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# A Molecular Dynamics Technique to Extract Forces in Soft Matter Systems Under Compression With Constant Solvent Chemical Potential

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**ABSTRACT:** Molecular dynamics simulations of opposing polymer brushes at varying surface separation distances were performed to develop a method for conducting a static compression of soft matter. As all separation distances were represented by independent simulations, the proper solvent density for every level of compression needed to be determined to acquire realistic data. This was accomplished by maintaining a constant solvent chemical potential for each separation distance. In doing so, each independent simulation is equilibrated with all others, reproducing conditions encountered experimentally in force spectroscopy measurements. Chemical potential was determined using the Widom test particle insertion method. Force information was extracted from pressure profiles, such that unphysical forces occurring within the surface layers were not accounted for in the calculation. Each individual simulation was a canonical ensemble molecular dynamics simulation, but taken together they approximate a grand canonical ensemble for the solvent particles by holding their chemical potential constant.

## ■ INTRODUCTION

Confined soft matter systems are encountered in biological science,[1,2] tribology,[3,4] and polymer science[5,6] and have numerous applications. The focus of this work is polymer brushes, which, for instance, have applications as lubricants[7] and colloidal stabilizers.[8,9] For any system where two layers are brought into contact, forces and structure should be examined in concert to understand their joint response. Molecular dynamics simulations are an effective means to study these systems. Structure, in the form of density profiles, is readily available in simulations, as the location of all particles is tracked throughout the span of the simulation. Likewise, forces are directly accessible by examining the particle trajectories.

When conducting a simulation of a confined material, it may be desirable to imitate conditions experienced in force spectroscopy measurements, such as the surface force apparatus (SFA)[10] or atomic force microscope (AFM), so that meaningful comparisons can be made. In a typical force experiment, two surfaces are brought into contact, and forces are measured statically for different separation distances. There is normally a large reservoir of solvent, allowing solvent to flow out of the space between the surfaces throughout the compression.

A number of simulation studies of confined polymer brush systems have been performed with implicit solvent models.[11−15] While these studies are useful in examining the polymer brush characteristics, details concerning the solvent are mostly lost. When using an explicit solvent, a question arises as to what solvent density should be used. Often the solvent density between the surfaces is kept constant throughout the compression.[16,17] Again, these methods can extract valuable information about structure−force relationships but do not exactly reproduce experimental conditions, as there is no restriction on solvent density between the surfaces during an experiment. Naturally, the solvent density within a large reservoir in an experimental apparatus will be constant, but the density between two surfaces under strong confinement will vary with separation distance. When keeping solvent density between the surfaces constant throughout the compression, it is assumed that the solvent will interact with the brush equally whether highly compressed or fully separated, and therefore configurational entropy changes within the system caused by confinement are ignored. Some recent studies have instead opted to hold the chemical potential constant during the compression, thereby imitating a system which is in equilibrium with its different levels of compression.[18−20] These studies were conducted in the grand canonical ensemble to maintain constant chemical potential in dissipative particle dynamics simulations, where the solvent is represented by large fluid elements rather than individual particles.

This paper details a procedure to conduct molecular dynamics simulations of confined soft matter with explicit solvent at a constant solvent chemical potential. Discrete simulations at different surface separations were performed allowing static compression of a polymer brush system. This is the same situation encountered in an experiment where the solvent between the surfaces at all separation distances has the same chemical potential as the solvent reservoir, as shown in Figure 1. For the simulation technique, no solvent reservoir is used. Instead, similar conditions are met by requiring the solvent chemical potential to be equal within a certain tolerance at each separation distance.

The method described was used specifically for opposing polymer brushes for development but can be straight forwardly extended to other confined soft matter systems. The process is distinct from previous constant chemical potential simulations[18−20] in that all individual simulations are performed in the canonical ensemble rather than the grand canonical ensemble.

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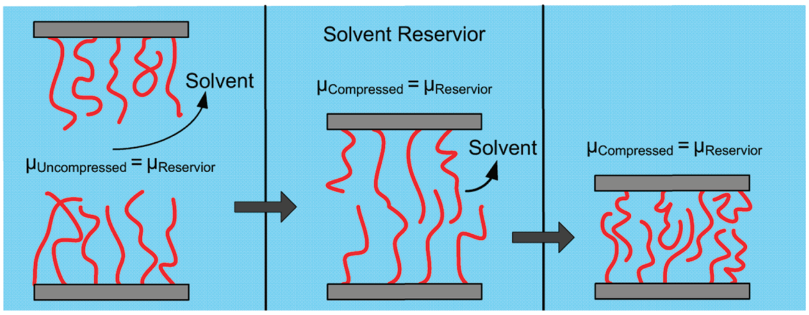

**Figure 1.** Schematic of experimental conditions encountered when compressing soft matter, where $\mu$ is the chemical potential of the solvent. The solvent between the surfaces at all separation distances has the same chemical potential as the solvent reservoir. As an example, an opposing polymer brush system is shown, which was the system used to develop the technique.

There is no solvent addition or removal during individual simulations. While the principle of holding chemical potential is the same, the method is entirely different. In this work, simulations are conducted, prior to a production run, which determine the solvent density required to provide a solvent chemical potential equal to that of the reference system. Essentially, work is put in ahead of time to set up the systems properly and from there can be simulated normally, without the need for additional calculations or changing the amount of solvent. The individual simulations hold the number of particles, volume, and temperature constant (NVT) but, as a whole, approximate the grand canonical ensemble with respect to the solvent by holding its chemical potential constant. For the purposes of this work, exactly reproducing the grand canonical ensemble is not important. What is desired is to most accurately simulate the experimental ensemble, which can be achieved by holding solvent chemical potential constant. When the simulations at different separations are viewed together, the number of solvent particles decreases with compression. This is comparable to solvent being expelled from between the surfaces as they come together in an experiment, and the polymer amount remains unchanged. An additional difference from the previous works in this area is that an explicit solvent is used to preserve detailed information concerning solvent interactions and configurations. This level of detail can be important when investigating solvent behavior or shear flow.[21]

As individual simulations conducted for each separation are conventional canonical ensemble molecular dynamics simulations, this method can be easily implemented in common molecular dynamics packages. Some programs, such as Gromacs,[22] have features which can implement the chemical potential calculations quite easily. In this paper, the methodology is presented. A second, application paper will detail findings of force and structure information of confined polymer brushes.

## ■ MODEL

The simulation model used in these studies has been validated and thoroughly described previously,[23] so it will only be briefly explained here. The coarse-grained MARTINI model[24] (version 1.4) was used due to the long simulation times and large number of simulations required. This is a generic coarse-grained model where each particle is set to a mass of 72 g/mol and is assigned van der Waals parameters that make it polar, nonpolar, or charged. Polar particles were used for all components, but the interaction strength of the surface particles was reduced by a factor of 3 to prevent surface adsorption. This model has been used successfully to characterize single unconfined polymer brushes.[23,25] A similar version of the MARTINI model has also been applied to diblock polymer systems.[26] All nonbonded interactions are represented by a 6-12 Lennard-Jones potential. Bonded interactions use a harmonic bonding potential and a cosine angle potential. The specific equations and constants used can be found in ref 23, which studied the same system with only a single surface of grafted polymer brushes.

The surfaces define the $x-y$ plane and were comprised of overlapping particles that remained fixed throughout all simulations and prevented any solvent or polymer particles from passing through. The first monomer of each polymer chain was fixed during the simulation 0.3 nm above the surface in a regular grafting pattern, yielding an end-grafted polymer brush. Nonbonded interactions were not considered between fixed particles. A grafting density of 0.347 chains/nm$^2$ and linear chains of 40 monomers were used to develop and test the method. Previous work[23] has shown that under these conditions, the polymer is in good solvent and in the brush regime. Periodic boundary conditions were employed in all three directions. The $x$ and $y$ box dimensions were 12 nm each, and the $z$ dimension was determined by the surface separation examined in the individual simulation. The Lennard-Jones cutoff was 1.2 nm, and the surfaces were 1.41 nm thick so that the two brushes do not affect one another through periodic boundaries. A Berendsen thermostat[27] was used to maintain the temperature at 350 K with a correlation time of $\tau_T$ = 1 ps. The time step for all production runs was 0.02 ps. The neighbor list was updated every 10 steps with a cutoff of 1.4 nm.

## ■ THEORY

The solvent chemical potential was kept constant between simulations at different fixed separations, imitating the conditions of a dynamic compression. Chemical potential, $\mu$, can be separated into an ideal portion and an excess component as shown in eq 1:

$$\mu = \mu_{\text{id}} + \mu_{\text{ex}} \tag{1}$$

Equation 2 gives the ideal chemical potential:

$$\mu_{\text{id}} = kT\ \ln(x_i) + \mu_0 \tag{2}$$

where $k$ is the Boltzmann constant, $T$ is temperature, $x_i$ is the mole fraction of solvent, and $\mu_0$ is a reference chemical potential.

In this case it is not appropriate to consider the mole fraction, as the systems contain chemically grafted brushes. All polymers of each brush are chemically connected to each other

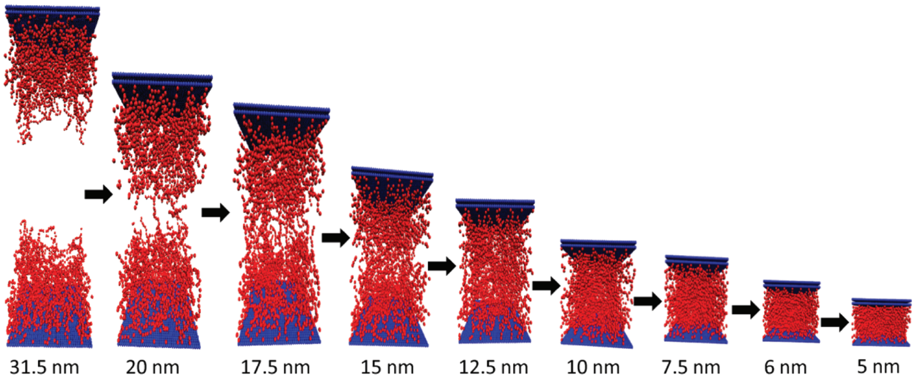

**Figure 2.** VMD[29] images of the brush system for each simulated separation distance examined. The series illustrates the static compression of the polymer brush system.

through the surface, essentially yielding one very large molecule for each brush. Experimentally brushes are often generated by adsorbing an insoluble part on the surface, but in the simulations, the polymers are permanently affixed to the surface. As desorption is not possible, each polymer chain will always be chemically linked to all others on the surface and therefore cannot be considered as a separate molecule. Thus, in this case, mole fraction is not an easily defined or meaningful quantity. Instead, the volume fraction of the solvent was used here technically assuming the monomers and not the polymers as second species for simplicity.

The excess component of the chemical potential was determined using the Widom test particle insertion method.[28] In this method, a ghost particle is inserted randomly into the system, and its interaction energy, $\Delta U_{\mathrm{tpi}}$, with all other particles is calculated. The particle does not remain in the system but is theoretically inserted solely for the purpose of the calculation. This process is then repeated many times to obtain an ensemble average $\langle \exp(-\Delta U_{\mathrm{tpi}}/kT)\rangle$ for the system. The excess chemical potential can then be calculated from eq 3:

$$\mu_{\mathrm{ex}} = -kT \ln\left\langle \exp\left(\frac{-\Delta U_{\mathrm{tpi}}}{kT}\right)\right\rangle \tag{3}$$

As the chemical potential is to be kept constant relative to a noninteracting system, the chemical potential of the fully separated system (noninteracting brushes), $\mu_{\mathrm{sep}}$, was subtracted from each compressed system's chemical potential, $\mu_{\mathrm{comp}}$. In doing so, the reference chemical potential $\mu_0$ cancels out and after simplification yields

$$\begin{aligned}\mu_{\mathrm{comp}} - \mu_{\mathrm{sep}} &= kT \ln\left(\frac{x_{i,\mathrm{comp}}}{x_{i,\mathrm{sep}}}\right)\\ &\quad + kT \ln\left[\frac{\left\langle \exp\left(\frac{-\Delta U_{\mathrm{tpi}}}{kT}\right)\right\rangle_{\mathrm{sep}}}{\left\langle \exp\left(\frac{-\Delta U_{\mathrm{tpi}}}{kT}\right)\right\rangle_{\mathrm{comp}}}\right]\end{aligned} \tag{4}$$

By definition, the difference on the left-hand side of eq 4 is zero when the two systems are in equilibrium.

To exactly reproduce the grand canonical ensemble, particle fluctuations would also need to be negligibly small. The data supports that they are indeed small, as relatively small particle additions or removals will significantly affect the chemical potential value.

## ■ COMPUTATIONAL DETAILS

Gromacs 4.0.4[22] was used for all simulations. All systems were initially solvated to an arbitrary density, and energy minimized using a steepest decent algorithm to remove particle overlaps. A brief molecular dynamics simulation of 10 000 steps with a time step of 0.001 ps followed to further remove bad contacts.

A zero point system which served as reference throughout this study was simulated first. The reference system was uncompressed with the two opposing brushes separated sufficiently that they were noninteracting. From previous simulations using this model,[23] the brush extension is known to be about 10 nm. Therefore, a separation distance of 30 nm between the surfaces was selected for the initial set up of the reference system. The reference system was equilibrated semi-isotropically under constant normal pressure and constant lateral area to obtain the correct density. As the brushes were fully separated, no normal forces were found. The pressure coupled simulation ran for 100 ns using a Berendsen barostat[27] with a correlation time of $\tau_{\mathrm{P}} = 2$ ps and a reference pressure of 1 bar. The total change to the box size was less than 1.5 nm, and it occurred within the first 5 ns. The average $z$ dimension obtained after equilibration was used for a subsequent 2 $\mu$s NVT simulation. This fully separated system was then used as a reference system, where all other compressed systems were required to have the same solvent chemical potential.

Each compressed system was initially set up with the desired surface separation distance and a total particle density close to the reference system. NVT simulations for each separation distance were run for 2−4 $\mu$s. The highly compressed systems needed to run longer to equilibrate. Equilibrium was defined as when the radius of gyration of the compressed polymer brush stabilized, as structural evolution is one of the slowest equilibration modes. All systems had at least 1.5 $\mu$s of data after equilibration for analysis. Separation distances of 20, 17.5, 15, 12.5, 10, 7.5, 6, and 5 nm were examined for the compressed systems. Snapshots of the compression are shown in Figure 2.

As discussed in the Theory Section, the solvent chemical potential was calculated using the Widom test particle insertion method,[28] which can be implemented in Gromacs 4.5.2.[22] We caution that earlier versions of Gromacs gave incorrect results when using this feature. If using a molecular dynamics package without this capability, a code can be written to perform random test particle insertions and to calculate the interaction energy.

A crucial aspect of the particle insertion method is to eliminate contributions from insertions into the surface layers. Any insertion into the surface will result in very large, positive contributions to $\Delta U_{\mathrm{tpi}}$. These values will not simply cancel out between systems, as the surface occupies a larger volume fraction of the box in the compressed systems than in the uncompressed. As the system is compressed, surface layer sampling becomes more pronounced and, if not accounted for, will result in a systematic reduction of the excess chemical potential (or lower density at equilibrium with the reference state) with greater compression. This problem can be avoided by disallowing random particle insertions within the surface which is physically sound, as in a real chemically grafted brush, no solvent can penetrate the surface. In this work, the test particle insertion function in Gromacs was modified to bias the random $z$ coordinate selected. The $z$ coordinate was required to be at least one particle diameter away from the surface, as even a small overlap would significantly impact the values obtained.

In each system for which the chemical potential was calculated, a solvent test particle was inserted at random positions in each frame examined. The number of insertions necessary was determined by finding when the value for $\mu_{\mathrm{ex}}$ from eq 3 converged. In general the number of insertions increased with system size and ranged from 100 million to 600 million. Denser systems may require a larger number of particle insertions. The test particle calculations are computationally cheap compared to the simulation runs, so efficiency for the Widom method is not a major concern. For each insertion, a random position in the box was selected, and the test particle was inserted randomly ten times into a 0.05 nm radius sphere around that point to obtain better statistics at relatively little computational cost, as the neighbor list had already been compiled. A depiction of the test particle insertion method is shown in Figure 3. As can be seen, the ghost particles are inserted in random locations between the surfaces. Higher levels of overlap with polymer or solvent particles lead to less favorable interaction energies. That energy, when put into eqs 3 and 4, gives a measure of how many solvent particles need to be added or removed from the system to be equilibrated with the reference system.

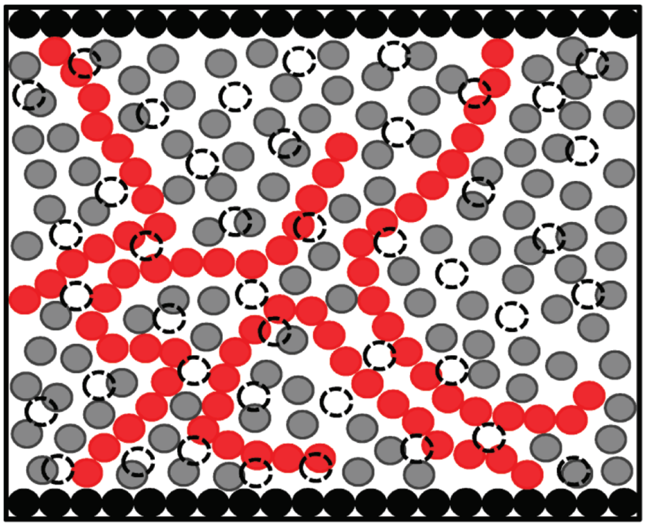

**Figure 3.** Illustration of the test particle insertion method. Surface particles are black, polymers are red, and solvent particles are gray. The dashed black circles indicate ghost particles which are randomly inserted for the purposes of the calculation but do not remain in the system.

Frames from which the chemical potential was calculated were initially each 5 ns apart to ensure that independent configurations were examined. Once it was determined from these tests what the solvent density should be, the chemical potential for that system was recalculated based on frames 1 ns apart to decrease the error and to confirm the findings, but overall values generally changed very little. The resulting chemical potential was calculated from independent configurations over the last 1.5 $\mu$s of the simulation. The excess contribution to the chemical potential was found from these insertions and combined with the ideal portion to find the total chemical potential for a given separation distance.

Once the chemical potential was calculated for the compressed and reference systems, the reference system's chemical potential was subtracted off as in eq 4. To be considered in equilibrium, the difference between the compressed and separated system's solvent chemical potential was required to be less than 0.05 $kT$ for all but the most highly compressed systems (5 and 6 nm separation). At these high compressions, the error due to increasing polymer density became much larger so they were required to be within 0.1 $kT$ of the reference system. If the difference $(\mu_{\mathrm{comp}} - \mu_{\mathrm{sep}})$ was negative, more particles were needed, while if it was positive, the system was too dense and particles had to be removed from the compressed system. Solvent particles were added or removed accordingly. After any solvent particle number change, a new simulation with the new amount of solvent ran again for 2−4 $\mu$s, and the new chemical potential was calculated.

Generally it took two to four iterations to settle on the right number of solvent particles. After two attempts, interpolation or extrapolation was used to give a reasonable next guess for the number of solvent particles. As there is error associated with the excess chemical potential obtained from the test particle insertions, it should be viewed as determining a range of solvent particle numbers which will provide a chemical potential in agreement close to the reference system. An example of the chemical potentials found for different amounts of solvent in a compressed system is shown in Figure 4. As stated earlier, final results for each separation distance were recalculated using more frames which brought down error bars to less than 0.1 $kT$, but were not done so for preliminary data. Figure 4 is shown for illustrative purposes as the system with the most iterations, but

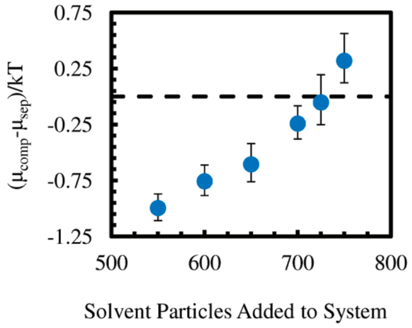

**Figure 4.** Chemical potential relative to the reference system versus particles added to the system starting at an arbitrary density. This data is from the system at 5 nm surface separation distance.

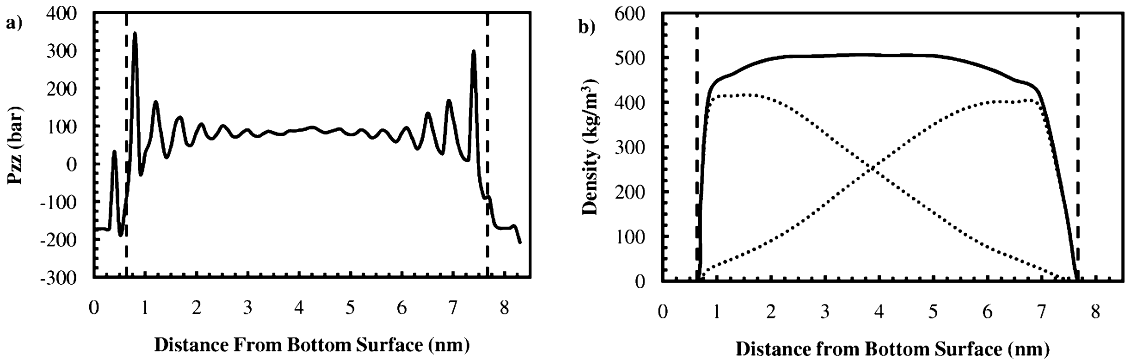

**Figure 5.** (a) Profile of the normal pressure versus distance from the bottom surface for a surface separation distance of 7.5 nm. Dashed lines indicate the edges of the surface. (b) Corresponding polymer density distribution for a separation of 7.5 nm. Dashed lines are the edges of the surfaces, dotted lines show the top and bottom density profiles of the brush independently, and the solid line gives the overall polymer density.

as stated earlier, in most cases fewer iterations yielded good results.

## PRESSURE AND FORCE CALCULATION

A primary interest of simulating confined soft matter is to obtain force information which can be compared to experimental results. A typical surface force apparatus experiment yields a profile of normal force versus separation distance.[30−32] The normal force data can be obtained by calculating profiles of the normal component of the pressure tensor ($\mathbf{P}_{zz}$). Including the frozen surface layers will lead to incorrect pressure calculations by conventional methods, as the surface layers do not interact with one another. They do, however, interact with the material between the surfaces, which leads to highly attractive, unrealistic energies. For the normal pressure, this means that within the surface there are large, negative values, which artificially lower the pressure if it is averaged over the entire box. For this reason, pressures must be calculated from a pressure profile and not averaged over the system in the conventional way.

To find pressures which omit the data within the surface layer, pressure profiles were calculated[33−35] and averaged only between the surfaces. A typical normal pressure profile, along with its corresponding polymer density profile, is given in Figure 5.

The details of the pressure profile in Figure 5a are not important for this discussion. What should be noted is that the normal pressure is positive in the fluid but becomes strongly negative within the surface. This negative pressure will lower the average normal pressure obtained and will contribute more to the average at higher compressions (smaller system sizes). For the pressure profile calculation, the system was binned into 0.1 nm segments, and the Coulomb cutoff was set to 2.0 nm. For comparison, the corresponding average density distribution is shown in Figure 5b, which helps illustrate where in the brush system the pressures are being calculated. Detailed analysis of this data and comparisons to other experimental and simulation work will be made in a subsequent, application paper.

## CONCLUSION

A method for conducting a static compression of soft matter with molecular dynamics was described. It allows for molecular dynamics simulations in the canonical (NVT) ensemble to be used in a way that approximates a grand canonical ensemble for the solvent. The chemical potential of each simulated separation distance was calculated using the Widom test particle insertion method. By fixing the solvent chemical potential at each separation distance, every simulation is in equilibrium with all others. This more realistically reproduces the conditions encountered experimentally by confined systems than simply using a constant solvent density. This approach resembles and can be compared to experimentally measured force profiles from the SFA or AFM. In the present case, the method was specifically used on confined polymer brush systems but can easily be adapted for confining other soft materials, such as polymer melts, proteins, etc.

As described, fixed surface layers can cause problems with both the chemical potential and the pressure calculations, and their effects need to be excluded from both calculations. In the case of the chemical potential, sampling the surface with test particle insertions will lead to a lower solvent density therefore not realistically simulating a compression. The test particle code needs to exclude the surfaces layers for all particle insertions to avoid this problem. Similarly, accurate pressure data were obtained by calculating pressure profiles and averaging over only the data in the fluid region, thereby omitting any nonrealistic pressure values within the frozen surface.

This method differentiates itself from previous work in that it allows for explicit solvent particles, which provides a greater level of detail on the solvent. While the initial computational requirements are somewhat large, once the system is set up it can be simulated or analyzed efficiently without the need to adjust solvent particles or density. This could be especially useful if a very long simulation is desired, then the initial set up costs are miniscule compared to the length of the run.

Using this method will allow molecular dynamics simulations to be conducted which realistically confine or compress various soft matter systems. Further work will be specifically focused on applying this method to polymer brushes and direct comparison to experimentally measured force profiles. The influence of variables such as grafting density and chain length on the force and structure can be obtained and compared. Additionally, once the compression is accurately described, the system can be sheared at each separation distance to investigate lubrication properties.

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### Notes

The authors declare no competing financial interest.

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