

Supporting Information: Design Rules for Graphene and Carbon-Nanotube Solvents and Dispersants

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Methodology

All systems were simulated in a rectangular box with periodic boundary conditions in all three dimensions.

Simulations of parallel graphene sheets (termed parallel-sheet simulations thereafter) were performed using a $7\text{nm} \times 7\text{nm} \times 7\text{nm}$ box and two finite $5.2\text{nm} \times 5.2\text{nm}$ sheets, separated by a distance d between the planes spanned by the centers of the graphene carbon atoms (Figure 1). The remaining space in the simulation box was filled with solvent molecules by overlaying it with pre-equilibrated solvent boxes and then removing any overlapping molecules.

After energy minimization of the initial configuration the temperature was equilibrated to 300K in the (NVT) ensemble for 300ps. This was followed by 8ns and 1ns pressure coupled

equilibration in the $(NP_{\parallel}s_zT)$ ensemble for CBrCl_3 and water, respectively, with a specified temperature of 300K and pressure of 1 bar (Table 1). Here $P_{\parallel} = P_{xx} = P_{yy}$ is the pressure on the box faces perpendicular to the plane of the sheets and s_z is the box size perpendicular to the sheets.

Initial box dimensions of the system for the Corresponding Distances Method (CDM) were $5.112\text{nm} \times 266.0\text{nm} \times 11.0\text{nm}$. Two graphene sheets were placed in the simulation box in the $x, y, z = 0$ plane, then one was rotated around the x -axis by two degrees (Figure 1). The lower the angle selected, the higher the accuracy of the method, but the larger the simulation box that is needed to achieve a given separation between the graphene sheets. The sheets were $5.112\text{nm} \times 258.126\text{nm}$, i.e. finite in y , but infinite and periodic in x . This graphene sheet size combined with the angle selected determines the maximum distance that is simulated (9 nm) at which the PMF is set as zero. Edge effects were eliminated in post-processing by ignoring 50 rows of carbon atoms (6.14nm) at the end of each sheet.

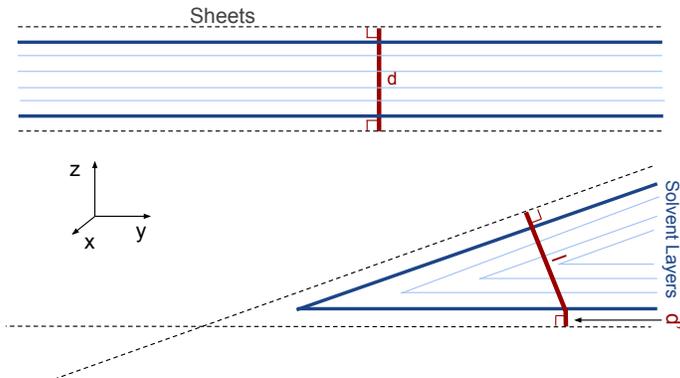


Figure 1: Schematic of the two simulation systems (top , parallel; bottom, CDM). The two systems are linked via the corresponding distances $d = \ell + d'$.

The box was populated with solvent as for the parallel-sheet simulations, then the configuration energy was minimized, followed by 300ps temperature coupled equilibration in the (NVT ensemble) and 2ns pressure coupled equilibration in the $(NP_{\perp}s_xT)$ ensemble, where $P_{\perp} = P_{yy} = P_{zz}$ is the pressure on the box faces perpendicular to the periodic direction of the sheet. NVT production runs were 10ns long for the CDM and water in parallel sheets

simulations, with the first 1ns discarded prior to post-processing; and 21ns long for CBrCl₃ parallel sheets simulations with the first 11ns discarded prior to post-processing. The central concept of the Corresponding Distances Method is that any distance d of the parallel-sheet simulations can be found in the angled system at $d = \ell + d'$ (Figure 1).^{1,2}

Table 1: Simulation Parameters

Production	
Ensemble	NVT
Simulation time (ns)	10 (water), 21 (CBrCl ₃), 10 (all CDM)
Averaging (ns)	9 (water), 10 (CBrCl ₃), 9 (all CDM)
Integrator	velocity verlet
Timestep (ps)	0.002
vdW and electrostatic cut-off (nm)	1.6
vdW scheme	Lennard Jones 12-6, potential shift
Electrostatic scheme	Reaction Field Zero, potential shift verlet
Thermostat ¹	velocity rescale
Thermostat coupling time/constant (ps)	0.1
Neighbour list update frequency (steps)	20
Neighbour list cut-off (nm)	1.9
Isothermal/Isobaric Equilibration	
Ensemble (see text)	($NP_{ s_z}T$) parallel-sheet, ($NP_{ -s_x}T$) CDM
Simulation time (ns)	1
Barostat	Berendsen
Barostat coupling constant (ps)	2.0
Isothermal Compressibility (bar^{-1})	$4 \cdot 10^{-5}$
Isothermal Equilibration	
Ensemble	NVT
Simulation time (ps)	300
Energy Minimization	
EM Type (CBrCl ₃)	conjugate gradient
EM Type (water)	steepest decent
Number of steps ²	10000
Convergence criteria, F_{\max} (kJmol^{-1})	10^3
Parameters for the energy minimization and equilibration steps are the same as for the production step unless otherwise stated. Descriptions of all other simulation parameters can be found in the GROMACS manual. ³	

¹Coupled only to the solvent.

²Or until machine precision or the specified max force is reached.

Validity of the Corresponding Distance Method

The parallel-sheet simulations needed to produce the PMF curves are demanding computationally and administratively. The relatively low density of data points in feature-rich regions of the force curve and the possibility of systematically missing low or high parts in oscillating regions can both lead to integration errors and therefore incorrect PMFs.²

An additional technical problem in these simulations may arise from the finite nature of the graphene sheets and the possibility of a diffusion barrier forming along the perimeter. Thermodynamic consistency, i.e. achieving the same bulk pressure and temperature in all simulations, is also problematic in dense systems and in this sense the set of parallel-sheet simulations represents an approximation of the true force curve.

The Corresponding Distances Method^{1,2} (CDM) avoids these problems and allows us to compute the complete force and PMF curves at very high resolution from a single simulation of crossed graphene sheets (Figure 2). The method guarantees thermodynamic consistency by design, i.e. all distances correspond to the same bulk system, and it can include graphene edges, although in this work the sheets are infinite.

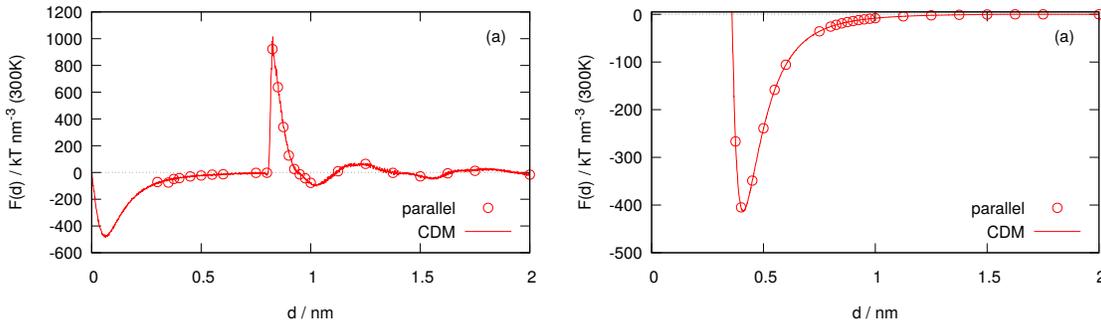


Figure 2: (a) The sm mean force between a pair of parallel graphene sheets immersed in CBrCl_3 to demonstrate the excellent agreement between results from the CDM (solid curve) and the parallel sheet simulations of the system (symbols). (b) The sm potential of mean force obtained from the mean force via integration. The slight disagreement between the two methods is introduced by integration of the sparse data from direct simulation.

As the mean force is obtained directly from the two methods without further processing, it represents the best benchmark for comparison. The example shown in Figure 2(a)

demonstrates the excellent performance of the Corresponding Distances Method.

The disagreement in the smPMF data is due to numerically integrating the sparse data from the parallel-sheet simulations (25 data points), whereas the high data density of the CDM (4200 data points) avoids this problem. This is especially important for the region around $d \approx 0.85\text{nm}$, where the sharp change in $F(d)$ is captured very well by the CDM, leading to a correct smPMF curve, whereas the parallel-sheet simulations would overestimate the smPMF.

We also show results from parallel-sheet simulations of Steele-graphene sheets in water in Figure 3. The agreement of the forces obtained from these direct simulations and those from the Corresponding Distances Method is excellent, verifying again the suitability of the CDM to study solvent quality for 2D materials. In addition the CDM is also computationally more efficient with, for this specific system, 2.1 CPUh/data point versus 136.0 CPUh/data point of the parallel-sheet simulations (e.g. almost two order of magnitudes). The agreement of the PMFs is good, but to a lesser extent, as is expected due to the numerical integration of the sparse force data from the parallel-sheet simulations.

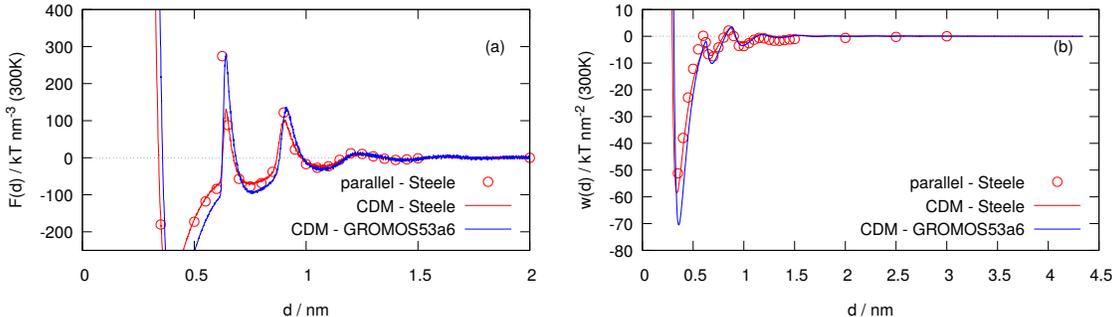


Figure 3: The force curves $F(d)$ (a) and the PMF curves $w(d)$ (b) for graphene immersed in water obtained via the CDM (lines) using the GROMOS force field (blue) and the Steele parameters (red), and computed directly from simulations of parallel graphene sheets (symbols). Visible are the good agreement of the force data between the CDM and the direct simulations and the lower force and PMF in the Steele case due to its lower interaction strength.

We have studied the water system using two different parameterizations for the graphene carbon atoms: the GROMOS force field, as for CBrCl_3 above, and the Steele potential

parameters.^{4,5} The key difference between the two is that the Steele C/C potential is 20% lower. As this reduces the O/C interaction via the mixing rules, we expect that the confined water monolayer is less stable for the Steele potential. This is indeed the case as the results in Figure 3 show.

In order to make a consistent comparison between the graphene and CNT free energy profiles, we performed the CDM free energy calculations also for two CNTs in water using the GROMOS force field. The simulation set up are the same as those reported in Ref.⁶ and the results are shown in Figure 5 of the main text.

References

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