

Supporting Information for: Derivation of Coarse Grained Models for Multiscale Simulation of Liquid Crystalline Phase Transitions

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Equilibration of the atomistic simulations in the sm A state

In the smA state the mean-squared displacement (MSD) of the molecules within the xy plane reaches the diffusive regime and the molecules have diffused several molecular lengths, which is one criterion that the system has been well equilibrated. To further check the equilibration of the system in the smA state at 460 K, we computed the orientational correlation of the 8AB8 molecules, shown in Figure S1 from a simulation of 100 ns. During this time there is partial orientational relaxation. Molecules in the smA state relax by a mechanism where they move from their original smectic layer to the inter-layer space (the molecular axes turning by ninety degrees in this process). Then a molecule can sometimes fully reorient ending up either in the next smectic layer or going back to the original layer from where it had started.

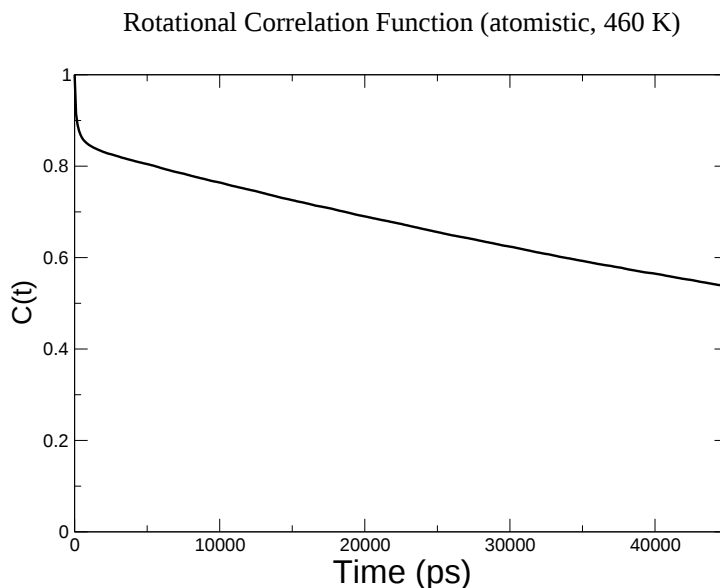


Figure S1: The orientational correlation function of the core of 8AB8 molecules in the smectic A phase at 460 K, calculated for the atomistic model.

The supercooled liquid reference state

The supercooled liquid was prepared, atomistically, by taking a fully disordered configuration at 480 K and then equilibrating it under constant temperature of 460 K and 1 atm pressure.

After an initial equilibration under constant pressure for about 5 ns, the average box dimensions were obtained. The system was further equilibrated at NVT conditions – initially for 15 ns, later for 50 ns. The target radial distribution functions were obtained from these NVT runs. No change in the radial distribution functions was observed in different windows of these simulations, indicating that over this timescale the isotropic state is structurally stable. The mean squared displacement shown in Figure S2 was monitored and the equilibration was continued until each molecule, on average, travelled its own length (~ 2.5 nm). During this time the eigenvalues of the tensor $Q_{\alpha\beta}$ (eq. 1 of the main manuscript), was monitored. It is evident from Figure S3, that no significant macroscopic nematic order developed in the system.

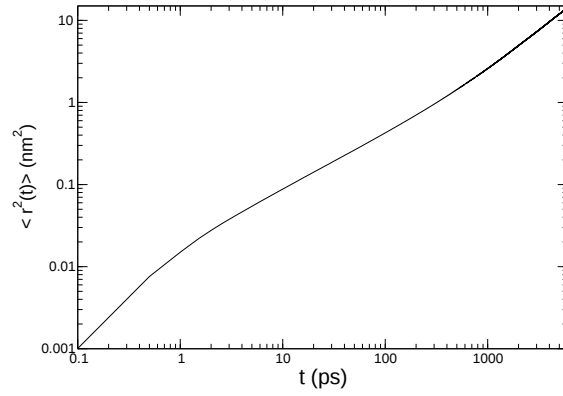


Figure S2: The mean squared displacement of the molecules in the supercooled, atomistic melt at 460 K. At long times, the MSD scales linearly with time, ensuring a diffusive behaviour.

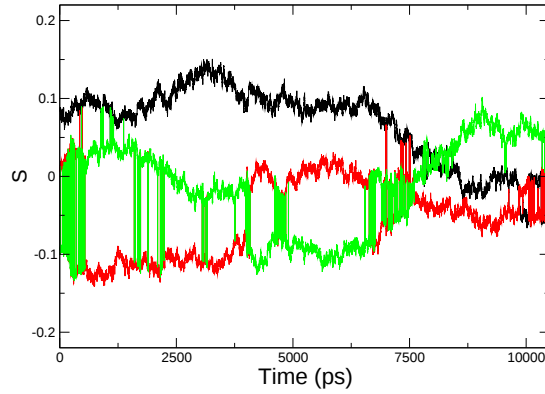


Figure S3: The three eigenvalues of the tensor, $Q_{\alpha\beta}$, of the supercooled, atomistic system at 460 K. The system does not develop any significant order.

Model I

In this version of the model the molecule is made up of three different types of CG beads. That makes six non-bonded interactions, which have to be determined. The comparison of the structure of the coarse grained and the atomistic melts, obtained after 100 steps of iterative Boltzmann inversion of the non-bonded potentials, is presented in Figure S4. The red curve is the atomistic target radial distribution function (RDF), while the black curve is the RDF calculated from the coarse grained simulations. The corresponding potentials are shown in Figure S5 and Figure S6. In this set, all six non-bonded potentials were iterated. It is clear from Figure S5 that in this version of the model, most of the attractive interaction is dumped on the AZ bead.

Model II

In this version, the molecule is again made up of three different types of CG beads. All interactions concerning the AZ bead are made repulsive. This means that three interactions are completely repulsive, namely, AZ-AZ, AZ-PH and AZ-AL. The AZ-AZ and the AZ-PH interactions are repulsive due to the way the WCA potential was constructed. The attractive portion of the two above interactions (obtained from model I) have been removed and the repulsive part has been shifted vertically so that the minima of the potential is at zero energy. The interaction between AZ and AL beads turns out to be repulsive in nature from model I and hence, this interaction has been kept the same as that in model I. We then performed iterative Boltzmann inversion on the remaining interactions. Figure S7 shows the comparison of the structures, the red curve being the atomistic target radial distribution function (RDF), while the black curve is the RDF calculated from the coarse grained simulations. Figure S8 and S9 show the potentials for coarse grained model II.

Model III

The parametrization of the final CG model is based on the observation that all six aliphatic beads are not of the same chemical type. The two beads which are closest to the core have an oxygen in the atomistic model, and are not exactly equivalent to the four other aliphatic beads. Hence in this final version we differentiate between two innermost and the four outermost aliphatic beads. This model thus has four different types of bead, AL, ALo, PH, and AZ. Figure S10 shows the comparison of the structure between CG model III and the atomistic reference. Figures S11 and S12 show the potentials obtained by iterative Boltzmann inversion. Finally, Figure S13 shows the comparison of the bond length distributions for coarse grained model III and the atomistic models.

We could observe phase transitions (smectic to isotropic upon heating and vice versa spontaneous formation of a smectic phase upon cooling) with CG model III. One can compare how the shape of the molecule changes across this phase transition in the atomistic and the CG representations. Figure S14 shows how the CG model reproduces the shape change of the underlying atomistic model across the phase transition.

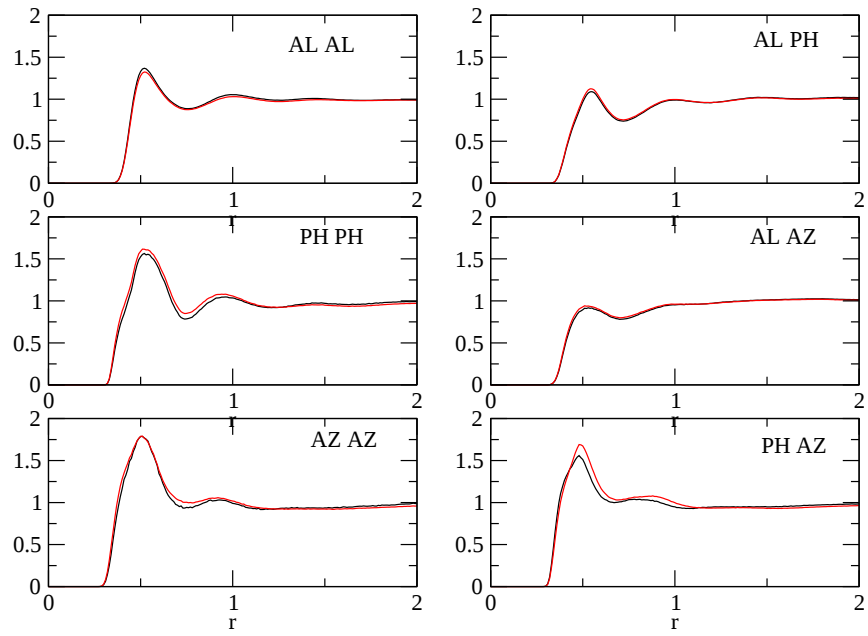


Figure S4: Comparison of the structure of the atomistic and the coarse grained melts for model I (black curves). The target radial distribution functions (red curves) are those of the supercooled liquid at 460 K.

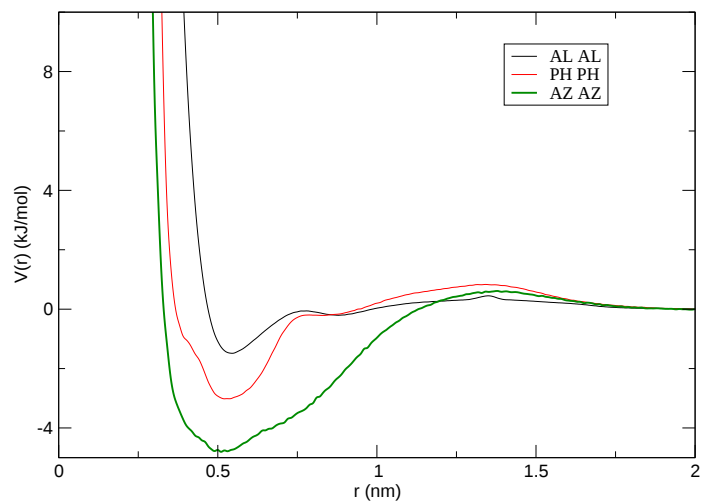


Figure S5: The potentials between like beads, obtained for model I after the iterative Boltzmann inversion. The target radial distribution functions are those of the supercooled liquid at 460 K. The molecule is made up of three different types of beads, which means six unknown non-bonded interactions. The above Figure shows the interactions between similar beads.

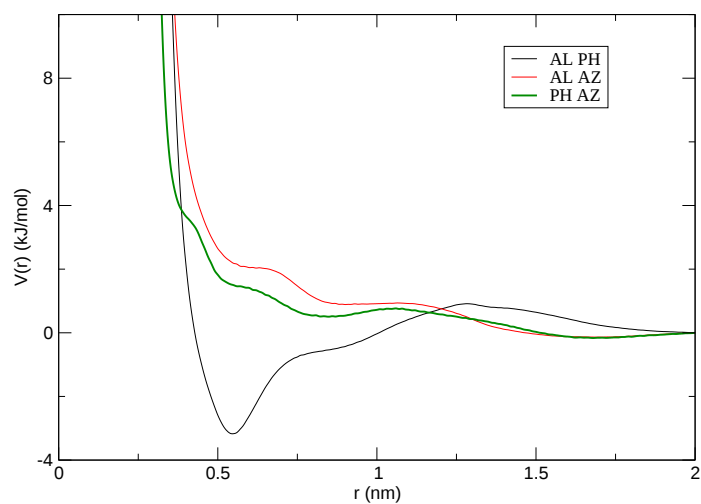


Figure S6: The potentials between unlike beads, obtained for model I after iterative Boltzmann inversion. The target radial distribution functions are those of the supercooled liquid at 460 K.

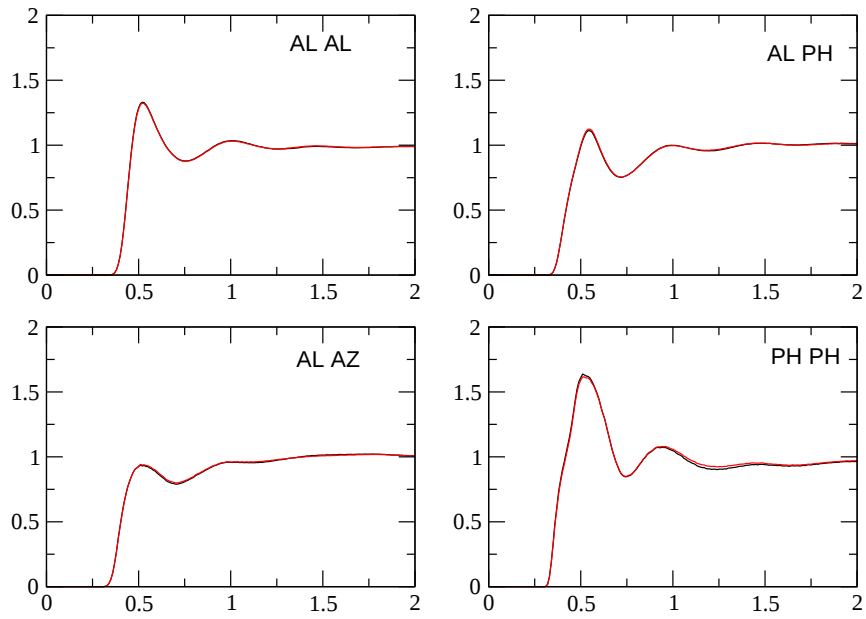


Figure S7: Comparison of the structure of the atomistic (red curve) and the coarse grained melt (black curve) in the supercooled liquid phase at 460K for CG model II. The interaction of the AZ bead with all other beads are repulsive. These interactions were held fixed during the iterations and the remaining interactions were obtained by iterative Boltzmann inversion.

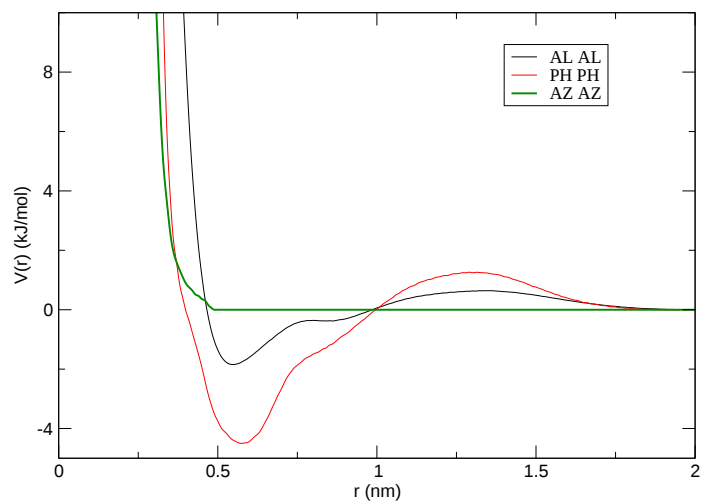


Figure S8: The potentials for model II, obtained after iterative Boltzmann inversion, with the constraint, that the interaction of the AZ bead with all other beads are repulsive. These interactions were held fixed during the iterations. The target radial distribution functions are those of the supercooled liquid at 460 K.

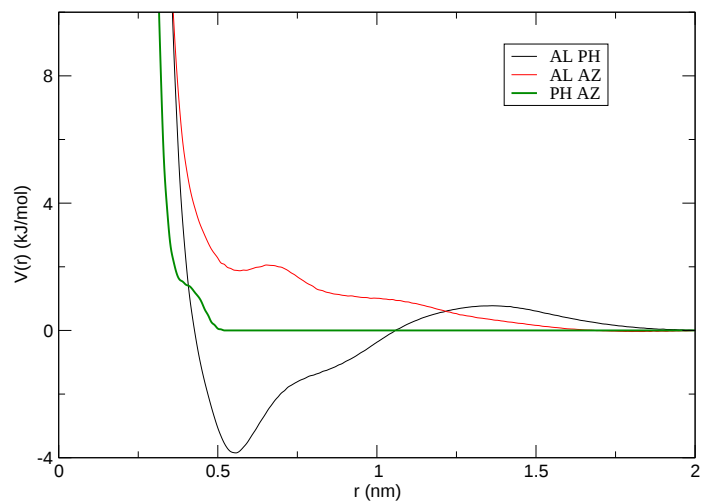


Figure S9: The potentials for model II obtained after iterative Boltzmann inversion, with the constraint, that the interaction of the AZ bead with all other beads are repulsive. These interactions were held fixed during the iterations. The target radial distribution functions are those of the supercooled liquid at 460 K.

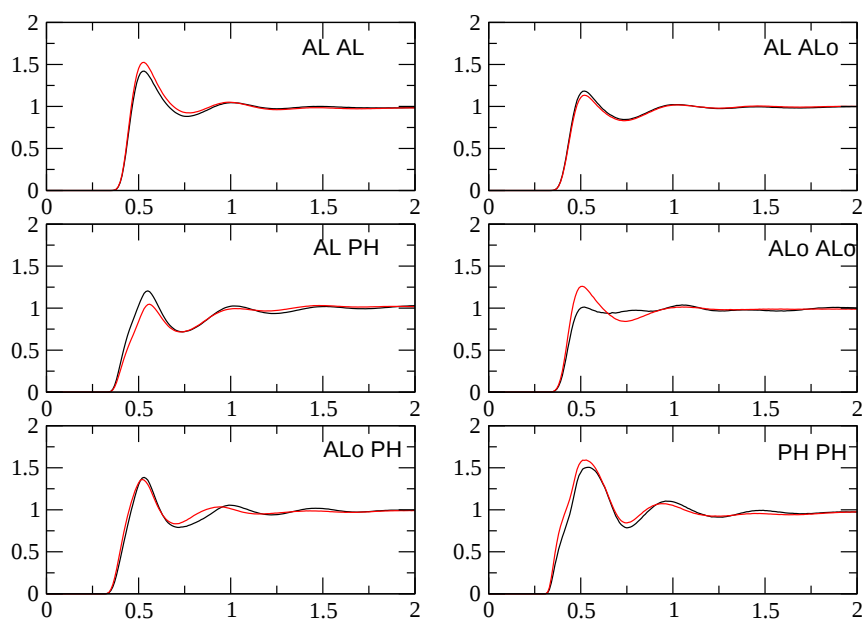


Figure S10: Comparison of the structure of the atomistic (red curve) and the coarse grained melt (black curve) in the supercooled liquid phase at 460K for coarse grained model III. The interaction of the AZ bead with all other beads are repulsive. In this set of iterations we differentiate between the aliphatic beads which are nearest to the core and those aliphatic beads which are further away (AL and ALo).

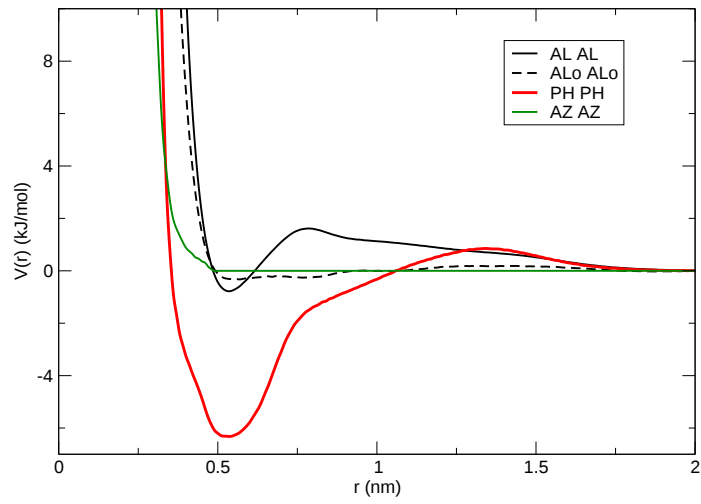


Figure S11: The potentials for model III obtained after iterative Boltzmann inversion. The interaction of the AZ bead with all other beads are repulsive. In this set of iterations we differentiate between the aliphatic beads which are nearest to the core and those aliphatic beads which are further away. Note that most of the attractive interaction is now between the benzene beads.

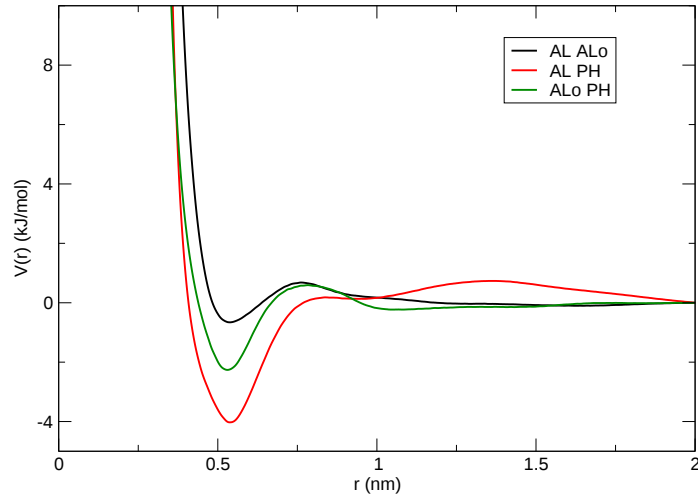


Figure S12: The potentials for model III obtained after iterative Boltzmann inversion. The interaction of the AZ bead with all other beads are repulsive. In this set of iterations we differentiate between the aliphatic beads which are nearest to the core and those aliphatic beads which are away. Note that the attraction between PH and all the AL beads, which was uniform in model II, now splits up into two categories. The interaction between PH and the inner AL bead is weak, whereas the attraction between PH and the outer AL beads is stronger. This has significant effects in the stabilisation of the layered smectic A structure.

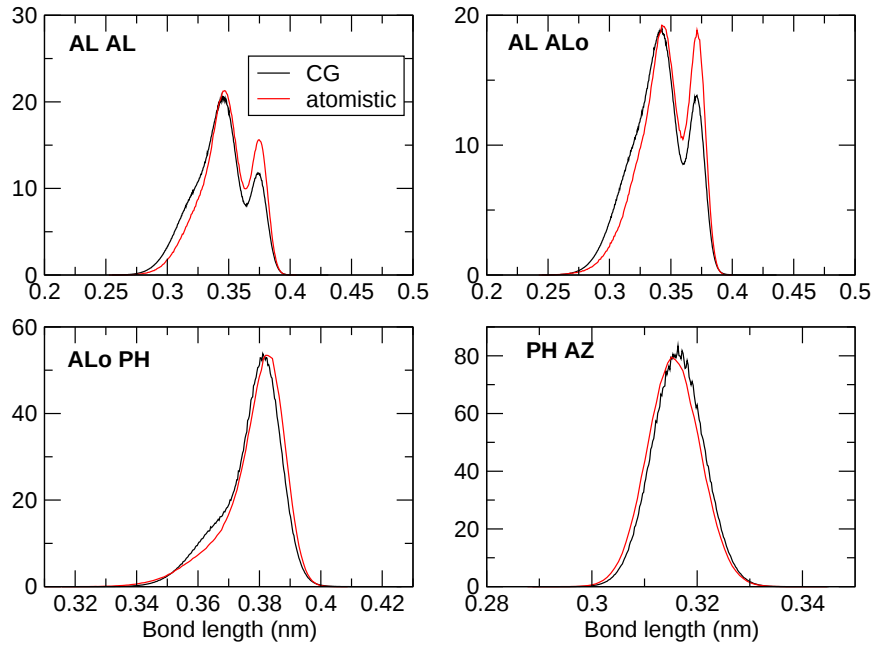


Figure S13: The comparison of distribution of bond lengths calculated from CG model III and atomistic trajectories. The bead types have been defined in Figure I of the main manuscript.

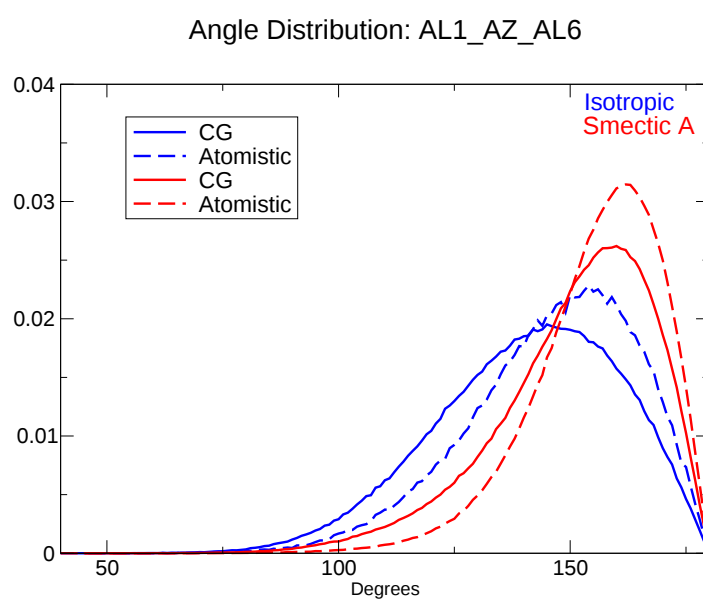


Figure S14: Comparison of the distribution of the angle formed by the first CG alkane bead, central CG azo bead and the end CG alkane bead in the atomistic and the coarse grained representation for the isotropic and the smectic A states. The CG model reproduces the shape change of the underlying atomistic model across the smectic A – isotropic phase transition.