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On the Properties of a Periodic Fluid

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The Born–Green equation is used to clarify and estimate the error introduced into Monte Carlo and molecular dynamics simulations of dense fluids by the use of periodic boundary conditions. This theory is applied to the Lennard-Jones fluid and the theoretical predictions are found to be in reasonable agreement with experiment. The implications for size dependence of pressure, for anisotropy of the radial distribution function, for size dependence of the supercooling limit for crystal nucleation, and for the orientations of nucleated crystals are discussed.

KEY WORDS: Liquids; computer simulations; molecular dynamics; radial distribution function; periodic boundary conditions.

1. THEORY

This paper points out a systematic error in data obtained by Monte Carlo or molecular dynamics simulations of small systems, estimates this error, and tests its predictions of the size dependence of pressure and the anisotropy of the radial distribution function for a periodic fluid against the results of computer simulations.

Consider a simulation of N particles at density ρ in a periodically continued cube of side $L = (N/\rho)^{1/3}$, and postulate a pairwise interaction

$$\phi(R_1, R_2) = \phi(R'_{12}) \tag{1}$$

where

$$\begin{aligned} \phi(R) &= [V(R) - V(R_{\max})] \quad &\text{for} \quad R < R_{\max} \\ \phi(R) &= 0 \quad &\text{for} \quad R > R_{\max} \end{aligned} \tag{2}$$

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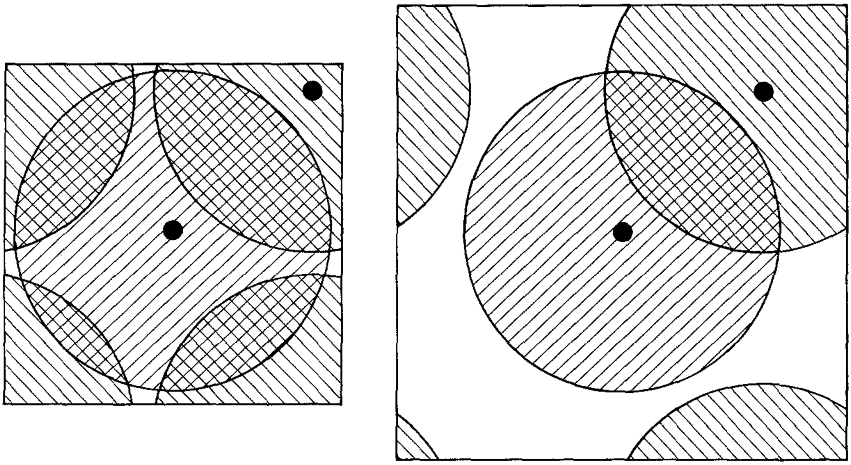

Fig. 1. Schematic illustration of the nearest neighbor prescription for 108-particle (left) and 256-particle (right) systems of density $N\sigma^3/V = 91$. The range of interaction (shown shaded) is 2.3σ. The figures are drawn to scale.

R'_{12} is the "nearest image" distance of (R_1, R_2), $R_{\max} < L/2$, and $V(R)$ is the potential of the bulk system whose thermodynamic properties are desired. (The nearest image prescription is illustrated schematically in Fig. 1.) The pressure is to be obtained via the virial relation

$$P = \rho T - (\rho^2/6) \int d^3R\, [RV'(R)G(R)] \tag{3}$$

where the radial distribution function $G(R)$ to be used in (3) is given by the computer simulation for $R < R_{\max}$, and is taken to be unity for $R > R_{\max}$. The "tail correction" is not small, but it is reasonable to assume it can be well estimated. (There is an additional small correction due to the fact that the center-of-mass velocity is zero. This point has been discussed by Hoover and Alder.(1))

Let us now compare the radial distribution function obtained by computer simulation with that of a bulk system. For either a bulk or a periodic system, the radial distribution is given by (for an excellent review, see Rushbrooke(2))

$$G(1, 2) = \frac{V^2 \int d3\, d4 \cdots dN \exp(-U/T)}{\int d1\, d2 \cdots dN \exp(-U/T)} \tag{4}$$

where V is the volume and U the total potential energy. The Born–Green equation

$$-T\,\nabla_1 G(1, 2) = G(1, 2)\,\nabla_1\phi(1, 2) + \rho \int d3\, G(1, 2, 3)\,\nabla_1\phi(1, 3) \tag{5}$$

which relates the radial distribution function to the triplet correlation function, is obtained by taking the gradient of (4). This may be rearranged to read

$$[T(\partial/\partial r_2) + \phi'(r_2)]G(r_2) = -\rho \int d3\, G(1, 2, 3)(\cos\theta)\phi'(r_3) \tag{6}$$

where, with no loss of generality, particle 1 has been placed at the origin, θ is the angle between $\mathbf{r}_2$ and $\mathbf{r}_3$, and gradients have been replaced by ordinary derivatives. Since Eq. (6) is derived from Eq. (4), it also applies equally well to a bulk or a periodic system under the assumption of pairwise interactions. For the periodic system the potential must be defined to include the "nearest image" prescription, and all particle coordinates may be restricted to the primary cell. The triplet function for the bulk is not known, and that for the periodic system may be obtained only with difficulty. However, a reasonable estimate (actually plus or minus a few tens of percent[(3)]) may be obtained using the superposition approximation

$$G(1, 2, 3) \simeq G(r_{12})G(r_{13})G(r_{23}) \tag{7}$$

Consider the triplet shown in Fig. 2, for which $R_{23} > R_{\max}$. Denoting bulk correlation functions by the subscript 0, for this case

$$G_0(1, 2, 3) \simeq G_0(r_{12})G_0(r_{13})(1) \tag{8}$$

if correlations in the bulk system beyond $R_{\max}$ are neglected. By contrast, in the periodic system particles 2 and 3 are highly correlated due to the "nearest image" prescription, so that

$$G(1, 2, 3) \simeq G_0(r_{12})G_0(r_{13})G_0(r'_{23}) \tag{9}$$

(The prime notation is now used to specify the nearest image distance not contained in the primary cell.) Denoting by the subscript 1 the difference

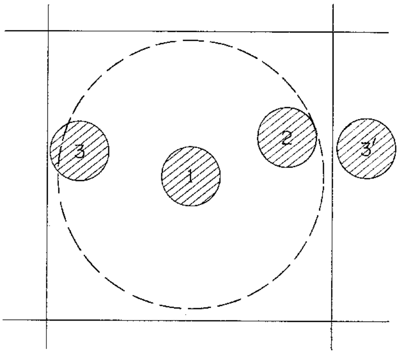

Fig. 2. Example of a triplet whose correlation function changes substantially between bulk and periodic systems. The dashed lines denote the boundaries of the primary cell.

between the correlation functions in the bulk and periodic systems, we have that Eqs. (8) and (9) lead to

$$G_1(1,2,3) \cong \begin{cases} G_0(r_{12})G_0(r_{13})[G_0(r'_{23}) - 1] & \text{for} \quad r'_{23} < R_{\max} \\ 0 & \text{otherwise} \end{cases} \tag{10}$$

Inserting (10) into (6), we obtain a first-order linear equation for $G(\mathbf{r}_{12})$ whose solution is

$$TG_1(\mathbf{r}) = \exp[-\phi(r)/T] \int_0^r dx\, G_0(x) I(x\mathbf{r}/r) \exp[\phi(x)/T] \tag{11}$$

$$I(\mathbf{r}_{12}) = \int d^3\mathbf{r}_3\, G_0(r_{13})[G_0(r'_{23}) - 1]\phi'(r_{13})(\mathbf{r}_{13}\cdot\mathbf{r}_{12}/|\mathbf{r}_{13}|\,|\mathbf{r}_{12}|) \tag{12}$$

The integral in (12) is over positions of particle 3 satisfying $r_{23} > R_{\max}$ and $r'_{23} < R_{\max}$. The pressure error is determined by inserting G_1 into the second term of (3) and spherically averaging the result.

2. RESULTS

This prescription has been carried out for two systems of 108 Lennard-Jones particles, one under triple-point conditions $[(\rho^*, T^*) = (0.8, 0.7)]$ and one under conditions of a supercooled fluid $[(\rho^*, T^*) = (0.91, 0.62)]$. {The Lennard-Jones potential is given by $V = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$. Units of density, temperature, and pressure are defined by $\rho^* = N\sigma^3/V$, $T^* = kT/\epsilon$, and $P = P\sigma^3/\epsilon$. Time is measured in units of $\tau = (M\sigma^3/\epsilon)^{1/2}$.} In both cases $R_{\max}$ was taken to be 2.3σ, and $G_0(r)$ was taken from a molecular dynamics run. Some results are shown in Table I. The calculations were done to first order in the correction, and have not been made self-consistent. The correction term $G_1(r)$ assumes positive values starting near the first neighbor peak, and may eventually go negative near the (100) superlattice direction. The spherically averaged correction never exceeds about 2%. For the supercooled case the 108-particle system gives a pressure low by about 0.15 Lennard-Jones unit, or about 60 atm for argon. This is in good agreement with the result of Mandell *et al.*(4) who find an error of about 90 atm. For the triple-point case the error is about one-third as large.

A more severe test is comparison of the anisotropic $G(r)$ predicted here with that measured by computer experiment. To that end we measured the anistropy of $G(r)$ for 108-particle molecular dynamics runs of length 90τ, and for a 256-particle run of 30τ. For the small systems, the results (Fig. 3) agreed with our prediction of the magnitude of the anisotropy and with the predicted sharp drop of $G(r)$ near the (100) superlattice direction. We had not predicted so deep a minimum in the neighborhood of 30° from (100), nor the rise beyond that angle. That the effect remained large for distances substantially less than

Table I. Calculated Corrections to Radial Distribution Function and Pressure of a 108-Particle Lennard-Jones Fluid for Superlattice Directions ($\cos\theta$, $\sin\theta$, 0)[a]

	Supercooled case		Triple-point case	
θ	$G_1(R_{max})$	ΔP	$G_1(R_{max})$	ΔP
0.0045	−0.44	−0.100	−0.098	−0.086
0.1714	−0.41	−0.139	−0.054	−0.093
0.2427	−0.34	−0.182	−0.0085	−0.097
0.2976	−0.25	−0.219	0.030	−0.096
0.3441	−0.16	−0.246	0.059	−0.092
0.3852	−0.06	−0.263	0.075	−0.085
0.4224	0.01	−0.267	0.079	−0.076
0.4569	0.07	−0.260	0.074	−0.067
0.4890	0.11	−0.244	0.063	−0.058
0.5194	0.12	−0.233	0.053	−0.050
0.5482	0.12	−0.199	0.044	−0.043
0.5756	0.11	−0.176	0.037	−0.038
0.6020	0.09	−0.155	0.031	−0.033
0.6274	0.09	−0.136	0.027	−0.028
0.6520	0.07	−0.120	0.024	−0.024
0.6757	0.06	−0.106	0.021	−0.021
0.6988	0.05	−0.093	0.019	−0.018
0.7213	0.05	−0.081	0.016	−0.015
0.7432	0.04	−0.070	0.014	−0.012
0.7646	0.04	−0.060	0.012	−0.010
0.7856	0.03	−0.051	0.010	−0.008
Spherical average	−0.02	−0.15	0.02	−0.05

[a] The unit of pressure is ϵ/σ^3.

$L/2$ was also unexpected. These errors seem to be due in roughly equal measure to failure of the superposition approximation and to lack of self-consistency in this calculation. For the 256-particle system under similar supercooled conditions the departure of $G(r)$ from isotropy was never more than 5%.

The anisotropy of the 108-particle system is also seen in the Fourier space reciprocal to the superlattice. The structure factor

$$S(\mathbf{k}) = (1/N)\sum_{i,j}\exp[i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)] \tag{13}$$

was measured for the 12 distinct (511) wave vectors and four (333) wave vectors (in units of $2\pi/L$), all of which have the same length. For the supercooled case the (511) structure factor 4.13 ± 0.79 is significantly larger than the (333) value 1.84 ± 0.23. Again, the effect is milder, but still present, in

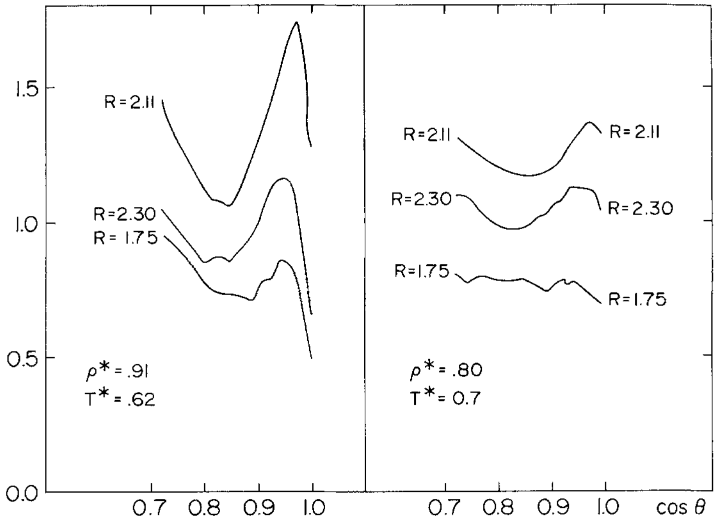

Fig. 3. Angular dependence of radial distribution function for two 108-particle systems.

the 108-particle triple-point liquid, for which the respective structure factors are 2.23 ± 0.07 and 1.93 ± 0.06. (The errors were obtained by assuming structure factors in different directions to be independent, uncorrelated measurements.)

3. DISCUSSION

Because the compressibility $\partial\rho/\partial P$ of the Lennard-Jones fluid under these conditions is fairly small, the effects discussed here, while they seem substantial in terms of absolute pressure, are small if the desired result is density as a function of pressure. If one wishes to relate computer simulation results to real substances, the errors caused by size dependence are surely less than those caused by uncertainty in the potential. For the case of the Lennard-Jones fluid a great deal of thermodynamic data have been published for systems far larger than 108 particles (in particular, Verlet(5) and Rahman(6) studied systems of 864 particles), and such work need not be considered suspect. However, one should be careful in studying systems that have relatively soft cores and long attractive tails. These are likely to show substantial size dependence in their thermodynamic properties.

For studies of phenomena more complex than equilibrium thermodynamic data, and particularly for nucleation studies,(4) the anisotropy of this effect is likely to be very important, and may be the explanation for the strong sample-size dependence of supercooling limit found by Mandell *et al.* This may also explain why in several crystal nucleation events crystals never formed with their (100) axes in the (100) superlattice directions. The present study shows that this orientation would have required the second neighbors to be at points where $G(r)$ is strongly depressed in the supercooled fluid.

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