [by Ref. [78]] for 18 separate samples, by sequential deposition of layers of Pb onto an insulating substrate [78]. The samples obtained in the first stages of deposition, i.e., the thinnest, expressed isolated regions with small inter-grain coupling energy [78]; such systems behave as superinsulators below a critical temperature. With the addition of more material [78], the system will exhibit stronger inter-grain coupling and transition to a phase-coherent thin-film superconductor below a critical temperature.

A complete description of the dual electrical transport properties of charged Josephson junction arrays, across the superconductor-to-superinsulator transition, derives from the uncertainty relation that applies to the model [95, 16, 18] (Eqn. 2.11). In the limit that a perfect 2D superconductor is obtained, i.e., for $g = 0$, the ground state is characterized by a complete absence of uncertainty in the scalar phase angle [18] throughout the system (i.e., $\Delta\phi = 0$). This is achieved by the binding of a balanced plasma of topological point defects into low-energy pairs [25, 71, 24]. These paired configurations are excitations from the phase-coherent ground state [25, 71, 24, 21], and minimize

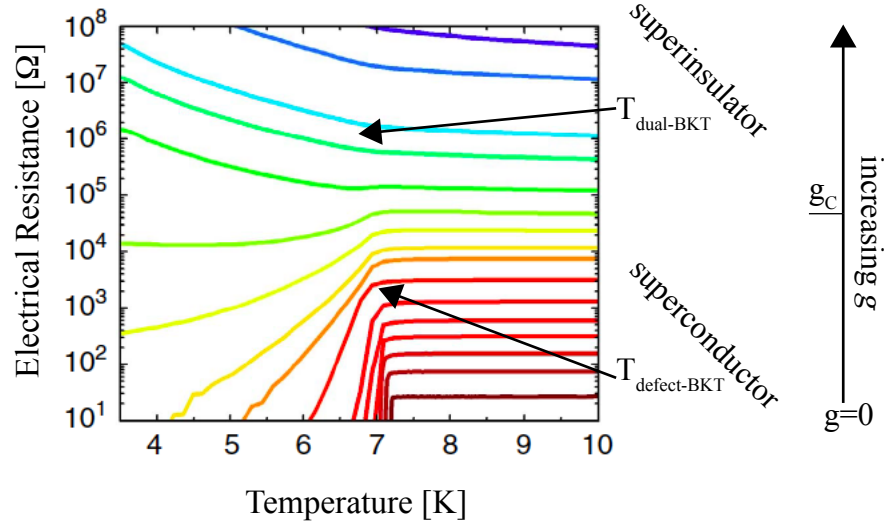


Figure 2.16: Measurements of the electrical resistance of planar charged JJAs [Ref [78]], across the superconductor-to-superinsulator transition. Electrical resistance goes sharply to zero in the superconducting regime ($g \rightarrow 0$), and inverse behavior is observed in the superinsulating regime ($1/g \rightarrow 0$).

the uncertainty in the scalar phase angle parameter at finite temperatures. Because charge and phase cannot be specified simultaneously [16], the absence of uncertainty in ϕ implies that the number of Cooper pairs transferred across a junction is entirely uncertain (i.e., $\Delta N \neq 0$). This enables the development of a macroscopic superconducting state in restricted dimensions, such that a supercurrent of condensed particles develops that cannot scatter and dissipate energy [18]. This superconducting state is one of “zero electrical resistance” at finite temperatures (i.e., by Eqn. 2.7 (Josephson phase relation), no voltage develops across the system).

In contrast, in the range of dominant kinetic energy, as condensed particles (Cooper pairs) get ‘pinned’ within separate islands [113, 16, 18] (as charge dipoles that carry no net charge) they block the flow of current. The pinning of electric charges eliminates the uncertainty in the total charge transferred (i.e., $\Delta N = 0$), and requires a maximized uncertainty in the global orientation of order parameters across the system (i.e., $\Delta\phi \neq 0$). This low-temperature state, known as superinsulation, is dual to the phase-coherent superconductor. In this low-temperature system, a finite voltage develops across the entire system [18] that is characterized by the Josephson phase angle relation (Eqn. 2.7). However, despite the voltage that develops, current remains blocked as any voltage potential is unable to drive the neutral charge dipoles. Charge pinning plays an important role in preventing charge fluctuations, that would otherwise destroy the low-temperature phase-incoherent state of superinsulation [113, 16, 18]. This low-temperature state exhibits “zero electrical conductivity” in the finite temperature range, i.e., as the temperature is decreased the electrical resistance sharply increases.

Chapter 3

$SU(2)$ orientational ordering

3.1 Ordering in bulk dimensions:

3.1.1 Free energy minimization:

Orientalional order in three-dimensional undercooled atomic liquids has been identified, by Nelson and Widom [15], with the tessellation of the three-sphere (S^3) by the preferred orientational symmetry of atomic clustering in three-dimensions $H \in SO(3)$. This is due to the fact that rotations in three-dimensions are non-commutative, and require conjugation by a quaternion for their representation. The group of unit quaternion numbers form the unitary group of degree two, i.e., $SU(2)$, which is the universal covering group [142, 20, 143] for the special group of rotations in three-dimensions $SO(3)$. The unitary group of degree two can be regarded as the surface of constant positive curvature that is embedded in four-dimensional Euclidean space (i.e., $S^3 \in \mathbb{R}^4$).

This hypersphere has the structure of a compact Lie group, because the quaternion group is closed under multiplication. The hypersphere S^3 and the circle S^1 are the only spheres (i.e., S^n) that admit compact Lie group structures. The relationship between the group of unit quaternion numbers ($SU(2)$) and S^3 is analogous to the fact that S^1 , i.e., the simplest compact Lie group, is isomorphic to the group of unit complex numbers ($U(1)$). The group of proper rotations in two-dimensions $SO(2)$ is described by the set of unit complex numbers (i.e., $U(1)$): $\mathbb{C} : e^{i\theta} = \cos \theta + \sin \theta \hat{i}$ where θ is the single scalar phase angle parameter.

Similarly, the group of proper rotations in three-dimensions, through an arbitrary angle 2θ around an arbitrary axis, is conveniently parameterized by the group of unit quaternion numbers (i.e., $SU(2)$). This parameterization is given as a versor^a, i.e., an extension of Euler's formula [28, 144] , as:

$$\mathbb{H} : e^{\hat{\tau}\theta} = \cos \theta + \sin \theta \hat{\tau} \quad \text{where, } \hat{\tau}^2 = -1 \quad (3.1)$$

^aA versor is a quaternion of norm 1. The norm of a quaternion $q = q_0 + q_1\hat{i} + q_2\hat{j} + q_3\hat{k}$ is $n(q) = \sqrt{q_0^2 + q_1^2 + q_2^2 + q_3^2}$.

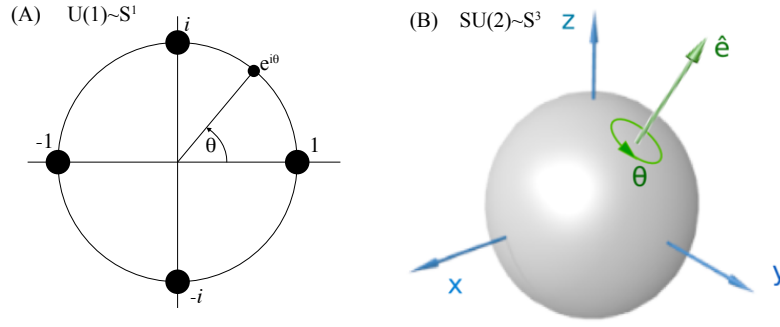


Figure 3.1: (A) The group of complex numbers is the $U(1)$ unitary group that parameterizes the unit circle (S^1) in the complex plane. (B) The group of quaternions give a simple way to encode rotations in three-dimensions $SO(3)$. The group of quaternion numbers is the $SU(2)$ unitary group, that is four-dimensional and parameterizes a unit hypersphere (S^3).

and $\hat{\tau}$ is a unit-length vector quaternion that consists of three separate imaginary components ($\hat{i}, \hat{j}, \hat{k}$). The full expression of $\hat{\tau}$ is:

$$\hat{\tau} = \cos \theta_1 \hat{i} + (\sin \theta_1 \cos \theta_2) \hat{j} + (\sin \theta_1 \sin \theta_2) \hat{k}, \quad (3.2)$$

where $(\theta \in [0, \pi], \theta_1 \in [0, \pi], \theta_2 \in [0, 2\pi])$. Multiplication of quaternion basis elements gives: $\hat{i}^2 = \hat{j}^2 = \hat{k}^2 = -1$ and $\hat{i}\hat{j} = \hat{k}, \hat{j}\hat{k} = \hat{i}, \hat{k}\hat{i} = \hat{j}$. To reiterate, quaternions give a simple way to describe rotations in three-dimensions. The group of rotations $SO(2)$ and the group of rotations $SO(3)$ are depicted in Figure 3.1. Importantly, two quaternions correspond to each rotation in three-dimensions (see Appendix C) and so the representation of $H \in SO(3)$ as quaternion elements (i.e., the lift of $H \in SO(3)$ into $SU(2)$) is twice the size of $H \in SO(3)$ and is hence known as the binary group [19, 20, 23, 27] $H' \in SU(2)$.

Above the melting temperature, the Landau free energy of a high-temperature fluid that possesses unbroken $SO(3)$ symmetry has a minimum at zero order parameter ($\psi = 0$) and forms a bowl as a function of the real and imaginary parts of a quaternion number. Below the melting temperature, the Landau free energy of the system is at a minimum along the surface of a hypersphere ($S^3 \in \mathbb{R}^4$) that is like a higher-dimensional ‘Mexican hat’ potential energy configuration (Fig. 2.2). The four degrees of freedom of the four-dimensional quaternion order parameter are: a set of three scalar phase angle parameters $(\theta \in [0, \pi], \theta_1 \in [0, \pi], \theta_2 \in [0, 2\pi])$, and the radius of the three-sphere that acts as the amplitude of the quaternion order parameter at any given temperature. For quaternion ordered systems that exist in a “bulk dimension” (seven), spontaneous symmetry breaking at the melting temperature occurs as the system chooses a particular ground state from among those available on the orientational ground state manifold $\mathcal{M} = SU(2)/H'$ that applies macroscopically. It is the choice of a particular ground state that breaks the symmetry of the high-temperature fluid. In the case of solidification, on spontaneous symmetry breaking at the melting temperature, the system chooses

a particular set of (three) scalar phase angle parameters that applies globally to the solid ground state. Despite the choice of a ground state along $\mathcal{M} = S^3$, the free energy of the ordered system remains invariant to rotation by a quaternion number: $\hat{\mathbf{n}} = |\hat{\mathbf{n}}|e^{\hat{\tau}\theta}$. Thus, the three scalar phase angle parameters represent the set of Nambu-Goldstone bosons [86, 34] that are anticipated on the spontaneous breakdown of the continuous symmetry group $SU(2)$.

Conventional global orientational ordering, by spontaneous symmetry breaking at finite temperatures, is forbidden in three- and four- dimensional spaces which are restricted dimensions for a four-dimensional quaternion order parameter (that is characterized by three scalar phase angles). It follows that undercooling below the melting temperature is necessary topologically in three- or four-dimensions. This is in contrast to the development of “conventional” global (macroscopic) orientational order at the melting temperature for quaternion order parameter systems that exist in the “bulk dimension” (i.e., $4 + 3 = 7$ [seven] dimensions). In considering orientational ordering during solidification in three- or four-dimensions, using a quaternion order parameter, the well-developed physical concepts that apply to complex n -vector (i.e., $n = 2$) ordered systems that exist in restricted dimensions must be extended to a higher-dimensional algebra domain.

3.1.2 Meissner effect and topologically stable defects:

A possible “Meissner-like effect” that applies to three-dimensional crystalline solids has been discussed by researchers in the field of condensed matter physics [92, 145] for many decades. On crystallization, the translational symmetry of the high-temperature atomic fluid is broken and misorientational fluctuations are expelled from the crystal. In three-dimensional crystalline solids, this has the consequence of grain formation by breaking the translational symmetry in three-dimensions and the formation of grain boundaries. The crystalline ground state rotates as a grain boundary is crossed, and the field of misorientations that develops as a consequence of the existence of a grain boundary dies away exponentially as one enters the grain [92]. This feature, where an expelled field (here, rotational deformation) dies away exponentially from the boundaries of the system and from the core of topological defects, is characteristic of an irrotational system [92, 82, 145] (Eqn. 2.4).

The expulsion of rotational deformations in an orientationally ordered state of matter originates because there is an energy cost to change the amplitude of the order parameter slightly away from its ideal value that defines the radius of the ground state manifold (here, $\mathcal{M} = S^3$) at any given temperature. In this way, the amplitude degree of freedom is unique from the scalar phase angle degrees of freedom, which are anticipated Nambu-Goldstone bosons [86] (massless). On the development of global orientational order in the crystalline solid state, the irrotational condition suggests [82] that the velocity of atomic displacements within the lattice only depends on the gradients of the set of scalar phase angles of the quaternion order parameter. For more details on the irrotational condition that applies to macroscopically orientationally-ordered phases in general, see Appendix D. An ap-

proach to determine the irrotational velocity field configuration in the orientationally-ordered solid state is suggested in Appendix D.2, the final solution is left for future work.

Just as in complex ordered systems, the enforcement of the irrotational constraint results in the expulsion of misorientational fields into topologically stable defects that allow for a quantized amount of rotational deformation to enter their core. In other words, in order for crystalline solid states to remain everywhere irrotational, angular deformation fields are pushed into topological defect elements that are available to the system. With the introduction of topological defects, the irrotational condition is satisfied everywhere within the crystalline solid state except for at the core of the defects [21]. The macroscopically orientationally-ordered solid state (in bulk dimensions) admits topological defects that belong to the third and first homotopy group of $\mathcal{M} = S^3/H'$; furthermore, these topological defects are crucial in understanding the prevention of conventional orientational order in restricted dimensions. These important groups of defects are discussed in turn in the following subsections.

Third homotopy group topological defects

The main type of topological defects that are available to n -vector ordered systems belong to the homotopy group [36] π_m of $\mathcal{M} = S^m$, where $m = n - 1$, i.e., $\pi_m(S^m) = \mathbb{Z}$. This homotopy group parameterizes the number of distinct ways that an m -sphere can wrap around the relevant topological manifold $\mathcal{M} = S^m$. The identification of the homotopy group $\pi_m(S^m)$ with the lattice of integers $\mathbb{Z} = 0, \pm 1, \pm 2$ indicates that there are an infinite number of topologically stable defect elements available to the group. Thus, the homotopy groups $\pi_m(S^m)$ are necessarily Abelian [21]. In the case of quaternion n -vector ordered systems, these topological defect elements belong to the third homotopy group of $\mathcal{M} = S^3$ (i.e., $\pi_3(S^3)$). These third homotopy group topological defects are the higher-dimensional analogue to the fundamental homotopy group defects (i.e., π_1) that are available to complex n -vector ordered systems (i.e., $U(1)$ superfluids), known as vortices.

In general, for each $\pi_m(S^m)$ homotopy group, there are topologically stable configurations indexed by an integer topological number that counts the number of times the m -dimensional sphere wraps around itself. As an example, the integer topological number known as the “winding number” ($k = 0, \pm 1, \pm 2, \dots$) characterizes the strength of a $\pi_1(S^1)$ vortex by counting the number of times the order parameter θ wraps around $\mathcal{M} = S^1$, when making a closed circuit in real space. Similarly, representatives of the third homotopy group are characterized by an integer topological number (which may be called $B = 0, \pm 1, \pm 2, \dots$) that is like the “winding number” of a vortex. The topological number B counts the number of times a map of the order parameter $\hat{\mathbf{n}}(\theta, \theta_1, \theta_2)$ wraps around the topological manifold $\mathcal{M} = S^3$, when considering the order parameter on a closed measuring hypersphere in real space.

Just as in the case of the winding number of a vortex, the topological charge B of the $\pi_3(S^3)$ topological defect is an arbitrary integral topological number (i.e., positive or negative) that measures

the number of times the mapping of the quaternion orientational order parameter wraps around the measuring three-sphere [146, 147]. It is important to note that, despite the infinity of states of $\pi_m(S^m)$ topological defects that are possible topologically, when an expelled field enters into the ordered system it should be pushed into topological defect elements of the lowest energy [23].

By the topological charge equation (Eqn. 1.7), $\pi_3(\mathcal{M})$ defects are three-dimensional in seven-dimensional “bulk” quaternion ordered systems. These topological defects are analogous to $\pi_1(\mathcal{M})$ defects that are linear in three-dimensional “bulk” complex ordered systems. In three-dimensional superfluid systems, a vortex line must pass through any closed loop that contains a singularity in the order parameter [92]. A similar configuration can be imagined for three-dimensional third homotopy group defects in “bulk” quaternion ordered systems that contain singularities in the orientational order parameter. Importantly, in bulk ordered systems, the possible existence of a finite density of topological defects just below the bulk critical transition temperature does not prevent the development of conventional global order at finite temperatures [99]. This is because the free energy cost to introduce such topological defects, with a dimension larger than zero, into the “bulk” ordered system is too high to produce them in the absence of an applied field [99].

On the other hand, by the topological charge equation (Eqn. 1.7), topological defects that belong to n -vector ordered systems become lower dimensional in restricted dimensions and prevent the development of conventional global orientational ordering at finite temperatures (recall, $\pi_1(S^1)$ topological point defects in the two-dimensional XY model [99, 25]). In general, for n -vector ordered systems that exist in the lower critical restricted dimension D_{low} equal to n , the topological defects that belong to the homotopy group $\pi_m(S^m)$ (where $m = n - 1$) are point defects [36] in the orientational order parameter field. As examples of point defects in order parameter fields, consider the $\pi_1(S^1)$ point defect in a system of 2-vectors in two-dimensions (Figure 3.2(A)) and the $\pi_2(S^2)$ point defect in a system of 3-vectors in three-dimensions (Figure 3.2(B)). These examples of point defects are available: in XY models (i.e., $O(2)$ symmetry) in two-dimensions [25], and in Heisenberg models (i.e., $O(3)$ symmetry) in three-dimensions respectively. The third homotopy group point defect, in a four-dimensional system with $O(4)$ symmetry, is the next higher-dimensional point defect.

At temperatures below the bulk critical transition temperature, ordered systems that exist in the lower critical restricted dimension D_{low} are prevented from establishing conventional global orientational order. This is because topological point defect elements are spontaneously generated, in the absence of any external fields. This is a consequence of the large configurational entropy term, that is characteristic of topological defects as points, that diverges logarithmically [25] with the system size L :

$$S_{config} = D \ln \left(\frac{L}{a} \right), \quad (3.3)$$

where D is the dimension of the system and a is the radius of the core of the point defect. To reiterate, these topologically stable point defects are of crucial importance in preventing spontaneous

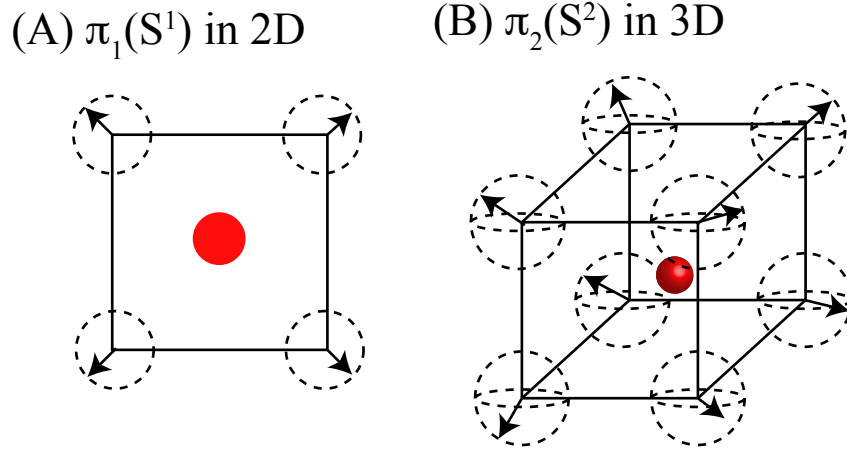


Figure 3.2: $\pi_m(S^m)$ topological defects (i.e., in the n -vector order parameter field) are points in $n = m + 1$ dimensions. The defect core sits in the center of a closed measuring m -sphere. (A) $\pi_1(S^1)$ point defect in two-dimensions. (B) $\pi_2(S^2)$ point defect in three-dimensions.

symmetry breaking by continuous (n -vector) order parameters at finite temperatures [99]. However, ultimately, it is the presence of these topological defects that enables a description of the novel topological phase transition that allows for the existence of a topologically-ordered phase-coherent low-temperature state for systems that exist in restricted dimensions (i.e., $D \leq D_{low}$).

First homotopy group topological defects

In addition to third homotopy group topological defects, another type of topological defect is available to atomic systems below the melting temperature. These defects are characterized by closed circuits (i.e., $\pi_1(\mathcal{M})$), and thus belong to the fundamental homotopy group of $\mathcal{M} = SO(3)/H \equiv S^3/H'$. These closed-loop topological defects are wedge disclinations that are defined on the three-sphere by making use of the $2 - to - 1$ homomorphism between the $SO(3)$ and $SU(2)$ groups. This is done because the three-dimensional surface of constant positive curvature, i.e., $SU(2) \cong S^3$, is simply connected [19, 20, 148] on its own (you cannot lasso a basketball [34, 145] Fig. 3.3), whereas $\pi_1(SO(3)) \cong \pi_1(\mathbb{RP}^3) \cong \mathbb{Z}_2$. It is by the identification of points (H') on the surface of $SU(2) \cong S^3$ that closed-loop topological defects may be defined; without points identified, on the simply connected surface of S^3 , any closed loop could be contracted to a point.

Closed paths [20, 149] in $SO(3)$ are best described by the simply connected group $SU(2)$ (which has a $2 - to - 1$ homomorphism with $SO(3)$). This is because $G = SO(3)$ does not distinguish rotation by 2π about an axis from no rotation, while these rotations are topologically distinct [20, 149]. Thus, the algebra of the fundamental homotopy group defects in systems for which $\mathcal{M} = SO(3)/H$ and

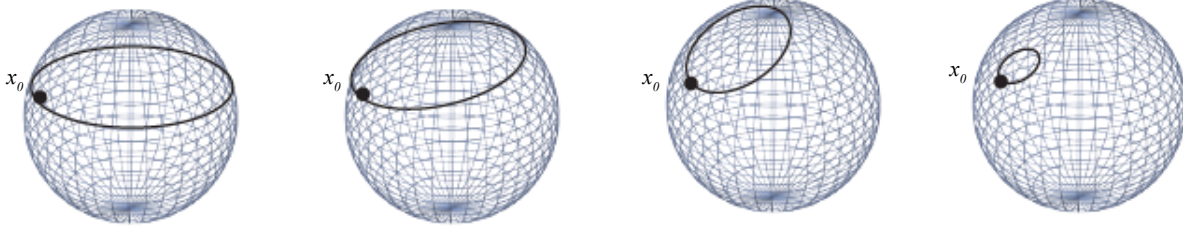


Figure 3.3: The two-sphere is simply connected, such that any closed measuring circuit can be shrunk to its base point [34], x_0 . This applies to all higher dimensional spheres $\mathcal{M} = S^m$. Thus, the fundamental homotopy group of any sphere other than S^1 is zero, i.e., $\pi_1(S^n) = 0$ for $n > 1$.

that express discrete orientational symmetry below the melting temperature is given as [19, 20]:

$$\pi_1 \left(\frac{S^3}{H'} \right) = H', \quad (3.4)$$

where H' is the binary representation of the preferred discrete orientational symmetry group of atomic clustering $H \in SO(3)$ (because H is discrete, H' is also discrete [19]). Topological defects that belong to this homotopy group are wedge disclinations. In three-dimensions, fundamental homotopy group defects are linear (by Eqn. 1.7) and are known to play a role in solidification processes [23, 15, 46].

3.2 Ordering in restricted dimensions (four- and three-): $O(4)$ quantum rotor model

In three-dimensions, all solidifying atomic systems will undercool as the temperature of the system is driven below the melting temperature T_M . This is so that atomic clusters can develop that exhibit a preferred orientational symmetry, in preparation for solidification. As previously discussed, the relevant topological order parameter manifold that describes orientational order in undercooled atomic systems is the three-sphere that is tessellated by the binary representation [19, 19, 15, 23] of the preferred discrete subgroup of proper rotations in three-dimensions $H \in SO(3)$ (defined by taking the lift of $H \in SO(3)$ into $SU(2)$).

By the isomorphism between the unitary group $SU(2)$ and the group of unit quaternions ($S^3 \in \mathbb{R}^4$), a quaternion orientational order parameter can therefore be applied to the undercooled atomic liquid systems below the melting temperature. Based upon the dimensionality of the orientational order parameter (i.e., $n = 4$), both four- and three- dimensions should be considered as restricted dimensions for quaternion orientational ordering. Therefore, conventional global orientational order (i.e., solidification at the melting temperature) cannot be obtained at finite temperatures [33] in four- or three-dimensions. Thus, undercooling below the melting temperature can be viewed as a

topological consequence of existing in restricted dimensions for the orientational order parameter.

In approaching a topological description of orientational order in solidification processes and in the solid state, solidification in both four- and three-dimensions should be studied. This is because the lower critical restricted dimension of a quaternion order parameter (i.e., the largest geometrical space dimension in which spontaneous symmetry breaking is prevented at finite temperatures [33]), is four [73]. Just below the melting temperature, in four- and three- dimensions, misorientational fluctuations throughout the system take the form of topologically stable defect elements that are spontaneously generated and prevent the development of global orientational order (thereby requiring undercooling). This is a higher-dimensional realization of the Mermin-Wagner theorem [29], which applies most directly to complex n -vector ordered systems that exist in two- and one-dimensions (although, by the Mermin-Wagner theorem, any system that exhibits continuous symmetries cannot spontaneously symmetry break these symmetries in two- and one-dimensions).

To mathematically model solidification in four- and three-dimensions (i.e., quaternion orientational ordering in restricted dimensions), for which the conventional global orientational order is prevented at finite temperatures, it is convenient to make use of an $O(n)$ quantum rotor model where $n = 4$. In particular, a four-dimensional plastic crystal phase that develops just below the melting temperature is well-described by a four-dimensional $O(4)$ quantum rotor model. This is a direct higher-dimensional analogue to planar Josephson junction arrays of complex n -vector order parameters, that develop below the bulk critical transition temperature and that are well-described by $O(2)$ quantum rotor models [39, 17] (see Section 2.2).

Just as in the case of planar Josephson junction arrays (just below the bulk critical transition temperature), 4D plastic crystalline phases (just below the melting temperature) are prevented from developing conventional orientational order as a consequence of the possible existence of a gas of misorientational fluctuations in the orientational order parameter throughout the system. Such plastic crystalline phases are mesomorphic states of matter between the liquid state and the solid state, that exist as liquid-like solids^b. This hypothetical mesomorphic 4D plastic crystal phase acts as a model of the undercooled atomic liquid system in three-dimensions, that develops just below the melting temperature and, that has not yet formed a solid state.

In the 4D plastic crystal phase, just below the melting temperature, an amplitude of orientational order develops on each of the sites of the plastic crystal but the system remains in a liquid-like state as a consequence of the possibility of the free rotation of its constituents. The internal orientational degrees of freedom of each of the constituents of the plastic crystal are characterized by an $O(4)$ rotor [17], that rotates in four-dimensions. Therefore, it is useful to introduce a set of three scalar phase angle parameters ($\theta \in [0, \pi]$, $\theta_1 \in [0, \pi]$, $\theta_2 \in [0, 2\pi]$) on each site, so that the orientation of

^bFor a review of mesomorphic states of matter, and plastic crystals in particular, see Appendix I.

each constituent of the plastic crystal takes the form:

$$\hat{\mathbf{n}}_m = (\cos \theta_m, \sin \theta_m \cos \theta_{1,m}, \sin \theta_m \sin \theta_{1,m} \cos \theta_{2,m}, \sin \theta_m \sin \theta_{1,m} \sin \theta_{2,m}). \quad (3.5)$$

The 4D plastic crystal is modeled by developing a four-dimensional lattice of such $O(4)$ rotors, that are able to interact with their nearest-neighbors. In general, the constituents of plastic crystal phases close-pack and retain artificial translational periodicity; as a consequence, a preferred mean orientation of the constituents of the plastic crystal develops [53]. This mean orientation which can be considered to be a director field ($\hat{\mathbf{n}}(\mathbf{r})$), that admits topologically stable defects. The gas of misorientational fluctuations that can develop as a consequence of the free rotation of constituents of the 4D plastic crystal takes the form of topological defects in this director field.

Despite the inability of the system to undergo a conventional disorder-order phase transition at the melting temperature, ordered low-temperature solid states may still be obtained by the minimization of the Hamiltonian energy of the $O(4)$ quantum rotor model. The $O(4)$ Hamiltonian, that mathematically models the 4D plastic crystalline system, allows for two distinct ground states as the temperature is lowered below a critical finite value. This follows from the fact that, just as in the case of the $O(2)$ quantum rotor model [75, 17, 39, 35, 33, 150] that applies to Josephson junction arrays, the kinetic and potential energy terms of the $O(4)$ quantum rotor model cannot be minimized simultaneously. The question of how these distinct/dual low-temperature solid states can be achieved is a primary focus of this section (Section 3.2).

Ultimately, distinct low-temperature states of $O(n)$ quantum rotor models can be realized as a consequence of uncertainty relations that apply to the operators of each $O(n)$ rotor [17]. These uncertainty relations are symmetric [16, 18], and can be recast as a duality between the important degrees of freedom which are: topological point defects and condensed atomic particles. For instance, in charged $O(2)$ Josephson junction arrays, the important degrees of freedom that present a duality are: $\pi_1(S^1)$ magnetic vortices and charged Cooper pairs; the transition between distinct ground states in charged JJAs is known as the superconductor-to-superinsulator quantum phase transition [16, 75] (Section 2.2). Similarly, one may consider that, the relevant uncertainty relations that apply in the four-dimensional plastic crystal phase can be recast as a duality between: third homotopy group point defects $\pi_3(S^3)$ and condensed atomic particles. In the four-dimensional plastic crystal, i.e., uncharged, the dual low-temperature states are a crystalline solid and an “orientational glass.” The critical transition point between the crystalline and noncrystalline ground states occurs where the kinetic and potential energy terms in the $O(4)$ Hamiltonian become comparable, and may be called a self-dual critical point [137, 151].

Moreover, because the constituents of the 4D plastic crystal (are polytope that) have the symmetry of $\mathcal{M} = S^3/H'$ (where H' is the lift of $H \in SO(3)$), the existence of a plasma of fundamental homotopy group defects is possible below the melting temperature. Topological defects that belong

to the fundamental homotopy group of $\mathcal{M}$ are planar in four-dimensions, and exist as line defects in three-dimensions (by the topological charge equation). Thus, unlike third homotopy group defects, these topological defect elements are visible in three-dimensions as lines (third homotopy group defects have a dimension -1 in 3D). The distinct low-temperature solid states that can derive from an undercooled atomic system are: crystalline solids (including geometrically frustrated topologically close-packed phases, e.g., Frank-Kasper crystalline structures) in the range of dominant potential energy, and orientationally-disordered (glassy) solids in the range of dominant kinetic energy.

The remainder of this section (Section 3.2) is organized as follows. In Section 3.2.1, crystallization in the range of dominant potential energy is discussed. Within Section 3.2.1, numerical Monte-Carlo simulations of orientationally-ordering in a four-dimensional $O(4)$ rotor model are presented [73]. These simulation results provide evidence for a Berezinskii-Kosterlitz-Thouless topological ordering transition, that allows for the existence of an orientationally-ordered solid state, in terms of the formation of low-energy bound pairs of third homotopy group topological point defects. The use of geometrical frustration as a non-thermal tuning parameter, that can drive the undercooled atomic system towards the self-dual critical point (crystalline-to-noncrystalline transition) in the range of dominant potential energy is also considered in Section 3.2.1. Section 3.2.2 focuses on the mechanism of formation of orientationally-disordered solid states, in the range of dominant kinetic energy. The inverse cooling rate that is applied to the undercooled atomic system is suggested as a tuning parameter, that can be utilized in the laboratory to drive a glass-forming system towards the self-dual critical point (crystalline-to-noncrystalline transition) from the extreme limit that potential energy effects are absent. Phase diagrams for solidification in four- and three-dimensions, across the self-dual critical point, are described in Section 3.2.3. These phase diagrams are discussed in terms of the important states of matter that exist, and the ordering processes by which they are obtained. Finally, in Section 3.2.4, the thermal transport properties of crystalline and non-crystalline solid states (above approximately 50 K) are considered within this topological framework.

3.2.1 Dominant potential energy:

As the temperature of a solidifying atomic fluid that exists in four- or three- dimensions is lowered below the melting temperature T_M , it is prevented from developing conventional global orientational order and will be forced to undercool. In four-dimensions, below the melting temperature, a plastic crystal phase can form for which an amplitude of quaternion orientational order is identified with each of the sites of a four-dimensional array (artificial translational periodicity); such systems are well-described by four-dimensional $O(4)$ quantum rotor models.

Despite the prevention of conventional global orientational order at the melting temperature, as a consequence of the free rotation of the constituents of the plastic crystal just below the melting temperature, an orientationally-ordered ground state may still be obtained by the minimization of

the potential energy term in the $O(4)$ quantum rotor model Hamiltonian. The potential energy due to interactions between the orientational order parameters, of nearest-neighbor constituents of the 4D plastic crystal, takes the form:

$$\hat{V} = -E_J \sum_{\langle mn \rangle} \hat{\mathbf{n}}_m \cdot \hat{\mathbf{n}}_n, \quad (3.6)$$

where $\hat{\mathbf{n}}_m$ is the director (Eqn. 3.5) located at site m , $E_J > 0$ is the coupling energy between nearest-neighbor order parameters and the sum is over all nearest-neighbors $\langle mn \rangle$.

Making use of the fact that $\hat{i}^2 = \hat{j}^2 = \hat{k}^2 = -1$, and using a standard cosine angle difference identity, the potential energy (Eqn. 3.6) can be re-written as [73]:

$$\hat{V} = -E_J \sum_{\langle mn \rangle} (\cos \theta_m \cos \theta_n + \sin \theta_m \sin \theta_n \times (\cos \theta_{1,m} \cos \theta_{1,n} + \sin \theta_{1,m} \sin \theta_{1,n} [\cos(\theta_{2,m} - \theta_{2,n})])). \quad (3.7)$$

As the temperature of the system is lowered towards zero Kelvin, this potential energy function is minimized by the ground state of perfectly aligned order parameters. This is a higher-dimensional analogue to the two-dimensional XY model [71], and an alternative form of a phase transition towards the orientationally-ordered low-temperature state should occur that is topological and defect-driven.

In four-dimensions, it is most straightforward to consider the process of orientational ordering by discretizing the gas of misorientational fluctuations that develop (just below T_M , as a consequence of the free rotation of constituents of the plastic crystal) as spontaneously generated topologically stable defects that are mobile. In particular, the spontaneous generation of third homotopy group point defects in four-dimensions is directly analogous to the spontaneous generation of fundamental homotopy group point defects in two-dimensional XY models just below the bulk critical transition temperature. In four-dimensions, spontaneously generated third homotopy group point defects cannot be removed by any continuous distortion of the order parameter field. Thus, in order to obtain an orientationally-ordered state at finite temperatures (below the melting temperature), a topological ordering event should occur within this gas of misorientational fluctuations that takes the form of topologically stable point defects (and disclinations).

Isolated topological point defects are stabilized at high-temperatures by a large configurational entropy [99], that is associated with the possible placement of an isolated point defect core within the system^c. Despite having a large configurational entropy, which stabilizes isolated point defects at high-temperatures, isolated point defect cores produce energetically costly distortions in scalar phase angle parameters far from their core. As a result, as the system minimizes its overall Helmholtz free energy ($F = V_{\text{gradient}} - TS_{\text{config}}$), isolated point defect cores are not favorable at low-temperatures.

^cIn four-dimensions, assuming a simple hyper-cubic lattice ($\mathbb{E}^4$), the possible positions for the placement of an isolated point defect core (located at the center of any closed hyper-volume made by nearest-neighbors) can be approximated as $(L/a)^4$ where L is the system size and a is the radius of the point defect core. The configurational entropy per point defect is then: $S_{\text{config}} = 4k_B \ln \left(\frac{L}{a} \right)$.

A topological description of solidification, in terms of third homotopy group point defects (π_3) in four-dimensions [73], goes beyond the historical way of thinking about solidification solely in terms of topological line defects in three-dimensions [23, 46] (π_1). It is owing to the Abelian nature of $\pi_m(S^m)$ homotopy groups (which are identified with the lattice of integers $\mathbb{Z} = 0, \pm 1, \pm 2, \dots$) that pairs of third homotopy group point defects (i.e., of $\mathcal{M} = S^3$) with equal and opposite sign (sum-0) are possible. These paired configurations do not require large energetically costly distortions [21] in the orientational order parameter field far from the pair. This is because the order parameter field far from the pair that can be continuously distorted to the uniform state [21]. It follows that, below a critical temperature, these low-energy pairs of point defects (which are topologically equivalent to the uniform state) minimize the overall Helmholtz free energy of the system. Thus, as the temperature is lowered below this critical value, a transition towards the orientationally-ordered crystalline solid state is anticipated that belongs to the defect-driven Berezinskii-Kosterlitz-Thouless universality class of topological ordering phase transitions.

Traditional crystalline systems (i.e., not geometrically frustrated):

The ground state of Eqn. 3.7, which mathematically models the internal orientational degrees of freedom of the constituents of the four-dimensional plastic crystal, is one of perfect alignment of $O(4)$ rotors. The perfectly orientational ordered state that is obtained by the minimization of Eqn. 3.7, as the temperature is lowered to zero Kelvin, is characteristic of a “traditional” crystalline solid ground state that is free of topological defects. The defect-free ground state that is obtained in this extreme limit, i.e., in the absence of kinetic energy effects, is considered to be “unfrustrated” geometrically [22].

In this classical (i.e., “unfrustrated”) limit, the gas of misorientational fluctuations that develops just below the melting temperature takes the form of concomitant plasmas of spontaneously generated π_3 and π_1 topological defects that are balanced in concentrations of defects with positive and negative signs. This gas of misorientational fluctuations is analogous to the gas of misorientational fluctuations that develops in planar superconducting systems at temperatures smaller than the bulk critical transition temperature. These defects are topologically stable and cannot be removed by any continuous distortion of the order parameter field. Thus, a topological ordering event is anticipated to occur within this gas of misorientational fluctuations in order to allow for the existence of an orientationally-ordered low-temperature state.

In four-dimensions, in order to minimize the overall free energy of the system, third homotopy group point defects should bind into low-energy sum-0 paired configurations below a critical transition temperature. Likewise, below a critical transition temperature, defects in the form of wedge disclinations should also become topologically ordered by binding into low-energy complementary pairs with equal and opposite angular deficit. These paired configurations of wedge disclinations are consid-

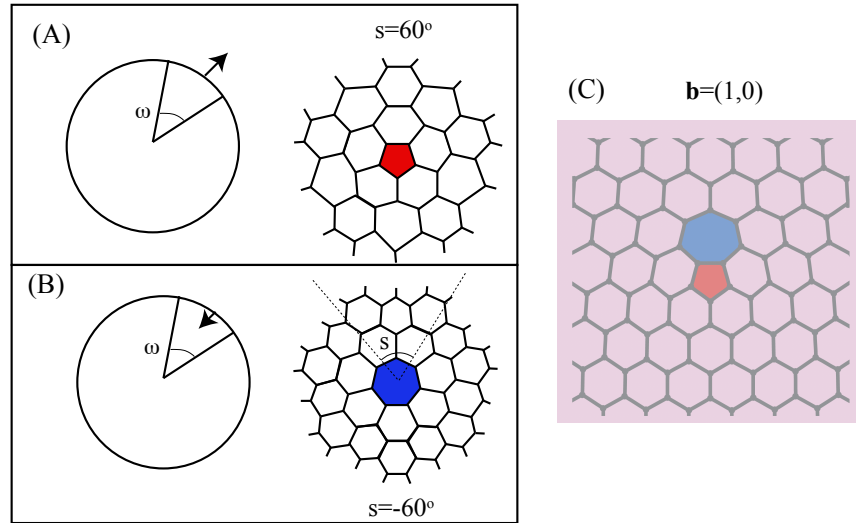


Figure 3.4: (A, B) Wedge disclinations are topological defects that are obtained by removing (or adding) a wedge of material characterized by a positive (or negative) angular deficit from (or to) an ideal structure. Shown are ($s = 60^\circ$, pentagons (red)) and ($s = -60^\circ$, heptagons (blue)) wedge disclinations, in a 2D honeycomb lattice, that carry positive and negative curvature respectively. (C) Edge dislocations are defects that are topologically equivalent to pairs of wedge disclinations whose angular deficits sum to zero. An edge dislocation in graphene, with the smallest allowable Burger's vector ($\mathbf{b}=(1,0)$), has the configuration of an edge-sharing heptagon-pentagon. [Image: Ref. [154]]

ered to be edge dislocations [152, 21, 153, 154], that belong to the fundamental homotopy group of the translational order parameter space of the orientationally-ordered crystalline lattice [145]. Edge dislocations form because isolated wedge disclinations, which are mobile in the undercooled system, are not permitted in the crystalline solid state that is orientationally-ordered and therefore exhibits a crystalline lattice.

The lack of geometrical frustration, in the absence of kinetic energy effects, is a consequence of the ability of vertices with the preferred orientational order of atomic clustering to fill ordinary space in three-dimensions. In three-dimensions, such atomic clusters are face-centered cubic (FCC) or hexagonally close-packed (HCP). Preferred orientational order that is space-filling in three-dimensions generates a tessellation of the surface of positive curvature in four-dimensions (i.e., $S^3 \in \mathbb{R}^4$), by its binary representation (i.e., $\mathcal{M} = S^3/H'$). In the absence of geometrical frustration, this tessellation is developable such that it can be flattened back into Euclidean space without distortion [155]. This is only possible because there is no finite Gaussian curvature attributed to any of the atomic vertices that are able to develop long-range translational periodicity in three-dimensional flat space (i.e., Euclidean). In systems that are not geometrically frustrated, it is owing to the absence of curvature attributed to atomic vertices that the gas of misorientational fluctuations that develops below the melting temperature takes the form of *balanced* plasmas of π_3 and π_1 topological defects (i.e., concentrations of defects with opposite signs are equal).

Figure 3.4(A) and (B) show two-dimensional examples of wedge disclinations, that are character-

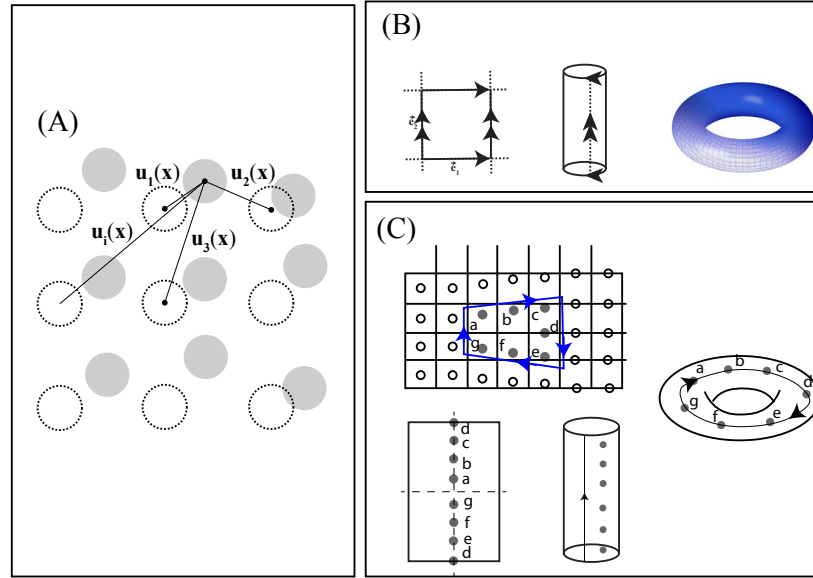


Figure 3.5: (A) A 2D crystalline lattice (ideal lattice points) and displaced atoms. The order parameter is a measurement of atomic displacements $\mathbf{u}(\mathbf{x})$, with respect to the ideal lattice. (B) The ideal lattice point that is associated with a given displaced atom is ambiguous [145]. Thus, there is an ambiguity in the definition of the order parameter such that, the set of distinct order parameters (that can describe atomic displacements in a crystalline solid) forms a square with periodic boundary conditions [145] that has the same topology as a two-dimensional torus (T^2). (C) The positions of atoms drift with respect to their ideal lattice positions as a closed loop is traversed around a dislocation. This corresponds to a loop around the order parameter space, that wraps around the hole of the torus that corresponds to an extra row of atoms. Rearranging the atoms slightly deforms the loop but does not change the number of times it wraps around the hole (this is why it is a topological defect). [Image reproduced from: Ref. [145]]

ized by either a positive or negative angular deficit (and hence carry signed curvature at their core). Figure 3.4(C) depicts a bound pair of complementary wedge disclinations, whose angular deficits sum to zero. Pairs of complementary wedge disclinations are considered to be edge dislocations [152, 21, 153, 154], that carry no curvature. Paired wedge disclinations (Fig. 3.4(C)) are favored energetically (over isolated wedge disclinations) below the finite temperature that marks crystallization. It follows that there is an absence of isolated wedge disclinations, in favor of dislocations, in the low-temperature orientationally-ordered crystalline solid state. Isolated wedge disclination are only able to persist in the solid state in the event of geometrical frustration. In fact, with the incorporation of geometrical frustration into Eqn. 3.7, the crystalline ground state that is obtained exhibits an ordered arrangement of topological defects that is known as the major skeleton network in topologically-close packed (TCP) crystalline structures (i.e., geometrically frustrated crystalline structures).

Further topological arguments for the existence of a topological ordering transition, that allows for the realization of the low-temperature crystalline solid state in four- and three-dimensions, may

be developed by considering the relationship between the topology of the system and curvature^d. Wedge disclinations and dislocations each belong to the fundamental homotopy group of the relevant order parameter space. Thus, the topological strength attributed to these topological defects is a topological invariant much like the winding number (of $\pi_1(S^1)$ vortices). Disclination topological defects are characterized by an angular deficit topological invariant (known as the Frank vector); the topological invariant that measures the strength of a dislocation is the Burger's vector, that represents the magnitude and direction of a lattice distortion. While a disclination topological defect introduces curvature into an initially flat geometry [22], a dislocation does not carry any curvature.

Topologically, a dislocation carries no curvature because the translational order parameter manifold of the crystalline solid state in m -dimensions is an m -dimensional torus (T^m) whose surface has a total Gaussian curvature of zero. The field of atomic displacements that is introduced in the vicinity of a dislocation defect core corresponds to a loop around the hole in the m -dimensional torus (T^m). A description of a dislocation in a two-dimensional crystalline lattice, in real space and on the topological manifold (two-dimensional torus), is provided in Fig. 3.5 (A, B, C). Unlike the spherical orientational order parameter manifold, the toroidal manifold has a total curvature of zero and is hence is flat (just like the Euclidean space). Thus, when two complementary wedge disclinations pair, the total Frank vector on taking a closed loop around the pair sums to zero and the space is once again flat. Such pairs of wedge disclinations are edge dislocations (Fig. 3.4 (C)), that is available to translationally ordered crystalline solid states that exist in flat space.

Numerical Monte-Carlo (MC) simulations, that have been performed in order to investigate the orientational-ordering process of a system of continuous quaternion n -vector order parameters in four-dimensions in the absence of kinetic energy effects, are presented below (Section 3.2.1). These simulation results provide evidence of a transition towards an orientationally-ordered low-temperature state, that favors the alignment of quaternion orientational order parameters throughout the system. The nature of the transition is determined by estimating thermodynamic response functions, in the vicinity of the transition. These Monte-Carlo simulations provide evidence that the orientationally-ordered low-temperature state may be considered to be obtained by a topological ordering event (i.e., Berezinskii-Kosterlitz-Thouless (BKT) type), within the gas of misorientational fluctuations that would otherwise prevent conventional global orientational order at finite temperatures.

Monte-Carlo simulations of an $O(4)$ quantum rotor model in four-dimensions In this section, a four-dimensional system of weakly-linked $O(4)$ rotors is studied using numerical Monte-Carlo (MC) simulations. The ground state, achieved by the minimization of potential energy (Eqn. 3.7), is one of perfectly aligned $O(4)$ rotors throughout the system. In these simulations, the rotors are arranged at the sites of a simple hyper-cubic ($\mathbb{E}^4$) lattice, such that each rotor has a set of eight nearest-neighbors, i.e., the kissing number [156] is eight. Periodic boundary conditions are utilized

^dFor discussion on the connection between topology and curvature, see Appendix J

in order to consider system sizes $L \times L \times L \times L$, for: $L = 3, 4, 5, 6, 7$.

Five separate samples, initialized with different random number generators, are used to compute the physical observables for each system size L . The initial configuration of quaternion n -vector order parameters within a 4D array is constructed by generating a randomized distribution of scalar phase angles $(\theta, \theta_1, \theta_2)$ throughout the system. At each temperature, 1000 Monte-Carlo steps are taken to achieve thermal equilibrium, and 2000 subsequent steps are used to collect the statistical data required to compute the physical observables. On each step, each of the $N = L \times L \times L \times L$ rotors are selected in turn (and at random), and an attempt is made to change its state. As the simulation proceeds, the physical observables of interest are computed.

The author notes that the limited number of steps taken, and sizes considered, is a consequence of the higher dimensionality of the model which pushes the limits of computational resources. Ultimately, this is due to the serial nature of this Monte-Carlo code; this type of Monte-Carlo simulation, in dimensions larger than three-, is an excellent candidate [157, 158, 159] for computation on graphical processing units (GPU) that have been shown to dramatically increase the speed of MC simulations.

The observed energy (Eqn. 3.7) and order parameter per site are plotted in Figure 3.6 (A) and (B). These results provide evidence of a transition resulting from the alignment of $O(4)$ rotors, as the temperature is lowered below a critical value. Furthermore, because there is no discontinuity in the order parameter (i.e., a first derivative of the free energy) this transition is not first order (in the Ehrenfest sense); thus, this transition appears to be a continuous phase transition.

In order to determine the nature of the continuous transition to the low-temperature state, it is instructive to consider the behavior of thermodynamic response functions (heat capacity (Eqn. 2.27) and susceptibility (Eqn. 2.24)) and their size-effects [71, 21]. The computed specific heat and susceptibility, for the five lattice sizes studied, are plotted versus temperature in Figures 3.6 (C) and (D). Importantly, there does not appear to be any regular singularity in the behavior of the observed susceptibility or specific heat at the transition; this points towards a continuous transition (i.e., that is not first order). Furthermore, the thermodynamic response functions remain smooth and finite at the transition, which is characteristic of a transition that has topological origins [127, 33, 128]. Thus, these simulation results (Fig. 3.6) provide evidence that the order of the continuous transition is higher than second; this is consistent with a topological ordering transition that is of infinite-order.

Further evidence for a topological ordering event is given by considering the size-effects of the thermodynamic response functions. For topological ordering transitions, the specific heat is independent of the system size for large enough systems [122, 73]. This is evidence of a lack of conventional long-range order [160], wherein the low-temperature system is only topological ordered (quasi-long-range-order [21, 33]). The observed specific heat (Fig. 3.6 (C)) does not depend on the system size, for large enough systems ($L = 5, 6, 7$). In the case of 2D BKT transitions, the fact that the specific heat is independent of the lattice size for large enough lattices is well-known and this behavior has been used by many authors as an indication of BKT character of the transition [122, 121, 71, 33].

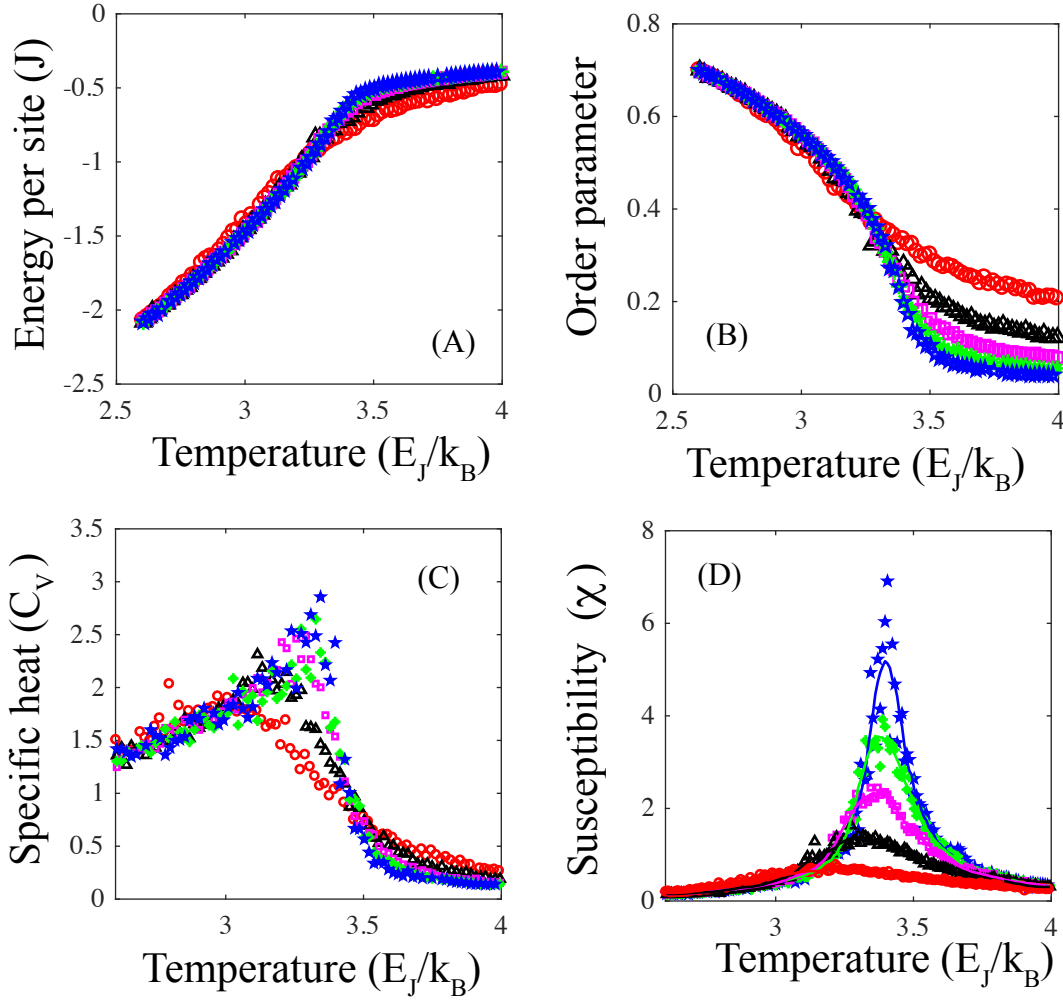


Figure 3.6: (A) Energy per site, (B) order parameter per site, (C) specific heat and, (D) susceptibility versus temperature for various lattice sizes ($L \times L \times L \times L$): $L = 3, 4, 5, 6, 7$ ($\circ, \triangle, \square, *, \star$). The units of temperature are E_J/k_B , where E_J is the nearest-neighbor coupling energy.

In contrast to the specific heat, the peak values of the observed susceptibility (Fig. 3.6 (D)) do scale with the system size over all length scales [120, 122, 71]. This is owing to an anticipated finite size scaling relationship between the susceptibility and a diverging correlation length [71]. As a two-dimensional example, consider Eqn. 2.28 (Kosterlitz [71] 1974). As a topological ordering transition is approached from high-temperatures, the correlation length (ζ) should tend rapidly towards the system size (L). According to the renormalization group work of Kosterlitz [71] (1974), the susceptibility χ in the vicinity of a topological ordering transition depends on the correlation length [120] as:

$$\chi \sim \zeta^\gamma, \quad (3.8)$$

where γ is a related to a critical exponent of the model.

As a consequence of this scaling relationship, the maximum in susceptibility (at the topological

ordering transition) depends linearly on the system size [120, 122] on a log-log scale. Recall, in the 2D XY model [71], consideration of the size-effects on the peak value of the susceptibility [71, 129, 33, 122, 120] allows for the determination of the critical exponent η at the transition temperature as $1/4$ (see Fig. 2.11). Figure 3.7 (A) plots the peak values of χ versus system size on a log-log scale. A linear fit to the data points, i.e., $\log(\chi_{\max}) = \gamma \log(L)$, can be made with a slope of $\gamma = 2.4 \pm 0.1$. This finding suggests the applicability of a finite size scaling relationship [71, 120, 122] between the susceptibility and the correlation length [71] (Eqn. 3.8) that is consistent with a topological ordering transition. An analytical prediction of the value of γ at $T_{\text{defect-BKT}}$, in this four-dimensional $O(4)$ model, requires analogous renormalization-group work to that of Kosterlitz [71] (1974).

An estimation of the critical transition temperature may be made by considering size-effects on the location of the susceptibility peak. This information is plotted in Fig. 3.7(B); in the limit of infinite system sizes, the peak location extrapolates to $3.5 E_J/k_B$ (where E_J is the nearest-neighbor coupling energy). Therefore, just as in the case of topological ordering in two-dimensions, the maximum in the heat capacity (Fig. 3.7(C)) is seen to be dislocated from this transition temperature [121, 21].

To summarize these simulation results, a phase transition has been detected within a four-dimensional system of continuous quaternion n -vector (i.e., $n = 4$) order parameters, i.e., $O(4)$. Owing to the dimensionality of the system, and of the orientational order parameter, this system undercools below the bulk critical transition temperature. In this model, the existence of a gas of misorientational fluctuations throughout the system prevents the development of conventional global orientational order at finite temperatures. This gas of misorientational fluctuations takes the form

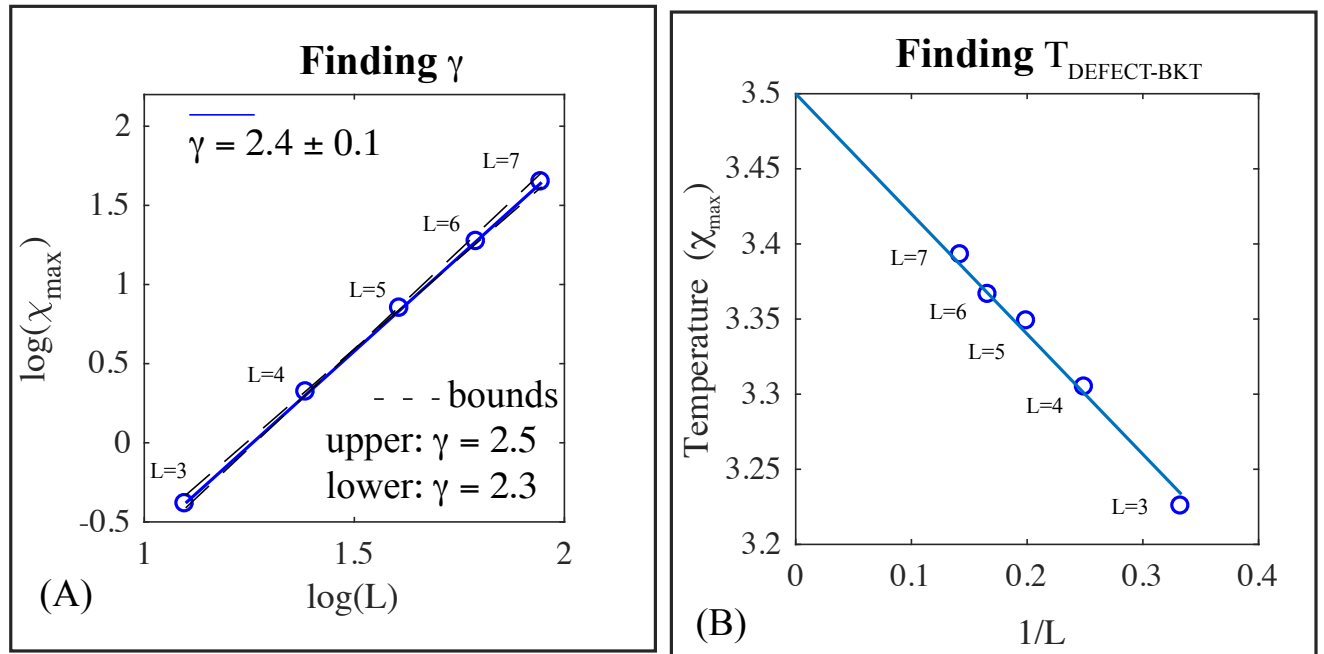


Figure 3.7: 4D quaternion n -vector ordered system: (A) $\chi_{\max}$ versus system length on a log-log scale (Eqn. 3.8). (B) Estimation of $T_{\text{defect-BKT}}$ by considering size-effects of the location of $\chi_{\max}$.

of spontaneously generated third homotopy group point defects, which are the only type of topologically stable defects that are available to the system studied in this simulation. The development of a ground state of perfect orientational-order, by the minimization of potential energy (Eqn. 3.7), requires that these topologically stable defects undergo an ordering transition. In light of this, the observed Monte-Carlo results (that display a transition towards the low-temperature orientationally-ordered state) have been considered within the context of a novel topological ordering transition of third homotopy group point defects.

By monitoring thermodynamic response functions (specific heat and susceptibility) for several lattice sizes, this transition has been found to show characteristic behavior of a Berezinskii-Kosterlitz-Thouless type topological ordering transition in four-dimensions. In particular, the specific heat has been found to be independent of the lattice size for large enough lattices, which is indicative of a topological ordering transition. Furthermore, strong finite size scaling of the susceptibility with the lattice size has been found. This kind of strong scaling is known to occur in the vicinity of defect-driven BKT topological ordering transitions. Thus, it may be concluded that these Monte-Carlo simulation results are consistent with topological arguments by providing evidence that the transition to the orientationally-ordered low-temperature state, of a quaternion n -vector ordered system in four-dimensions, belongs to the Berezinskii-Kosterlitz-Thouless universality class of defect-driven topological ordering transitions.

Topologically close-packed crystalline systems (i.e., geometrically frustrated):

In the range of dominant potential energy, the role of geometrical frustration is to introduce finite kinetic energy effects. Geometrical frustration in the crystalline solid state is akin to magnetic frustration of the phase-coherent superconducting state that is realized in restricted dimensions. For charged JJAs, in the absence of an applied magnetic field [110], the concentrations of topological point defects with opposite signs are equal [35]; as such, in the absence of frustration, perfect topological ordering below a critical temperature and no topological defects persist to the ground state. Similarly, crystalline ground states that are not geometrically frustrated are not plagued by topological defects and the space in which it inhabits is flat everywhere.

Geometrical frustration is evident when the preferred orientational order of atomic clustering in three-dimensions (i.e., $H \in SO(3)$) is incompatible with a space-filling arrangement [22]. Geometrical frustration, evident in flat space, is relieved by allowing for positive curvature to enter into each of the atomic clusters. This produces a tessellation of the three-dimensional space of constant positive curvature [15] that is not developable in flat space, i.e., as the polytope $\mathcal{M} = S^3/H'$. This is because $\mathcal{M}$ has a curvature mismatch with flat three-dimensional Euclidean space [15], such that finite positive Gaussian curvature is attributed to each atomic vertex of the tessellation $\mathcal{M}$.

The positive curvature that is attributed to geometrically frustrated atomic vertices drives an

asymmetry in the plasma of topological defects towards the concentration of those that carry a negative sign. With the incorporation of geometrical frustration, the biased nature of the plasmas of topological defects ensures that the three-dimensional Euclidean space remains flat on average [15, 23]. In three-dimensions, the excess negative wedge disclination lines concentrate negative curvature at their core [23, 161, 22] and balance out the positive curvature of geometrically frustrated atomic vertices (third homotopy group defects should also become biased). Excess negative topological defects are structural constituents of geometrically frustrated systems, because the vertices of $\mathcal{M}$ inherit positive curvature and cannot be flattened back into Euclidean space without introducing permanent deformations (such that the Euclidean space remains flat on average). The difference in the positive Gaussian curvature of $\mathcal{M}$ and flat three-dimensional Euclidean space quantifies the geometrical frustration that is characteristic of the particular undercooled atomic liquid. With increasing geometrical frustration, i.e., with increasing positive curvature of $\mathcal{M}$, the plasma becomes increasingly biased towards the concentration of topological defects with a negative sign.

In solidifying undercooled atomic liquids that are geometrically frustrated, the excess negatively signed topological defects are unable to form low-energy paired configurations on crystallization and will persist to the solid ground state. These unpaired topological defects form a periodic arrangement, so that the crystalline ground state is characterized by zero configurational entropy. In three-dimensions, this periodic arrangement of topological defects (in geometrically frustrated crystalline solid states) is known as the major skeleton network [58, 57] that consists of negative disclination lines [15, 23]. In general, geometrically frustrated crystalline solid states that form are known as topologically close-packed (TCP) structures. Topologically close-packed structures are comprised exclusively of tetrahedral interstices [54], i.e., without octahedral interstices. On the other hand, space-filling FCC and HCP packings have both tetrahedral and octahedral interstices.

As an example of orientational order in geometrically frustrated undercooled atomic systems, in contrast to FCC and HCP clustering, one is drawn to the fact that there is an energetic preference for icosahedral coordination surrounding atoms in dense liquids [15, 23] (Sir Charles Frank [56] (1952)). Despite the incompatibility of icosahedral coordination with a space-filling crystal, icosahedral coordination shells do tessellate the three-sphere in four-dimensions forming the $\{3, 3, 5\}$ polytope [55, 15]. The 120 vertices of the $\{3, 3, 5\}$ polytope are the symmetry elements of the binary icosahedral group Y' (i.e., the lift of $Y \in SO(3)$ into $SU(2)$). Geometrical frustration of icosahedral coordination drives a global excess in the concentration of topological defects with a negative sign [15].

Frank-Kasper structures [57, 58], are three-dimensional examples of geometrically frustrated crystalline solid states that express preferred icosahedral local orientational order. Frank-Kasper structures are able to exist as stable ground states as a result of the development of a major skeleton network [58, 57] of ordered negative disclination lines [15, 23]. In Frank-Kasper crystalline structures, atomic sites of icosahedral coordination ($Z = 12$) are referred to as minor sites [57] and, sites with more than 12-coordination ($Z > 12$) are identified as major sites. Atoms with $Z > 12$ combine

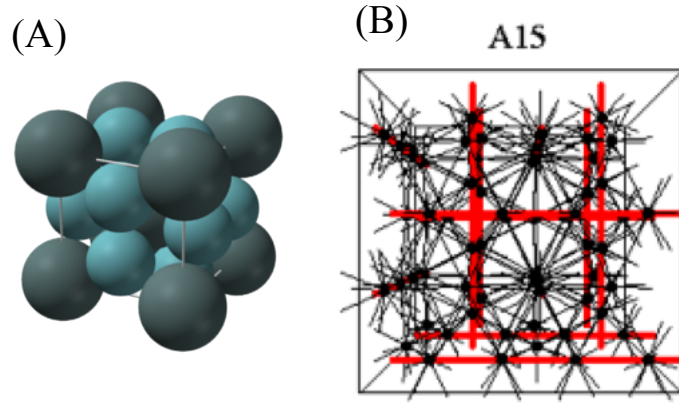


Figure 3.8: (A) The $A15$ structure is one of the most common members of the family of Frank-Kasper topologically close-packed (TCP) crystalline phases, that are comprised of atoms with icosahedral coordination $Z = 12$ and higher coordination $Z = 14$. (B) The contiguous major skeleton network in $A15$ compounds is composed of three orthogonal grids of $Z = 14$ coordinated atoms which are in fact -72° disclination lines [23].

to form the major skeleton network, that threads through an otherwise icosahedral medium [23, 65, 15]. For example, in $A15$ compounds, the major skeleton consists of [23] orthogonal grids of $Z = 14$ atoms in three-dimensions (as shown in Fig. 3.8). The icosahedral orientational order parameter vanishes at $Z = 14$ atoms, which form lines that correspond to -72° disclinations (that belong to the fundamental homotopy group [19, 23] $\pi_1(SO(3)/Y) = Y'$).

With increasing geometrical frustration, the positive Gaussian curvature that is attributed to each of the vertices on $\mathcal{M}$ increases. Consequently, the spacing between topological defects in the crystalline ground state becomes smaller. Figure 3.9 depicts an anticipated phase diagram of the four-dimensional plastic crystal, in the limit of dominant potential energy, that proves useful to modelling crystallization in three-dimensions. With increasing geometrical frustration, the topological ordering transition temperature should become suppressed. Above a critical value of geometrical frustration, the process of crystallization is forbidden as topological defects become entirely biased towards those of a single sign and the formation of bound pairs of topological defects that act as excitations from the crystalline ground state is not possible.

It is important to note that the quantity of geometrical frustration in atomic systems with discrete symmetry is not a continuous variable. This is because the preferred orientational symmetry of atomic clustering $H \in SO(3)$ is a discrete group. For geometrically frustrated atomic clusters, i.e., that are not compatible with a space-filling arrangement in ordinary three-dimensions, the Gaussian curvature of $\mathcal{M}$ is inversely proportional to the radius of $\mathcal{M}$ [14]. If fewer vertices are identified (i.e., for smaller symmetry groups $H \in SO(3)$), $\mathcal{M}$ has a smaller radius and hence the positive Gaussian curvature attributed to each vertex on its surface increases.

To reiterate, with the incorporation of a geometrical frustration, the crystalline ground state is

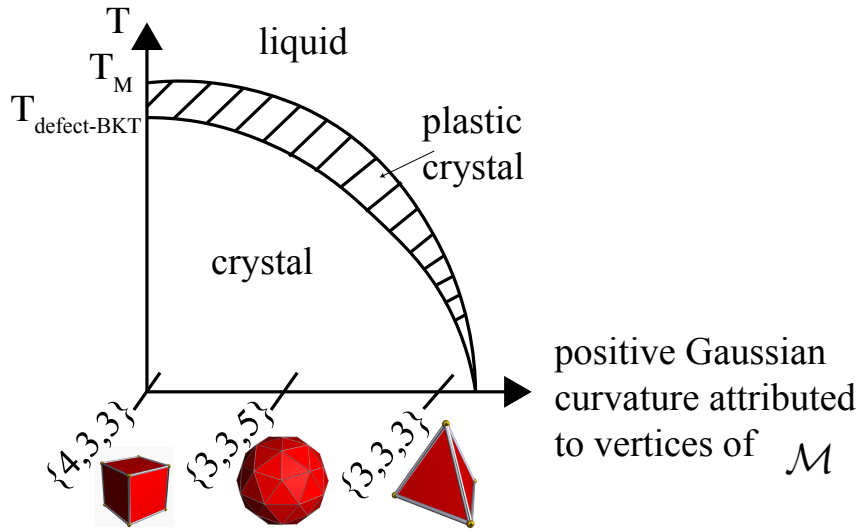


Figure 3.9: Schematic phase diagram of a 4D plastic crystal, in the range of dominant potential energy, plotted as geometrical frustration versus temperature. Geometrical frustration is driven by the positive Gaussian curvature attributed to the vertices of $\mathcal{M}$. In geometrically frustrated undercooled systems, the topological ordering transition temperature ($T_{\text{defect-BKT}}$) becomes suppressed; above a critical value of geometrical frustration, the crystalline solid is no longer a ground state and $T_{\text{defect-BKT}}$ is driven to zero. Geometrically frustrated crystalline (orientationally-ordered) low-temperature solid states of the 4D plastic crystal exhibit a major skeleton of disclinations, and a periodic arrangement of third homotopy group point defects. The distance between topological defects in the ground state is inversely proportional to geometrical frustration.

no longer one of perfect orientational order. Instead, the set of scalar phase angle parameters that characterize the orientational order parameter will vary from site to site in order to facilitate the incorporation of a periodic arrangement of topological defects into the ground state (major skeleton). In four-dimensions, the ground state now consists of a periodic configuration of third homotopy group point defects and a major skeleton of planar disclinations. The corresponding ground state in three-dimensions is that of a TCP crystalline phase, which exhibits a major skeleton network of disclination lines (e.g., Frank-Kasper crystalline structures).

3.2.2 Dominant kinetic energy:

In the range of dominant rotor kinetic energy, just below the melting temperature, an undercooled atomic system in four-dimensions develops as a plastic crystal that exists in metastable equilibrium. In this state of matter, molecular rearrangements (that are necessary to remain in metastable equilibrium) are thermally activated such that average relaxation times follow the Arrhenius law [162]. Orientationally disordered low-temperature solid states of the 4D plastic crystal phase are favored in this limit. In the absence of potential energy effects, the low-temperature solid state that is obtained (by minimizing the rotor kinetic energy term) is one of maximal uncertainty in the orientation of order parameters throughout the system [17] (i.e., $\Delta\theta_i = \text{max. for } i = 0, 1, 2$).

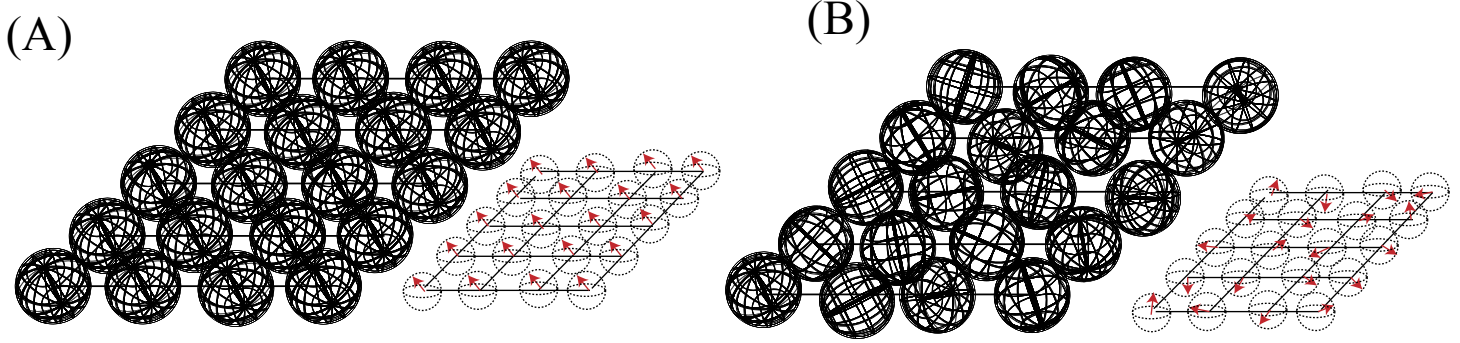


Figure 3.10: A plane of molecules in distinct low-temperature states of a 3D plastic crystal: (A) orientationally-ordered and, (B) “orientational glass.”

Such low-temperature solid states of plastic crystals, that have quenched disorder in orientational degrees of freedom, are commonly referred to as “orientational glasses.” For reference, Figures 3.10 (A) and (B) depict planes of molecules in orientationally-ordered (crystalline) and “orientational glass” low-temperature states of a 3D plastic crystal. Four-dimensional “orientational glass” solid states are considered to be higher-dimensional (uncharged) analogues to the states of superinsulation, that can be realized in charged planar Josephson junction arrays that are well-described by $O(2)$ quantum rotor models (Section 2.2).

As the temperature of a glass-forming undercooled system is lowered below some critical value (the glass transition temperature) it will fall out of metastable equilibrium upon the formation of an orientationally-disordered solid state^e (i.e., non-crystalline). In the absence of potential energy effects, no internal relaxations are possible and glasses that form by the minimization of the kinetic energy term are maximally orientationally-disordered. Owing to the symmetry of the uncertainty relations that apply to this model [17], it is implied that all condensed particles should become thermally pinned in this extreme limit at the glass transition. This process may be considered as akin to the formation of neutral charge dipoles at the transition to the phase-incoherent superinsulating state [132, 16, 18].

With the incorporation of finite potential energy effects, the system can become increasingly undercooled as internal relaxations that are necessary in order to adequately sample configurations are possible to lower temperatures. With finite potential energy effects, the system is partially internally relaxed on glass formation such that some orientational correlations between neighboring components of the plastic crystal are characteristic of the non-crystalline low-temperature solid state. In the limit that the undercooled system is driven towards the self-dual critical point, at which the potential energy becomes comparable to the kinetic energy, a hypothetical “ideal” non-crystalline

^eBy convention, glass formation occurs as the viscosity of an undercooled atomic system rises above a critical value (10^{13} Poise).

solid state can be achieved that is entirely internally relaxed such that it exhibits the maximum orientational correlations of any glass.

In the laboratory, the applied cooling rate is the most obvious tuning parameter that can be utilized to drive a glass-forming undercooled system towards the self-dual critical point, by introducing finite potential energy effects into the $O(4)$ quantum rotor model Hamiltonian. The applied cooling rate competes with the thermally activated process of internal relaxation, such that the system may only undergo internal relaxation processes in the time allowed by the applied cooling rate [163, 162, 164]. Eventually, as the temperature is lowered below a critical value, molecules rearrange so slowly that the undercooled system will be unable to adequately sample configurations in the time allowed by the cooling rate and will become frozen [163] at the glass transition. Undercooled systems can only become entirely internally relaxed, at the self-dual critical point, in the limit of an infinitely slow cooling rate (Figure 3.11). Any real glass transition occurs owing to constraints on cooling rates that can be achieved in the laboratory, as the system falls out of metastable equilibrium at some higher temperature (the real glass transition temperature) than the transition temperature at the self-dual critical point.

As the glass-forming system falls out of metastable equilibrium, i.e., on glass formation, condensed atomic particles that are not internally relaxed become thermally pinned within the system. Thus, by the inclusion of finite potential energy effects, there is a trade-off between the thermal pinning

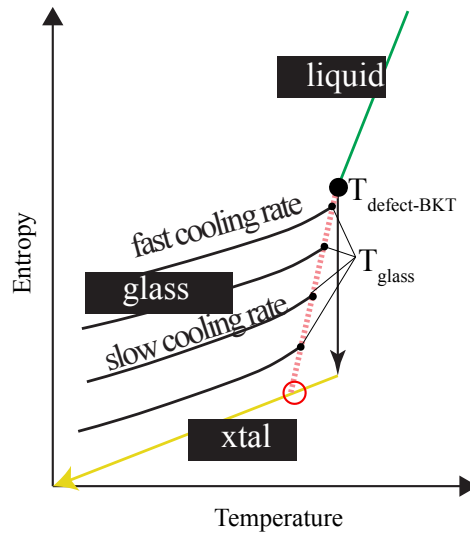


Figure 3.11: In the laboratory, the glass transition temperature can be controlled by the applied cooling rate. With slower cooling rates, the metastable liquid can become increasingly undercooled. An entropy paradox is exhibited in the limit of an infinitesimal cooling rate (open circle), where the entropy difference between the glass-forming liquid and its crystalline phase is zero.

of condensed particles (that are not internally relaxed) and the development of orientational correlations between constituents of the plastic crystal (by internal relaxation). This can be viewed as a consequence of the symmetric uncertainty relations that relate the uncertainties in the amplitude and scalar phase angle parameters of the quaternion orientational order parameters. In three-dimensions, these orientational correlations that develop are between *groups of atoms* that have broken the full symmetry of the high-temperature liquid by the formation of atomic clusters with preferred orientational coordination $H \in SO(3)$. The glass-forming undercooled system with the most orientational correlations on solidification exists at the self-dual critical point, where the system has become entirely internally relaxed yet lacks translational order. There is an anticipated entropy paradox at this point, for which the configurational entropy of the glass-forming undercooled system should be the same as its crystalline counterpart. This entropy paradox is reminiscent of the Kauzmann paradox [165, 163] at the “ideal” glass transition temperature in three-dimensions.

3.2.3 Phase diagrams:

$O(4)$ quantum rotor model in four-dimensions

The relevant mathematical models of n -vector ordered systems that exist in restricted dimensions are $O(n)$ quantum rotor systems, which act as rotating Bose-Einstein condensates [17]. These models apply in cases where conventional orientational ordering cannot be obtained due to the possible existence of a gas of misorientational fluctuations (in the form of topological point defects), just below the bulk critical transition temperature. For quaternion n -vector ordered systems that exist in four- and three-dimensions, owing to the dimensions of the orientational order parameter, undercooling below the bulk critical transition temperature is a topological necessity.

Quaternion n -vector ordered systems in four-dimensions can be described using four-dimensional $O(4)$ quantum rotor models, in which third homotopy group topological defects are discretized as points that are spontaneously generated. These point defects coexist with four-dimensional ordered regions just below the bulk critical transition temperature (compare with the discussion of Josephson junction arrays in Section 2.2). Distinct ground states of the $O(n)$ quantum rotor model can be realized by the minimization of either the potential energy term or the kinetic energy term of the $O(n)$ quantum rotor model Hamiltonian. The potential energy term is minimized by the complete alignment of rotors in the ground state. On the other hand, the low-temperature state that minimizes the kinetic energy term exhibits a maximum uncertainty in rotor orientations throughout the system.

These distinct low-temperature states of matter, and their mechanisms of formation, can be understood by considering the uncertainty relations that apply to the ordered system [95, 16, 17]. These uncertainty relations, defined for each $O(n)$ rotor between its angular momentum operators and its orientational position [17], may be recast as a duality between topological point defect (scalar phase angle) and condensed particle (amplitude) degrees of freedom [16, 17]. The orientationally-ordered

low-temperature state is obtained by a defect-driven Berezinskii-Kosterlitz-Thouless transition within a gas of misorientational fluctuations; low-energy bound pair configurations minimize the uncertainty in the scalar phase angle parameters in the ground state. By duality, in analogy with the mechanism of formation of the phase incoherent low-temperature states of $O(2)$ Josephson junction arrays [113, 18], orientationally-disordered low-temperature states of the $O(4)$ quantum rotor model (which are dual to orientationally-ordered low-temperature states) are anticipated to exist as a result of a Berezinskii-Kosterlitz-Thouless transition that takes place within a gas of fluctuations in the amplitude of the order parameter throughout the system.

Figure 3.12 shows the anticipated phase diagram of a generic (continuous) $O(4)$ quantum rotor model in four-dimensions. This phase diagram shows a transition between distinct orientationally-ordered and orientationally-disordered low-temperature states of a quaternion ordered system. This phase diagram will be shown to be useful in understanding solidification in four- and three-dimensions. The important states of matters, identified as regions *I*, *II*, *III*, *IV* (Fig. 3.12), and their mechanisms of formation are discussed below.

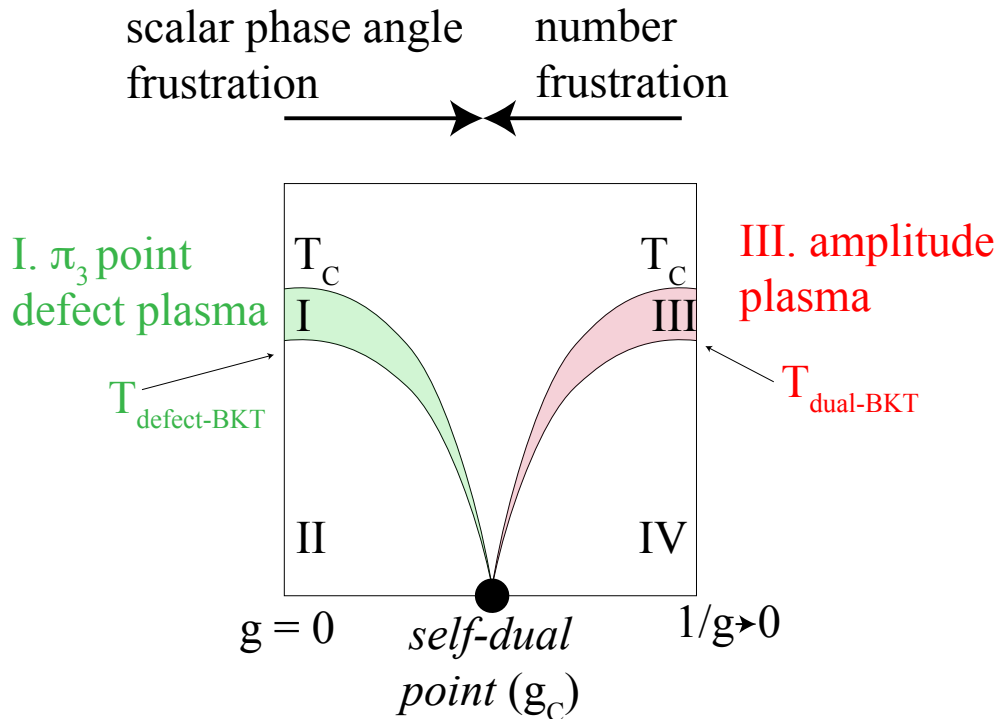


Figure 3.12: Anticipated phase diagram of an uncharged $O(4)$ ordered system in 4D. Below the bulk critical transition temperature, T_C , orientational order is characterized by a quaternion n -vector (i.e., $n = 4$) order parameter ($\psi = |\psi|e^{i\theta}$) that is four-dimensional, and is characterized by three scalar phase angle parameters. The amplitude and scalar phase angle parameters cannot be specified simultaneously to arbitrary precision; this leads to a transition between (dual) orientationally-ordered and orientationally-disordered low-temperature states, at a self-dual critical point.

1. Region I. Below the bulk critical transition temperature T_C , a network of four-dimensional ordered regions forms that each express a well-defined amplitude of quaternion orientational order and that are only weakly-coupled to their nearest-neighbors. As a consequence of weak-linking, this system is prevented from obtaining conventional global orientational order at finite temperatures. In the range of dominant potential energy, it is the existence of a gas of misorientational fluctuations that take the form of spontaneously generated topological point defects ($\pi_3(S^3)$) that prevents the development of global orientational order at finite temperatures. Just below T_C , these topological point defects are stabilized by configurational entropy as isolated entities that are mobile and unbound. In the absence of phase angle frustration, the plasma of topological point defects is balanced (i.e., the concentrations of point defects with opposite signs are equal). With the introduction of phase angle frustration, the plasma becomes biased towards the concentration of topological defects that carry a particular sign. This suppresses the critical transition temperature, to the orientationally-ordered low-temperature state ($T_{\text{defect-BKT}}$) to zero at the self-dual critical point (where potential and kinetic energies are comparable).
2. Region II. The temperature $T_{\text{defect-BKT}}$ marks a defect-driven topological ordering transition, that allows for the existence of the orientationally-ordered low-temperature state. For temperatures below $T_{\text{defect-BKT}}$, excitations from the ground state are low-energy sum-0 pairs of third homotopy group point defects. This orientationally-ordered low-temperature state of the four-dimensional $O(4)$ quantum rotor model, in which $O(4)$ rotors are aligned, mathematically describes an $SU(2)$ Bose-Einstein condensate that is characterized by a macroscopic orientational order parameter. In the absence of phase-angle frustration, all of the topological point defects that exist as isolated entities in Region I ($T_{\text{defect-BKT}} < T < T_C$) will form low-energy sum-0 pairs at $T_{\text{defect-BKT}}$. With the incorporation of phase-angle frustration, the orientationally-ordered low-temperature state will no longer be one of perfectly aligned rotors; instead, the scalar phase angle parameters in the ground state will vary from node to node by the inclusion of a periodic arrangement of unpaired topological point defects (of a single sign).
3. Region III. In the range of dominant kinetic energy, a quaternion n -vector ordered system develops as a network of weakly-linked four-dimensional ordered regions with small coupling energy between nearest-neighbors. Just below the bulk critical transition temperature T_C , a plasma of fluctuations in the amplitude of the quaternion n -vector order parameter (condensed particle number) develops throughout the system. These amplitude fluctuations are identified with condensed particle transport, which is thermally activated. With the incorporation of finite potential energy effects, frustration of this state of matter leads to the suppression of the transition to the orientationally-disordered low-temperature state.
4. Region IV. The transition towards an orientationally phase-incoherent low-temperature state,

by the minimization of the kinetic energy term, occurs at a finite temperature $T_{\text{dual-BKT}} < T_C$. For temperatures below $T_{\text{dual-BKT}}$, the low-temperature state that has formed by the minimization of the kinetic energy term is orientationally-disordered. This low-temperature solid state is considered to be dual to the orientationally-ordered solid state (Region II). By the uncertainty relations that apply to the operators of $O(4)$ rotors, the kinetic energy term favors localization of amplitude fluctuations throughout the system that would otherwise destroy the low-temperature state. In the extreme limit that potential energy effects are absent, the low-temperature system is maximally orientationally-disordered and all condensed particles should become pinned. With the incorporation of potential energy effects, on approaching the self-dual critical point (from $1/g \rightarrow 0$), frustration of the orientationally-disordered low-temperature state leads to increased orientational correlations.

Solidification in four-dimensions

Four-dimensional $O(4)$ quantum rotor models can be utilized to describe 4D plastic crystals, whose internal orientational degrees of freedom are characterized by quaternion rotors. Hypothetical 4D plastic crystal phases develop as the temperature of a four-dimensional atomic fluid (that possesses $SO(3)$ symmetry) is lowered below the melting temperature T_M . This plastic crystal system is a “liquid-like solid” mesomorphic phase [166], that is an intermediate state of matter between the liquid and solid states. As the temperature is lowered below a critical value, such a plastic crystal may solidify as either orientationally-ordered (crystalline) or orientationally-disordered (“orientational glass”) depending on the ratio of the potential and kinetic energy terms in the $O(4)$ quantum rotor model Hamiltonian that describes the system.

In considering the phase diagram of four-dimensional plastic crystals, which have the possibility for the realization of distinct low-temperature states, it is convenient to recast the uncertainty relations that apply to the operators of $O(4)$ rotors as a duality between topological point defects and condensed atomic particles. In this way, one can consider the structure of the dual low-temperature states (on either side of the self-dual critical point) in terms of the important degrees of freedom that characterize the four-dimensional undercooled quaternion ordered system.

In the range of dominant potential energy, just below the melting temperature T_M , conventional orientational ordering is prevented due to the existence of a gas of misorientational fluctuations that takes the form of spontaneously generated topological defects that belong to the third and first homotopy groups of $\mathcal{M}$. A Berezinskii-Kosterlitz-Thouless transition within this gas of misorientational fluctuations, at $T_{\text{defect-BKT}}$, drives the system towards the orientationally-ordered (crystalline) low-temperature state. In the classical potential energy limit, a perfectly orientationally-ordered ground state is favored that does not contain any topological defects at zero Kelvin; with the incorporation of kinetic energy effects, the critical temperature $T_{\text{defect-BKT}}$ gets reduced until, above some critical

value, a crystalline ground state is no longer possible.

By duality, in the range of dominant kinetic energy, it is a plasma of condensed particles that prevents the development of the solid state at the melting temperature and that must undergo localization to achieve the solid state. In a classical kinetic energy limit, minimization of the kinetic energy term favors the complete localization of condensed particles; this low-temperature state therefore exhibits maximal uncertainty in the orientation of polytope constituents throughout the four-dimensional “orientational-glass” low-temperature state. The existence of a zero-temperature transition between the distinct ground states is due to the fact that the potential energy and kinetic energy of the Hamiltonian model cannot be minimized simultaneously [17].

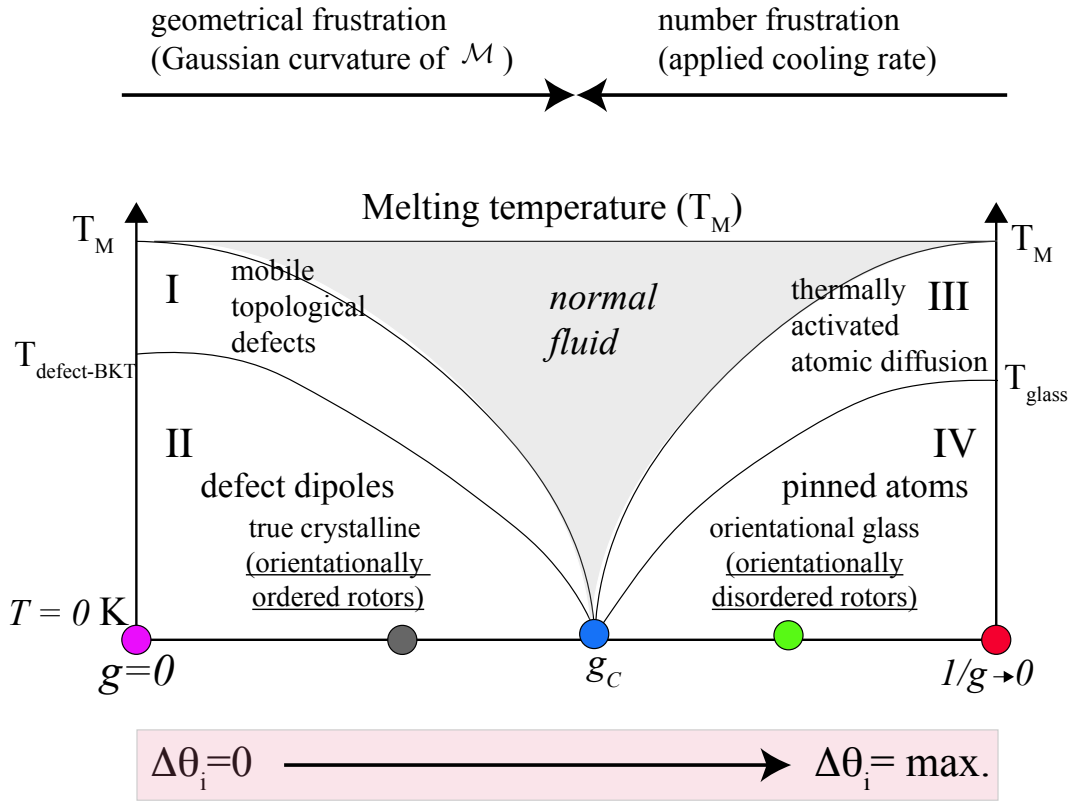


Figure 3.13: Anticipated phase diagram for solidification of 4D plastic crystals, as described using a four-dimensional $O(4)$ quantum rotor model. An orientationally-ordered low-temperature state (Region II) forms in the range of dominant potential energy ($g < g_C$). A dual “orientational glass” low-temperature solid state (Region IV) forms in the range of dominant kinetic energy ($g > g_C$). The crystalline low-temperature state is obtained at $T_{\text{defect-BKT}}$, by a defect-driven Berezinskii-Kosterlitz-Thouless transition within the gas of misorientational fluctuations that prevents conventional orientational order at finite temperatures (Region I). In contrast, the “orientational glass” low-temperature state is obtained at the critical glass transition temperature $T_{\text{dual-BKT}}$, as the metastable plastic crystal phase (Region III) falls out of its metastable equilibrium on cooling.

Figure 3.13 shows a schematic of the predicted phase diagram of four-dimensional plastic crystals, that shows a transition between dual orientationally-ordered (crystalline) and orientationally-disordered (“orientational glass”) low-temperature states. Below, the states of matter that exist within each important region (I, II, III, IV) and their mechanism of formation are identified.

1. Region I. In the range of dominant potential energy, below the melting temperature T_M , a four-dimensional plastic crystal phase forms in which each constituent of the system is well-coupled to its nearest-neighbors. The free rotation of constituents in this plastic crystal phase leads to a gas of misorientational fluctuations in the form of concomitant plasmas of spontaneously generated topological defects that belong to the third and first homotopy groups of $\mathcal{M} = S^3 \in H'$ (i.e., point defects and disclinations in 4D). The critical temperature $T_{\text{defect-BKT}}$ marks a defect-driven transition within the concomitant plasmas of topological point defects, that belongs to the Berezinskii-Kosterlitz-Thouless universality class. In the absence of geometrical frustration, the plasmas of topological defects are balanced in concentrations of topological defects with positive and negative sign. For increasing geometrical frustration, the concentrations of topological defects become biased towards those with negative sign and, the critical temperature $T_{\text{defect-BKT}}$ becomes reduced to zero above some critical value.
2. Region II. For temperatures below $T_{\text{defect-BKT}}$, topological defects are bound as low-energy paired configurations that allow for the existence of low-temperature orientationally-ordered solid states. Explicitly, the excitations from the ground state are sum-0 paired configurations of third homotopy group point defects and low-energy pairs of wedge disclinations that are considered to be edge dislocations. This 4D low-temperature orientationally-ordered solid state is an uncharged $SU(2)$ Bose-Einstein condensate of atomic particles, and is hence translationally ordered and crystalline. In the absence of geometrical frustration (kinetic energy effects), all topological defects that are mobile and unbound in Region I form low-energy paired configurations and none persist to the ground state which is perfectly orientationally ordered (such that $\Delta\theta_i = 0$ for $i = 0, 1, 2$). Geometrical frustration of the crystalline solid state forces a periodic arrangement of unpaired topological defects (of a single sign) to persist to the ground state. Despite the periodic arrangement of topological defects (zero configurational entropy), their presence in the geometrically frustrated crystalline ground state leads to a finite uncertainty in the orientation of the order parameter throughout the system, i.e., $\Delta\theta_i \neq 0$ for $i = 0, 1, 2$.
3. Region III. In the range of dominant kinetic energy, below the melting temperature T_M , a plastic crystal phase forms in which there is little interaction between the separate ordered regions. Such a plastic crystal phase is glass-forming, and will avoid crystallization. For temperatures between T_M and T_{glass} , which marks the critical glass transition temperature, rearrangements of atomic constituents are thermally activated and follow Arrhenius-like relaxation behavior.

In the limit of an extremely fast cooling rate, the plastic crystal mesomorphic phase will fall out of metastable equilibrium instantaneously as all atomic components within the system become thermally pinned (being unable to achieve internal relaxation within the given cooling rate). With finite cooling rates, the glass-forming plastic crystal phase can become increasingly undercooled by allowing for some rearrangements of atomic constituents that allow for internal relaxation of the structure. With progressive undercooling, internal relaxation of the glass-forming plastic crystal phase (Region III) ensures that fewer atomic components are thermally pinned at the critical glass formation transition temperature.

4. Region IV. For temperatures below T_{glass} , “orientational glass” low-temperature solid states form that have frozen in quenched disorder in some rotational degrees of freedom. These low-temperature orientationally-disordered solid states are non-crystalline and may be considered to be dual to crystalline solid states (Region II). In a classical limit, minimization of the kinetic energy term favors complete localization of condensed atomic particles in the solid state that is maximally orientationally-disordered (i.e., $\Delta\theta_i \equiv \text{max. for } i = 0, 1, 2$). By duality, this low-temperature solid state (Region IV) may be considered to be an $SU(2)$ Bose-Einstein condensate of topological defects. Real “orientational-glass” low-temperature states form when the constraint on the cooling rate is relaxed, such that some atomic constituents become internally relaxed by molecular rearrangements in the undercooled system (Region III). In the limit of an infinitesimal cooling rate, the self-dual critical point can be achieved at zero Kelvin that represents the limit in which a glass-forming plastic crystal phase becomes completely internally relaxed (i.e., $\Delta\theta_i \equiv \text{self-dual for } i = 0, 1, 2$) yet does not become translationally ordered. At this self-dual critical point, there is an entropy paradox where the difference in the configurational entropy of the glass-forming phase (Region III) and its crystalline counterpart is zero.

Solidification in three-dimensions

Three-dimensional undercooled atomic liquids, that develop below the melting temperature T_M , are related to mesomorphic 4D plastic crystal phases that may be described by four-dimensional $O(4)$ quantum rotor models. Just like mesomorphic 4D plastic crystalline phases, the undercooled atomic liquid can solidify as either an orientationally-ordered or orientationally-disordered solid state (i.e., crystalline and structural glass) as the temperature is lowered below a critical value. This is a consequence of the inability to simultaneously minimize the kinetic and potential energy terms of the Hamiltonian that describes the system. Figure 3.14 shows a schematic of the anticipated phase diagram for solidification processes in three-dimensions. A transition between dual crystalline and non-crystalline solid ground states is anticipated, at the critical point for which the potential and kinetic energy terms become comparable. The states of matter that exist within the important regions I, II, III, IV , and their mechanisms of formation, are discussed below.

1. Region I. In the range of dominant potential energy ($g < g_c$), below the melting temperature T_M , the system is driven to form atomic clusters that break the symmetry of the high-temperature liquid ($SO(3)$) to a discrete subgroup $H \in SO(3)$. The relevant orientational order parameter manifold is $\mathcal{M} = S^3/H'$ where H' is the binary representation of H . The three-dimensional atomic liquid is prevented from developing conventional long-range order at the melting temperature due to the existence of a gas of misorientational fluctuations in the form of spontaneously generated topological defects (disclination line defects and third homotopy group defects). In the limit that the undercooled atomic system is geometrically frustrated, the concentrations of topological defects become biased towards those with a negative sign – so that the overall Euclidean space remains flat in the presence of geometrical frustration. Just below the melting temperature, these spontaneously generated topological defects are mobile and destroy global orientational order.
2. Region II. In the range of dominant potential energy, below a critical temperature ($T_{\text{defect-BKT}}$), a crystalline ground state is obtained via a Berezinskii-Kosterlitz-Thouless transition within the

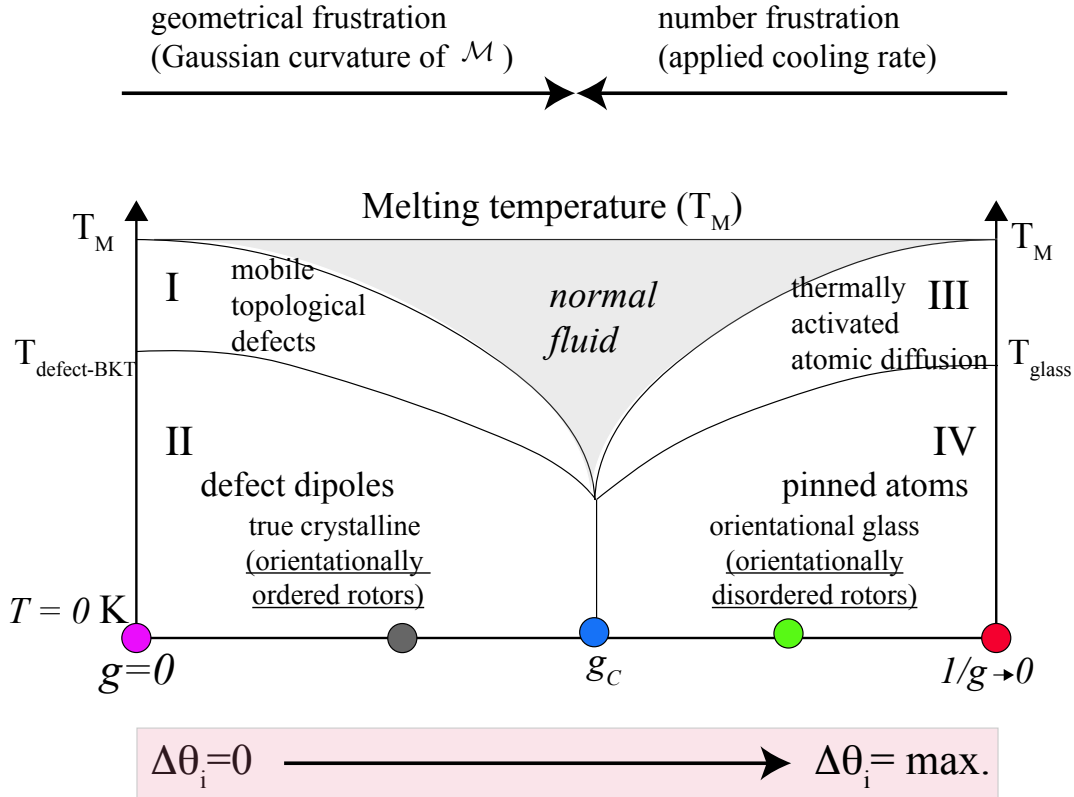


Figure 3.14: Schematic phase diagram of the three-dimensional $O(4)$ quantum rotor model, that describes solidification of undercooled atomic liquids in three-dimensions. The diagram is plotted in the coordinates of temperature versus the ratio of importance of kinetic and potential energies g .

gas of misorientational fluctuations that would otherwise destroy global orientational order at finite temperatures (Region I). On the formation of the crystalline solid state, disclination line defects in the undercooled atomic liquid form bound pairs of equal and opposite angular deficit. These bound pairs are considered to be edge dislocations [152, 21, 153, 154], which act as excitations from the crystalline ground state. A perfect crystal forms in the absence of geometrical frustration ($\Delta\theta_i = 0$ for $i = 1, 2, 3$). In cases of geometrical frustration, a major skeleton network of periodically arranged disclination line defects persists in the ground state ($\Delta\theta_i \neq 0$ for $i = 1, 2, 3$). The major skeleton network is comprised of frustration induced negative disclination lines that form an orthogonal grid in three-dimensions. With increasing geometrical frustration, the topological ordering transition temperature $T_{\text{defect-BKT}}$ is suppressed; above a critical value of geometrical frustration, a crystalline solid ground state can no longer form.

3. Region III. In the range of dominant kinetic energy ($g > g_C$), below the melting temperature T_M , the system is a viscous glass-forming undercooled liquid that is in a metastable equilibrium. This system is characterized by small interaction energy between neighboring atomic clusters. In order for the undercooled atomic system to remain in a metastable equilibrium, as the temperature is lowered below T_M , the atomic system must undergo irreversible motion by atomic rearrangements that are thermally activated. Glass formation occurs, at a critical temperature T_{glass} , as the system becomes frozen into a non-equilibrium configuration by falling out of metastable equilibrium. The absence of potential energy effects corresponds to an infinitely fast cooling rate, such that the undercooled atomic liquid system is unable to undergo any thermally activated atomic rearrangements (that would otherwise allow it to remain in metastable equilibrium, and undergo further undercooling). In the hypothetical limit of an infinitesimal cooling rate, an “ideal” structural glass forms at the point where the potential and kinetic energy terms are approximately equal.
4. Region IV. In the range of dominant kinetic energy, structural glass solid states exist for temperatures below T_{glass} . These structures are considered to be related to the 4D “orientational glass” low-temperature solid state of the 4D plastic crystal phase, which does not retain any artificial translational periodicity in the related three-dimensional solid state. In the limit of an infinitely fast cooling rate, i.e., in the absence of potential energy effects, each of the atomic constituents in the solid state are completely localized (thermally pinned) and the solid state is maximally orientationally disordered. Any real glass forms in the limit of a finite applied cooling rate, and does not exhibit complete localization (thermal pinning) of condensed atomic particles. This is due to the the partial internal relaxation of the undercooled atomic liquid from which it derived. In the limit of an infinitely slow cooling rate, one can extrapolate to a critical point where a system is maximally undercooled and forms a completely internally relaxed solid state that is not translationally-ordered.

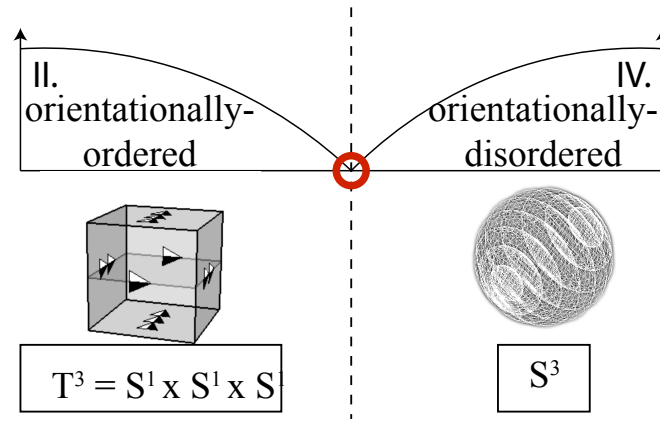


Figure 3.15: The three-dimensional torus is the translational order parameter manifold of a 3D crystalline lattice. In contrast, the order parameter manifold remains a hypersphere (S^3) in 3D systems that lack translational periodicity.

Importantly, the translational order parameter manifold of three-dimensional crystalline solid states (i.e., $g < g_C$) is a three-dimensional torus (T^3). This is due to the periodic boundary conditions that develop as a consequence of global translational order [145] (for a two-dimensional example, see Fig. 3.5). The torus manifold has zero total (integral) curvature, and therefore admits dislocations as fundamental homotopy group defects (i.e., instead of disclinations). On the other hand, the order parameter manifold of non-crystalline solids remains as the three-dimensional sphere (S^3) owing to the lack of translational order. Dislocations are not able to exist in relationship to S^3 , which has positive overall curvature and (thus) does not present a handle/hole that is characteristic of the torus. These statements are summarized graphically in Fig. 3.15.

The low-temperature ordered state of matter that exists at the point at which the potential and kinetic energy terms becomes comparable is of considerable interest. The order parameter manifolds on either side of this critical point are not topologically equivalent to one another (i.e., T^n is not S^n for $n > 1$). This is different than in the case of the $O(2)$ quantum rotor model, for which the order parameter on either side of the quantum phase transition resides on the topological manifold S^1 (in fact, $T^1 \equiv S^1$). The system at the self-dual critical point, that is achieved for a sufficiently geometrically frustrated system in the limit of an infinitely slow cooling rate, is entirely internally relaxed such that there are significant orientational correlations between neighboring groups of atoms yet there is no translational order. At this critical point, bound defects are unable to form and no atomic constituents are thermally pinned because the system is completely internally relaxed.

This hypothetical state of matter presents a bridge between the crystalline and non-crystalline solid state structures. Crystalline phases have both discrete translational and orientational order, and real non-crystalline solids lack both translational and orientational order; as a bridge, the state of matter at the self-dual critical point lacks translational order, but does possess significant orientational ordering (Fig. 3.16). Despite the critical point being both interesting and important, from

	TCP	Ideal glass	Real glass
Translational:	Discrete	none	none
Orientalional:	Discrete	Discrete	none

Figure 3.16: Crystalline solids have both discrete translational and orientational order. Real glasses have neither translational nor orientational order. At the self-dual critical point (i.e., crystalline-to-noncrystalline transition), an “ideal glass” can hypothetically form that has no translational symmetry but does exhibit long-range orientational correlations. This state of matter is akin to a quasicrystal, which has no translational symmetry but does exhibit long-range orientational order [167].

the point of view of topology and orientational ordering, a liquid-solid transition is not achievable at this point due to limitations on the cooling rate in the laboratory. This is because the solidification temperature at this critical point, defined at point of intersection of the crystal entropy curve with the supercooled liquid entropy curve (Kauzmann point [165, 168, 163]), falls below the real glass transition temperature T_{glass} at which the system falls out of metastable equilibrium as a consequence of a finite cooling rate.

Schematic diffraction patterns of the anticipated ground states, in the vicinity of the crystalline to non-crystalline transition that is located at a critical value of g (i.e., g_C), are shown in Figure 3.17 (A). Crystalline ground states are realized by the minimization of potential energy (i.e., for $g < g_C$), and non-crystalline ground states are realized by the minimization of kinetic energy (i.e., for $g > g_C$). The structures of the various ground states are discussed below.

- Perfect crystal. The diffraction pattern of a traditional crystalline solid state, that is free of topological defects and hence is not geometrically frustrated, shows discrete orientational symmetry and the diffraction spots are sharp. This structure may be considered to be obtained by the minimization of the potential energy term of the $O(4)$ quantum rotor model Hamiltonian in three-dimensions, via a defect-driven topological ordering transition.
- Topologically close-packed crystal. Geometrical frustration forces a finite density of topological line defects into the crystalline ground state, as the set of scalar phase angle parameters of the orientational order parameter vary from site to site. These topological line defects are arranged periodically, to ensure zero configurational entropy. In three-dimensions, such geometrically frustrated crystalline structures (commonly referred to as topologically close-packed [54] (TCP)) are identified by the network of topological line defects that persist to the ground state which is known as a major skeleton network [58, 23, 65, 54]. The major skeleton network is a contiguous network of atoms with coordination that is greater than the preferred coordination of the geometrically frustrated atomic vertices, which create orthogonal grids of negative disclination

lines. For example, in Frank-Kasper crystalline structures, atoms with $Z > 12$ coordination combine to form the major skeleton network that threads through an otherwise icosahedral medium that consists of atoms with $Z = 12$ coordination. Negative curvature is concentrated at the core of disclination line defects that comprise the major skeleton network, which balances the positive curvature that is attributed to geometrically frustrated atoms (such that the overall Euclidean space remains flat on average). In topologically close-packed systems, which exhibit the discrete symmetry of the major skeleton network of disclination lines, the diffraction spots are more diffuse than in the case of a perfect crystal that is free of geometrical frustration.

- Extreme orientational glass. This solid state may hypothetically be formed in the limit of an infinitely fast cooling rate, such that the entire $SO(3)$ symmetry group is frozen in globally. This ground state has maximal orientational disorder, and therefore exhibits a complete absence of orientational correlations between neighboring groups of atoms. This hypothetical non-crystalline solid state exhibits an especially broad and diffuse ring diffraction pattern.
- Real orientational glass. Lifting the constraint on the applied cooling rate, a real structural glass may form from the undercooled atomic liquid that is quenched using a finite applied cooling rate. A real glass exhibits some orientational correlations between its atomic clusters, and is partially internally relaxed. The global orientational order of real structural glasses remains trivial (i.e., the structural glass has frozen in $SO(3)$ symmetry globally), but there are increased orientational correlations as compared with the (hypothetical) extreme orientational glass. The ring diffraction pattern, characteristic of non-crystalline solids, is less diffuse than in the case of the (hypothetical) extreme orientational glass but remains broad.

The configurational entropy of the ground state depends on the spatial arrangement of topological defects that persist to zero Kelvin (if any). In the crystalline ground state, topological defects that persist to zero Kelvin form an ordered arrangement such that the crystalline solid state has zero configurational entropy at zero Kelvin (in accord with the third law of thermodynamics). On the other hand, the configurational entropy of real structural glasses at zero Kelvin is proportional to the amount of quenched in orientational disorder and increases proportional to the cooling rate (i.e., with faster cooling rates the undercooled liquid quenches in additional orientational disorder). However, it is anticipated that the configurational entropy of the completely internally relaxed structural glass, i.e., that forms at g_C , yet that is not translationally ordered is zero at zero Kelvin. Figure 3.17 (B) summarizes these statements.

3.2.4 Thermal transport properties

The dependence on temperature of the thermal transport properties of solid state systems is intimately related to the structure that forms from the undercooled atomic liquid. It is well-known

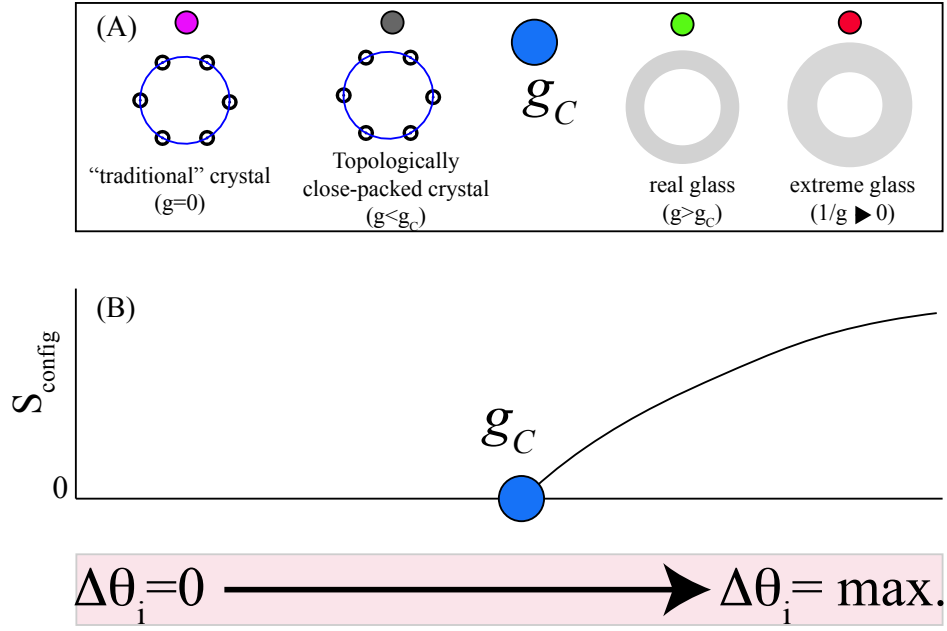


Figure 3.17: (A) Schematic diffraction patterns of anticipated ground states for various ratios of kinetic to potential energy (g). To the left of the self-dual critical point (located at g_c), the diffraction patterns are crystalline; to the right, the diffraction patterns are amorphous. (B) Configurational entropy is zero in the crystalline ground state, despite topological defects that may persist to the ground state in the case of geometrical frustration. On the other hand, configurational entropy at zero Kelvin is non-zero in non-crystalline solids – and is maximized in the absence of potential energy effects. An entropy paradox is evident at the self-dual critical point (g_c), for which the difference in configurational entropy of the glass-forming phase and its crystalline counterpart is zero (much like the Kauzmann paradox [165]).

that, crystalline and non-crystalline materials exhibit an inverse dependence of the thermal conductivity on temperature above approximately 50 K. Figure 3.18(A) shows the measured thermal conductivities of crystalline and “orientational glass” low-temperature states of a 3D plastic crystal; Figure 3.18(B) shows the measured thermal conductivities of 3D crystalline α -quartz and vitreous silica. The fact that the thermal conductivity of crystalline solid states increases rapidly with decreasing temperatures, while the thermal conductivity of non-crystalline solid states decreases with decreasing temperatures, was first pointed out by Eucken [2] (1911).

By applying the topological framework that has been presented in this thesis, the inverse temperature dependence of the thermal transport properties of crystalline and non-crystalline solid states (above approximately 50 K) may be viewed as a consequence of the realization of distinct ground states of $O(4)$ quantum rotor models. It follows that the thermal transport properties of the solid state may be viewed as an analogue to the well-studied example of the electrical transport properties of charged $O(2)$ Josephson junction arrays [16, 78], which display a singularity at the superconductor-to-superinsulator transition (Section 2.2: see Figures 2.15 and 2.16). Likewise, a singularity in the

thermal transport properties (as a function of temperature) is anticipated at the self-dual critical point (i.e., $g = g_C$) that belongs to the $O(4)$ quantum rotor model.

This kind of singularity, in the relevant material transport properties at a non-thermal transition between distinct ground states, is a characteristic of $O(n)$ quantum rotor models in general [17]. The inverse behavior of the material transport properties as a function of temperature on either side of the singularity is characteristic of dual low-temperature states that are ‘mirror images’ of one another [16, 132, 18] (in the context that the phase-coherent state acts as a Bose-Einstein condensate of condensed particles while the phase-incoherent state acts as a condensate of topological defects [138, 18]). Whereas electrical conductivity in superconductors is mediated by Cooper pair charge transport, thermal transport in a lattice is adequately described by the phonon gas model^f.

In the phonon gas model, lattice vibrational modes (plane wave collective oscillations, known as phonons) propagate heat. Lattice vibrational modes possess well-defined group and phase velocities [11], and develop wave-packets which incur multiple scattering mechanisms [11]. At high-temperatures, the thermal conductivity of crystalline solid states is determined primarily by the anharmonicity of lattice forces [170, 11]. Anharmonicity leads to phonon-phonon interactions, which result in phonons being scattered by other phonons (Normal and Umklapp scattering processes). Only Umklapp phonon-phonon scattering processes can affect the conduction of heat, because the total momentum of interacting phonons is not conserved which leads to finite thermal resistance. As

^fSee Appendix A for a discussion of the phonon gas model.

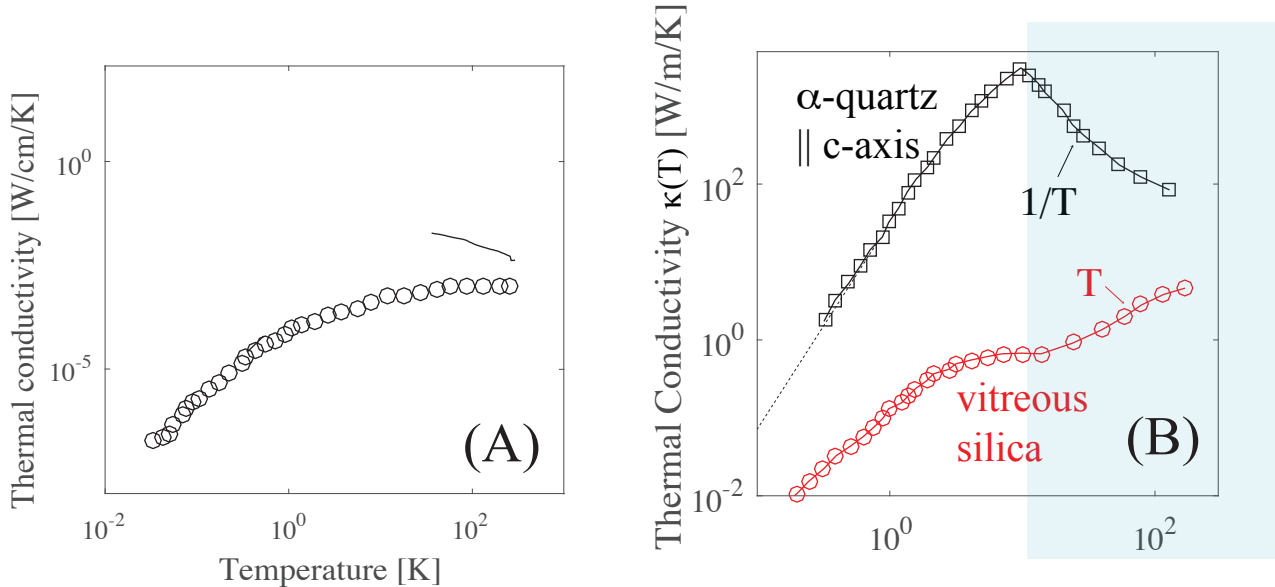


Figure 3.18: (A) The measured thermal conductivity of: single-crystal C_{60} (solid line, Ref. [169]), and solid C_{60}/C_{70} compacts (open circles, Ref. [13]). (B) Measured thermal conductivities of 3D structural crystalline and non-crystalline solid states (Ref. [79]).

the temperature is lowered, the frequency of resistive (anharmonic) Umklapp scattering processes becomes reduced and the thermal conductivity increases sharply.

In contrast, solid states that form from viscous undercooled atomic liquids (i.e., in the range of dominant kinetic energy) do not express a periodic lattice and so phonon collective excitations are unable to exist. The thermal conductivity in non-crystalline solids, above approximately 50 K, is well described by Einstein's picture [6] of a random walk of thermal energy between localized oscillators vibrating with random phases [13]. In his model of a random walk of thermal energy, heat exchange takes place within a distance that is approximately equal to the interatomic spacing [5]. The thermal conductivity predicted by this model decreases with decreasing temperatures [8, 4, 12], like the thermal conductivity of non-crystalline solids. The main difference between Einstein's model of thermal transport and thermal transport in the phonon gas picture is the critical assumption of a random phase of vibration of groups of atoms [13, 5]. Within the context of the topological framework presented herein, the random phase assumption in the random walk model of thermal transport has its origin in the fact that the kinetic energy term in the $O(4)$ Hamiltonian favors orientational disorder in non-crystalline solid states.

The thermal conductivity as a function of temperature of crystalline and non-crystalline systems, i.e., on either side of the anticipated singularity at $g = g_C$, are shown in Figure 3.19. Undercooled atomic liquids that are not geometrically frustrated are obtained by the minimization of potential energy (i.e., in the absence of kinetic energy effects), and are free of topological defects. This is possible because, as the temperature is lowered towards zero from the critical defect-driven Berezinskii-Kosterlitz-Thouless transition temperature, bound pairs of logarithmically interacting topological defects are brought together and annihilate (despite their topological stability as isolated entities). The ground state (at zero Kelvin) that is free of topological defects is perfectly orientationally ordered such that the uncertainty in the scalar phase angle parameters is completely eliminated, i.e., $\Delta\theta_i = 0$ for $i = 1, 2, 3$.

With the incorporation of geometrical frustration (i.e., with finite kinetic energy effects), the orientational order in the crystalline ground state is no longer perfect due to the presence of a finite density of frustration induced topological defects that form an ordered network. The Frank-Kasper phases [58, 57] (e.g., A15 and Laves phases [54]) are interesting examples of condensed matter systems that exhibit an ordered array of frustration induced negative disclination lines [15], in order to permit a crystalline solid state with local orientational order that has icosahedral symmetry. Despite the periodic arrangement of the frustration induced topological defects in the crystalline ground state, their presence generates a finite uncertainty in the global orientational order parameter such that $\Delta\theta_i \neq 0$ for $i = 1, 2, 3$.

For a given material composition, a maximum magnitude of thermal conductivity should occur in the limit that the crystalline ground state is not geometrically frustrated ($g = 0$, pink). As the self-dual critical point is approached from $g = 0$, i.e., with the incorporation of geometrical frustration,

it is anticipated (by analogy with $O(2)$ Josephson junction arrays) that the overall magnitude of the thermal conductivity is suppressed (finite $g < g_C$, grey). The quantity of geometrical frustration, that is quantified by the difference in Gaussian curvature of the ideal polytope (i.e., order parameter manifold) $\mathcal{M}$ with flat space, is inversely proportional to the distance between frustration induced topological defects in the crystalline ground state. With a critical value of geometrical frustration (i.e., at the self-dual critical point), the distance between topological defects that persist to zero Kelvin becomes small enough that their cores overlap and the ground state is no longer crystalline.

With a critical value of geometrical frustration, the system whose ground state is no longer crystalline is no longer subject to resistive Umklapp scattering processes. Thus, at the self-dual critical point, the characteristic features of translational order are no longer displayed in the thermal transport properties such that the thermal conductivity does not increase with decreasing temperatures (see Fig. 3.19). Despite lacking translational order, this system does express orientational order and therefore acts as a bridge between the crystalline and non-crystalline structures (see Fig. 3.16). It

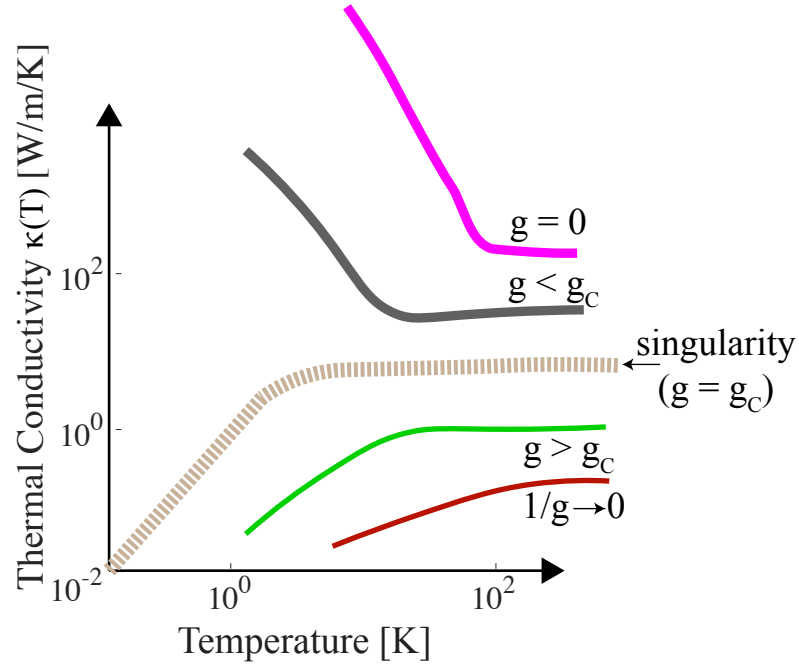


Figure 3.19: Anticipated thermal conductivity κ of solid states above approximately 50 K. κ of crystalline solids increases sharply with decreasing temperatures. With the incorporation of geometrical frustration (gray), the overall magnitude of κ should become suppressed as compared with an unfrustrated crystalline counterpart (pink). In contrast, κ of non-crystalline solids decreases with decreasing temperatures over the same temperature range. For a given material composition, the thermal conductivity of the non-crystalline solid state is anticipated to be proportional to the amount of undercooling prior to glass formation. This is because increasingly undercooled systems (green) exhibit more orientational correlations than those that derive from less undercooled systems (red). A singularity in the thermal transport properties, with respect to temperature, is anticipated to exist at the self-dual critical point that belongs to the $O(4)$ quantum rotor model (dashed).

follows that this hypothetical solid state (at $g = g_C$) should present thermal transport properties that are similar to quasicrystals (which have orientational order but do not possess periodic translational order). The thermal transport properties of quasicrystalline materials have been shown [171, 172, 173] to be comparable to those observed in amorphous systems.

In non-crystalline solids, which form because of limited interactions between neighboring groups of atoms, orientational disorder is favored at low-temperatures (i.e., by the minimization of kinetic energy). In the complete absence of potential energy effects, an “extreme” glass low-temperature solid state forms that exhibits a complete lack of orientational correlations between neighboring groups of atoms, i.e., $\Delta\theta_i$ ($i = 0, 1, 2$) is maximum. In this limit, all atomic constituents are thermally pinned at the glass transition. This is a realization of a system of Einstein oscillators that are entirely uncoupled, and thus cannot transmit thermal energy from one group of atoms to another [5, 6] ($1/g \rightarrow 0$, red). Real non-crystalline solid states derive from viscous undercooled atomic liquids that have small (finite) interactions between neighboring groups of atoms.

The incorporation of finite potential energy effects can also be achieved in the laboratory with finite cooling rates; specifically, the inverse cooling rate can be utilized as a tuning parameter that drives the quantity $1/g$ from 0 towards the self-dual critical point, where the kinetic and potential energies are comparable. With slower cooling rates, progressive undercooling becomes possible as internal relaxations are achieved by performing necessary molecular rearrangements (thermally activated) within the time allowed by the cooling rate. In the limit that kinetic and potential energies are comparable, which can be achieved in the case of an infinitely slow cooling rate, the undercooled atomic liquid becomes entirely internally relaxed prior to the formation of the solid state.

Real non-crystalline solids exhibit only incomplete internal relaxation, and atomic constituents that are not internally relaxed become thermally pinned on glass formation. As a result of internal relaxation, real glassy solids exhibit some orientational correlations between neighboring groups of atoms such that $\Delta\theta_i$ for $i = 0, 1, 2$ is finite and not maximum. These orientational correlations allow for heat transfer to occur by a random walk mechanism ($g > g_C$, green). That is, as the self-dual critical point is approached from $1/g \rightarrow 0$, orientationally correlated regions that develop become larger and additional heat transfer can occur between neighboring groups of atoms by the random walk mechanism.

Chapter 4

Summary and Conclusions

The current thesis is based on seminal work from across a wide range of fields in order to offer a topological perspective on the development of the solid state from undercooled atomic liquids. The hypotheses on which this thesis is based (Section 1.8) have been shown to be self-consistent in that they enable the consideration of the entire range of solid state structures (i.e., perfect crystals, topologically close-packed crystals and glassy solids), and their thermal transport properties, in a way that does not lead to inconsistencies with what has been observed experimentally. This should open the door for the classification of solid state materials, and their thermal transport properties, in terms of topological defects. The interplay between topological defects and material transport properties is a concept that applies generally in the field of materials science, for which real structures at temperature are never perfect and always contain such defects.

Atomic fluids in the symmetric high-temperature phase, i.e., above the melting temperature, exhibit continuous rotational symmetry in three-dimensions $G = SO(3)$. This symmetry group has a 2-to-1 homomorphism with the group of quaternion numbers that are four-dimensional. As the backbone of this work, parallels have been drawn between orientational ordering processes in systems that are characterized by a quaternion order parameter versus those that are characterized by a complex order parameter. In particular, in this thesis, the emphasis has been on the mechanisms of orientational ordering in restricted dimensions. By comparing solidification of undercooled atomic liquids in four- and three- dimensions (characterized by a quaternion orientational order parameter) with the development of low-temperature states of complex ordered systems that exist in restricted dimensions (Mermin-Wagner theorem), undercooling below the melting temperature can be viewed as a topological consequence of ordering in restricted dimensions.

A distinguishing feature of complex ordered systems that exist in restricted dimensions is the possible existence of a gas of misorientational fluctuations, just below the bulk critical transition temperature, in the form of spontaneously generated topological defects that belong to the fundamental homotopy group of the complex order parameter manifold (i.e., $\pi_1(S^1)$ vortices). In this thesis, an analogous phenomena has been considered for quaternion ordered systems that exist in re-

stricted dimensions for which misorientational fluctuations take the form of spontaneously generated topological defects that belong to the third homotopy group (i.e., $\pi_3(S^3)$). These third homotopy group defects are points in four-dimensions. Just as vortex topological defects are of crucial importance in preventing conventional global orientational order at finite temperatures in complex ordered systems that exist in restricted dimensions, third homotopy group topological defects play the same role quaternion ordered systems that exist in restricted dimensions.

Numerical Monte-Carlo simulations have been performed on a model quaternion ordered system in four-dimensions, i.e., $O(4)$ quantum rotor model in four-dimensions, in order to investigate the nature of the transition to the orientationally-ordered low-temperature state. The $O(4)$ rotor model studied with these simulations is continuous, and so only third homotopy group point defects are admitted as topologically stable defect elements. On lowering the temperature below a critical value, a phase transition has been detected within the quaternion ordered system in four-dimensions. The thermodynamic response functions (susceptibility and heat capacity), in the vicinity of the transition, show behavior that is characteristic of topological ordering. Specifically, the observed susceptibility shows evidence of a strong finite size scaling with the lattice size. This kind of strong scaling behavior is known to occur in the vicinity of Berezinskii-Kosterlitz-Thouless type transitions. Moreover, the specific heat was found to be independent of the lattice size for large enough lattices, which is indicative of the absence of conventional long-range order at finite temperatures. Thereby, the author concludes that the Monte-Carlo simulation results support heuristic topological arguments that suggest the binding of point defects into low-energy sum-0 pairs below a critical temperature. These paired configurations lead to distortions in the order parameter field far from the pair that can be continuously deformed to the uniform state, and thereby allow for the existence of an orientationally-ordered state at finite temperatures in restricted dimensions.

In addition to novel topological ordering phenomena, ordering in restricted dimensions brings with it the possibility for the realization of distinct low-temperature states that are either orientationally-ordered or orientationally-disordered – and *frustration* of such ground states. This is a consequence of the mathematical applicability of $O(n)$ quantum rotor models, which are characterized by both potential and kinetic energies, to describe n -vector ordered systems (e.g., complex 2-vector, quaternion 4-vector) that exist in restricted dimensions. The $O(4)$ quantum rotor model applies in cases of solidification in four- and three-dimensions, just as $O(2)$ quantum rotor models describe ordering phenomena in Josephson junction arrays of complex order parameters (i.e., two- and one-dimensions). The defect-driven topological ordering transition that belongs to the $O(4)$ quantum rotor model, that has been detected with numerical Monte-Carlo simulations, thereby indicates that crystallization does not occur by spontaneous symmetry breaking and instead is obtained by a transition that is driven by topological defects. In three-dimensional atomic systems, this defect-driven transition towards the crystalline solid state is most evident as the formation of dislocation line defects as dipoles of complementary wedge disclinations (on crystallization).

Herein, a complete phase diagram for solidification in terms of an $O(4)$ quantum rotor model has been developed. Geometrical frustration, quantified by the positive Gaussian curvature attributed to atomic vertices that are unable to tessellate flat space, has been used as a tuning parameter that leads to finite kinetic energy effects. Owing to the positive curvature associated with atomic vertices that are geometrically frustrated, the gas of misorientational fluctuations in the form of topological defects becomes biased towards the concentration of defects that carry negative curvature – keeping the overall Euclidean space flat on average. These excess negatively signed topological defects are unable to form bound pairs at the topological ordering transition temperature, and persist to the crystalline ground state in a periodic fashion (major skeleton). Such geometrically frustrated crystalline ground states are topologically close-packed (Frank-Kasper structures, that express local icosahedral orientational symmetry, are a particular example). At a critical value of geometrical frustration, the gas of misorientational fluctuations in the form of topological defects (just below the melting temperature) becomes entirely biased towards the concentration that carries a negative sign. In this critical limit, crystallization is forbidden as low-energy paired configurations of topological defects (that allow for the existence of the crystalline solid state) are no longer able to develop. Within the context of the $O(4)$ quantum rotor model, solidification of undercooled atomic liquids to non-crystalline solid states occurs in the range of dominant kinetic energy (which is minimized in the limit of maximal orientational disorder in the solid state).

By the nature of the non-thermal transition between distinct ground states (here, crystalline and glassy), one expects a singularity in the relevant transport properties at the transition. Such a singularity is evident in the thermal transport properties of the solid state, at the self-dual critical point that belongs to the $O(4)$ quantum rotor model. While the thermal conductivity of crystalline matter increases rapidly with decreasing temperatures, the thermal conductivity of non-crystalline matter decreases rapidly with decreasing temperatures. The thermal conductivity of the solid state, that exhibits a singularity at the non-thermal transition between distinct ground states, has been considered in analogy to the electrical transport properties of charged $O(2)$ Josephson junction arrays that exhibit a singularity at the superconductor-to-superinsulator transition. On the formation of the phase-coherent (superconductor) low-temperature state in restricted dimensions, the electrical resistance tends rapidly to zero; in contrast, on the formation of the phase-incoherent (superinsulator) low-temperature state, the electrical resistance tends rapidly to an infinite value. Thus, ordering characteristics of the distinct ground states of an $O(n)$ quantum rotor model match the behavior of the relevant material transport properties.

The hypotheses listed in Section 1.8 have been shown to be self-consistent and, hence, can be used to further elucidate the topological origins of solid state structures. This thesis has been designed to enable others to pursue the concept, and the author hopes that these pursuits will open a new field of research into the role of topology in the change of phase of the undercooled liquid to the solid state and in their thermal transport properties.

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Glossary

References are denoted with brackets []. Page numbers in dissertation are without brackets.

Abrikosov vortex lattice A lattice of parallel vortices that develop in a type-II superconductor (i.e., a superconductor with negative surface energy) in an applied magnetic field [97]. 28

binary group A binary group H' is related to the group H by a 2-to-1 group homomorphism, on taking the lift of H into its simply connected covering group (universal). Hence, the binary group H' contains twice the number of symmetry elements as H . Examples arise by taking the lift of $H \in SO(3)$ into $SU(2)$; the lifted group $H' \in SU(2)$ is the binary group of H . H' contains twice the number of symmetry elements as H , because two quaternions correspond to each rotation in three-dimensions [19, 20, 23, 27]. *See also* universal covering group and lift. 4

bulk dimension The bulk dimension, for a particular n -vector order parameter, is the dimension in which spontaneous symmetry breaking of the symmetric phase can occur. In general, the bulk dimension is greater than n . *See also:* restricted dimension. 54, 55

bulk critical transition temperature For systems that exist in the bulk dimension, the bulk critical transition temperature (T_C) is the temperature at which the symmetry of the high-temperature phase is spontaneously broken. In bulk $U(1)$ superfluids (i.e., three-dimensional), T_C marks the second-order transition to the superfluid in three-dimensions (T_λ or T_{BCS}). For n -vector ordered systems that exist in restricted dimensions, below the bulk critical transition temperature, n -dimensional ordered regions form that are weakly-linked to their nearest-neighbors. That is, in restricted dimensions, a conventional disorder-order phase transition at the bulk critical transition temperature (T_C) is prevented. 18, 48

Burger's vector The Burger's vector ($\vec{b}$) is a topological invariant that measures the strength and direction of a dislocation in a crystalline lattice, upon taking a closed loop around the topological defect core. For example, the fundamental homotopy group of the 3-dimensional torus (i.e., the Cartesian product of three circles: $\mathbb{T}^3 = S^1 \times S^1 \times S^1$) is $\pi_1(\mathbb{T}^3) = \mathbb{Z} \times \mathbb{Z} \times \mathbb{Z}$, where $\mathbb{Z}$ is the lattice of integers. That is, a dislocation line defect in a three-dimensional lattice is represented by a Burger's vector that consists of three integers (b_1, b_2, b_3) where b_i represents an extra plane of atoms in a direction i . A non-zero value of b_i defines a closed loop

in order parameter space that winds b_i times around the torus along the coordinate i . For a two-dimensional example see Fig. 3.5. In the case of an edge dislocation, the Burger's vector is perpendicular to the line direction, for a screw dislocation, the Burger's vector is parallel to the line direction. *See also* Dislocation, fundamental homotopy group and, $\mathbb{T}^m$. 9, 10, 37, 67

Chern class The m^{th} Chern class describes the behavior of the set of tangent vectors on manifolds of dimension $d = 2m$, where m is an integer. The Chern class measures the number of source/sink singularities that are forced into a tangent vector configuration on a surface. Any tangent vector field on an even-dimensional sphere will contain source and sink singularities unlike for even-dimensional tori. The Chern number is the Euler characteristic of the surface. 155

compact Lie group A compact Lie group is a compact smooth manifold together with a group structure for multiplication. The only spheres that admit a compact Lie group structure are S^1 (unit complex numbers) and S^3 (unit quaternions numbers). 53

configurational entropy The total entropy of a thermodynamic system can be separated into multiple components including thermal entropy due to thermal energy (S_{TM}), and configurational (residual) entropy due to misorientations (S_0). The thermal entropy, which is a measure of the thermal energy that cannot be converted into useful work, goes to zero at zero Kelvin ($S_{TM} = \int (C_V/T)$, where C_V is the heat capacity at constant volume). On the other hand, the configurational entropy is not a function of temperature; instead, the configurational entropy depends on the number of molecules N and the number of distinct orientations available to them Ω ($S_0 = Nk_B \ln \Omega$, where k_B is the Boltzmann constant). The total entropy of a thermodynamic system is then the sum of its multiple components. The configurational entropy may remain non-zero at zero Kelvin in systems that are not orientationally-ordered (hence, not in equilibrium). *See also:* third law of thermodynamics. 16, 36, 57

critical exponents Traditionally, critical exponents describe the scaling behavior of thermodynamic variable in the vicinity of continuous (second-order) phase transitions, e.g., $c_V \sim (T - T_C)^{-\alpha}$ and $\zeta \sim (T - T_C)^{-\nu}$. Critical exponents depend on the universality class to which the model belongs. The scaling behavior of physical quantities near higher-order topological ordering transitions are also characterized by critical exponents; in particular, for XY models in two-dimensions, the susceptibility (χ) depends on the correlation length (ζ) as $\chi \sim \zeta^{2-\nu}$ where $\nu = 1/4$ is the critical exponent at the topological ordering transition. *See also:* universality class. 41

developable surface A surface $\mathcal{M}$ is a developable surface if, and only if, its Gaussian curvature K is equal to zero (i.e., Euler characteristic is zero). A developable surface can be "flattened" into Euclidean space without distortions such as tearing (i.e., without the introduction of permanent topological defects) *See also:* Euler characteristic and Gaussian curvature. 14

director In mesomorphic states of matter, a director ($\hat{\mathbf{n}}$) denotes the special molecular orientation that is characteristic of the mesomorphic state. For instance, the anisotropic molecules of a liquid crystal are oriented along the director. 61, 152

dislocation A dislocation is a topological defect that is available in crystalline lattices, i.e., an irregularity within the crystalline structure. Dislocation topological defect elements belong to the fundamental homotopy group of the m -dimensional torus (T^m) that defines the translational order parameter space of the n -dimensional crystalline lattice (see Fig. 3.5), i.e., $\pi_1(T^m)$. Translational order is lost at the core of a dislocation. The two basic kinds of dislocation are edge dislocations and screw dislocations. A three-dimensional dislocation line is characterized by its line direction and its Burger's vector (topological invariant) that describes the magnitude and direction of distortion in the lattice. 9, 67

first Brillouin zone A translationally ordered crystalline solid structure, defined by primitive translation vectors ($\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$), is characterized by a reciprocal lattice that is defined by reciprocal lattice vectors ($\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$). The boundaries of the first Brillouin zone are the planes normal to the six reciprocal lattice vectors ($\pm\mathbf{b}_1, \pm\mathbf{b}_2, \pm\mathbf{b}_3$) at their midpoints [11]. This central cell, the first Brillouin zone (also known as the Wigner-Seitz primitive cell of a reciprocal lattice [11]), is especially important in the study of electron and phonon dispersion relationships and in diffraction experiments. 21, 122

Frank-Kasper crystalline structure Frank-Kasper phases are topologically close-packed crystals that express preferred icosahedral orientational order, that is geometrically frustrated from filling three-dimensional Euclidean space. The non-icosahedral environments form a network of disclination lines (that belong to the fundamental homotopy group) that is called the major skeleton network. *See also:* major skeleton network and topologically close-packed. 12

Frank vector A Frank vector ($\vec{\omega}$) is the topological invariant that characterizes a disclination, that is introduced by the Volterra process. The rotation on the cut surface (angular deficit) is the vector ω that is known as the Frank vector (see Fig. 1.5). *See also* Wedge disclination and Volterra process. 9, 10, 67

fundamental homotopy group The fundamental (first) homotopy group of a topological space X , i.e., $\pi_1(X)$, records information about the topological properties of X by classifying closed paths (loops/circuits) into homotopy classes of loops. Elements that belong to the same homotopy class are homotopic to one another (they can be continuously deformed into each other). While all higher homotopy groups ($\pi_i, i \geq 2$) are necessarily Abelian [21, 148], the fundamental group is in general non-Abelian [174, 20]. *See also* homotopy and homotopy group. 16

Gaussian curvature The Gaussian curvature K at a point on a surface is the product of its principle curvatures, κ_1 and κ_2 : $K = \kappa_1 \kappa_2$. The two principal curvatures measure how the surface bends by different amounts in different directions. In the case of a sphere (S^2) of radius R , the Gaussian curvature everywhere is $1/R^2$. A surface with zero integral Gaussian curvature is a developable surface, i.e., a surface that has Euclidean geometry and can therefore be “flattened” into Euclidean space without distortion (i.e., Euler characteristic zero, e.g., T^2) *See also*: Euler characteristic and developable surface. 14, 71

geometrical frustration Geometrical frustration is the phenomenon in condensed matter systems where it is not possible for atoms to sit simultaneously in the potential energy minimum presented by all of its neighbors. Geometrical frustration is the result of preferred local orientational order that is incompatible with a space-filling arrangement in ordinary Euclidean space. For example, regular tetrahedra and icosahedra are geometrically frustrated in three-dimensions. *See also*: major skeleton network and Gaussian curvature. v, 62

Ginzburg-Landau parameter The value of the Ginzburg-Landau (G-L) parameter distinguishes [97] type-I superconductors from type-II superconductors, which allow for the penetration of magnetic field into vortex topological defects. The G-L parameter is the ratio of the magnetic field penetration depth and the superconducting coherence length. As the G-L parameter increases above $1/\sqrt{2}$, the surface energy between the superconducting and normal layers becomes negative and applied magnetic field above a critical value can penetrate the sample as an Abrikosov vortex lattice. *See also*: Abrikosov vortex lattice and vortices. 29

glass A glassy solid (i.e., amorphous or non-crystalline solid) is a state of matter that resists shear deformation (i.e., its shear modulus of rigidity is nonzero) but that does not possess long-range order. By convention, any non-crystalline material whose viscosity is greater than 10^{13} Poise is called a glassy solid [175]. 10, 15, 82

Hamiltonian The Hamiltonian ($\hat{\mathcal{H}}$) corresponds to the total energy of the system, i.e., $\hat{\mathcal{H}} = \hat{T} + \hat{V}$ where $\hat{T}$ is the kinetic energy and $\hat{V}$ is the potential energy. 18

homeomorphic Homeomorphisms are mappings that preserve all of the topological properties of a topological space. Two spaces with a homeomorphism between them are topologically equivalent (they are the same from a topological point of view). In order to explain homeomorphisms, one is drawn to the joke: “when is a coffee mug a donut (torus)?” Topologically, these spaces are homeomorphic because they each contain a single hole (i.e., a single genus). An example of a homeomorphism in physics is the homeomorphism between the three-sphere S^3 and the unitary group of degree two $SU(2)$. 154

homomorphism A homomorphism between two groups (G_1 and G_2) is a map $f : G_1 \rightarrow G_2$ such that the group operation is preserved. Therefore, a group homomorphism maps the identity element in G_1 to the identity element in G_2 . There are many types of group homomorphisms, including: one-to-one and two-to-one (e.g., between $SU(2)$ and $SO(3)$ are related by a 2-to-1 homomorphism). 4, 9, 58

homotopy Two continuous functions are homotopic if they can be continuously deformed into one another, this continuous deformation is known as a homotopy between the two functions. An important use of homotopy is in the characterization of topological defects as elements that belong to particular homotopy groups. *See also:* homotopy group and fundamental homotopy group and topological defect. 9

homotopy group Homotopy groups classify the topological properties of a topological space $\mathcal{M}$. The i^{th} homotopy group $\pi_i(\mathcal{M})$, is the group of all topological defects that are defined using maps of an i -dimensional sphere onto the given topological space $\mathcal{M}$ (with a law for the combination of topological defects) *See also* homotopy and fundamental homotopy group. 7

icosahedral symmetry The icosahedral rotation group (532) has 60 rotational (orientation-preserving) symmetry elements, i.e., Y is of order 60. The full icosahedral group Y_h ($\bar{5}32/m$) has a center of inversion such that it has order 120. (The full icosahedral group Y_h is a subgroup of $O(3)$, while the rotational icosahedral group Y is a subgroup of $SO(3)$.) Icosahedral symmetry contains five-fold symmetry elements, which are incompatible with a space-filling arrangement in three-dimensions. Hence, atomic systems that exhibit icosahedral symmetry are geometrically frustrated in flat space. *See also:* isotropy subgroup. 91

infinite-order phase transitions Infinite order phase transitions do not show any *regular* singularity in any finite derivative of the free energy (in an Ehrenfest sense). A most famous example of an infinite order phase transition is the Berezinskii-Kosterlitz-Thouless topological ordering transition in two-dimensions. 41

inner product An inner product is a generalization of the dot product for real numbers to vectors with imaginary components. The standard definition of the inner product of two vectors with imaginary components ($\mathbf{v}$ and $\mathbf{w}$) is defined as: $\langle \mathbf{v} | \mathbf{w} \rangle = v_1 w_1^\dagger + v_2 w_2^\dagger + \dots + v_n w_n^\dagger = \sum v_i w_i^\dagger$ where $\dagger$ is the complex conjugate. 35

irrotational An irrotational vector field has a vanishing curl. Irrotational flow occurs when the curl of the velocity is zero: $\omega = \nabla \times v = 0$. This behavior is evident in $U(1)$ superfluids for which the velocity field is the gradient of a scalar phase angle parameter, i.e., $v = \nabla \theta$, because the curl of a gradient of a scalar field is zero. 26

isotropy subgroup The isotropy subgroup (H) is the group of elements in G that describes the remaining symmetry of the ordered parameter [19, 20] (leaves the order parameter (ground state) invariant). The topological order parameter manifold ($\mathcal{M}$) is the quotient of the symmetry group of the symmetric phase G and the isotropy subgroup H of the state of broken symmetry, i.e., $\mathcal{M} = G/H$. For example, the uncharged superfluid breaks the $U(1)$ group to the trivial group and has a topological manifold: $\mathcal{M} = U(1)/1 = S^1$. 5

Josephson junction A (charged) Josephson junction is a device that is composed of two macroscopic superconductors that are coupled by a weak-link, that typically consists of a thin insulating barrier. The Josephson effect is an example of a “macroscopic quantum phenomenon” in which a supercurrent of condensed particles can tunnel across the insulating junction. The two characteristic energies of a charged Josephson junction are the Josephson coupling energy E_J and the charging energy E_C . 30

Josephson junction array A Josephson junction array (JJA) is a network of Josephson junctions. In restricted dimensions (for complex order parameters), a naturally occurring Josephson junction array forms as the temperature is lowered below the bulk critical transition temperature (T_C). That is, separate 2D complex ordered regions develop that are weakly-linked to their nearest-neighbors forming Josephson junctions. 3

Kauzmann paradox The Kauzmann paradox [165, 176] is an entropy paradox where the entropy of a glass-forming liquid is equal to the crystal entropy, on extrapolating to the Kauzmann point. The Kauzmann paradox is hypothetical, because no real glass-former can be cooled sufficiently slowly to achieve the Kauzmann temperature; any real glass transition occurs at a temperature above the Kauzmann temperature, as the system forms a glass on falling out of metastable equilibrium. 89

lift Taking a “lift” makes use of a 2-to-1 homomorphism between two groups in order to describe the group on a simply connected covering space. The lift of the subgroup $H \in SO(3)$ into $SU(2)$, is obtained by making use of a 2-to-1 homomorphism. The lifted group, $H' \in SU(2)$, is called a binary group because it is twice the size of $H \in SO(3)$ (two quaternions correspond to each rotation in three-dimensions [19, 20, 23, 27] (see Appendix C)). For example, consider taking the “lift” of the identity element, which corresponds to a 0 or 2π rotation in three-dimensions, into $SU(2)$. The lifted group now consists of two elements that are represented by 2×2 unitary matrices: $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ and $\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$. Thus, the lifted group of $I \in SO(3)$ gives the three-sphere with diametrically opposite points identified [20], i.e., $\mathcal{M} = S^3/\mathbb{Z}_2$. The topological manifold now allows for a single non-trivial topological defect element [149, 52] measured by a closed loop that connects the antipodal points on S^3 . *See also:* binary group, homomorphism and

universal covering space. 4, 59, 72, 114

liquid crystal Liquid crystals are mesomorphic states of matter that behave as solid-like liquids (anisotropic liquids). Liquid crystals are composed of anisotropic (e.g., rod-like) molecules that develop a preferred orientational alignment along a special axis, known as the director. A liquid crystalline phase transitions towards a crystalline solid state at a lower temperature, by breaking the remnant translational symmetry of the liquid crystal. *See also:* director. 10

long-range order Long-range order (LRO) means that the order parameter in an ordered system is periodic, such that if the value of the order parameter is known at $\mathbf{x} = 0$ it is also known at $\mathbf{x} = \infty$. In solids, the existence of Bragg peaks in x-ray diffraction scattering patterns is indicative of LRO. 5, 16, 84

lower critical restricted dimension The lower critical restricted dimension (D_{low}) is the largest geometric space dimension for which spontaneous symmetry cannot be broken by a continuous n -vector order parameter, e.g., two- and one-dimensions for complex ordered systems, and four- and three- for quaternion ordered systems. *See also:* restricted dimension. 5

major skeleton network A major skeleton network forms because topologically close-packed crystalline phases (e.g., Frank-Kasper phases), which are based on tetrahedral units only, are geometrically frustrated. While some atoms in the crystalline solid state express the local geometrically frustrated coordination (minor network, e.g., $Z = 12$) others have higher coordination numbers (e.g., $Z > 12$). The atoms with higher coordination number form contiguous disclination lines, that result in the major skeleton network of three orthogonal grids of negative disclination lines in three-dimensions. *See also:* geometrical frustration. 13

Meissner effect The Meissner effect in a superconductors (i.e., charged $U(1)$ superfluid) is the expulsion of a magnetic field by the superconducting phase. The Meissner effect is a consequence of the energy cost to change the amplitude degree of freedom of the superconducting order parameter (away from its ideal position on the basin $\mathcal{M}$). 25

Mermin-Wagner theorem The Mermin-Wagner theorem states that, for systems that exist in two- or one-dimensions (restricted dimensions), continuous symmetries cannot be spontaneously broken at finite temperatures by developing conventional long-range order. 32, 94

mesomorphic phase Mesomorphic phases have mechanical properties and symmetry properties that are intermediate between those of liquid and solid states. The term mesomorphic applies to materials of “middle” (Greek: mesos) “form” (Greek: morphe) that are classified as either liquid-like solids (plastic crystals) or solid-like liquids (liquid crystals). *See also:* plastic crystal and liquid crystal. 10, 80

Nambu-Goldstone boson A set of Nambu-Goldstone bosons are anticipated in models that exhibit the spontaneous breakdown of continuous symmetries. The number of Nambu-Goldstone bosons that necessarily appear are equal to the number of generators that belong to the continuous symmetry group that characterizes the high-temperature system. Nambu-Goldstone bosons are long-wavelength massless fluctuations of the order parameter that have no energy cost associated with them. Phonons are Nambu-Goldstone bosons. For example, $U(1)$ superfluids have a single Nambu-Goldstone boson ($\theta \rightarrow \theta + \theta_0$) and crystalline solid states have three Nambu-Goldstone bosons ($1L + 2T$). *See also:* spontaneous symmetry breaking. 24, 55

non-Abelian group Elements of a non-Abelian group do not commute (i.e., the order of operation matters). That is, in a non-Abelian group G , there exists at least one pair of elements g_1 and g_2 such that $g_1 \cdot g_2 \neq g_2 \cdot g_1$. Examples of non-Abelian groups are the group of quaternion numbers $SU(2)$ or (equivalently) the rotation group in three-dimensions ($SO(3)$). 4

$O(n)$ symmetry The $O(n)$ symmetry group is the group of all vectors pointing to a point on the surface of the unit sphere in n -dimensions, i.e., $S^{n-1} \in \mathbb{R}^n$, that leave the origin fixed. Physical realizations of $O(n)$ symmetry include [21]: XY spin models ($O(2)$ symmetry) and the Heisenberg model ($O(3)$ symmetry). 4

octonion The octonions ($\mathbb{O}$) are an algebra domain that is an extension of the quaternion numbers, with seven imaginary components and one real component. Thus, any octonion o can be written in the form: $o = x_0\hat{e}_0 + x_1\hat{e}_1 + x_2\hat{e}_2 + x_3\hat{e}_3 + x_4\hat{e}_4 + x_5\hat{e}_5 + x_6\hat{e}_6 + x_7\hat{e}_7$ with real coefficients $\{x_i\}$. The multiplication table of unit octonions is given in Fig. E.1. 142

order parameter An order parameter is a measure of the degree of order that develops by symmetry breaking, and that distinguishes an ordered phase from a disordered phase. The order parameter is zero in the symmetric (i.e., disordered) phase, and takes on a non-zero value in the ordered phase. Using the Landau mean-field theory of phase transitions, the free energy (F) of a system near the disorder-order transition is defined as an analytic Taylor series expansion of the order parameter (Ψ). In general, $F = \frac{1}{2}\alpha\Psi^2 + \frac{1}{3}b\Psi^3 + \frac{1}{4}c\Psi^4 + H\Psi\ldots$ where $\alpha = a(T - T_C)$, T_C is the critical transition temperature, a, b, c are constants, and H is an external field. The actual series expansion that describes F must only contain terms that respect the symmetry of the order parameter. The observed order parameter minimizes the free energy. 3

phonon Phonons are Nambu-Goldstone bosons, of broken symmetry, that are quantized collective excitations of a well-ordered state of matter. Phonons exhibit a linear dispersion relationship in the long-wavelength and do not have an energy gap. In crystalline solids, phonons are quantized vibrations of the crystalline lattice that play a major role in material transport properties (e.g., thermal conductivity). 1, 90, 122

plastic crystal Plastic crystals are mesomorphic states of matter that behave as liquid-like solids.

Plastic crystals are comprised of nearly spherical (slightly anisometric) particles, that are weakly-linked to their neighbors and, that are afforded nearly unhindered rotation [53]. It is easy for artificial translational periodicity to be established as the temperature of a liquid of nearly spherical molecules is lowered below a critical value. The plastic crystal phase develops by breaking translational symmetry on establishing lattice sites about which the constituents of the plastic crystal rotate. The melting temperature (associated with broken translational symmetry) separates the high-temperature liquid and the plastic crystal phase. A plastic crystal phase can form an crystal low-temperature state on cooling, or an orientational glass as the result of a glass transition. 10

quantum rotor model A quantum rotor model describes the internal degrees of freedom of a system of continuous n -vector order parameters that are positioned on the sites of a lattice and interact [17]. One of the important features of the quantum rotor model, that applies to n -vector ordered systems that exist in restricted dimensions, is its $O(n)$ symmetry. Importantly, a quantum rotor model considers both potential and kinetic energy terms. 6

quaternion Quaternions ($\mathbb{H}$) are an algebra domain that is an extension of the complex numbers ($\mathbb{C}$). Quaternions have one real and three imaginary components ($\hat{i}, \hat{j}, \hat{k}$) and are generally represented in the form: $a + b\hat{i} + c\hat{j} + d\hat{k}$ where a, b, c and d are real numbers and $\hat{i}^2 = \hat{j}^2 = \hat{k}^2 = -1$. The multiplication of two quaternions is non-commutative, such that: $\hat{i}\hat{j} = \hat{k}$ ($\hat{j}\hat{i} = -\hat{k}$), $\hat{j}\hat{k} = \hat{i}$ ($\hat{k}\hat{j} = -\hat{i}$), $\hat{k}\hat{i} = \hat{j}$ ($\hat{i}\hat{k} = -\hat{j}$) (Fig. E.1). Quaternions give a simple way to describe a rotation in three-dimensions (see Appendix C). Furthermore, the unit quaternions have the group structure of the three-sphere (S^3) which is homeomorphic to $SU(2)$. 4, 53

restricted dimensions A system exists in a restricted dimension if it is unable to spontaneously break the continuous symmetry of a high-temperature phase at finite temperatures, by the development of conventional global orientational order characterized by an n -vector order parameter. Two- and one- dimensions are restricted dimensions for complex n -vector ($n = 2$) ordered systems, and four- and three- dimensions are restricted dimensions for quaternion n -vector ($n = 4$) ordered systems. 2, 3, 47, 50, 57, 58, 60, 77

S^m The m -sphere is the space of constant positive curvature that is embedded in $(m+1)$ dimensions. For example, the two-dimensional space of constant positive curvature is the surface of the two-sphere S^2 that is embedded in three-dimensions. 7

simply connected A simply connected surface $\mathcal{M}$ has a fundamental homotopy group that is trivial, i.e., $\pi_1(\mathcal{M}) = 0$. x, 58, 59

spontaneous symmetry breaking During a spontaneous symmetry breaking event, at a critical transition temperature, the full symmetry group G of a high-temperature phase is broken to a isotropy subgroup $H \in G$ that applies globally. Spontaneous symmetry breaking of a continuous symmetry group can only occur in the bulk dimension for that particular symmetry group (e.g., three-dimensions for $G = U(1)$ and seven-dimensions for $G = SU(2)$). *See also:* bulk dimension. 3

tessellation Periodic or non-periodic tilings of a surface with one or more shapes with no overlaps or gaps. For example, icosahedral cells are unable to tessellate ordinary three-dimensional space (i.e., Euclidean), but it can tessellate the surface of a sphere in four-dimensions (S^3). 71

third law of thermodynamics By the third law of thermodynamics, the entropy of a system approaches a constant value as the temperature approaches zero Kelvin. The entropy of a system is related to the number of microstates that are accessible; for well-ordered systems, the entropy at 0 K will be exactly zero. 88

topological invariant A topological invariant is a property of a given topological space $\mathcal{M}$ that is preserved under homeomorphism. That is, it is a property that depends on the topology of the space and not on its metrics. A common example of a topological invariant is the topological charge of a topological defect (e.g., the winding number of a vortex, the angular deficit of a disclination, the Burger's vector of a dislocation). 67

topological ground state manifold A topological ground state manifold ($\mathcal{M}$) describes the degenerate ground states of a low-temperature ordered system. The topological ground state manifold is given by the quotient: $\mathcal{M} = G/H$ where G is the symmetry group of the symmetric phase and $H \in G$ is the isotropy subgroup that applies to the ordered system. The topological properties of the manifold inform the types of topologically stable defects that are available to the ordered system. For example, consider the rim of the 'Mexican hat' potential energy configuration in $U(1)$ superfluids (Fig. 2.2), which admits π_1 vortices. 5

topological defect Topological defects may be anticipated as a result of the lowering of symmetry during phase transitions. The ordered system is classified by a topological ground state manifold ($\mathcal{M}$, of degenerate ground states), and the topological defects that are available to the ordered system are classified by identifying the non-trivial homotopy groups of $\mathcal{M}$, i.e., $\pi_i(\mathcal{M})$. In particular, in order to classify topological defects of dimensionality d in D dimensional space, one has to consider the homotopy group $\pi_i(\mathcal{M})$ where $i = D - d - 1$ is the topological charge of the defect. Topological defects are topologically stable and cannot be removed by any continuous distortion of the order parameter field. 5, 66

topologically close-packed Topologically close-packed (TCP) structures are crystalline systems that are comprised entirely of tetrahedral interstices [54]. Because tetrahedra cannot fill space in three-dimensions, an ordered network of topological defects is a structural constituent of TCP crystalline phases (i.e., major skeleton network). The most common example of TCP phases are Frank-Kasper crystalline structures, which express local icosahedral orientational order. *See also:* Frank-Kasper crystalline structure. 88

Umklapp scattering Umklapp scattering is a resistive phonon-phonon interaction (unlike Normal phonon-phonon interactions, which are not resistive). A phonon-phonon interaction occurs when two incoming phonons with wave-vectors k_1 and k_2 create one outgoing phonon with a wave-vector k_3 , i.e., $k_1 + k_2 = k_3$. If the sum of the two incoming wave-vectors is outside of the first Brillouin zone, an Umklapp scattering process occurs where the outgoing phonon is brought back inside the first Brillouin zone by the subtraction of a reciprocal lattice vector G . That is, in Umklapp scattering processes there is a change in the total phonon momentum during the process which limits the thermal conductivity in crystalline materials (unlike Normal phonon-phonon interactions). 1, 21, 90, 92, 124

uncertainty relations Uncertainty relations assert the limit on precision with which pairs of complementary variables can be known simultaneously, e.g., position and momentum. In $U(1)$ superfluids whose complex order parameter ($\psi = |\psi|e^{i\theta}$) has both an amplitude and a scalar phase angle parameter degree of freedom, for example, a quantum uncertainty principle [95, 16, 18] applies that relates the uncertainties in the phase $\Delta\theta$ and the number of condensed particles in the condensate: $\Delta\theta\Delta n_S \geq 1$. 19, 61, 75, 77, 80

undercooling Undercooling (i.e., supercooling) is the process of lowering the temperature of a liquid or gas below its freezing point by avoiding solidification. All atomic liquids in three-dimensions are forced to undercool in order to overcome a free energy barrier to form critical nuclei. The opposite process to undercooling is to superheat a liquid above its boiling point. The presence of a hysteresis in cycling through the processes of superheating and undercooling is a signature of first-order phase transitions [21]. 3, 8, 55

universal covering group A universal covering group is a simply connected covering group [143]. In general [143], $SO(N)$ has the universal covering group $Spin(N)$. That is, $Spin(2) = U(1) = SO(2)$ and $Spin(3) = SU(2) = SO(3)$. *See also* binary group. 4, 9, 53

universality class In the classification of phase transitions, a universality class is a collection of models whose phase transitions share the same scaling behavior and are described by the same critical exponents. The universality hypothesis [32] suggests that the critical properties of model systems are based on two important dimensions: the spatial dimension of the model (D)

and the dimensionality of the order parameter (n). Critical properties of all systems within the same (D, n) class will be the same, and these models belong to the same universality class [33].

See also: critical exponents. 5, 17, 71

Volterra process A Volterra process [177] can be used to generate disclinations and dislocations. For example, a wedge disclination line in three-dimensions can be created in an elastic cylinder by cutting the structure along a line and adding (or removing) a wedge of material between the two lips of the cut (Fig. 1.5). 9, 13

vortices Vortices are topological defects that belong to the fundamental homotopy group of $\mathcal{M} = S^1$. Vortices are available to $U(1)$ superfluids, below the bulk critical transition temperature (T_C). Vortices in uncharged $U(1)$ superfluids carry quantized rotation; vortices in charged $U(1)$ superfluids (i.e., superconductors) carry quantized magnetic flux [82]. Vortices are points in two-dimensions, and are linear in three-dimensions. *See also:* winding number. 8, 16

wedge disclination A wedge disclination is a topological defect, that belongs to the fundamental homotopy group, for which orientational order is destroyed at its core. A disclination is characterized by a quantized angular deficit (i.e., Frank vector) in one circuit around the defect core, that can be positive or negative. Wedge disclinations are introduced by the Volterra process [178], by adding or removing a wedge of material between two lips of a cut in an elastic cylinder. The defect core of a wedge disclination, for which the Frank vector is parallel to the cylinder's axis, can be viewed as a concentration of curvature (see Fig. 1.6(B)) that is proportional to the angular deficit [22]. *See also* Frank vector and Volterra process. 9

winding number The winding number is a topological invariant that classifies the strength of topological defect elements that belong to the fundamental homotopy group of $\mathcal{M} = S^1$ (i.e., $\pi_1(S^1)$ vortices). The winding number may be any arbitrary integer (i.e., positive or negative) because a clockwise path can be distinguished from a counterclockwise path; the winding number is therefore a $\mathbb{Z}$ topological invariant. *See also:* vortices. 16, 33, 44, 56, 67

Appendix A

History of models of thermal properties

Understanding the transport of thermal energy within crystalline and non-crystalline solid state materials is not entirely straightforward. Heat conduction in solids is governed by the phenomenological Fourier's law [1] which, expressed in three-dimensions, is:

$$\mathbf{q} = -\kappa \nabla T. \quad (\text{A.1})$$

where the heat flux density $\mathbf{q}$ (W/m^2) is the amount of energy that flows through a unit area per unit time, ∇T (K/m) is the temperature gradient and κ is the thermal conductivity ($W/m/K$). A temperature difference between two faces results in the transport of heat from the side maintained at the higher temperature. The thermal conductivity is a temperature dependent property that is unique to a specific material. In dielectric materials (the focus of the current work), the thermal conductivity results entirely from contributions from internal degrees of freedom in the form of vibrational modes.

Prior to the advent of low-temperature physics, the high-temperature values of κ were known to be approximately constant. The high-temperature value for the thermal conductivity depends on the classical value for the heat capacity of solids, which was proposed by Dulong and Petit [2] (1819). Their finding that, at high-temperatures, many solids exhibit a molar heat capacity of $3R$ where R is the universal gas constant is consistent with equipartition theory (there are 3 vibrational mode degrees of freedom per atomic component in three-dimensions and each possesses kinetic and potential energy components). It was not until much later, with the advent of low-temperature physics (Nernst 1906), that quantum theories became important in order to understand both heat capacity and thermal conductivity experiments. These advents in low-temperature physics established the limiting thermodynamic behavior of systems as the temperature approached zero. In particular, the heat capacity does not remain constant but does decrease to zero and does not follow the Dulong-Petit law to low-temperatures.

A. Einstein (1907) [3] was the first to provide a description of the heat capacity of solids that extended to low-temperatures, by successfully introducing a first set of elementary excitations in

condensed matter systems [4]. Einstein first approached the specific heat by assuming that all atomic constituents in the solid act as independent quantum harmonic oscillators, that oscillate with the same frequency. By applying Planck's quantization assumption to the thermal energy [5], originally derived for black-body radiation, Einstein determined the following expression for the volumetric heat capacity of a three-dimensional solid:

$$C_{V, \text{Einstein}} = 3nk_B x^2 \frac{e^x}{(e^x - 1)^2}, \quad (\text{A.2})$$

where n is the number density of oscillators in the system, and the dimensionless argument x equals Θ_E/T where $\Theta_E = \hbar\omega_E/k_B$ is the Einstein temperature at which all degrees of freedom are saturated at the Einstein frequency ω_E . This formulation determined the specific heat with only a single free (material-dependent) parameter, i.e., the so-called Einstein temperature Θ_E . The high-temperature specific heat of an Einstein solid recovers the well-known Dulong-Petit limit and, for the first time, the low-temperature thermal properties were approached. Using Einstein's model, as the temperature is lowered towards zero Kelvin, the specific heat approaches zero exponentially fast because all oscillations possess the same frequency (ω_E).

The next major developments of the model of the heat capacity in solids were suggested by Debye [6] (1912), and by Born and von Karman [7, 8] (1912), who were quick to point out (after Einstein's original model) that coherence^a is in fact produced between the sites of translationally ordered lattices of harmonic oscillators that comprise crystalline solids. A vibrational dispersion results due to the expected coherence between lattice vibrational modes, known as phonons. Born and von Karman derived the vibrational dispersion relationship, by imposing cyclic boundary conditions, given the equations of motion of atomic constituents of a lattice^b. The vibrational dispersion that applies to a one-dimensional monatomic chain^c is plotted, as frequency versus wavevector, in Fig. A.1(A). The spectrum becomes continuum-like for lattices in the infinite limit ($L \rightarrow \infty$), and each wavevector represents a normal mode (there are $3N$ normal modes in a three-dimensional crystalline solid). Lattice vibrational modes that superimpose, within a range of frequencies, form wave-packets that can be treated as particles. As the first Brillouin zone boundary is approached, the group velocity of the derived vibrational dispersion:

$$v_g = \frac{\partial\omega(q)}{\partial q}, \quad (\text{A.3})$$

which is the velocity with which a wave-packet propagates through space, reduces to zero.

Following the derivation of the dispersion relationship of lattice vibrational modes (Born and von

^aCoherence between waves implies an in-phase nature.

^bDerived by applying Hooke's linear law to relate the force needed to displace an atom from its ground position to the spring stiffness, k , and displacement amplitude u .

^cThe vibrational dispersion of a one-dimensional monatomic chain follows the form: $\omega(q) = \sqrt{\frac{4K}{m}} \left| \sin\left(\frac{qa}{2}\right) \right|$, where m is the atomic mass, a is the lattice constant, K is the spring constant, and $q = 2\pi n/L$ is the wavevector where $n = 0, \pm 1, \pm 2, \dots, N$ and N and L are the number of atoms in the crystal and the size of the crystal.

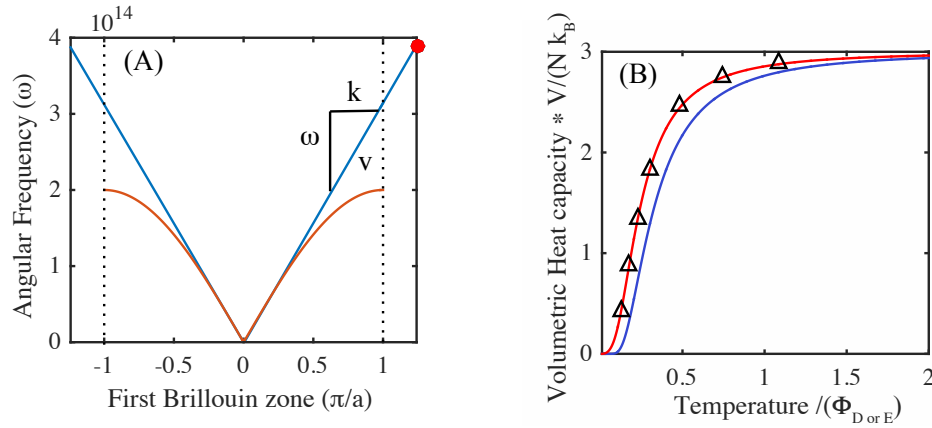


Figure A.1: (A) Phonon dispersion relationship of a one-dimensional monatomic chain, and the corresponding Debye approximation. (B) Volumetric specific heat of a 3D Einstein solid (blue) and a 3D Debye elastic continuum solid (red); Δ 's represent data onto which the heat capacity of dielectric crystalline materials converge.

Karman), P. Debye sought to calculate the contribution to the heat capacity from the spectrum of possible vibrational modes in the crystalline solid [6]. The Debye model treats the vibrations of a lattice as “phonons in a box.” This is the solid state equivalent to the law of black body radiation, for which electromagnetic radiation is considered as a gas of photons in a box [5]. Debye’s model is in contrast to Einstein’s model, which approximates the internal energy of the solid state as an ensemble of many individual quantum harmonic oscillators that all oscillate with the same frequency and are hence incoherent. The essential approximation of the Debye model was to treat the lattice vibrational modes as dispersionless (i.e., $v_g = v_p = v$, where $v_p = \omega/q$ is the phase velocity), in a way that is identical to the electromagnetic waves in an empty cavity [9]. Debye’s model of elastic waves in three-dimensional crystalline solids considers $3N$ normal modes (N is the number density of atoms), which make up three separate branches of the vibrational dispersion (one longitudinal and two transverse). With these assumptions, the Debye model correctly predicts the T^3 dependence of the heat capacity of three-dimensional solids at low-temperatures (as such, it is commonly known as the Debye T^3 model). The agreement of the Debye model with the low-temperature measurements of the specific heat, with no free parameters, improves upon Einstein’s model which employs the Einstein temperature as a free parameter. A comparison of the Einstein and Debye models of heat capacity is shown in Fig. A.1(B).

Perhaps the most important success of the theory of elastic waves, by Born and von Karman and by Debye, was that it paved the way for a qualitative understanding of the observed high thermal conductivity of crystalline solids and its temperature dependence [12, 13] (as compared with non-crystalline solids). By allowing for the definition of wave-packets, which can be treated as particles, the heat transfer mechanisms in crystalline solids can be analyzed through the kinetic theory of gases [12, 14] (Ref. [15]). Understanding this, Debye [16] presented a model of the thermal

conductivity κ as:

$$\kappa = \frac{1}{3} C_V v \Lambda \quad (\text{A.4})$$

where v is the phonon velocity and Λ is the mean free path of scattering. In crystalline solids, which allow for coherent phonons, the mean free path is the result of multiple scattering mechanisms and the overall lifetime of a wave-packet is assessed using the empirical Matthiessen's rule [17]. In contrast, in non-crystalline solids, wave-packets do not develop and (as the common notion of multiple independent scattering mechanisms becomes invalid) Matthiessen's rule no longer applies. A schematic of a non-crystalline structure (continuous random network), characterized by irregular orientations, as distinguished from its crystalline counterpart is illustrated in Fig. A.2(A).

As was originally pointed out by Eucken [13] (1911), while the thermal conductivity of crystalline solids increases with decreasing temperatures [18] the thermal conductivity of glasses (universally) decreases with decreasing temperatures. Measurements of the thermal conductivity, as a function of temperature, for crystalline α -quartz and non-crystalline vitreous SiO_2 , are shown in Fig. A.2(B). In crystalline solids, at high-temperatures, heat transport by lattice vibrational modes (phonons) is determined by the anharmonicity of lattice forces [19]. With decreasing temperatures, the thermal conductivity of crystalline solids increases (proportional to temperature) as the dominant resistive (anharmonic) Umklapp scattering processes [20] become less frequent.

On the other hand, the thermal conductivity of non-crystalline systems decreases with decreasing temperature. Straightforwardly, this is due to the lack of resistive Umklapp scattering processes which is a result of a lack of translational order within the glassy solid state. The heat transport mechanism in non-crystalline solids, at high-temperatures, is described by an early model [21] by Einstein (1911). Einstein started from his 1907 model [3] of atomic vibrations as localized harmonic oscillators, that vibrate with the same frequency. In order to conduct heat, Einstein coupled his oscillators to their nearest-neighbors using harmonic forces [12] with random phases. In doing so,

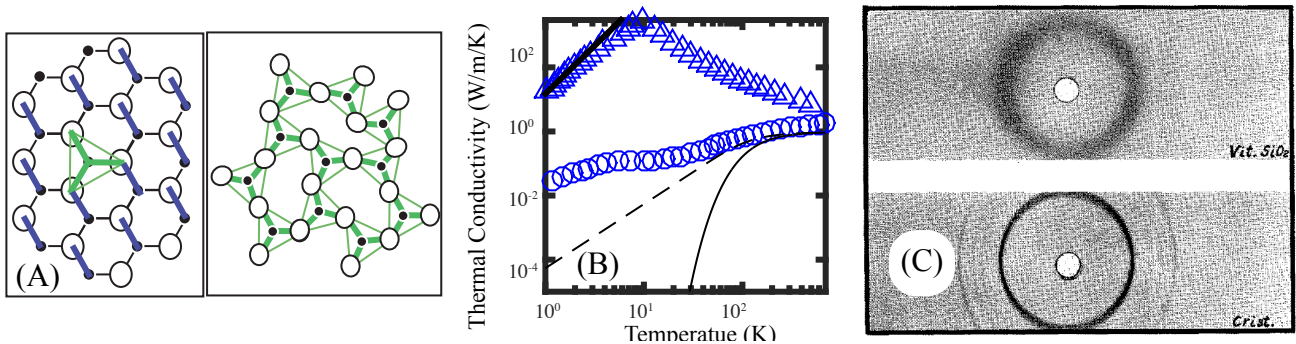


Figure A.2: (A) Schematic 2D solid state systems. A translationally periodic crystalline lattice [left] and a continuous random network structural glass [right]. (B) Measured thermal conductivity of vitreous SiO_2 and α -quartz (Ref. [10]). (C) X-ray powder diffraction patterns of amorphous silica (top) and crystalline α -quartz (Ref. [11]).

the thermal energy of each atom is transferred during one half of each period of oscillation of the atom [12]. This gives the relaxation time of each oscillator as equal to one half of the period of vibration [12]: $\tau = \pi/\omega$; this kind of relaxation mechanism is characteristic of strong-scattering [22], and leads to a mean free path on the order of a single interatomic spacing [23]. Einstein's model of the thermal conductivity decreases with decreasing temperatures, as is characteristic of non-crystalline solids above approximately $50K$.

The thermophysical properties (e.g., heat capacity and thermal conductivity) of solid state systems are intimately related to their structure, which can be interrogated through experimental diffraction patterns. The diffraction patterns of crystalline solids, which have translational periodicity and are orientational ordered, show high intensity peaks by scattering from specific planes of atoms within the solid. A powder diffraction pattern for crystalline solid (α -quartz) is shown in Fig. A.2(C), and shows numerous sharp rings [11]. On the other hand, x -ray diffraction patterns of glassy solids (shown for vitreous silica in Fig. A.2(C)) show one or more broad and diffuse rings [11]. Based on these diffraction experiments [11], the term continuous random network [24, 25, 26] became popular as a description of the structure of silicate glasses. Within the continuous random network, groups of atoms are misoriented with respect to neighboring groups of atoms such that the vitreous state is not afforded the long-range periodicity of the crystal; a definite coordination and continuity of the system is expressed by the terminology "continuous random network."

In 1949, C. Kittel was the first to consider correlations between the structure of glassy solid states and their thermal transport properties [18]. C. Kittel interpreted the magnitude of the thermal conductivity of silica glass, as a function of temperature, within the framework of original x -ray diffraction patterns of vitreous silica by B. E. Warren [11] (shown in Fig. A.2(C)). Kittel noted that in non-crystalline solids, due to a lack of LRO, the average distance that a thermal energy carrier can travel will be limited by impediments on the length scale that is associated with the lack of periodicity. By assessing the measured thermal conductivity as limited exclusively by this length scale of disorder Λ_0 , as $\kappa \approx \frac{1}{3}C_V v \Lambda_0$, Kittel calculated values of Λ_0 on the order of approximately 7 Å. Kittel concluded that these results directly support [18] the original continuous random network model that had been developed earlier by Zachariasen [27] and Warren [11].

Appendix B

Relevant Group Theory

B.1 Definition of a group

A group G is a set of elements g , together with an operation that combines each two elements g_1 and g_2 to form another element of the group G . The set of elements and operation that combines them must satisfy four requirements (known as group axioms) in order to qualify as a group:

- **Closure:** For all g_1 and g_2 in G , the element $g_1 \cdot g_2$ must also be in G .
- **Associativity:** For all g_1, g_2, g_3 in G : $(g_1 \cdot g_2) \cdot g_3 = g_1 \cdot (g_2 \cdot g_3)$.
- **Identity element:** There exists an element $e \in G$ such that for every element $g \in G$, $e \cdot g = g \cdot e = g$. This element e is the identity element.
- **Inverse element:** For an element $g \in G$, an element $g^{-1} \in G$ exists such that $g \cdot g^{-1} \in G = e$ where e is the identity element.

One way that groups can be classified is as either Abelian or non-Abelian, depending on whether or not the order of two operands changes the result. Groups that are commutative (Abelian) are include $SO(2)$ and $U(1)$, while the groups $SO(3)$ and $SU(2)$ are characterized by generators that do not commute with each other (non-Abelian). Unitary groups ($U(1)$ and $SU(2)$) and orthogonal groups ($SO(2)$ and $SO(3)$) are introduced below.

B.2 Unitary groups and special unitary groups

A unitary group of degree n , $U(n)$ is the group of all $n \times n$ unitary matrices. A complex square matrix U is unitary if:

$$UU^\dagger = U^\dagger U = I \tag{B.1}$$

where $U^\dagger$ is the complex conjugate of U and I is the identity matrix. The subgroup of all unitary matrices of degree n with a determinant $+1$ form a group called the special unitary group $SU(n)$. The analogue to a unitary matrix U is an orthogonal rotation matrix R , for which: $RR^T = R^T R = I$ where R^T is the transpose of R and I is the identity matrix.

B.2.1 $U(1)$ unitary group

The group $U(1)$ is the set of all 1D complex unitary matrices, with unit determinant. The group has a single generator, and is characterized by a single real scalar phase angle parameter, θ . The real scalar phase angle parameter θ is used to specify an element of the group, which are points on the unit circle. The name “ $U(1)$ ” is used since complex numbers $e^{i\theta}$ are by definition 1×1 unitary matrices. The $U(1)$ Lie group can be written using a single exponential:

$$E(\theta) = \exp(i\theta T) \quad (\text{B.2})$$

that produces a complex phase change.

Complex multiplication defines the combination law of group elements:

$$E(\theta_m)E(\theta_n) = e^{i\theta_m}e^{i\theta_n} = e^{i(\theta_m+\theta_n)}. \quad (\text{B.3})$$

That is, the result of two rotations by complex numbers corresponds to their complex multiplication, which is accomplished by the simple addition of their scalar angles θ_1 and θ_2 . Thus, the $U(1)$ group is Abelian due to the fact that the generator T commutes with itself, and so the elements of the group also are commutative.

B.2.2 $SU(2)$ special unitary group

The unitary group $SU(2)$ is the set of all 2×2 complex unitary matrices, with unit determinant. The constraint on the determinant removes one generator from the $U(2)$ group, such that the group $SU(2)$ has three generators (F_x, F_y, F_z) and is characterized by three scalar phase angle parameters ($\theta, \theta_1, \theta_2$). Thus, the $SU(2)$ group manifold is isomorphic to the three-sphere (S^3) that is embedded in four-dimensions. The three generators are related to the set of three Pauli matrices:

$$F_x = \sigma_x/2 ; \quad F_y = \sigma_y/2 ; \quad F_z = \sigma_z/2, \quad (\text{B.4})$$

where:

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (\text{B.5})$$

These generators do not commute with one another, and so $SU(2)$ is a non-Abelian group.

B.3 Orthogonal groups and special orthogonal groups

Orthogonal transformations preserve length in a particular ordinary Euclidean n -dimensional space. This length preserving restriction requires that:

$$x_1'^2 + x_2'^2 + \dots + x_n'^2 = x_1^2 + x_2^2 + \dots + x_n^2. \quad (\text{B.6})$$

An orthogonal transformation $R : V \rightarrow V$ is a linear transformation on a real inner product space V (e.g., the Euclidean space $\mathbb{R}^n$) that preserves the inner product by preserving lengths and angles between vectors. A linear transformation:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}, \quad (\text{B.7})$$

is an orthogonal transformation if it satisfies the orthogonality condition:

$$a_{ij}a_{ik} = \delta_{jk} \quad (\text{B.8})$$

where Einstein summation is used and δ_{jk} is the Kronecker delta. A length-preserving transformation R in n dimensions can be represented by a $n \times n$ orthogonal matrix; if R is orthogonal, then: $\det(R) = \pm 1$.

The group of all orthogonal transformations in n dimensions is the $O(n)$ group. The subgroup of orthogonal matrices with a positive determinant (proper rotations) is the special group of rotations in n -dimensions $SO(n)$. The full orthogonal group in n -dimensions $O(n)$ consists of all proper and improper rotations (as generated by reflections, determinant -1). A square matrix R is orthogonal if:

$$RR^T = R^T R = I \quad (\text{B.9})$$

where R^T is the transpose of R and I is the identity matrix. The analogue to an orthogonal rotation matrix, R , is a unitary matrix U for which: $UU^\dagger = U^\dagger U = I$ where $U^\dagger$ is the complex conjugate of U and I is the identity matrix.

B.3.1 $SO(2)$ special orthogonal group

In two-dimensions, a rotation $\mathbf{x}' = R\mathbf{x}$ may be represented as:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}, \quad (\text{B.10})$$

where $\det(A) = a_{11}a_{22} - a_{21}a_{12} \neq 0$. In two-dimensions, in order to satisfy Eqn. B.6 using the transformation (B.10) it is required that [28, 29]:

$$x'^2 + y'^2 = (a_{11}x + a_{12}y)^2 + (a_{21}x + a_{22}y)^2. \quad (\text{B.11})$$

$$= (a_{11}^2 + a_{21}^2)x^2 + 2(a_{11}a_{12} + a_{21}a_{22})xy + (a_{22}^2 + a_{12}^2)y^2. \quad (\text{B.12})$$

In order for is to be true for all x and y , the following must be true:

$$(a_{11}^2 + a_{21}^2) = 1 \quad (a_{11}a_{12} + a_{21}a_{22}) = 0 \quad (a_{22}^2 + a_{12}^2) = 1. \quad (\text{B.13})$$

Thus, there are three constraints imposed on the four parameters $(a_{11}, a_{12}, a_{21}, a_{22})$ leaving a single free scalar phase angle parameter (θ) . These conditions can be used to determine that:

$$(a_{11}a_{22} - a_{12}a_{21})^2 = 1. \quad (\text{B.14})$$

Recognizing $a_{11}a_{22} - a_{12}a_{21}$ as the determinant of R , $\det(R) = \pm 1$. Those orthogonal matrices with the determinant equal to +1 do not change the parity of the coordinate system upon transformation, and are called *proper* rotations. The *special* orthogonal group in two-dimensions $SO(2)$ is the group of all proper rotations in two-dimensions.

The $SO(2)$ group (i.e., the group of orthogonal matrices with positive determinant) may be parameterized as:

$$R(\theta) = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \quad (\text{B.15})$$

where $\theta \in [0, 2\pi]$ is the single scalar phase angle parameter that characterizes the transformation. To check that this matrix transformation is an orthogonal transformation, it must satisfy the orthogonal conditions (Eqn. B.8)

$$a_{11}a_{11} + a_{21}a_{21} = (\cos^2 \theta + \sin^2 \theta) = \delta_{11} = 1, \quad (\text{B.16})$$

$$a_{12}a_{12} + a_{22}a_{22} = (\sin^2 \theta + \cos^2 \theta) = \delta_{22} = 1, \quad (\text{B.17})$$

$$a_{11}a_{12} + a_{21}a_{22} = (-\cos \theta \sin \theta + \cos \theta \sin \theta) = \delta_{12} = 0. \quad (\text{B.18})$$

The product of two rotation matrices $R(\theta_1)$ and $R(\theta_2)$ commutes, as can be shown using trigonometric identities.

$$R(\theta_1)R(\theta_2) = \begin{bmatrix} \cos \theta_1 & -\sin \theta_1 \\ \sin \theta_1 & \cos \theta_1 \end{bmatrix} \begin{bmatrix} \cos \theta_2 & -\sin \theta_2 \\ \sin \theta_2 & \cos \theta_2 \end{bmatrix} \quad (\text{B.19})$$

$$= \begin{bmatrix} \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 & -\cos \theta_1 \sin \theta_2 - \cos \theta_2 \sin \theta_1 \\ \cos \theta_1 \sin \theta_2 + \cos \theta_2 \sin \theta_1 & \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \end{bmatrix} = \begin{bmatrix} \cos(\theta_1 + \theta_2) & -\sin(\theta_1 + \theta_2) \\ \sin(\theta_1 + \theta_2) & \cos(\theta_1 + \theta_2) \end{bmatrix}. \quad (\text{B.20})$$

Therefore, $R(\theta_1 + \theta_2) = R(\theta_1)R(\theta_2) = R(\theta_2)R(\theta_1)$ and so the $SO(2)$ group is Abelian. This group may be parameterized by the complex numbers that comprise the unitary group $U(1)$, by the 1-to-1 homomorphism (isomorphism): $e^{i\theta} \rightarrow \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix}$.

B.3.2 $SO(3)$ special orthogonal group

In three-dimensions, the relevant rotation R is 3×3 matrix:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \quad (\text{B.21})$$

where $\det(A) = a_{11}\det \begin{bmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{bmatrix} - a_{12}\det \begin{bmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{bmatrix} + a_{13}\det \begin{bmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{bmatrix} \neq 0$. In three-dimensions, in order to satisfy Eqn. B.6 using the transformation (B.21) it is required that:

$$x'^2 + y'^2 + z'^2 = (a_{11}x + a_{12}y + a_{13}z)^2 + (a_{21}x + a_{22}y + a_{23}z)^2 + (a_{31}x + a_{32}y + a_{33}z)^2. \quad (\text{B.22})$$

$$\begin{aligned} &= (a_{11}^2 + a_{21}^2 + a_{31}^2)x^2 + (a_{12}^2 + a_{22}^2 + a_{32}^2)y^2 + (a_{13}^2 + a_{23}^2 + a_{33}^2)z^2 + \\ &2(a_{11}a_{12} + a_{21}a_{22} + a_{31}a_{32})xy + 2(a_{11}a_{13} + a_{21}a_{23} + a_{31}a_{33})xz + 2(a_{12}a_{13} + a_{22}a_{23} + a_{32}a_{33})yz. \end{aligned} \quad (\text{B.23})$$

In order for this expression to hold for all x, y and z , the following must be true:

$$\begin{aligned} (a_{11}^2 + a_{21}^2 + a_{31}^2) &= 1 & (a_{22}^2 + a_{12}^2 + a_{32}^2) &= 1 & (a_{22}^2 + a_{12}^2 + a_{32}^2) &= 1 \\ (a_{11}a_{12} + a_{21}a_{22} + a_{31}a_{32}) &= 0 & (a_{11}a_{13} + a_{21}a_{23} + a_{31}a_{33}) &= 0 & (a_{12}a_{13} + a_{22}a_{23} + a_{32}a_{33}) &= 0. \end{aligned} \quad (\text{B.24})$$

There are six constraints imposed on the nine parameters $(a_{11}, a_{12}, a_{13}, a_{21}, a_{22}, a_{23}, a_{31}, a_{32}, a_{33})$ leaving three free scalar phase angle parameter $(\theta, \theta_1, \theta_2)$. It turns out that these conditions are satisfied provided that $\det(R) = \pm 1$. The group of all proper rotations ($\det(R) = +1$) in three-dimensions is the special orthogonal group in three-dimensions $SO(3)$. Any such rotation acts as a two-dimensional rotation in the plane orthogonal to an axis of rotation. It follows that a rotation in three-dimensions is defined by an arbitrary angle about a specified axis of rotation.

For example, rotation by arbitrary angles θ , ϕ and Φ about the x -, y - and z - axes:

$$R_x = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix} \quad R_y = \begin{bmatrix} \cos \phi & 0 & -\sin \phi \\ 0 & 1 & 0 \\ \sin \phi & 0 & \cos \phi \end{bmatrix} \quad R_z = \begin{bmatrix} \cos \Phi & \sin \Phi & 0 \\ -\sin \Phi & \cos \Phi & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (\text{B.25})$$

Euler angles (θ , ϕ , Φ) are one way to describe the orientation of a rigid body with respect to a fixed axis in three-dimensions. These matrices satisfy the orthogonal condition (Eqn. B.8). Consider the orthogonal conditions for R_x :

$$a_{11}a_{11} + a_{21}a_{21} + a_{31}a_{31} = 1 + 0 + 0 = \delta_{11} = 1, \quad (\text{B.26})$$

$$a_{12}a_{12} + a_{22}a_{22} + a_{32}a_{32} = 0 + \cos^2 \theta + \sin^2 \theta = \delta_{22} = 1, \quad (\text{B.27})$$

$$a_{13}a_{13} + a_{23}a_{23} + a_{33}a_{33} = 0 + \sin^2 \theta + \cos^2 \theta = \delta_{33} = 1, \quad (\text{B.28})$$

$$a_{11}a_{12} + a_{21}a_{22} + a_{31}a_{32} = 1 * 0 + 0 * \cos \theta - 0 * \sin \theta = \delta_{12} = 0, \quad (\text{B.29})$$

$$a_{11}a_{13} + a_{21}a_{23} + a_{31}a_{33} = 1 * 0 + 0 * \sin \theta + 0 * \cos \theta = \delta_{13} = 0, \quad (\text{B.30})$$

$$a_{12}a_{13} + a_{22}a_{23} + a_{32}a_{33} = 0 * 0 + \cos \theta * \sin \theta - \sin \theta \cos \theta = \delta_{23} = 0. \quad (\text{B.31})$$

Using Euler angles, any rotation R can be decomposed in terms of rotation about three axes: $R = R_x R_y R_z$ where the order of operations is important in the definition of R . Hence, the group of rotations in three-dimensions is a non-Abelian group. Unit quaternions, which are isomorphic to the unitary group $SU(2)$, are useful in the definition of rotations in three-dimensions. This is discussed in more detail in Appendix C.

Appendix C

Quaternions as 3D rotations: $SO(3)$ to $SU(2)$ homomorphism

Quaternions give a simple way to encode a rotation through a principle angle around a principle axis in four numbers [30]. Any Euclidean vector $\mathbf{a} = (a_x, a_y, a_z)$ can be rewritten as a pure imaginary quaternion $a_x\hat{\mathbf{i}} + a_y\hat{\mathbf{j}} + a_z\hat{\mathbf{k}}$. Any desired rotation through an angle θ , around the axis defined by a unit vector $\mathbf{v} = (u_x, u_y, u_z) = v_x\hat{\mathbf{i}} + v_y\hat{\mathbf{j}} + v_z\hat{\mathbf{k}}$, can be applied to any position vector $\mathbf{a}$. This rotation can be described as a quaternion versor, as an extension of Euler's formula:

$$\mathbf{q} = e^{\frac{\theta}{2}(v_x\hat{\mathbf{i}}+v_y\hat{\mathbf{j}}+v_z\hat{\mathbf{k}})} = \cos \frac{\theta}{2} + (v_x\hat{\mathbf{i}} + v_y\hat{\mathbf{j}} + v_z\hat{\mathbf{k}}) \sin \frac{\theta}{2}. \quad (\text{C.1})$$

The desired rotation can be applied to any Euclidean vector $\mathbf{a}$ in three-dimensional space, which is written as a quaternion with a real coordinate equal to zero.

The desired rotation is evaluated by taking the conjugation of $\mathbf{a}$ by a unit quaternion $\mathbf{q}$:

$$\mathbf{a}' = \mathbf{q}\mathbf{a}\mathbf{q}^{-1} \quad (\text{C.2})$$

where $\mathbf{q}^{-1} = (a_1 - b_1\hat{\mathbf{i}} - c_1\hat{\mathbf{j}} - d_1\hat{\mathbf{k}})$ is the conjugate of $\mathbf{q}$, and $\mathbf{a}' = (a'_x, a'_y, a'_z)$ is the Euclidean vector in three-dimensional space after the rotation. This conjugation is evaluated using the quaternion distributive law (Hamilton product), i.e., quaternion distributive multiplication. Thus, the map $\mathbf{a}' \rightarrow \mathbf{q}\mathbf{a}\mathbf{q}^{-1}$ is a rotation in three-dimensions. Furthermore, the map $(-\mathbf{q})\mathbf{a}(-\mathbf{q})^{-1}$ is the same as $\mathbf{q}\mathbf{a}\mathbf{q}^{-1}$. This shows that there is a 2-to-1 homomorphism from quaternions of unit norm to the group of proper rotations in three-dimensions $SO(3)$.

By letting $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ be the following matrices:

$$\hat{\mathbf{i}} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \hat{\mathbf{i}} = \begin{bmatrix} \hat{i} & 0 \\ 0 & -\hat{i} \end{bmatrix} \quad (\text{C.3})$$

$$\hat{\mathbf{j}} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \quad \hat{\mathbf{k}} = \begin{bmatrix} 0 & \hat{i} \\ \hat{i} & 0 \end{bmatrix} \quad (\text{C.4})$$

the set of quaternions (of unit norm) is isomorphic to the unitary group of degree two $SU(2)$, via a map:

$$\mathbf{q} = a\hat{\mathbf{1}} + b\hat{\mathbf{i}} + c\hat{\mathbf{j}} + d\hat{\mathbf{k}} = \alpha + \beta\hat{j} = \begin{bmatrix} \alpha & -\bar{\beta} \\ \beta & \bar{\alpha} \end{bmatrix} = U \quad (\text{C.5})$$

where $\alpha = (a\hat{\mathbf{1}} + b\hat{\mathbf{i}})$ and $\beta = (c + d\hat{i})$, such that $\alpha, \beta \in \mathbb{C}$ and $U \in SU(2)$. This 2-to-1 homomorphic mapping between $SO(3)$ and $SU(2)$ may be denoted [31]:

$$R(\hat{n}, \theta) \leftrightarrow \pm q(\hat{n}, \theta) \quad (\text{C.6})$$

where $R(\hat{n}, \theta)$ is a rotation through the angle θ about the axis $\hat{n}$, and $q(\hat{n}, \theta)$ is a quaternion number.

The quaternions $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ can also be written as:

$$\hat{\mathbf{i}} = \begin{bmatrix} \hat{i} & 0 \\ 0 & -\hat{i} \end{bmatrix} = \hat{i}\sigma_z \quad \hat{\mathbf{j}} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} = \hat{i}\sigma_y \quad \hat{\mathbf{k}} = \begin{bmatrix} 0 & \hat{i} \\ \hat{i} & 0 \end{bmatrix} = \hat{i}\sigma_x \quad (\text{C.7})$$

where

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -\hat{i} \\ \hat{i} & 0 \end{bmatrix} \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (\text{C.8})$$

are the Pauli matrices (Eqn. C.8). Thus, any arbitrary quaternion can be written in terms of the Pauli matrices as:

$$q = a\hat{\mathbf{1}} + b\hat{\mathbf{i}} + c\hat{\mathbf{j}} + d\hat{\mathbf{k}} = a\hat{\mathbf{1}} + \hat{i}(d\sigma_x + c\sigma_y + b\sigma_z). \quad (\text{C.9})$$

Moreover, the quaternion $q(\hat{n}, \theta)$ (i.e., Eqn. C.1) that describes a rotation in three-dimensions can be conveniently parameterized in terms of the Pauli matrices as [31, 32]:

$$q(\hat{n}, \theta) = e^{\hat{i}(\theta/2)\hat{n} \cdot \sigma_i}. \quad (\text{C.10})$$

Here, the 2-to-1 nature of the homomorphism between $SU(2)$ and $SO(3)$ can be seen from the fact that $q(\hat{n}, \theta + 2\pi) = -q(\hat{n}, \theta)$ provides the same rotation [32] in three-dimensions as $q(\hat{n}, \theta)$.

C.1 Example 1:

C.1.1 $\mathbf{qaq}^{-1}$

Consider the rotation by the arbitrary angle α around the x -axis ($\mathbf{v} = 1\hat{i} + 0\hat{j} + 0\hat{k}$). The length of $\mathbf{v}$ is 1 and the half angle is $\alpha/2$. In this case, one deals with conjugation by the unit quaternion:

$$\mathbf{q} = \cos \frac{\alpha}{2} + \sin \frac{\alpha}{2} \cdot \mathbf{v}. \quad (\text{C.11})$$

Letting $X = \cos \frac{\alpha}{2}$ and $Y = \sin \frac{\alpha}{2}$, the conjugation can be written as:

$$\mathbf{a}' = (X + Y\hat{i})(a_x\hat{i} + a_y\hat{j} + a_z\hat{k})(X - Y\hat{i}). \quad (\text{C.12})$$

One first solves for $(X + Y\hat{i})(a_x\hat{i} + a_y\hat{j} + a_z\hat{k})$, using the quaternion distributive law:

$$(X + Y\hat{i})(a_x\hat{i} + a_y\hat{j} + a_z\hat{k}) = (Xa_x\hat{i} + Xa_y\hat{j} + Xa_z\hat{k}) + (-Ya_x + Ya_y\hat{k} - Ya_z\hat{j}). \quad (\text{C.13})$$

Next, multiplication by $\mathbf{q}^{-1}$ conjugates as:

$$\begin{aligned} & \left[(Xa_x\hat{i} + Xa_y\hat{j} + Xa_z\hat{k}) + (-Ya_x + Ya_y\hat{k} - Ya_z\hat{j}) \right] (X - Y\hat{i}) = \\ & (X^2 + Y^2)a_x\hat{i} + (a_x(X^2 - Y^2) - 2XYa_z)\hat{j} + (a_z(X^2 - Y^2) + 2XYa_y)\hat{k}. \end{aligned} \quad (\text{C.14})$$

Recalling the values for X and Y (noting that: $X^2 + Y^2 = 1$, and using trigonometric half-angle identities $X^2 - Y^2 = \cos \alpha$ and, $\frac{1}{2} \sin \alpha = \cos \frac{\alpha}{2} \sin \frac{\alpha}{2}$), in terms of α :

$$\mathbf{a}' = a_x\hat{i} + (a_y \cos \alpha - a_z \sin \alpha)\hat{j} + (a_z \cos \alpha + a_y \sin \alpha)\hat{k}. \quad (\text{C.15})$$

From Eqn. C.15 one easily arrives at the expected three-dimensional rotation matrix:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & -\sin \alpha \\ 0 & \sin \alpha & \cos \alpha \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (\text{C.16})$$

The matrices for rotations about y - and z -axes are constructed in the same manner.

C.1.2 $(-\mathbf{q})\mathbf{a}(-\mathbf{q})^{-1}$

Now consider the rotation by the arbitrary angle α around the x -axis, by the unit quaternion $-\mathbf{q}$, as: $\mathbf{a}' = (-\mathbf{q})\mathbf{a}(-\mathbf{q})^{-1}$. In this example, the fact that the map $\mathbf{a}' = (-\mathbf{q})\mathbf{a}(-\mathbf{q})^{-1}$ leads to the

same result as $\mathbf{a}' = (\mathbf{q})\mathbf{a}(\mathbf{q})^{-1}$ is shown. This equivalence is owing to the 2-to-1 homomorphism that exists between the group of unit quaternions and the group of rotations in three-dimensions. The quaternion $-\mathbf{q}$ is: $-\mathbf{q} = -X - Y \cdot \mathbf{v}$, where $X = \cos \frac{\alpha}{2}$ and $Y = \sin \frac{\alpha}{2}$. The conjugation can be written as:

$$\mathbf{a}' = \left(-X - Y\hat{i}\right) (a_x\hat{i} + a_y\hat{j} + a_z\hat{k}) \left(-X + Y\hat{i}\right). \quad (\text{C.17})$$

First, solve for $\left(-X - Y\hat{i}\right) (a_x\hat{i} + a_y\hat{j} + a_z\hat{k})$, using the quaternion distributive law:

$$\left(-X - Y\hat{i}\right) (a_x\hat{i} + a_y\hat{j} + a_z\hat{k}) = (-Xa_x\hat{i} - Xa_y\hat{j} - Xa_z\hat{k}) + (Ya_x - Ya_y\hat{k} + Ya_z\hat{j}) \quad (\text{C.18})$$

Next, multiplication by $(-\mathbf{q})^{-1}$ conjugates as:

$$\begin{aligned} & \left[(-Xa_x\hat{i} - Xa_y\hat{j} - Xa_z\hat{k}) + (Ya_x - Ya_y\hat{k} + Ya_z\hat{j})\right] (-X + Y\hat{i}) = \\ & X^2a_x\hat{i} + X^2a_y\hat{j} + X^2a_z\hat{k} - XYa_x\hat{j} - XYa_y\hat{i} - XYa_z\hat{k} - XYa_x + \\ & + XYa_y\hat{k} - XYa_z\hat{j} + Y^2a_x\hat{i} - Y^2a_y\hat{k} + Y^2a_z\hat{j}. \end{aligned} \quad (\text{C.19})$$

Thus, $(-\mathbf{q})\mathbf{a}(-\mathbf{q})^{-1} = ((X^2 + Y^2)a_x)\hat{i} + ((X^2 - Y^2)a_y - 2XYa_z)\hat{j} + ((X^2 - Y^2)a_z + 2XYa_y)\hat{k}$. In terms of α :

$$\mathbf{a}' = (a_x)\hat{i} + (\cos \alpha a_y - \sin \alpha a_z)\hat{j} + (\cos \alpha a_z + \sin \alpha a_y)\hat{k} \quad (\text{C.20})$$

This expression is equivalent to $\mathbf{a}' = \mathbf{q}\mathbf{a}\mathbf{q}^{-1}$ (Eqn. C.15), and produces the same rotation matrix. This proves the 2-to-1 homomorphism between the $SU(2)$ group and rotations in three-dimensions.

C.2 Example 2:

Consider the rotation around the $[111]$ -axis ($\mathbf{v} = \hat{i} + \hat{j} + \hat{k}$) by the angle $\alpha = 120^\circ$ or $\frac{2\pi}{3}$ radians. The length of $\mathbf{v}$ is $\sqrt{3}$, and α is $\pi/3$. One needs to consider conjugation by the unit quaternion:

$$\mathbf{q} = \cos \frac{\alpha}{2} + \sin \frac{\alpha}{2} \cdot \frac{1}{\|\mathbf{v}\|} \mathbf{v} \equiv \cos \frac{\pi}{3} + \sin \frac{\pi}{3} \cdot \frac{1}{\sqrt{3}} \mathbf{v}. \quad (\text{C.21})$$

$$\mathbf{q} = \frac{1}{2} + \frac{\sqrt{3}}{2} \cdot \frac{\hat{i} + \hat{j} + \hat{k}}{\sqrt{3}} \equiv \frac{1 + \hat{i} + \hat{j} + \hat{k}}{2}. \quad (\text{C.22})$$

The conjugation is:

$$\mathbf{a}' = \left(\frac{1 + \hat{i} + \hat{j} + \hat{k}}{2}\right) (a_x\hat{i} + a_y\hat{j} + a_z\hat{k}) \left(\frac{1 - \hat{i} - \hat{j} - \hat{k}}{2}\right). \quad (\text{C.23})$$

Appendix D

Irrotational condition: velocity field distribution

The definitions of the curl in 3D and in 7D (Appendix E) are useful in determining the velocity field configurations ($\mathbf{v}$) that satisfy the irrotational flow condition (Eqn. 2.4): $\nabla \times \mathbf{v} = 0$, in complex [33] and quaternion n -vector ordered systems respectively.

D.1 $U(1)$ ordered system and the $\pi_1(S^1)$ topological defect

The 3D curl is useful in providing a description of the velocity field that is required in order to satisfy the irrotational condition in $U(1)$ ordered systems. By satisfying the irrotational condition everywhere along a closed ring, a topological defect core is contained at the center of the ring where the orientational order parameter is not defined [33]. This topological defect ($\pi_1(S^1)$) is commonly referred to as a “potential vortex” because it develops by satisfying the irrotational condition that applies to potential flow [34, 35].

In general, the superfluid velocity within a closed ring can be written in component form as:

$$\mathbf{v} = v_\theta \hat{\theta} \quad (\text{D.1})$$

where $\hat{\theta}$ is the unit vector in the θ direction at a point $\mathbf{r} = (r, \theta)$ (and $v_r = 0$). The cylindrical gradient in polar coordinates is:

$$\nabla \equiv \frac{\partial}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial}{\partial \theta} \hat{\theta}. \quad (\text{D.2})$$

The rotation associated with the velocity field configuration in its general form is, therefore:

$$\omega = \nabla \times \mathbf{v} = \hat{r} \times \frac{\partial \mathbf{v}}{\partial r} + \frac{\hat{\theta}}{r} \times \frac{\partial \mathbf{v}}{\partial \theta}. \quad (\text{D.3})$$

This expression must be solved in order to determine the appropriate velocity field configuration that

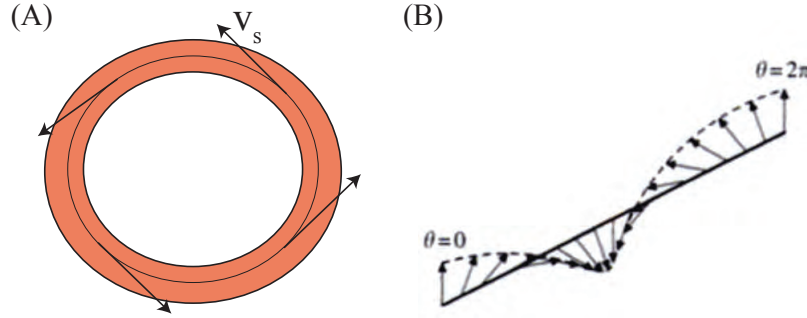


Figure D.1: (A) The flow of a $U(1)$ superfluid condensate within a closed ring must be everywhere irrotational. This condition is satisfied by a velocity field configuration shown here. (B) In order to ensure that the velocity field configuration around a closed ring is everywhere irrotational, the scalar phase angle parameter θ must change from zero continuously to 2π . [Figure from Ref [33]].

satisfies the irrotational constraint (Eqn. 2.4).

Noting the general definition of $\mathbf{v}$ (Eqn. D.1), this is expanded as:

$$\nabla \times \mathbf{v}_S = \hat{r} \times \left(\frac{\partial v_\theta}{\partial r} \hat{\theta} + \frac{\partial \hat{\theta}}{\partial r} v_\theta \right) + \frac{\hat{\theta}}{r} \times \left(\frac{\partial v_\theta}{\partial \theta} \hat{\theta} + \frac{\partial \hat{\theta}}{\partial \theta} v_\theta \right). \quad (\text{D.4})$$

In order to solve this expression, the derivatives of the polar unit vectors and their cross products must be considered. For the definition of the polar unit vectors $\hat{r}$ and $\hat{\theta}$ see Appendix D.1.1. Importantly, in the polar coordinate system, the cross products of the unit vectors are determined using quaternion multiplication rules (see Appendix E). This is accomplished by the identification of $\hat{x}$, $\hat{y}$ and $\hat{z}$ with the imaginary number $\hat{i}$, $\hat{j}$ and $\hat{k}$. The cross product of $\hat{r}$ with $\hat{\theta}$ is:

$$\hat{r} \times \hat{\theta} = (\cos \theta \hat{i} + \sin \theta \hat{j}) \times (-\sin \theta \hat{i} + \cos \theta \hat{j}). \quad (\text{D.5})$$

Using the quaternion multiplication rules: $\hat{i}^2 = \hat{j}^2 = \hat{k}^2 = -1$, $\hat{i}\hat{j} = \hat{k}$, $\hat{j}\hat{k} = \hat{i}$ and $\hat{k}\hat{i} = \hat{j}$ (see Fig. E.1), this expression solves as:

$$\hat{r} \times \hat{\theta} = -\cos \theta \sin \theta (\hat{i} \times \hat{i}) + \cos^2 \theta (\hat{i} \times \hat{j}) - \sin^2 \theta (\hat{j} \times \hat{i}) + \cos \theta \sin \theta (\hat{j} \times \hat{j}) = (\cos^2 \theta + \sin^2 \theta) \hat{k} \equiv \hat{z}. \quad (\text{D.6})$$

By the properties of cross-products: $\hat{\theta} \times \hat{r} = -\hat{z}$ and $\hat{r} \times \hat{r} = \hat{\theta} \times \hat{\theta} = 0$.

Utilizing the necessary expressions for the derivatives of the unit vectors (see Appendix D.1.1), and the cross products of the polar vectors defined above:

$$\nabla \times \mathbf{v} = \left(\frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \right) \hat{z}. \quad (\text{D.7})$$

This simplifies to:

$$\nabla \times \mathbf{v} = \frac{1}{r} \frac{\partial}{\partial r} (rv_\theta) \hat{z}. \quad (\text{D.8})$$

Therefore, in order that the ordered system remain everywhere irrotational around a closed path the velocity field configuration must satisfy:

$$\frac{1}{r} \frac{\partial}{\partial r} (rv_\theta) = 0. \quad (\text{D.9})$$

It follows that the system will remain irrotational around a closed path provided that the flow velocity has the form [33]:

$$v_\theta \propto \frac{k}{r} \quad (\text{D.10})$$

where k is the winding number (topological strength) of the vortex defect core that is enclosed within the closed ring.

In order that the flow remain everywhere irrotational (zero curl), the scalar phase angle parameter θ must change from zero to 2π (Fig. D.1(A)) on the closed path [33] (S^1). This leads to the development of a topological defect core at the center of the closed ring that belongs to the homotopy group, i.e., $\pi_1(S^1)$, and is thus characterized by an integer winding number (topological strength) k that counts the number of times the scalar angle parameter θ changes by 2π on the closed path. A schematic $\pi_1(S^1)$ defect of single strength (i.e., $k = 1$), on a one-dimensional line, is shown in Fig. D.1(B). A final expression for $\mathbf{v}$ within the irrotational system, in terms of the scalar phase angle parameter of the complex order parameter, can be derived by considering the order parameter field that satisfied the circuit constraint for any closed loop that encloses a $\pi_1(S^1)$ defect core [36]:

$$\oint d\theta = 2\pi k. \quad (\text{D.11})$$

The field: $\theta = k\phi$ where $\phi = \tan^{-1}(\frac{y}{x})$ satisfies this circuit constraint [36]. The cylindrical gradient (Eqn. D.2) of θ is:

$$\nabla\theta = \frac{k}{r} \hat{\theta} \quad \text{where } r = \sqrt{x^2 + y^2}. \quad (\text{D.12})$$

Thus, the potential flow velocity $\mathbf{v}$ (Eqn. D.10) can be re-written as [33]:

$$\mathbf{v} \propto \nabla\theta. \quad (\text{D.13})$$

D.1.1 Polar unit vectors and their derivatives:

Unit vectors:

The forwards and reverse coordinate transformations in polar coordinates are:

$$r = \sqrt{x^2 + y^2} \quad x = r \cos \theta \quad (D.14)$$

$$\theta = \tan^{-1} \left(\frac{y}{x} \right) \quad y = r \sin \theta, \quad (D.15)$$

where $r \in [0, \infty]$ and $\theta \in [0, 2\pi]$. In Cartesian coordinates, the position vector is therefore given as:

$$\mathbf{r} = r \cos \theta \hat{x} + r \sin \theta \hat{y}. \quad (D.16)$$

The unit vectors in the cylindrical coordinate system are:

$$\hat{r} \equiv \frac{\frac{d\mathbf{r}}{dr}}{\left| \frac{d\mathbf{r}}{dr} \right|} = \cos \theta \hat{x} + \sin \theta \hat{y}, \quad \text{where} \quad \left| \frac{d\mathbf{r}}{dr} \right| = 1, \quad (D.17)$$

and,

$$\hat{\theta} \equiv \frac{\frac{d\mathbf{r}}{d\theta}}{\left| \frac{d\mathbf{r}}{d\theta} \right|} = -\sin \theta \hat{x} + \cos \theta \hat{y}, \quad \text{where} \quad \left| \frac{d\mathbf{r}}{d\theta} \right| = r. \quad (D.18)$$

Derivatives of unit vectors:

The derivatives of the polar unit vectors are all zero except for:

$$\frac{\partial \hat{r}}{\partial \theta} = -\sin \theta \hat{x} + \cos \theta \hat{y} \equiv \hat{\theta} \quad \text{and,} \quad \frac{\partial \hat{\theta}}{\partial \theta} = -\cos \theta \hat{x} - \sin \theta \hat{y} \equiv -\hat{r}. \quad (D.19)$$

D.2 $SU(2)$ ordered system and the $\pi_3(S^3)$ topological defect

Just as the 3D curl is useful in determining the velocity field configuration that satisfies the irrotational flow condition in complex ordered systems (Appendix D.1), the 7D curl should be able to provide a description of the velocity field configuration ($\mathbf{v}$) that satisfies the equivalent condition in macroscopically orientationally-ordered systems that possess $SU(2)$ symmetry. The irrotational condition must be satisfied everywhere on a measuring hypersphere. This ensures that a topological defect core that belongs to the third homotopy group of $\mathcal{M} = S^3$ is located at the origin of the measuring surface.

The velocity of particles in the orientationally-ordered solid is assumed to have the general form:

$$\mathbf{v} = v_\theta \hat{\theta} + v_{\theta_1} \hat{\theta}_1 + v_{\theta_2} \hat{\theta}_2 \quad (D.20)$$

where $\hat{\theta}$, $\hat{\theta}_1$ and $\hat{\theta}_2$ are the unit vectors in the θ , θ_1 , and θ_2 directions at a point $\mathbf{r} = (r, \theta, \theta_1, \theta_2)$. The hyperspherical gradient is:

$$\nabla \equiv \frac{\partial}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial}{\partial \theta} \hat{\theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta_1} \hat{\theta}_1 + \frac{1}{r \sin \theta \sin \theta_1} \frac{\partial}{\partial \theta_2} \hat{\theta}_2. \quad (\text{D.21})$$

Therefore, the rotation associated with the velocity field configuration is:

$$\vec{\omega} = \nabla \times \mathbf{v} = \hat{r} \times \frac{\partial \mathbf{v}}{\partial r} + \frac{\hat{\theta}}{r} \times \frac{\partial \mathbf{v}}{\partial \theta} + \frac{\hat{\theta}_1}{r \sin \theta} \times \frac{\partial \mathbf{v}}{\partial \theta_1} + \frac{\hat{\theta}_2}{r \sin \theta \sin \theta_1} \times \frac{\partial \mathbf{v}}{\partial \theta_2}. \quad (\text{D.22})$$

Considering the general definition of $\mathbf{v}$ (Eqn. D.20), this can be expanded as:

$$\begin{aligned} \vec{\omega} = \nabla \times \mathbf{v} = & \hat{r} \times \left(\frac{\partial v_\theta}{\partial r} \hat{\theta} + \frac{\partial v_{\theta_1}}{\partial r} \hat{\theta}_1 + \frac{\partial v_{\theta_2}}{\partial r} \hat{\theta}_2 + \frac{\partial \hat{\theta}}{\partial r} v_\theta + \frac{\partial \hat{\theta}_1}{\partial r} v_{\theta_1} + \frac{\partial \hat{\theta}_2}{\partial r} v_{\theta_2} \right) + \\ & \frac{\hat{\theta}}{r} \times \left(\frac{\partial v_\theta}{\partial \theta} \hat{\theta} + \frac{\partial v_{\theta_1}}{\partial \theta} \hat{\theta}_1 + \frac{\partial v_{\theta_2}}{\partial \theta} \hat{\theta}_2 + \frac{\partial \hat{\theta}}{\partial \theta} v_\theta + \frac{\partial \hat{\theta}_1}{\partial \theta} v_{\theta_1} + \frac{\partial \hat{\theta}_2}{\partial \theta} v_{\theta_2} \right) + \\ & \frac{\hat{\theta}_1}{r \sin \theta} \times \left(\frac{\partial v_\theta}{\partial \theta_1} \hat{\theta} + \frac{\partial v_{\theta_1}}{\partial \theta_1} \hat{\theta}_1 + \frac{\partial v_{\theta_2}}{\partial \theta_1} \hat{\theta}_2 + \frac{\partial \hat{\theta}}{\partial \theta_1} v_\theta + \frac{\partial \hat{\theta}_1}{\partial \theta_1} v_{\theta_1} + \frac{\partial \hat{\theta}_2}{\partial \theta_1} v_{\theta_2} \right) + \\ & \frac{\hat{\theta}_2}{r \sin \theta \sin \theta_1} \times \left(\frac{\partial v_\theta}{\partial \theta_2} \hat{\theta} + \frac{\partial v_{\theta_1}}{\partial \theta_2} \hat{\theta}_1 + \frac{\partial v_{\theta_2}}{\partial \theta_2} \hat{\theta}_2 + \frac{\partial \hat{\theta}}{\partial \theta_2} v_\theta + \frac{\partial \hat{\theta}_1}{\partial \theta_2} v_{\theta_1} + \frac{\partial \hat{\theta}_2}{\partial \theta_2} v_{\theta_2} \right). \quad (\text{D.23}) \end{aligned}$$

In order to satisfy the irrotational constraint, Eqn D.23 must equal zero everywhere (except for the core of a third homotopy group topological defect).

In order to solve Eqn D.23, the derivatives of the hyperspherical unit vectors and their cross products must be determined. For the definition of the hyperspherical unit vectors $\hat{r}$, $\hat{\theta}$, $\hat{\theta}_1$ and $\hat{\theta}_2$ see Appendix D.2.1. The cross products of these coordinate axes may be determined using octonion multiplication rules (see Fig. E.1), just as quaternion multiplication rules enable the definition of the cross products of polar unit vectors. This may be accomplished by identifying the coordinates $(\hat{x}, \hat{y}, \hat{z}, \hat{t})$ with the imaginary numbers $(\hat{i}, \hat{j}, \hat{k}, \hat{l})$. The determination of the cross products of the unit vectors $(\hat{r}, \hat{\theta}, \hat{\theta}_1, \hat{\theta}_2)$, and their derivatives, is left for future work.

D.2.1 Hyperspherical unit vectors and their derivatives:

Unit vectors:

The forwards and reverse coordinate transformations are:

$$r = \sqrt{x^2 + y^2 + z^2 + t^2}, \quad x = r \sin \theta \sin \theta_1 \cos \theta_2 \quad (\text{D.24})$$

$$\theta = \cos^{-1} \left(\frac{t}{r} \right), \quad y = r \sin \theta \sin \theta_1 \sin \theta_2 \quad (\text{D.25})$$

$$\theta_1 = \cos^{-1} \left(\frac{z}{r_1} \right), \quad z = r \sin \theta \cos \theta_1 \quad (\text{D.26})$$

$$\theta_2 = \tan^{-1} \left(\frac{y}{x} \right), \quad t = r \cos \theta \quad (\text{D.27})$$

where $r_1 = \sqrt{x^2 + y^2 + z^2}$. In Cartesian coordinates, the position vector is given as:

$$\mathbf{r} = r \sin \theta \sin \theta_1 \cos \theta_2 \hat{x} + r \sin \theta \sin \theta_1 \sin \theta_2 \hat{y} + r \sin \theta \cos \theta_1 \hat{z} + r \cos \theta \hat{t}. \quad (\text{D.28})$$

The unit vectors of this coordinate system are:

$$\hat{r} = \frac{\frac{d\mathbf{r}}{dr}}{\left| \frac{d\mathbf{r}}{dr} \right|} = \sin \theta \sin \theta_1 \cos \theta_2 \hat{\mathbf{x}} + \sin \theta \sin \theta_1 \sin \theta_2 \hat{\mathbf{y}} + \sin \theta \cos \theta_1 \hat{\mathbf{z}} + \cos \theta \hat{\mathbf{t}}, \quad \text{where } \left| \frac{d\mathbf{r}}{dr} \right| = 1. \quad (\text{D.29})$$

$$\hat{\theta} = \frac{\frac{d\mathbf{r}}{d\theta}}{\left| \frac{d\mathbf{r}}{d\theta} \right|} = \cos \theta \sin \theta_1 \cos \theta_2 \hat{\mathbf{x}} + \cos \theta \sin \theta_1 \sin \theta_2 \hat{\mathbf{y}} + \cos \theta \cos \theta_1 \hat{\mathbf{z}} - \sin \theta \hat{\mathbf{t}}, \quad \text{where } \left| \frac{d\mathbf{r}}{d\theta} \right| = r. \quad (\text{D.30})$$

$$\hat{\theta}_1 = \cos \theta_1 \cos \theta_2 \hat{\mathbf{x}} + \cos \theta_1 \sin \theta_2 \hat{\mathbf{y}} - \sin \theta_1 \hat{\mathbf{z}}, \quad \text{where } \left| \frac{d\mathbf{r}}{d\theta_1} \right| = r \sin \theta. \quad (\text{D.31})$$

$$\hat{\theta}_2 = -\sin \theta_2 \hat{\mathbf{x}} + \cos \theta_2 \hat{\mathbf{y}}, \quad \text{where } \left| \frac{d\mathbf{r}}{d\theta_2} \right| = r \sin \theta \sin \theta_1. \quad (\text{D.32})$$

Derivatives of unit vectors:

The important non-zero derivatives are:

$$\frac{\partial \hat{\theta}}{\partial \theta}, \quad \frac{\partial \hat{\theta}}{\partial \theta_1}, \quad \frac{\partial \hat{\theta}}{\partial \theta_2}, \quad \frac{\partial \hat{\theta}_1}{\partial \theta_1}, \quad \frac{\partial \hat{\theta}_1}{\partial \theta_2}, \quad \frac{\partial \hat{\theta}_2}{\partial \theta_2}. \quad (\text{D.33})$$

Appendix E

Curl in 3D and 7D:

In the Cartesian coordinate system, R^n with coordinates $(x_1, \dots, x_n)$ and a standard basis $\{\bar{e}_1, \dots, \bar{e}_n\}$, ∇ (*Del*) is defined in terms of partial derivatives as:

$$\nabla = \left(\frac{\partial}{\partial x_1}, \dots, \frac{\partial}{\partial x_n} \right) = \sum_{i=1}^n \bar{e}_i \frac{\partial}{\partial x_i} \quad (\text{E.1})$$

For example, in a three-dimensional Cartesian coordinate system R^3 , with coordinates (x, y, z) and standard basis $\{\bar{e}_1, \bar{e}_2, \bar{e}_3\}$:

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = \bar{e}_x \frac{\partial}{\partial x} + \bar{e}_y \frac{\partial}{\partial y} + \bar{e}_z \frac{\partial}{\partial z}. \quad (\text{E.2})$$

Similarly, in a seven-dimensional Cartesian coordinate system R^7 , with coordinates (x, y, z, w, m, n, o) and standard basis $\{\bar{e}_1, \bar{e}_2, \bar{e}_3, \bar{e}_4, \bar{e}_5, \bar{e}_6, \bar{e}_7\}$, *Del* is written as:

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial w}, \frac{\partial}{\partial m}, \frac{\partial}{\partial n}, \frac{\partial}{\partial o} \right) = \bar{e}_x \frac{\partial}{\partial x} + \bar{e}_y \frac{\partial}{\partial y} + \bar{e}_z \frac{\partial}{\partial z} + \bar{e}_w \frac{\partial}{\partial w} + \bar{e}_m \frac{\partial}{\partial m} + \bar{e}_n \frac{\partial}{\partial n} + \bar{e}_o \frac{\partial}{\partial o}. \quad (\text{E.3})$$

The curl is the result of crossing the Del operator with a vector field, for example:

$$\nabla \times \vec{F} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \times (f_1, f_2, f_3). \quad (\text{E.4})$$

The result of the curl is a vector field; that is, the curl operator turns a vector field into another vector field. The concept of the curl in three-dimensional space E^3 is important in both mathematics and physics [37]. The most notable examples are contained in Maxwell's equations for electromagnetism that characterize the induction of the electric field $\mathbf{E}$ and the magnetic field $\mathbf{B}$ in three-dimensions using the curl operator. In this section, it is shown that the curl in three-dimensions is based on the quaternion algebra, and that the curl in seven-dimensions is based on the octonion algebra (which is an eight-dimensional vector space analogous to the quaternions). In particular, the three-dimensional

Octonion

Quaternion							
Complex							
1	<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i>	<i>o</i>
<i>i</i>	-1	<i>k</i>	<i>-j</i>	<i>m</i>	<i>-l</i>	<i>-o</i>	<i>n</i>
<i>j</i>	<i>-k</i>	-1	<i>i</i>	<i>n</i>	<i>o</i>	<i>-l</i>	<i>-m</i>
<i>k</i>	<i>j</i>	<i>-i</i>	-1	<i>o</i>	<i>-n</i>	<i>m</i>	<i>-l</i>
<i>l</i>	<i>-m</i>	<i>-n</i>	<i>-o</i>	-1	<i>i</i>	<i>j</i>	<i>k</i>
<i>m</i>	<i>l</i>	<i>-o</i>	<i>n</i>	<i>-i</i>	-1	<i>-k</i>	<i>j</i>
<i>n</i>	<i>o</i>	<i>l</i>	<i>-m</i>	<i>-j</i>	<i>k</i>	-1	<i>-i</i>
<i>o</i>	<i>-n</i>	<i>m</i>	<i>l</i>	<i>-k</i>	<i>-j</i>	<i>i</i>	-1

Figure E.1: Octonion group multiplication table, with quaternion and complex group multiplication tables as subgroups. Note that, while the complex group is Abelian, the quaternion and octonion groups are non-abelian since their group operation is non-commutative.

curl is obtained by defining the multiplication of two pure imaginary quaternions^a and the seven-dimensional curl is obtained by defining the multiplication of two pure imaginary octonions^b. This is accomplished using the multiplication table in Figure E.1. Interestingly, Maxwell originally wrote his famous relations for electromagnetism in the quaternion form and they were only later rewritten in modern vector notation.

E.1 Three-dimensions:

Quaternions have some properties that make them behave like three-dimensional vectors. The multiplication of two pure imaginary quaternions $p = (p_b\vec{e}_1 + p_c\vec{e}_2 + p_d\vec{e}_3)$ and $q = (q_b\vec{e}_1 + q_c\vec{e}_2 + q_d\vec{e}_3)$, using the quaternion multiplication table (Fig. E.1) is:

$$p \times q = (p_cq_d - p_dq_c)\vec{e}_1 + (p_dq_b - p_bq_d)\vec{e}_2 + (p_bq_c - p_cq_b)\vec{e}_3. \quad (\text{E.5})$$

This three-dimensional cross product is of particular importance in electrodynamics, as the definition of the $\mathbf{B}$ field in terms of the curl of the three-dimensional magnetic vector potential A^i :

$$B = \nabla \times A^i \text{ for, } i = 1, 2, 3. \quad (\text{E.6})$$

^aA pure imaginary quaternion has a zero real part, i.e., $q = 0 + b\vec{e}_1 + c\vec{e}_2 + d\vec{e}_3$.

^bA pure imaginary octonion has a zero real part, i.e., $o = 0 + b\vec{e}_1 + c\vec{e}_2 + d\vec{e}_3 + e\vec{e}_4 + f\vec{e}_5 + g\vec{e}_6 + h\vec{e}_7$.

This expression can be expanded in terms of Cartesian coordinates A_x , A_y and A_z :

$$\nabla \times A = \begin{vmatrix} e_1 & e_2 & e_3 \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{vmatrix} \begin{matrix} p \\ q \end{matrix} \quad (\text{E.7})$$

where (e_1, e_2, e_3) play the role of unit vectors for the x – y – and z – axes. Recalling the cross-product of the pure imaginary quaternions (where $p = \nabla$ and $q = A$), this expands as:

$$B = \nabla \times A^i = \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) e_1 + \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) e_2 + \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) e_3. \quad (\text{E.8})$$

Note that Eqn. E.8 and Eqn. E.5 have the same form.

E.2 Seven-dimensions:

When considering the curl in higher dimensions than three, the next dimension in which a cross product may be defined is in seven-dimensions [38]. In fact, it is well-known that the cross-product in one-, three-, and seven-dimensional spaces derive from the algebra domains: complex $\mathbb{C}$, quaternion $\mathbb{H}$ and octonion $\mathbb{O}$, which possess one, three, and seven imaginary components. This suggests that the curl in seven-dimensional space can be developed using octonion multiplication (Fig. E.1), by the same method that was used to develop the curl in three-dimensions using quaternion algebra.

The multiplication of two pure imaginary octonion numbers, where $(e_1, e_2, e_3, e_4, e_5, e_6, e_7)$ play the role of unit vectors along the Cartesian axes in seven-dimensions defines the cross-product in seven-dimensions. Allowing one of the octonions to play the role of a gradient, and the other as an arbitrary vector potential A^i , one can define a field $\mathbf{B}$ as their cross product:

$$B_g = \nabla \times A^i \text{ for, } i = 1, 2, 3, 4, 5, 6, 7. \quad (\text{E.9})$$

Using the octonion multiplication law (Fig. E.1), this expands as:

$$\begin{aligned}
B_g = \nabla \times A^i = & \left(\left(\frac{\partial A_{d_3}}{\partial d_2} - \frac{\partial A_{d_2}}{\partial d_3} \right) + \left(\frac{\partial A_{d_5}}{\partial d_4} - \frac{\partial A_{d_4}}{\partial d_5} \right) + \left(\frac{\partial A_{d_6}}{\partial d_7} - \frac{\partial A_{d_7}}{\partial d_6} \right) \right) \vec{e}_1 + \\
& \left(\left(\frac{\partial A_{d_1}}{\partial d_3} - \frac{\partial A_{d_3}}{\partial d_1} \right) + \left(\frac{\partial A_{d_6}}{\partial d_4} - \frac{\partial A_{d_4}}{\partial d_6} \right) + \left(\frac{\partial A_{d_7}}{\partial d_5} - \frac{\partial A_{d_5}}{\partial d_7} \right) \right) \vec{e}_2 + \\
& \left(\left(\frac{\partial A_{d_2}}{\partial d_1} - \frac{\partial A_{d_1}}{\partial d_2} \right) + \left(\frac{\partial A_{d_7}}{\partial d_4} - \frac{\partial A_{d_4}}{\partial d_7} \right) + \left(\frac{\partial A_{d_5}}{\partial d_6} - \frac{\partial A_{d_6}}{\partial d_5} \right) \right) \vec{e}_3 + \\
& \left(\left(\frac{\partial A_{d_1}}{\partial d_5} - \frac{\partial A_{d_5}}{\partial d_1} \right) + \left(\frac{\partial A_{d_2}}{\partial d_6} - \frac{\partial A_{d_6}}{\partial d_2} \right) + \left(\frac{\partial A_{d_3}}{\partial d_7} - \frac{\partial A_{d_7}}{\partial d_3} \right) \right) \vec{e}_4 + \\
& \left(\left(\frac{\partial A_{d_4}}{\partial d_1} - \frac{\partial A_{d_1}}{\partial d_4} \right) + \left(\frac{\partial A_{d_2}}{\partial d_7} - \frac{\partial A_{d_7}}{\partial d_2} \right) + \left(\frac{\partial A_{d_6}}{\partial d_3} - \frac{\partial A_{d_3}}{\partial d_6} \right) \right) \vec{e}_5 + \\
& \left(\left(\frac{\partial A_{d_7}}{\partial d_1} - \frac{\partial A_{d_1}}{\partial d_7} \right) + \left(\frac{\partial A_{d_4}}{\partial d_2} - \frac{\partial A_{d_2}}{\partial d_4} \right) + \left(\frac{\partial A_{d_3}}{\partial d_5} - \frac{\partial A_{d_5}}{\partial d_3} \right) \right) \vec{e}_6 + \\
& \left(\left(\frac{\partial A_{d_1}}{\partial d_6} - \frac{\partial A_{d_6}}{\partial d_1} \right) + \left(\frac{\partial A_{d_5}}{\partial d_2} - \frac{\partial A_{d_2}}{\partial d_5} \right) + \left(\frac{\partial A_{d_4}}{\partial d_3} - \frac{\partial A_{d_3}}{\partial d_4} \right) \right) \vec{e}_7. \quad (\text{E.10})
\end{aligned}$$

Appendix F

Derivation of $U(1)$ Josephson relations

The four important degrees of freedom that characterize a $U(1)$ Josephson junction belong to the complex order parameter on the left- and right-hand sides of the junction: $\psi_L = \sqrt{n_{S,L}}e^{i\theta_L}$ and $\psi_R = \sqrt{n_{S,R}}e^{i\theta_R}$, where $n_{S,L}$ and $n_{S,R}$ are the density of the condensate on either side of the junction and θ_L and θ_R are the scalar phase angle parameters that characterize the order parameter on either side of the junction. By defining the time-evolution of these four degrees of freedom, one can determine the general theory of $U(1)$ Josephson junctions [39].

The time-evolution of the amplitude and scalar phase angle degrees of freedom are determined by considering the imaginary and real parts of the coupled Schrödinger equations for the wave functions that comprise the junction [39]:

$$\hat{i}\hbar\frac{\partial\psi_L}{\partial t} = \mu_L\psi_L + K\psi_R \quad \text{and,} \quad \hat{i}\hbar\frac{\partial\psi_R}{\partial t} = \mu_R\psi_R + K\psi_L \quad (\text{F.1})$$

where K is a coupling constant that is characteristic of the junction (and is symmetric across the junction), μ_i is the lowest energy state on either side of the junction, and $\hbar$ is Planck's constant divided by 2π . In the event that K were zero, these equations would describe the lowest-energy states of each domain; non-zero K allows for leakage of information between the two sides [39].

These equations depend upon the time derivative of the wave function. The time derivative of the wave function may be solved for using the product rule, and the chain rule:

$$\frac{\partial\psi}{\partial t} = \frac{\partial(\sqrt{n_S}e^{i\theta})}{\partial t} \equiv \left[\frac{1}{2\sqrt{n_S}}\frac{\partial n_S}{\partial t} + i\sqrt{n_S}\frac{\partial\theta}{\partial t} \right] e^{i\theta}. \quad (\text{F.2})$$

Substituting this expression into Eqn. F.1, and dividing everything by $e^{i\theta_L}$, gives:

$$i\hbar \left[\frac{1}{2\sqrt{n_{S,L}}}\frac{\partial n_{S,L}}{\partial t} + i\sqrt{n_{S,L}}\frac{\partial\theta_L}{\partial t} \right] = \mu_L\sqrt{n_{S,L}} + K\sqrt{n_{S,R}}\frac{e^{i\theta_R}}{e^{i\theta_L}}. \quad (\text{F.3})$$

It is owing to the Abelian nature of complex numbers that the term $\frac{e^{i\theta_R}}{e^{i\theta_L}}$ can be rewritten using Euler's

expansion: $\frac{e^{i\theta_R}}{e^{i\theta_L}} = e^{i(\theta_R - \theta_L)} \equiv \cos \delta + i \sin \delta$, where $\delta \equiv \theta_R - \theta_L$. Using this expression, Eqn. F.3 can be re-written as (carrying through the multiplication by $i\hbar$):

$$\frac{i\hbar}{2\sqrt{n_{S,L}}} \frac{\partial n_{S,L}}{\partial t} - \hbar\sqrt{n_{S,L}} \frac{\partial \theta_L}{\partial t} = \mu_L\sqrt{n_{S,L}} + K\sqrt{n_{S,R}} (\cos \delta + i \sin \delta) \quad (\text{F.4})$$

The time derivative of the density of condensed particles gives a current of condensed particles across the junction, solved for by considering the imaginary part of Eqn. F.4; the time-evolution of the scalar phase angle is related to the real part of Eqn. F.4. The four important expressions are defined as [40]:

$$\dot{n}_{S,L} = +\frac{2}{\hbar}K\sqrt{n_{S,R}n_{S,L}} \sin \delta \quad \text{and,} \quad \dot{n}_{S,R} = -\frac{2}{\hbar}K\sqrt{n_{S,R}n_{S,L}} \sin \delta \quad (\text{F.5})$$

$$\dot{\theta}_L = -\frac{\Delta\mu}{2\hbar} - \frac{K}{\hbar} \sqrt{\frac{n_{S,R}}{n_{S,L}}} \cos \delta \quad \text{and,} \quad \dot{\theta}_R = +\frac{\Delta\mu}{2\hbar} - \frac{K}{\hbar} \sqrt{\frac{n_{S,L}}{n_{S,R}}} \cos \delta \quad (\text{F.6})$$

where $\Delta\mu = \mu_L - \mu_R$ is the chemical potential difference between the two superfluids, where $\mu_L = +\Delta\mu/2$ and $\mu_R = -\Delta\mu/2$ are the lowest-energy states on either side of the junction.

In a charged Josephson junction, one can consider connecting the two superconducting regions to the terminals of a battery in order to develop a potential difference V across the Josephson junction. Then, $\mu_L - \mu_R = qV$ where q is the charge of a Cooper pair (Josephson [40, 41] (1962) was the first to predict the tunneling of composite bosons known as Cooper pairs). These expressions also apply to Josephson junctions that are comprised of two baths of helium superfluid, wherein a difference in the head across the junction will generate a difference in chemical potential of $\mu = m_4gz$ between the two baths [42, 43], where z is the head, m_4 is the mass of an He^4 atom and g is the acceleration due to gravity [43]. z acts just like a potential voltage V in charged Josephson junctions.

The time evolution of the relative scalar phase across the junction is:

$$\dot{\delta} = \dot{\theta}_R - \dot{\theta}_L = \frac{\mu}{\hbar}. \quad (\text{F.7})$$

It follows that:

$$\delta = \delta_0 + \frac{1}{\hbar} \int \mu(t) dt. \quad (\text{F.8})$$

On the other hand, in the absence of an applied external flow of particles [39], $\dot{n}_{S,L} = -\dot{n}_{S,R}$. In a charged Josephson junction, upon connecting the two terminals within current-based circuit, an overall current develops to keep the potential constant and the current from one side the other is [39]:

$$I = n_S = I_C \sin \delta \quad (\text{F.9})$$

where $I_C = 2Kn_S/\hbar$ is a “critical current” that is characteristic of a particular junction.

Appendix G

Angular momentum components

G.1 $O(2)$

The $O(2)$ model has a single angular momentum component, i.e., $n(n-1)/2 = 1$ for $n = 2$. The angular momentum component is determined as:

$$L_1 = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right), \quad (\text{G.1})$$

where

$$x = r \cos \theta \quad y = r \sin \theta \quad \text{and,} \quad r = (x^2 + y^2)^{1/2} \quad \theta = \tan^{-1} \left(\frac{y}{x} \right). \quad (\text{G.2})$$

One can use the chain rule to convert the angular momentum component from Cartesian to polar form:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} = \frac{x}{r} \frac{\partial}{\partial r} - \frac{y}{x^2} \cos^2 \theta \frac{\partial}{\partial \theta} \quad (\text{G.3})$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} = \frac{y}{r} \frac{\partial}{\partial r} + \frac{x}{x^2} \cos^2 \theta \frac{\partial}{\partial \theta} \quad (\text{G.4})$$

These expressions can be substituted into Eqn. G.1 in order to find L_1 in polar coordinates:

$$L_1 = -i\hbar \left(\cancel{\frac{xy}{r} \frac{\partial}{\partial r}} + \cancel{-\cos^2 \theta \frac{\partial}{\partial \theta}} - \cancel{\frac{xy}{r} \frac{\partial}{\partial r}} + \frac{y^2}{x^2} \cos^2 \theta \frac{\partial}{\partial \theta} \right) = -i\hbar \cos^2 \theta \frac{\partial}{\partial \theta} \left(1 + \frac{y^2}{x^2} \right). \quad (\text{G.5})$$

Noting that $\left(1 + \frac{y^2}{x^2} \right) = 1/\cos^2 \theta$, the single angular momentum operator of the $O(2)$ rotor is [44]:

$$L_1 = \frac{1}{i} \hbar \frac{\partial}{\partial \theta}. \quad (\text{G.6})$$

G.2 $O(4)$

An $O(4)$ quantum rotor possesses six angular momentum components. The six angular momentum components are [45]:

$$L_1 = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad L_2 = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad L_3 = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right), \quad (\text{G.7})$$

$$M_1 = -i\hbar \left(w \frac{\partial}{\partial x} - x \frac{\partial}{\partial w} \right), \quad M_2 = -i\hbar \left(w \frac{\partial}{\partial y} - y \frac{\partial}{\partial w} \right), \quad M_3 = -i\hbar \left(w \frac{\partial}{\partial z} - z \frac{\partial}{\partial w} \right). \quad (\text{G.8})$$

The six generators of the group more conveniently written in terms of a four-dimensional spherical coordinate system that is characterized by 3 angles θ , θ_1 and θ_2 as:

$$x = r \sin \theta \sin \theta_1 \cos \theta_2 \quad y = r \sin \theta \sin \theta_1 \sin \theta_2, \quad z = r \sin \theta \cos \theta_1 \quad w = r \cos \theta. \quad (\text{G.9})$$

The angle θ describes the angle between a rotation axis [45] and a fixed Cartesian z -axis. The angles θ_1 and θ_2 characterize the rotation in a three-dimensional subspace with a fixed rotation axis [45]. The operators of infinitesimal rotations are [45]:

$$L_3 = \frac{1}{i} \hbar \frac{\partial}{\partial \theta_3}, \quad L^\pm = e^{\pm i \theta_3} \left(\pm \frac{\partial}{\partial \theta_1} + i \cot \theta_1 \frac{\partial}{\partial \theta_3} \right), \quad (\text{G.10})$$

$$M_3 = i \cos \theta_1 \frac{\partial}{\partial \theta} - i \sin \theta_1 \cot \theta \frac{\partial}{\partial \theta_1} \quad (\text{G.11})$$

$$M^\pm = e^{\pm i \theta_3} \left(\cot \theta \left[\mp \frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_2} + i \cos \theta_1 \frac{\partial}{\partial \theta_1} \right] + i \sin \theta_1 \frac{\partial}{\partial \theta} \right), \quad (\text{G.12})$$

where $L^\pm = L_1 \pm i L_2$ and $M^\pm = M_1 \pm i M_2$. The operator $\hat{\mathbf{L}}^2$ gives the magnitude of the three angular momentum components $\hat{\mathbf{L}}$ that describe 3D rotations, and the additional generator $\hat{\mathbf{M}}$ of three angular momentum components makes the fourth dimension accessible [45] by determining the transitions from 3D space to the true 4D manifold.

Appendix H

1D Josephson junction chains: (1D+1t) space-time approach

The $O(2)$ Hamiltonian applies to one-dimensional chains of complex tunnel junctions [46, 47] and can be tuned by a dimensionless parameter $g = E_C/E_J$ that characterizes each Josephson junction. Just as in two-dimensions, when g is tuned at zero temperature [48, 46], a transition between distinct (dual) ground states takes place. In the vicinity of this transition, the distinct low-temperature states are obtained by transitions that belong to the same Berezinskii-Kosterlitz-Thouless class as in planar Josephson junction arrays. As shown in Ref. [48], this is because the partition functions of the Josephson junction chain and array models are isomorphic [46] when one maps the 1D configurations of Josephson junctions to the 2D problem by taking a time (τ) direction to act as a second spatial direction [49, 50]. A schematic of a (1D+1t) space-time model of a Josephson junction chain is shown in Fig. H.1. At zero Kelvin, the time direction becomes infinite (i.e., forwards and backwards) and the relevant topological excitations can be viewed as $\pi_1(S^1)$ vortex point defects in the (1D+1t) space-time manifold [51, 52, 53]. Such a system cannot exhibit a transition to the ordered low-temperature state without the consideration of topology or the topological ordering of misorientational fluctuations [54].

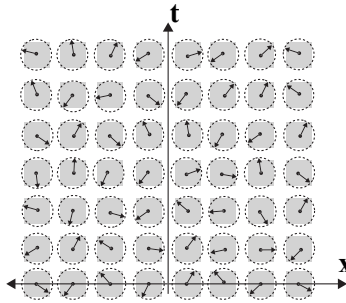


Figure H.1: A chain of Josephson junctions in (1D+1t) spacetime. Space-time vortices (in θ) proliferate just below the bulk critical transition temperature.

Appendix I

Mesomorphic states of matter: Plastic crystals and liquid crystals

There are two mesomorphic states of matter that exist as intermediate between the liquid and solid states [55]. Solid-like liquids are referred to as liquid crystals, and liquid-like solids are given the name plastic crystals [55]. These mesoscopic phases exist because there are two types of randomization that occur during a melting process between solid and liquid states [55, 56]: translational (T) and rotational (R). While in many materials translational and rotational order establish themselves concurrently, in mesoscopic phases there are two separate transitions (between the true solid and the true liquid) because it is substantially easier to disorder one type than the other.

It was with the early discovery of the liquid crystalline state, over 150 years ago (in 1888, by the Austrian botanist Freidrich Reinitzer while he was investigating the physical properties of cholesterol [57]), that it became clear that melting processes are a two-stage process that is a superposition of both translational and rotational ordering effects [58]. The discovery of plastic crystalline phases is more recent [58, 59], dating back to the 1960s. The study of plastic crystals exploded with the discovery of fullerene molecules [60] in 1985; a schematic of the nearest-neighbor environment in a three-dimensional fullerene plastic crystal is shown in Fig. I.1.

Liquid crystalline phases are typically comprised of very anisotropic (elongated shape) molecules that tend to establish a parallel orientation. Such molecules are unable to rotate freely [55]; it follows that, on cooling, the (freely rotating) molecules that comprise the high-temperature isotropic liquid will first become orientationally-ordered as their rotations are restricted to be about the special axis of the molecule [55]. The liquid crystalline state transitions towards a true crystalline solid, that is translationally ordered, at a subsequently lower temperature on breaking the remnant translational symmetry that is possessed by the liquid crystal [56].

On the other hand, nearly spherical (i.e., anisometric^a) molecules that allow for an almost uninhibited rotation in space [61, 55, 62] comprise plastic crystalline phases (Fig. I.1). Despite the

^aWithout full spherical symmetry.

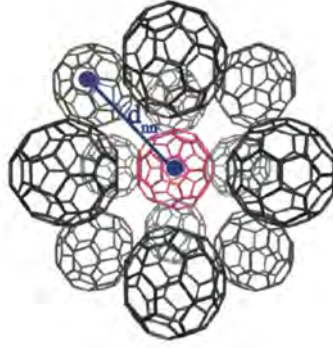


Figure I.1: Nearest-neighbor environment within a 3D fullerene plastic crystal (FCC arrangement).

nearly free rotation of the constituents within the plastic crystalline phase, artificial translational periodicity is retained [58] as the anisometric constituents fluctuate around mean lattice positions. Thus, plastic crystalline phases express (artificial) positional order of its constituents without orientational order. Both orientationally ordered and orientationally disordered low-temperature states of the plastic crystal phase are able to exist, as the temperature of the system is lowered below a critical value. These statements, regarding positional and orientational ordering in mesomorphic states of matter, are summarized in Fig. I.2. Here, the melting transition is identified with the translational ordering process. From this point of view, the liquid crystal and plastic crystal are complementary mesomorphic states of matter [58, 55].

In developing an understanding of the topological structure of plastic crystalline systems, via a continuum description [61], it is first convenient to introduce the continuum description of uniaxial nematic liquid crystals. The continuum description of uniaxial nematics [63], from which the topological structure of the ordered media is understood, is based on the assignment of a “average molecular orientation” to every point in space [63] that acts as a local order parameter. This configuration of order parameters creates what is known as the director field [36]. In the case of uniaxial nematic liquid crystals, owing to the symmetry of the ordered media, the average molecular orientation takes the form of a rodlike object. Thus, the director field is a line field (headless vector field) instead of a vector field; that is, the local order parameter (the director) at each point in space may be taken to be a unit vector $\hat{\mathbf{n}}$ for which $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ are identified.

Similarly, despite the nearly uninhibited rotation of constituents of plastic crystalline phases, an “average molecular orientation” can be defined at every point in the sample creating a director field [61, 63]. Here, the symmetry of the director field is discrete (i.e., not continuous) and the constituents of the plastic crystal phase have multiple molecular orientations that can be adopted without statistical preference. Just as in the case of the director field in liquid crystalline phases [63, 32] (e.g., nematic or biaxial), the director field of plastic crystalline phases can bear topological defects [61]. Thus, plastic crystalline phases are characterized by a non-trivial topological structure.

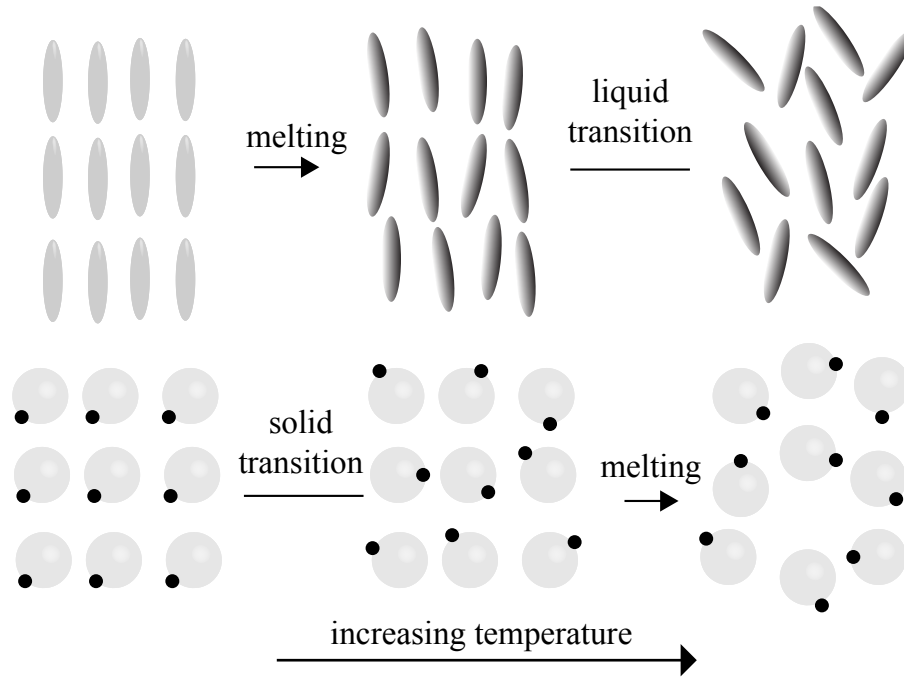


Figure I.2: Positional and orientational ordering occur separately in mesomorphic systems: liquid crystals and plastic crystals. On heating, liquid crystals lose positional order before orientational order, while the sequence is reversed in plastic crystals.

While the topological structures of three-dimensional liquid crystalline phases (uniaxial and biaxial nematics) have been well-studied by many authors [63, 64], there has been much less exploration into the topological structure of plastic crystalline phases. However, two works by Cremer et al. [61] and Achim et al. [65] have provided the framework for further study into the topological structure of plastic crystalline phases.

Appendix J

Connection between Topology and Curvature: Gauss-Bonnet theorem

Topology has a strong relationship with curvature. This may seem counter-intuitive because of the homeomorphisms that topology allows; for example, a torus may be stretched it to its homeomorphic equivalent which is a coffee cup. Even though the metric and curvature are changing, it turns out that, topology and curvature are linked via the Gauss-Bonnet theorem. The Gauss-Bonnet theorem that applies to two-dimensional closed manifolds $\mathcal{M}$ (e.g., T^2 and S^2) is:

$$\int_{\mathcal{M}} K \, dA = 2\pi\chi \quad (\text{J.1})$$

where χ and K are the Euler characteristic and the Gaussian curvature of the surface. That is, the integral of the Gaussian curvature over the two-dimensional topological manifold $\mathcal{M}$ is equal to a constant (2π) time the Euler characteristic. For example, consider the standard two-dimensional sphere (S^2); the Gaussian curvature is constant everywhere $1/R^2$, where R is the radius of the sphere. Thus, the integral of the Gaussian curvature over the surface: $\int_{S^2} K \, dA$, is just the area times the curvature, i.e., $4\pi R^2 \cdot 1/R^2 = 4\pi$. Therefore, the Euler characteristic of the two-dimensional sphere is 2. This holds for any metric on the sphere; that is, the Euler characteristic is a topological invariant that does not change no matter how much the sphere is deformed. Thus, positive curvature that is added by deforming the surface is exactly canceled out by reduced positive curvature somewhere else on the surface of the sphere.

The total curvature of the surface can only change if the topology of the surface changes, for instance, by tearing a hole in the surface. This process is also known as adding a handle to the surface, which changes the genus of the surface g that counts the number of holes/handles that the surface consists of. The Euler characteristic of two-dimensional manifolds depends on the genus of the manifold as $\chi = 2(1 - g)$. The most simple example is given by considering adding a handle to a two-dimensional sphere (Fig. J.1), the resulting manifold is the two-dimensional torus (T^2). The

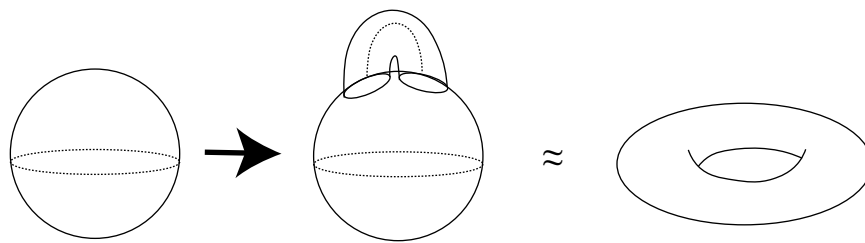


Figure J.1: A two-dimensional torus surface is homeomorphic to a sphere with a single handle sewn into it, i.e., the genus of a 2D torus is one and the genus of a 2D sphere is zero.

two-dimensional torus (which is homeomorphic to a donut or a coffee mug) has a genus of 1, while the genus of the sphere is zero. That is, because the two-dimensional torus has the topology of a two-dimensional sphere with a single handle/hole. It follows that the toroidal surface is restricted to having zero total curvature (positive curvature on the outside edge and negative curvature on the inside edge that cancel out exactly) no matter how the surface is deformed. Fig. J.2(A) and (B) shows a two-dimensional sphere and a two-dimensional torus. While the sphere has zero handles (thus, $\chi = 2$), the two-dimensional torus (which is homeomorphic to a donut or a coffee mug) has a single hole/handle and so its Euler characteristic is zero.

The validity of the Gauss-Bonnet theorem in two-dimensions (Eqn. J.1) extends to higher-dimensional even compact orientable manifolds as a generalized Gauss-Bonnet theorem [66, 67, 68]. The Euler characteristic of a manifold with dimension $2m$ (m is an integer), is related to the m^{th} Chern class [69, 70], e.g., the first Chern class applies to 2D manifolds, and the second Chern class is important for 4D manifolds. For 3D compact orientable manifolds (e.g., S^3 and T^3), even though the generalized Gauss-Bonnet theorem does not apply (odd-dimensional manifolds have a Euler characteristic of zero [71]), the strong relationship between curvature and topology still holds.

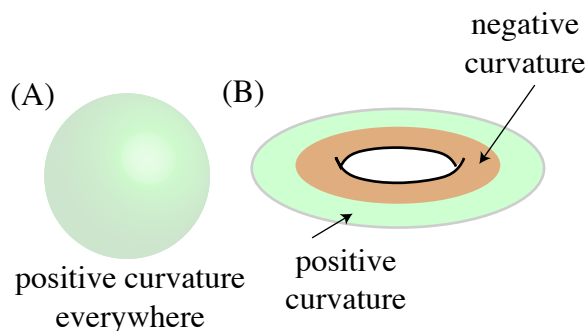


Figure J.2: (A) A sphere has no handles/holes, and has positive Gaussian curvature everywhere. Therefore, the Euler characteristic of S^2 is 2. (B) A two-dimensional torus has a Euler characteristic of zero, because the total curvature of the surface is zero no matter how the surface is deformed.

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Manuscripts prepared by the author

- [1] C. S. Gorham and D. E. Laughlin. “SU(2) orientational ordering in restricted dimensions: evidence for a Berezinskii-Kosterlitz-Thouless transition of topological point defects in four dimensions”. *Journal of Physics Communications* 2.7 (2018). DOI: 10.1088/2399-6528/aace2a.
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Original theoretical and computational work, performed in the preparation of this thesis, is being communicated in academic journals. A first manuscript, detailing the topological arguments and Monte-Carlo simulations that provide evidence for the existence of a topological ordering transition of point defects in four-dimensions, has recently been published in *Journal of Physics Communications* (Ref. [1]). A second article (Ref. [2]), detailing the application of $O(4)$ quantum rotor models to solidification phenomena is in the preparation phase.