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Drying/Self-Assembly of Nanoparticle Suspensions

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Abstract

The most feasible way to disperse particles in a bulk material or control their packing at a substrate is through fluidization in a carrier that can be processed with well-known techniques such as spin, drip and spray coating, fiber drawing, and casting. The next stage in the processing is often solidification involving drying by solvent evaporation. While there has been significant progress in the past few years in developing discrete element numerical methods to model dense nanoparticle dispersion/suspension rheology which properly treat the hydrodynamic interactions of the solvent, these methods cannot at present account for the volume reduction of the suspension due to solvent evaporation. As part of LDRD project FY-101285 we have developed and implemented methods in the current suite of discrete element methods to remove solvent particles and volume, and hence solvent mass from the liquid/vapor interface of a suspension to account for volume reduction (solvent drying) effects. To validate the methods large scale molecular dynamics simulations have been carried out to follow the evaporation process at the microscopic scale.

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1. INTRODUCTION

By controlling the rate of evaporation one can control the local order and packing of nanoparticles. Physically, the removal of solvent from a nanoparticle suspension occurs at the liquid/vapor interface whereas in most computational codes volume reduction is done by simply changing the dimensions of the simulation cell. In general, current coarse-grained solvent models do not allow for a free surface. Since volume-reduction occurs by external-boundary mass-flux which is controlled externally through a variable driving-force such as temperature and humidity, it is critical to develop thermodynamically consistent coarse-grained models and numerical algorithms to remove the solvent mass and heat flux. These methods must properly account for solvent mass/volume flux at a free surface which in turn leads to local (near surface) density changes of the nanoparticles.

A relatively recent technique, closely related to Lattice Boltzmann, for capturing hydrodynamics at the mesoscale is stochastic rotation dynamics (SRD).[1-4] This technique is based on simple fluid-particle interactions and dynamics. The fluid particles are considered massive, ideal, point particles which do not interact with each other in a pairwise sense, but interact through a "coarse-grained" collision operator in such a way as to conserve energy and momentum and produce fluctuating hydrodynamic behavior. Additionally, the fluid particles can interact with suspended nanoparticles through collisions. This method has been used to model colloidal suspensions both in equilibrium and under steady shear. Previously we have shown that one can parameterize the SRD fluid to provide a one to one match in the shear viscosity and density of real fluids such as water. As part of the present project we have developed methods to model the evaporation of solvent from nanoparticle suspensions as illustrated in Figure 1. We have implemented in the parallel molecular dynamics code LAMMPS[5] a procedure to explicitly remove the solvent near the boundary in a manner consistent with the limit of very slow evaporation. To achieve this the bounding wall is moved at a constant velocity and SRD particles are deleted. However, in many cases the increase in density of the nanoparticles near the interface reduces the evaporation rate since the solvent has to diffuse through this dense layer. In these cases the evaporation rate cannot be assumed to be constant. A feedback mechanism based on the local environment must be incorporated into the model to properly describe rate of the volume reduction/evaporation process and the heat transfer at the interface as the density of the nanoparticles at the interface increases. Molecular dynamics (MD) simulations of the evaporation of model systems were carried out as the first step in simulating the drying of nanoparticle suspensions to verify the proposed models used in the SRD simulations. Initial simulations of evaporation of solvent from nanoparticle droplets demonstrated the feasibility of following the drying of nanoparticle suspensions using MD simulations.

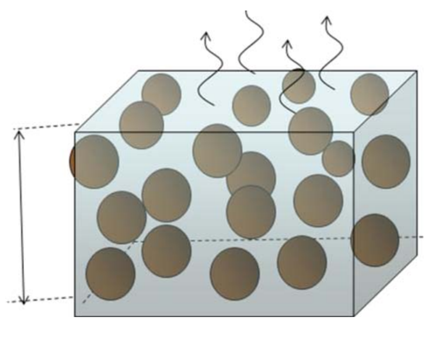

Figure 1 – Illustration of the evaporation of solvent from a nanoparticle suspension.

2. MODEL AND METHODOLOGY

To investigate the evaporation process at the microscopic scale we carried out large scale MD simulations of three simple liquids. In the first the interaction between atoms is described by the standard Lennard-Jones 12-6 interaction

$$U(r) = 4\varepsilon\,[\,(\sigma/r)^{12} - (\sigma/r)^{6}]$$

where r is the distance between two atoms and ε is the unit of energy and σ the diameter of the atom. The interaction is truncated at r_c=2.5σ. While a very commonly used model to simulate liquids, the Lennard-Jones model has one serious draw backs when modeling the evaporation process, namely it has a very high vapor pressure.[6,7] This results in a very large vapor density which does not correspond well to most liquids. One simple way to make the model more realistic but still retain the simplicity of the Lennard-Jones interaction is to model the solvent is short chains of Lennard-Jones atoms. Here we show that by modeling dimers which consists of two atoms and trimers consisting of a linear chain of three atoms we obtain the required slower evaporation rates. The bonded atoms are connected by an additional finitely extensible nonlinear elastic (FENE) potential

$$U_{FENE}(r) = -1/2\ k\ R_o^{2}\ \ln\,(1 - (r/R_o)^{2})$$

where $k = 30k_BT/\sigma^2$, T is the temperature and R_o=1.5σ.[8] The interactions between nanoparticles and between nanoparticles and the Lennard-Jones solvent atoms are described in ref. xx.

To simulate the evaporation process we modeled N=3,000,000 atoms in a parallelepiped of dimension L_x x L_y x L_z, where L_x=L_y=200σ. The simulation cell was periodic in the x and y directions and had upper and lower confining walls in the z direction. Both upper and lower z-walls interacted with the monomers with a Lennard-Jones 9-3 potential which depended only on the distance z from the wall,

$$U(z) = \varepsilon_{wall}\,[2/15(\sigma/r)^{9} - (\sigma/r)^{3}],$$

where $\varepsilon_{wall} = 2\varepsilon$. For the lower wall the interaction was truncated at z_c=2.5σ, while at the upper wall z_c=0.72σ. Each liquid film was constructed near its bulk density and placed in contact with an attractive flat lower wall in the xy plane at L_z=0. The position of the upper wall varied depending on the chain length and temperature of the system so that the thickness of the vapor phase was at least 50σ. Each system was constructed by placing the N atoms randomly in the simulation cell. The „fix nve/limit' command in LAMMPS was used to remove all overlaps. For each temperature, the system was allowed to come to equilibrium with its vapor for a few hundred thousand time steps before the evaporation process initiated.

The equations of motion were integrated using a velocity-Verlet algorithm with a time step Δt =0.005τ, where $\tau = \sigma(m/\varepsilon)^{1/2}$ for the dimer and trimers and 0.01τ for the monomers. During the equilibration, T was held constant by a Langevin thermostat weakly coupled to all of the atoms. Once the liquid vapor interface was equilibrated, the Langevin thermostat was removed except for those atoms within 15σ of the lower boundary at L_z=0. These atoms were thermostated for an additional 20,000-100,000 time steps before the evaporation process was initiated. After which a region of thickness 20σ approximately 50σ above the interface was defined where atoms were removed at a specified rate. In the first set of simulations all atoms which entered this region were removed which modeled the system in contact with a vacuum. In the second set of simulations the atoms were removed at a specified rate using the „fix evaporate' command in LAMMPS. For the dimer and trimer system, once one atom from the molecule was removed, the entire molecule was removed. During the entire evaporation process the thermostat remained coupled only to those atoms which were within 15σ of the lower boundary so that the kinetics of the evaporation process at the interface could be followed.

For the monomer system the liquid/vapor phase diagram is well known.[xx] However this is not the case for the dimer and trimer systems. Therefore for these two systems we also simulated the liquid/vapor interface by removing the walls in the z direction and replacing them with periodic boundary conditions. The resulting liquid and vapor densities ρ_L and ρ_V respectively along the coexistence curve for all three systems is shown in Figure 2. The liquid/vapor critical temperature T_c for each system is determined from fitting the calculated densities to[9,10]

$$\rho_L + \rho_V = a - b^* T$$

$$\rho_L - \rho_V = A^* (1-T/T_c)^{0.318}.$$

The best fits give T_c = 1.085, 1.565 and 1.741ε/k_B for the monomer, dimer and trimer systems respectively.

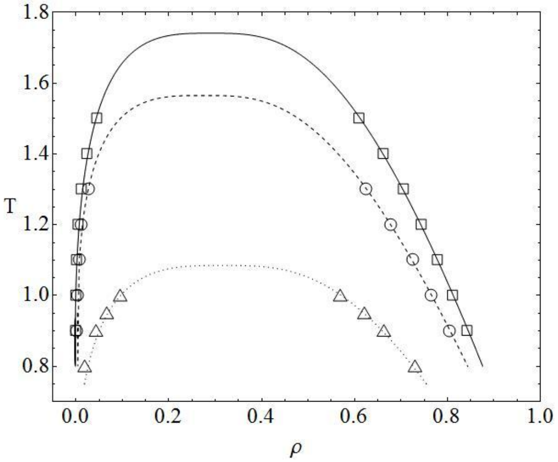

Figure 2. Liquid/vapor phase diagram for Lennard-Jones monomers (triangles), dimers (circles) and trimers (squares).

The SRD method is a member of a class of techniques referred to as multiparticle collision dynamics, which are off lattice, particle-based simulation techniques that attempt to efficiently resolve important "mesoscale" phenomena, such as fluctuating hydrodynamics (mass and momentum conservation) at the cost of losing detailed microscopic information. The SRD algorithm consists of two steps: (i) particle streaming and (ii) particle velocity update. These are described in detail in ref. 4.

3. EXPLICIT ATOM SIMULATIONS

When placed in contact with a vacuum, the evaporation of the Lennard-Jones monomer system occurs very rapidly as shown in Figure 3. Note the increase in density by 20% compared to its equilibrium value near the interface as there is significant evaporative cooling of the liquid film. Also note the increase in both the density and temperature gradients as the evaporation process continues. By the end of the simulation the temperature decreases across the interface from its initial value of $0.9\varepsilon/k_B$ to $0.7\varepsilon/k_B$, which is very close to the melting point for this system. Similar results are found for T=0.8 and $1.0\varepsilon/k_B$. This large decrease in density and temperature near the interface is much stronger than most simple fluids such as water which is one reason we considered the dimer and trimer system. Before presenting those results we show in Figure 4 the density profiles for the monomer system at a controlled rate of evaporation. Note that as expected the size of the decrease in density and temperature near the interface is reduced as the evaporation rate decreases. Only for the slowest rate does the vapor density remain at its equilibrium value.

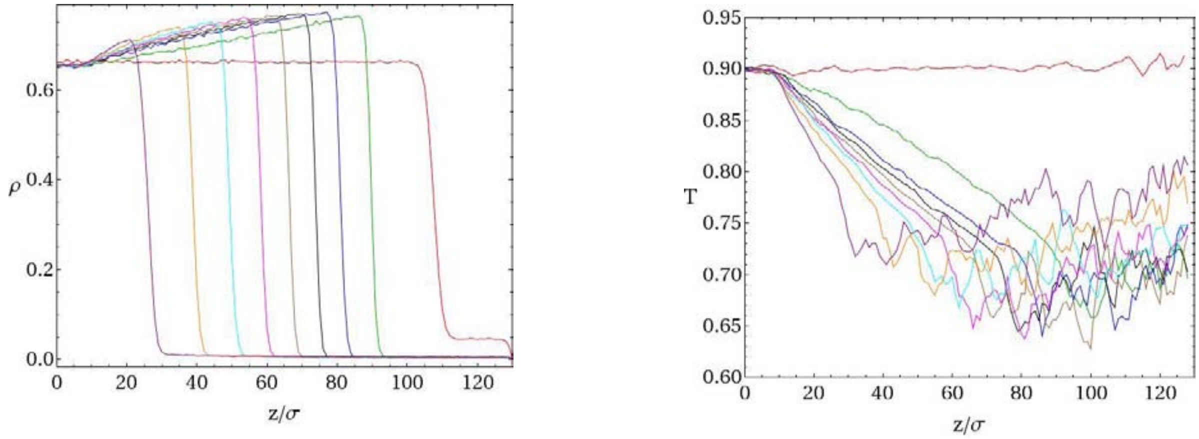

Figure 3. Density (left) and temperature (right) for a Lennard-Jones monomer fluid at T=0.9 ε/k_B in contact with a vacuum. From right to left the profiles are plotted every 2000τ since the evaporation process began at t=0 (right most curve).

Results for the dimer in contact with a vacuum and for controlled evaporation rate are shown in Figure 5. Similar results are observed for the trimer. The evaporation rate depends sensitively on both the temperature and length of the chain. For example in Figure 6 we present results the number of atoms evaporated versus time for T=1.1 ε/k_B for the three architectures while in Figure 7 results for the dimer system in contact with the vacuum is shown for five temperatures. Detailed analysis of the kinetics of the evaporation process and comparison to previous theories is underway.

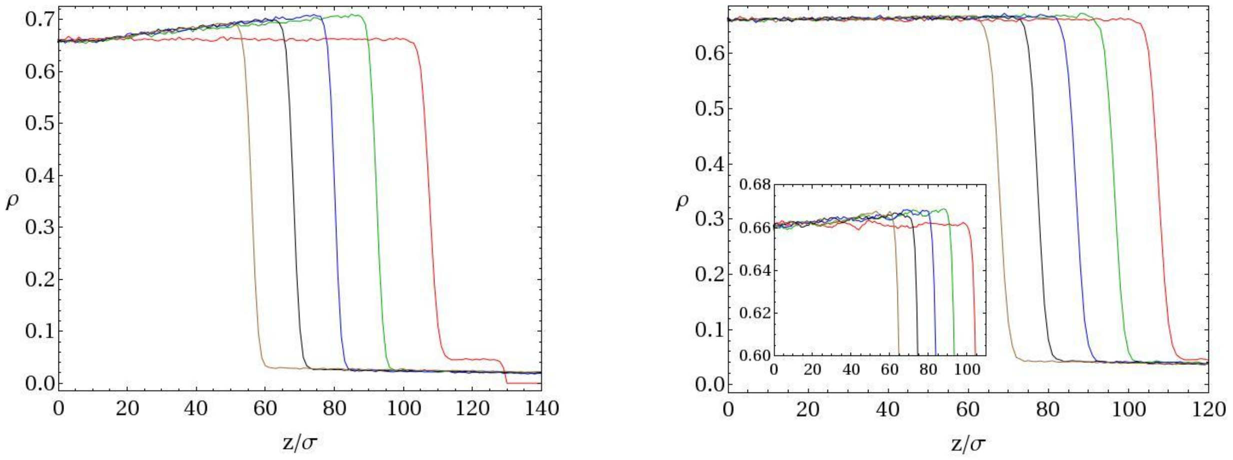

Figure 4. Density profiles for Lennard-Jones monomer system at $T=0.9\ \varepsilon/k_B$ evaporating at a rate of $1.0\text{x}10^{-3}/\tau\sigma^2$ (left) and $2.5\text{x}10^{-4}/\tau\sigma^2$ (right). The curves are plotted every 28,000τ (left) and 214,000τ (right) since the evaporation process began at t=0 (right most curve). The inset in the right figure is a blow up of the interfacial region.

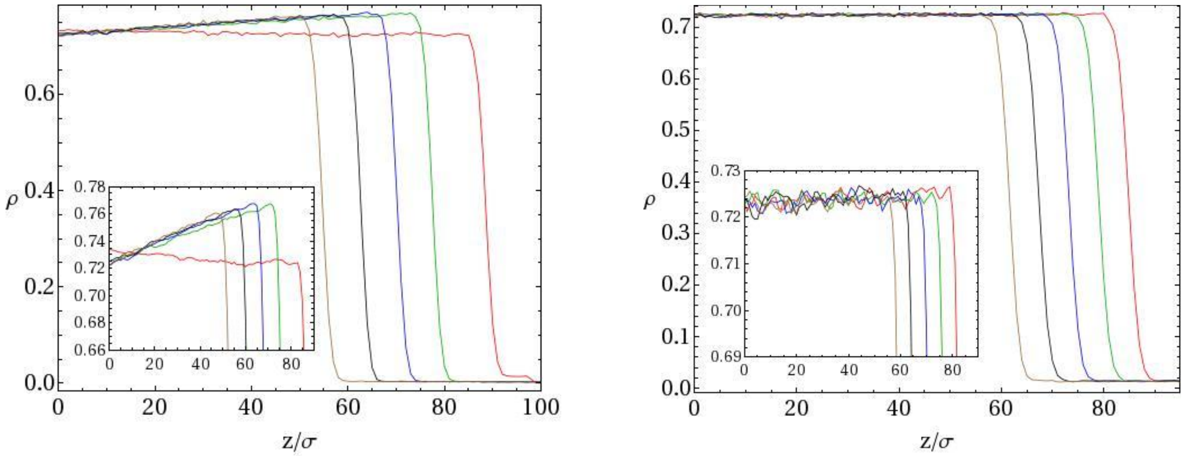

Figure 5. Density profiles for a Lennard-Jones dimer fluid at $T=1.1\ \varepsilon/k_B$ in contact with a vacuum (left) and at a fixed rate of $5.0\text{x}10^{-5}/\tau\sigma^2$ (right). From right to left the profiles are plotted every 4000τ since the evaporation process began at t=0 (right most curve).

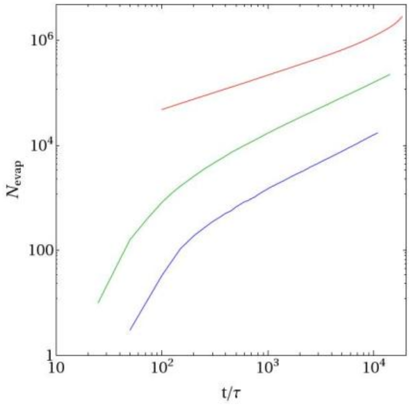

Figure 6. Number of evaporated atoms versus time for Lennard-Jones monomer (red), dimer (green) and trimer (blue) system at $T=0.9\ \varepsilon/k_B$ in contact with a vacuum.

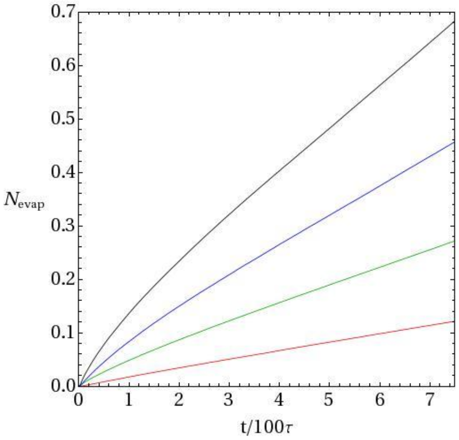

Figure 7. Number of evaporated atoms versus time for a dimer system in contact with a vacuum for T=0.9, 1.0, 1.1, and 1.2 ε/k$_B$ (from top to bottom).

The evolution of a nanoparticle suspension during solvent evaporation is shown in Figure 8. This shows that explicit atom simulations of nanoparticles suspensions are feasible with current computational resources.

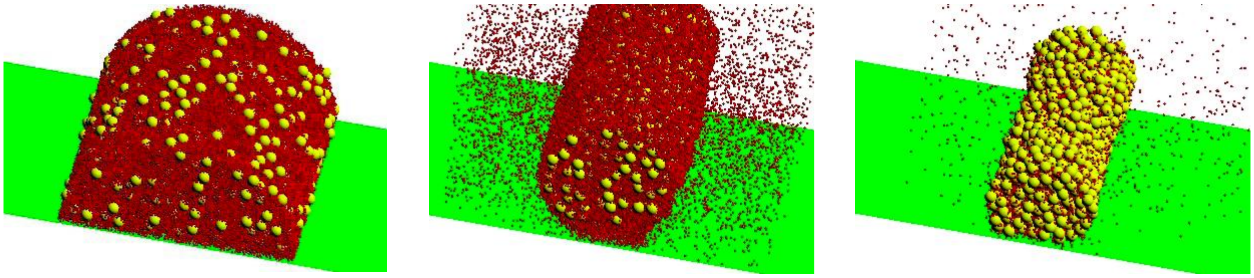

Figure 8. Evolution of a droplet of nanoparticles (yellow) in a Lennard-Jones monomer solvent (red) for nanoparticles which have a diameter 5 times that of solvent.

4. ENHANCEMENT TO LAMMPS

As part of this LDRD a number of new capabilities have been added to Sandia parallel molecular dynamics code LAMMPS.[5]

Evaporation of molecules: The ability to delete individual atoms to model evaporation of a simple atomic fluid previously existed in LAMMPS. The user specifies a geometric region and an evaporation rate. Particles within the region are searched for periodically and deleted. This was extended to allow entire molecules to be deleted. This is more complicated in LAMMPS, because individual processors don't know about entire molecules; they may only own one or a few atoms within the molecule. Extra logic was added to flag entire molecules when any single atom in the molecule was selected for deletion. All the processors then search for other atoms in the flagged molecule and delete them in a coordinated fashion. This means water or polymer-based solvents can now be "evaporated" in an analogous manner to idealized atomic solvents. Simulations for water evaporating at specified rates were run to verify that the additions work properly.

Walls for SRD fluid models: LAMMPS has various models for idealized (flat) walls that interact with normal fluids and particles. The added complexity for a fluid modeled via stochastic rotation dynamics (SRD), which consists of point particles which bounce off solute particles (colloids or nanoparticles), is twofold. First, a grid is overlaid on the system to assist in finding nearby solute particles that interact with an SRD particle. Normally that grid is static during a simulation and is sized so as to insure an integer number of bins in each dimension. Now the moving wall intersects or even eliminates grid cells at the boundaries. Second, the fluid properties of SRD particles, such as viscosity, depend on adequate particle counts in each bin, so that statistically valid operations can be performed on each bin's particles, such as the rotation operation which alters their velocities. As grid cells shrink and vanish due to moving walls, these statistical properties change or may become invalid. This issue is an area of open research and is something we hope to be able to test and quantify for the first time with LAMMPS.

Our strategy for the moving wall model is as follows. The wall itself interacts with SRD particles as if it were an infinite-diameter nanoparticle. This mediates the kind of collisions (slip or no-slip) that occur at the wall surface. Periodically, as the wall moves, and SRD particles are reflected back into the simulation box, SRD particles must be added or deleted to the overall system, to keep the SRD particle density constant, since its fluid properties like viscosity depend on the density. The removal is done similar to the evaporation of atomic solvent over the entire simulation box volume. Insertion is done randomly within the simulation box, without checking for overlaps with colloidal particles. This is relatively simple, since an SRD particle inside a nanoparticle will be quickly pushed out of the nanoparticle within a few subsequent time steps. Both the deletion and insertion operations are coordinated between processors to work effectively in parallel.

Drying of SRD fluid models: As with more traditional solvents, evaporation of SRD particles can be performed by removing the particles, lowering their density and altering the solvent properties. By removing the SRD particles at a surface (mimicking physical evaporation) we can observe changes in colloid or nanoparticle morphology resulting from the drying, e.g. aggregation or "skin"-formation near a free surface. The difference with SRD is that we want to do this as the SRD particles bounce off a wall (representing a free surface), as opposed to within a geometric volume. We are experimenting with several strategies for this approach. Some remove particles with a fractional probability when they bounce off the wall. Others remove the first N particles up to a computed limit, or remove based on a criterion related to the particle's kinetic energy. We plan to experiment with these approaches to see which best fits the explicit atom simulations discussed in Sec III.

5. CONCLUSIONS

We have implemented in the parallel molecular dynamics code LAMMPS[5] a procedure to explicitly remove the solvent near the boundary in a manner consistent with the limit of very slow evaporation. Explicit atom molecular dynamics simulations for three model systems were carried out to validate the model. In future work we will incorporate a feedback mechanism based on the local environment into the model to describe rate of the volume reduction/evaporation process and the heat transfer at the interface as the density of the nanoparticles at the interface increases. Simulations of solvent evaporation from a nanoparticle suspension are underway.

6. REFERENCES

1. A. Malevanets and R. Kapral, Journal of Chemical Physics **110**, 8605 (1999); **112**, 7260 (2000).
2. G. Gompper, T. Ihle, D. M. Kroll, and R. G. Winkler, Advances in Polymer Science **221**, 1 (2009).
3. R. Kapral, Advances in Chemical Physics **140**, 89 (2008).
4. M. K. Petersen, J. B. Lechman, S. J. Plimpton, G. S. Grest, P. J. in ’t Veld, and P. R. Schunk, Journal of Chemical Physics **132**, 174106 (2010).
5. S. Plimpton, Journal of Computational Physics **117**, 1 (1995); LAMMPS molecular dynamics package (http://lammps.sandia.gov).
6. V. V. Zhakhovski and S. I. Anisimov, JETP **84**, 734 (1999).
7. S. W. Sides, G. S. Grest, and M.-D. Lacasse, Physical Review E **60**, 6708 (1999).
8. K. Kremer and G. S. Grest, Journal of Chemical Physics **92**, 5057 (1990).
9. P. Adams and J. Henderson, Molecular Physics **73**, 1383 (1991).
10. B. Smit, Journal of Chemical Physics **96**, 8639 (1992).

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