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Letters

Structure and Pressure of a Hard Sphere Fluid in a Wedge-Shaped Cell or Meniscus

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Simulations of hard spheres in a wedge-shaped cell are reported. There is a tendency for the spheres near the vertex to have a solidlike structure and for those further from the vertex to have a fluidlike structure. The simulation density profiles exhibit discontinuities that are characteristic of structural changes in the fluid. Also, the density profile and pressure on the walls of the cell are computed by means of an integral equation. The pressure is large near the vertex and oscillates as the distance from the vertex increases or as the angular variable changes. The asymptotic value of the pressure is the bulk hard sphere pressure.

Introduction

The assembly of materials based on nanometer-sized particles, such as colloidal suspensions, to form "nano-structured materials" is a rapidly expanding area of material science.[1,2] It has been found that the properties of nanometer-sized colloidal suspensions confined to submicrometer-sized pores or thin films differ from the properties of the same suspensions in the bulk. For example, latex aqueous suspensions, at concentrations of a few percent and trapped between two solid surfaces, order themselves into colloid crystals.[3] A sequence of structures and the corresponding structural transitions are observed when the thickness of the confined suspension is increased progressively from zero.[4] In the plane−plane wedge geometry with a wedge angle of about 10^{-2} rad (0.5°), the suspension particles form a monolayer that has a fluidlike structure in a very narrow band in the region of the vertex, i.e., in the wedge area with the diameter smaller than the particle diameter. However, with the increasing wedge thickness, two-dimensional crystalline layers with triangular or square interplanar ordering have been identified.[4] When the wedge film thickness is several times the particle diameter, the particles are disordered.

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The phenomenon of particle structuring and structural transitions due to confinement is not well understood. It is believed that the microscopic transitions are entropically driven transitions.[5]

The goal of this paper is to analyze the effect of the wedge angle on the structure formation and pressure of a fluid inside a wedge-shaped cell or meniscus by means of computer simulations and integral equation techniques. For simplicity, we assume the fluid to be a fluid of hard spheres. This is consistent with the hypothesis that the transitions are entropy driven.

Simulation/Theory

We have studied a system of hard spheres in a wedge-shaped cell by simulations and by an integral equation. First, the simulations are discussed. We consider a wedge-shaped simulation cell of dimension $R_0 = 57.3d$, $\Theta_0 = 2\pi/90$ rad (=4°), and $ZL = 10d$ (note that R_0 is the length of the "effective" cell, namely, the region where the centers of the spheres can be positioned). We use 4° rather than the experimental value of 0.5° because we found it difficult to obtain good statistics when Θ_0 is very small. The parameter d is the hard sphere diameter. The walls at $\theta = 0$ and $\theta = \Theta_0$ and $r = R_0$ are hard. A periodic boundary condition is applied in the z direction. The coordinates of a particle are (r,θ,z). We placed $N = 802$ hard spheres in the cell. The reduced average density of hard spheres in the cell is $\rho d^3 = 0.7$ (for the "effective" volume that is accessible to the centers of the spheres). Moves are attempted for each hard sphere in sequence and any moves resulting in an overlap with any other spheres or with the bounding walls are rejected (using the convenient term of the "effective" cell, the inclusion in the cell can be expressed by the simple conditions: $0 \le r \le R_0$ and $0 \le \theta \le \Theta_0$). To save computer time, a linked cell method was applied for checking overlaps. The trajectories of the spheres are recorded over 200 moves in steps of 4. These are not time ordered trajectories but still give a sense of where the particles move. The density profile $\rho(r,\theta)$ can be computed by averaging. It is not so easy to obtain a smooth curve near $r = 0$ from simulations because there are so few spheres in this region. However, we can adapt the method of Henderson et al.,[6] where the density profile is calculated by means of an integral equation, using a modified Verlet closure, for the density between two nearly parallel walls. Since $\Theta_0 = 0.5°$ is small, the walls are very nearly parallel. For a given value of r, we compute the density profile between two nearly parallel walls whose separation is $r\Theta_0$. Because Θ_0 is small, the arc and straight line joining points a distance r from the vertex are nearly the same. The density profile at $r = 0$ (the so-called squeezed limit) is $e^{\beta\mu}$,[7] where μ is the chemical potential and $\beta = 1/kT$.

The pressure on the wall at r can be obtained from the contact value theorem

$$\beta p(r) = \rho(r,0) \tag{1}$$

Equation 1 express that fact that the pressure equals the momentum transfer to the wall, as given by the contact value of the density.

Results

First we consider the simulation results. Some density profiles are plotted in Figure 1. It is interesting that $\rho(r)$ exhibits discontinuities, similar to those seen by Pieranski et al.[4] as new layers of hard spheres can be accommodated between the walls of the wedge. These discontinuities do not disappear even when the number of moves becomes exceedingly large. These discontinuities are indicative of structural changes in the fluid.

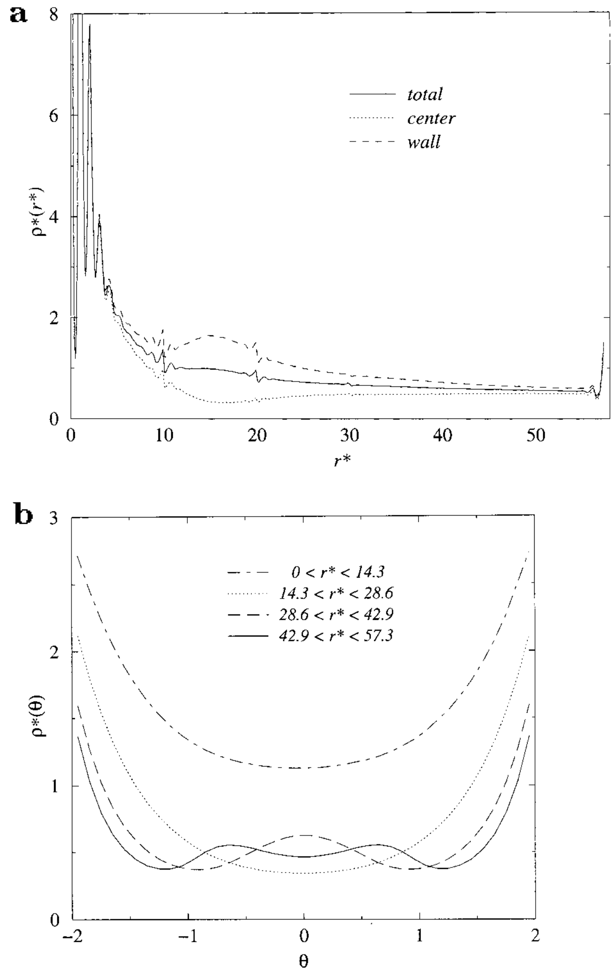

Figure 1. Density profile, in units of d^3, of hard spheres in a wedge for $\Theta_0 = 4°$. These profiles were obtained from simulations. In part a, the density profile is displayed as a function of r at the wall (upper curve) and at the center (lower curve). In part b, the profile is displayed as a function of θ. The curves, from top to bottom, display the integrated density over the r ranges, 0−14.3, 14.3−28.6, 28.6−42.9, and 42.9−57.3, respectively. These are the ranges of r in which one, two, three, and four layers of particles can be accommodated. All distances are in units of d.

The trajectories of the centers of the spheres near the edge of the cell at $\Theta_0 = 0$ and viewed from the side of the cell, obtained from our simulations, are shown as functions of r and z, in Figure 2. For $\Theta_0 = 0.5°$ there does not seem to be a clear distinction between the structure of the spheres near the vertex and further away. Evidently, the widening of the wedge is too gradual. This is one of the reasons why we considered $\Theta_0 = 4°$. In this case, there is a clear distinction between the spheres near and far from the vertex. Near $r = 0$ the hard spheres form a hexagonal, or triangular, lattice-like structure whereas further from the vertex the hard spheres are clearly fluidlike. The transition between the two regions is about 10 diameters from the vertex, even though the arc between walls is still small. A superficial examination of Figure 2 might lead one to the conclusion that the density is greater at large r than at small r. This contradicts the profiles shown in Figure 1 and is not a correct conclusion. The solidlike

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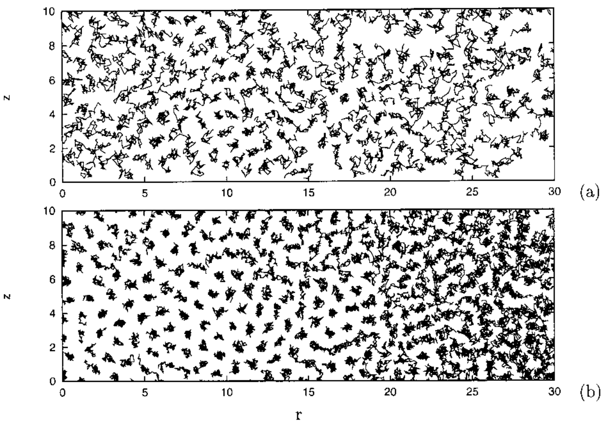

Figure 2. Trajectories of the centers of the hard spheres in a wedge near $\theta = \Theta_0/2$ and viewed from the side of the wedge. The trajectories were obtained from our simulations. The average density in the simulation cell is about $\rho d^3 = 0.7$. In part a, $\Theta_0 = 0.5°$, and in part b, $\Theta_0 = 4°$. All distances are in units of d.

trajectories near $r = 0$ show what appears to be empty space because the sphere centers are "confined" and do not range over space. The liquidlike trajectories at large r range widely over space and fill space. However, this does not indicate a greater value for density profile at large r than at small r.

For $\Theta_0 = \pi$, there is no solidlike region near the wall[7] since any location on a flat wall is equivalent to the region far from a vertex. Thus, it appears that the solidlike region near the vertex develops as Θ_0 is decreased from π. When Θ_0 is sufficiently small, structural changes are not observable from the trajectories. However, their presence is still manifest in the discontinuities seen in the density profile. The density profile $\rho(r,\theta)$, computed from the integral equation, is plotted in Figure 3. The figure is symmetric about $\theta = \Theta_0/2$, but the left-hand side is cut off for easier viewing. The peak at $r = 0$ is very large (about 135 for $\rho d^3 = 0.6$). The rise to this peak is monotonic. The apparent secondary peaks near $r = 0$ are a result of the plotting algorithm and are not real. We have computed $\rho(r,\theta)$ from our simulations too. The integral equation results are consistent with the simulation results but do not exhibit any discontinuities. Finally, in Figure 4 we plot the pressure on the sides of the cell that is obtained from the integral equation. The pressure is high near the vertex since the hard spheres are "pushed" into this region by the spheres further out. The pressure oscillates as additional layers of hard spheres can be accommodated between the walls at $\theta = 0$ and Θ_0 and ultimately becomes the bulk hard sphere pressure.

It would be interesting to see if density functional methods will exhibit density profiles with discontinuities.

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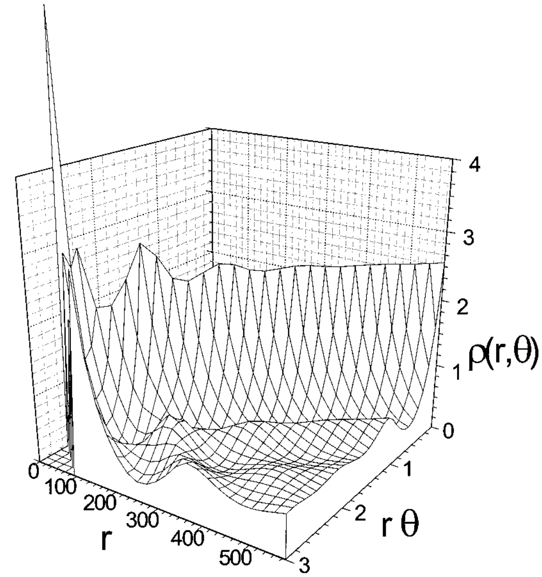

Figure 3. Integral equation density profile $\rho(r,\Theta)$, in units of d^3, of a hard sphere fluid in a wedge for $\Theta_0 = 0.5°$. The profile is symmetric about $\Theta_0/2$, the line running from the vertex to approximately $r\Theta_0 = 2.5$. The left-hand side is cut off for easier viewing. The bulk hard sphere density is $\rho d^3 = 0.6$. All distances are in units of d.

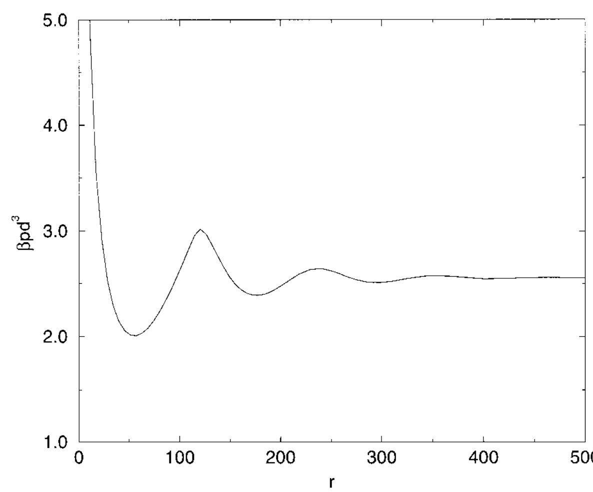

Figure 4. Integral equation reduced pressure, $\beta p(r)d^3$, on the walls at 0 and Θ_0 for $\Theta_0 = 0.5°$, as a function of the distance r along the edge. The bulk hard sphere density is $\rho d^3 = 0.6$. All distances are in units of d.

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