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Monte Carlo simulation of hard-sphere fluid and solid in a confined geometry

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We study the structure of hard-sphere solids and fluids in a spherical cavity with Monte Carlo simulation for samples with up to 1024 particles. We found that at high densities for a fixed number of particles the density of the solid near the wall oscillates as the density is changed, as a consequence of the commensuration of the cavity radius with the hard-sphere spacing. As the size of the system is increased, the region in density over which this oscillation occurs is decreased; the amplitude of variation remains strong. We also computed the structure factor averaged over particles at different distances from the center. Even though the density exhibits a peak at the boundary, this local structure factor is much smaller at the boundary, indicating a decrease of crystalline order at the interface because of the presence of the wall. Our result suggests that it is melting and not nucleation that starts at the walls. Density-functional-type methods, which assume this local structure factor to be small, may still be useful to study melting in confined geometries.

Over the last ten years there has been much study of the thermal, electrical, and magnetic properties of materials in different matrices, such as metal clusters in an insulator (granular metals) and fluids in Vycor and rocks. Takagi,[1] Buffat and Borel,[2] Awschalom and Warnock,[3] and Jackson and McKenna[4] studied melting behavior in different systems and found suppressions in the melting temperatures. Unruh *et al.*[5] found that for Bi and SiO_2, there is wide fluctuation in the freezing temperature while in SiO_2 there is no fluctuation in the freezing temperature. There has been speculation that the nucleus starts forming at the surface; this is contrary to recent evidence[6,7] which indicates that the order is less at the surface. There are also claims of surface melting for small clusters.[8] Pawlow,[9] Matsubara, Iwase, and Momkita,[10] Hasegawa, Hoshino, and Watabe,[11] and Sheng, Cohen, and Schrieffer[12] investigated the finite-size effects of melting by applying different analytic approximations. They found a suppression in the melting temperature and a temperature dependence of the specific heat similar to that observed experimentally. The size of a pore can be less than or equal to the size of a nucleus. The meaning of nucleation is not clear.

In addition to the melting behavior, other effects that require a knowledge of the structure have also been studied. The electrical resistivity exhibits interesting temperature dependence, the origin of which has been much discussed.[13] The coercivity of magnetic materials is found to increase for granular systems.[14] The physics of this is not understood.

There has been much computer simulation of the structure of *fluids* near a *flat* wall.[15,16] Not much is known about the *solid* phase in *spherical* boundaries, however. Because of the spherical wall, the atoms in the solid phase cannot sit at regular lattice positions at the interface. On the other hand, their positions will be useful to understand other physical properties. As a first step towards such an understanding, we have approximated the cavity in these materials by a sphere[17] of radius a and carry out a Monte Carlo study of the structure of solids and fluids surrounded by spherical walls. Particular attention is paid to the properties near the melting point. We hope this understanding of the structure will serve as a basis from which other physical quantities can be computed. Experimental solid boundaries will have an atomic structure on a comparable scale to that of the solidifying liquid and this may affect the local structure. A more realistic calculation should include these effects as well.

We find an increase in the density of both the solid and the fluid at the wall. For a fixed number of particles the density of the solid near the wall oscillates as the density is changed. This comes about because the radius of the cavity is not always commensurate with the lattice constant. As the size of the system is increased, the region in density over which this oscillation occurs is decreased; the amplitude of variation remains strong.

There has been some suggestion that the solid phase nucleates at the boundary in porous material. This would imply that the system is more solidlike at the boundary. To explore this question, we calculate a local structure factor defined as the structure factor averaged over particles at different distances from the origin. Whereas the local density is increased at the wall, no corresponding increase is seen in this local structure factor. This suggests that for the cavity sizes we looked at, growth does not start at the boundaries. As has been previously pointed out,[18] this suppression of order is peculiar for small spherical systems; for flat walls, we expect the local structure factor to increase near the walls. In that case, fluids will nucleate at the surface.

We have performed Monte Carlo (MC) simulations for a collection of hard spheres of unit radius in spherical shells such that the total number of particles $N=256$, 512, and 1024. The shells possess no structure. Their only effect is to confine the articles inside. Typically, 1000 N steps were used to thermalize the particles while another 1000 N steps were run for data to be collected. We have also performed test runs so that the number of MC steps is doubled. The final result for the density at the wall differs by less than 10%. A typical Metropolis scheme was used. The systems we have in mind can exchange energy with an external thermal bath. Thus a canonical ensemble is more appropriate. If energy cannot be exchanged, then a microcanonical ensemble will be more reasonable. For small systems, these two ensembles may not provide the same results. The question of ensembles in small systems have recently been investigated by Labastie and Whetten.[19]

The resulting density distribution as a function of the radial distance is shown in Figs. 1(a)–1(d) for densities from 0.8 to 1.1 for $N=512$. The density exhibits a peak at the spherical boundary. The density near the center is noisy because there are very few particles there and the statistics are not very good. The density of the fluid phase has been discussed in detail in a previous publication.[20] We found that the magnitude of the peak is less than that for a plane boundary. At low densities, it corresponds approximately to a linear theory by Henderson, Abraham, and Barker.[21]

The magnitude of the density at the boundary, which can be interpreted as p/kT, is shown in Fig. 2 for both the fluid (solid line) and the solid (dashed line) branch as a function of the density of the system. Also shown is the result from the Carnahan-Sterling equation of state (dotted line). Most dramatic is the oscillation of this quantity as a function of density at high densities. This is a consequence of the commensuration of the sphere box radius with the hard-sphere spacing.

The density at the boundary for 256, 512, and 1024 particles in the solid branch is shown in Fig. 3. As the size of the system is increased, the region in density over which this oscillation occurs is decreased, but the amplitude of variation remains strong.

We expect this commensuration effect to affect the freezing instability of a supercooled granular metal that interacts strongly with the matrix. Bismuth expands in the solid phase and is one such candidate. When the density of the granules is so high that the granules are connected, the pressure has to be the same in all the pores. The density of a granule in the fluid phase is often incommensurate with forming a solid in the corresponding pore if the solid interacts strongly with the pore walls. Frustration is introduced. On the other hand, there are density fluctuations in each pore inversely proportional to the volume of the pore. Thus we expect a small probability for some granules to be commensurate and able to initiate the fluid-solid instability transition. When a sufficient number of granules satisfies this condition, melting occurs. In this way, we expect to see a distribution of freezing temperature. This is what is experimentally observed.[5]

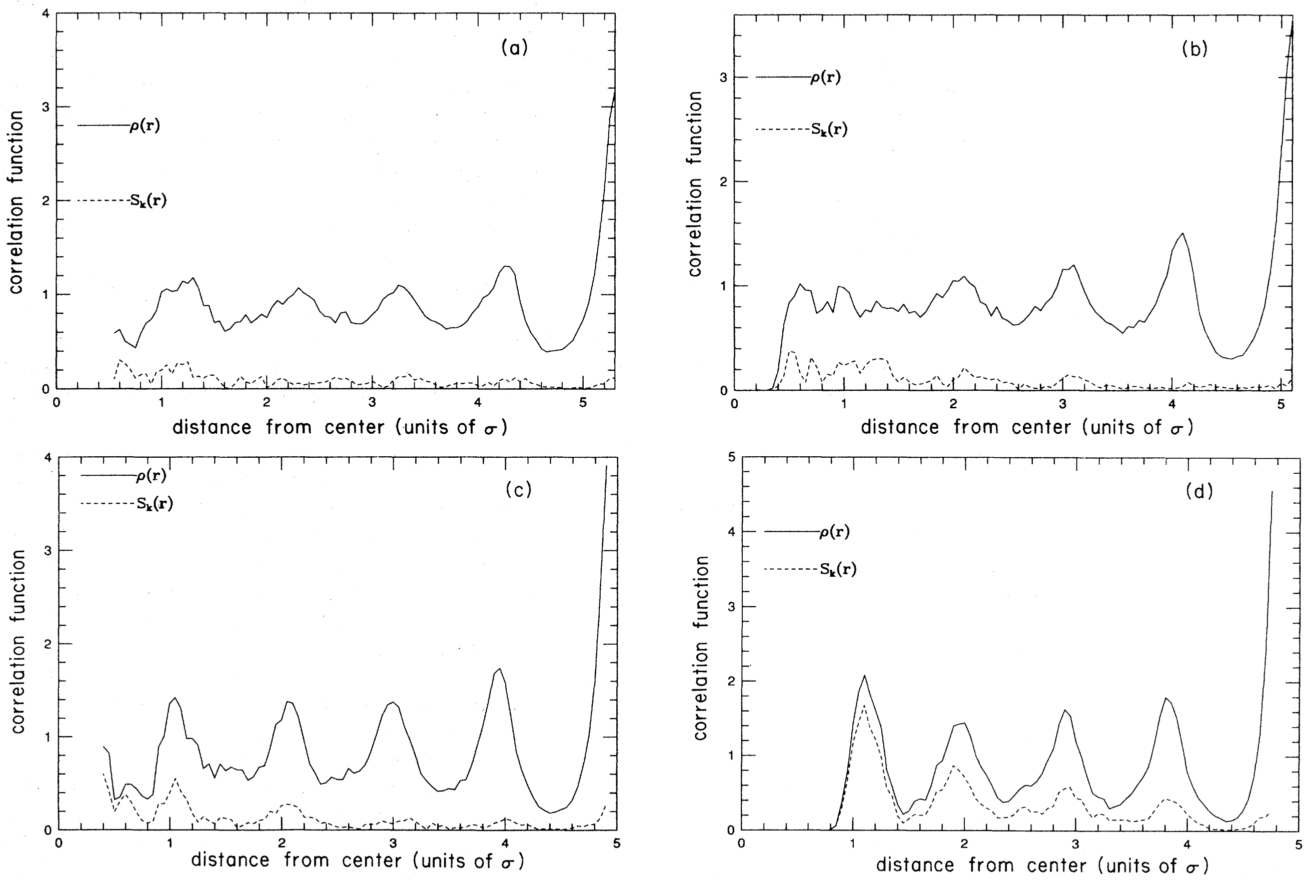

FIG. 1. (a)–(d) Monte Carlo results for the density profile and local structure factor next to a spherical wall for hard-sphere fluids of 512 particles of density (a) 0.8, (b) 0.9, (c) 1.0, (d) 1.1. All units are expressed in terms of the hard-sphere radius σ.

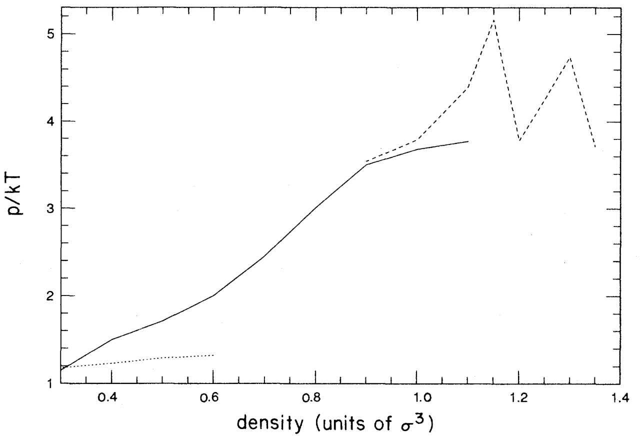

FIG. 2. The density at the wall as a function of the density in units of the hard-sphere radius of the system of 512 particles.

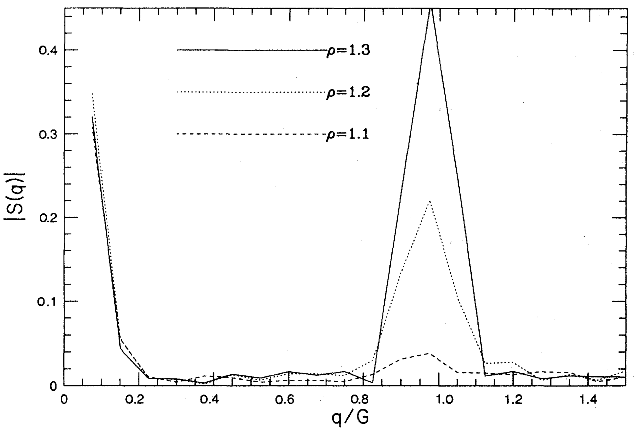

FIG. 4. Structure factor $S(q)$ as a function of the momentum transfer in units of the reciprocal-lattice vector at three different densities.

Freezing is a dynamical phenomena; a more careful study requires the inclusion of the dynamics of the system.

To quantitatively assess the surface-crystalline order, in addition to calculating the density distribution, we have also investigated a local structure $S_K(r)$ defined as the average of $\exp(i\mathbf{K}\cdot\mathbf{r}_j)$ for those electrons j at different distances r from the center of the spherical box. The amplitude of this local structure factor is the key order parameter in the density-functional-type theory for melting. Its evaluation will thus provide us with insight into its validity. The local structure factor as a function of the radial distance is also shown in Figs. 1(a)–1(d) for densities from 0.8 to 1.1 for $N=512$. The initial configuration at the start of the MC simulation was assumed to be a solid. Thus these correspond to a *solid* branch. As the density is increased, the system becomes more solidlike with well-defined local structure factors. The first clear sign of a solid occurs near a density of 1.1. In all cases, the local structure factor decreases as the distance from the center is increased, whereas the opposite is true for the local density. If melting starts at the center, the local structure factor should be higher at the boundary. Thus our result suggests that melting starts at the wall. Physically, the spherical boundary makes it difficult to form a solid at the outer wall. This is consistent with a recent picture of premelting for small clusters[8] and suggests that because of the spherical wall, there is less order near the wall. This result is also consistent with recent self-consistent Einstein model calculations of Zhou and Sheng[6] and Mössbauer experiments by Chien.[7]

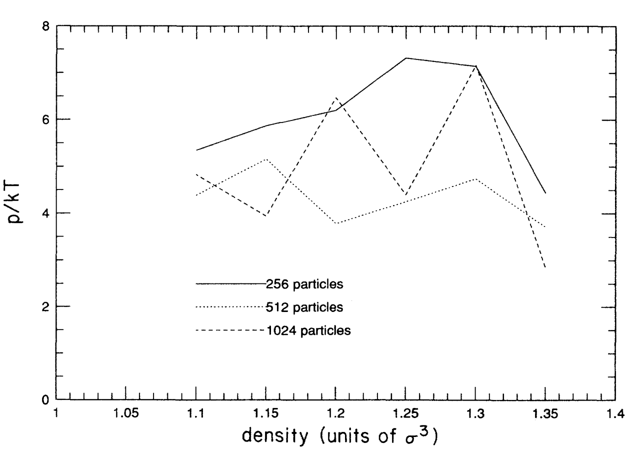

FIG. 3. The density at the wall at high densities as a function of the density in units of the hard-sphere radius of the system of 256, 512, and 1024 particles.

In density-functional-type theories,[22] one defines an amplitude function so that the local structure factor is written as $\mu(r)\exp(i\mathbf{K}\cdot\mathbf{r}_j)$. One usual assumption in these theories is that $\mu(r)$ is slowly varying. This is certainly true in the present case.

Furthermore, there does not exist any region where the local structure factor is flat, indicating that the cavity size that we looked at (of ten atomic distances in diameter), is smaller than or equal to a typical nucleus size. Our result for the small magnitude of μ at the boundary together with its nonconstant nature implies that for the cavity sizes we looked at, growth does not start at the boundaries simply because the cavity size is of the size of a single nucleus.

The total structure factor $S(q)$ as a function of the momentum q is shown in Fig. 4 for three different densities at high densities. A peak is seen at a wave vector close to what we expect to be the reciprocal-lattice vector. As the density is increased, the magnitude of this peak is increased. This is consistent with our expectation that the order is more solidlike as the density is increased. In principle, there is no genuine phase transition for any finite-size systems in that the magnitude of $S(G)$ is never infinite. The fact that $S(G)$ is finite does not mean one is in a solid phase. We shall consider the freezing completed when the amplitude of the local structure factor is nonzero for all values of r.

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