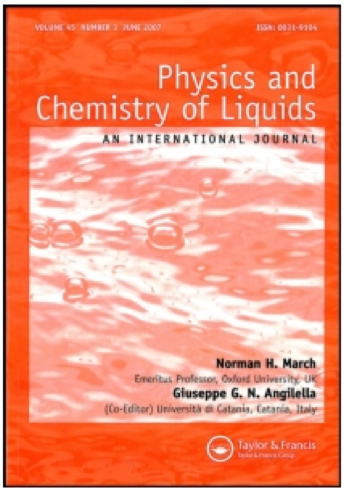

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A Theoretical Study of the Hard-Sphere Fluid-Solid Interface II. Test of an Alternative Variational Form

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A Theoretical Study of the Hard-Sphere Fluid-Solid Interface

II. Test of an Alternative Variational Form

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We examine the hard-sphere fluid-solid interface using a form for the inhomogeneous density that differs significantly from those in our previous paper. As before, our approach avoids the square-gradient approximation. We present results for the [111] interface which qualitatively support our earlier findings. While the new density profile closely resembles those observed in computer simulations of Lennard-Jones systems, the surface free energy calculated from this ansatz is almost 2.5 times as large as the earlier estimates.

Key Words: Coexistence, grand potential, inhomogeneous density, freezing.

I INTRODUCTION

Much current research[1] has focused on the phenomenon of hard-sphere freezing. This interest stems from successes of density functional descriptions of freezing, the availability of extensive simulation data[2] to compare with the theoretical predictions, and the existence of accurate approximation schemes for obtaining the hard-sphere properties. Considerably less research has been directed toward understanding the fluid-solid interface of this system. Contrary to hard-sphere freezing, convincing simulations of the interface have not yet been published. Recently, however, two theoretical papers[3,4] on the subject have appeared, both based on the inhomogeneous density functional formalism. The present discussion supplements our earlier work[3] (we will refer to this as paper I). We submit it as additional evidence of several of our previous findings, and as a test of the theory's sensitivity to the variational form chosen for the density.

The present paper is not a self-contained discussion of either hard-sphere interfaces or freezing, and we refer the reader to I and the references cited there for the theoretical foundations. We introduce our ansatz for the inhomogeneous density in Section II, and use it to estimate the surface free energy of the [111] interface. After tabulating and discussing our numerical results in Sections III and IV, we end the paper with a few brief conclusions.

II ANSATZ FOR THE DENSITY

The grand potential of an inhomogeneous system includes contributions from interfaces as well as from the bulk, coexisting phases. When two phases coexist, the contributions per unit volume from either bulk phase are equal. The difference between the total grand potential and that of an equal volume of one of the homogeneous phases is the surface free energy. The grand potential difference,

$$\begin{aligned}\beta(\Omega_{\text{inhomogeneous}} - \Omega_{\text{liquid}}) &= \beta\Delta\Omega[\rho(\mathbf{r})] \qquad (1)\\ &= -\int d\mathbf{r}_1 \Delta\rho(\mathbf{r}_1) + \int d\mathbf{r}_1 \rho(\mathbf{r}_1) \ln \frac{\rho(\mathbf{r}_1)}{\rho_0}\\ &\quad -\frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 c(r_{12}) \Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2)\\ &\quad -\frac{1}{6}\iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 c^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13})\\ &\quad \times \Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2)\Delta\rho(\mathbf{r}_3) - \cdots\end{aligned}$$

is variational with respect to the nonuniform density, $\rho(\mathbf{r})$, subject to the boundary conditions (applicable to a planar interface),

$$\rho(\mathbf{r}) \to \rho_0 = \rho_{\text{liquid}}, \; z \to -\infty,$$

and

$$\rho(\mathbf{r}) \to \rho_{\text{solid}}(\mathbf{r}), \; z \to \infty.$$

The minimum value of the functional is the free energy due to the interface of area A, $\beta\gamma_{SL}A$, in units of kT. In Eq. (1), $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$, and $c(r_{12})$, $c^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13})$, ... are two-, three-, etc. body direct correlation functions (dcf's) of the liquid phase. We know little about the higher-order dcf's and approximate Eq. (1) by

$$\beta\Delta\Omega[\rho(\mathbf{r})] = -\int d\mathbf{r}_1\Delta\rho(\mathbf{r}_1) + \int d\mathbf{r}_1\rho(\mathbf{r}_1)\ln\frac{\rho(\mathbf{r}_1)}{\rho_0} \tag{2}$$

$$-\frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 c(r_{12})\Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2)$$

$$-\rho_0^3/6c_{00}^{(3)}\int d\mathbf{r}_1\mu_0^3(z_1),$$

where

$$c_{00}^{(3)} = \iint d\mathbf{r}_2 d\mathbf{r}_3 c^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13})$$

and $\mu_0(z)$ is the fractional difference between the local and bulk-liquid number densities. As $z \to \infty$,

$$\mu_0(z) \to \frac{1}{\rho_0 V}\int d\mathbf{r}\Delta\rho(\mathbf{r}).$$

As discussed previously, we locate the transition density using the superposed Gaussians

$$\rho_{\text{solid}}(\mathbf{r}) = (\alpha/\pi)^{3/2}\sum_i \exp[-\alpha|\mathbf{r}-\mathbf{R}_i|^2] \tag{3}$$

for the homogeneous solid, and the coexistence condition,

$$\beta\Delta\Omega = 0. \tag{4}$$

The density of the homogeneous solid can be represented as the Fourier sum,

$$\rho_{\text{solid}}(\mathbf{r}) = \rho_0\left[1 + \sum_{\mathbf{q}}\mu_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r})\right]. \tag{5}$$

To account for variations in the density through the interface, we write

$$\rho(\mathbf{r}) = \rho_0\left[1 + \sum_{\mathbf{q}}\mu_{\mathbf{q}}(z)\exp(i\mathbf{q}\cdot\mathbf{r})\right] \tag{6}$$

with

$$\mu_{\mathbf{q}}(z) \to 0, \quad z \to -\infty$$

and

$$\mu_{\mathbf{q}}(z) \to \mu_{\mathbf{q}}, \quad z \to \infty,$$

We assume the variational forms

$$\mu_0(z) = \mu_0/2[1 + \tanh \gamma_0(z - z_0)] \tag{7}$$

and

$$\mu_1(z) = \mu_1/2[1 + \tanh \gamma_1(z - z_1)]. \tag{8}$$

Fourier inversion of Eqs (3) and (5) then gives

$$\mu_{\mathbf{q}} = (1 + \mu_0) \exp(-q^2/4\alpha), \quad \mathbf{q} \neq 0. \tag{9}$$

Let a equal the lattice constant in the bulk solid and $\mathbf{q}_1$, the first nonzero set of reciprocal lattice vectors. Substituting Eq. (9) into Eq. (8), using $q_1 = 2\pi/a\sqrt{3}$, and solving for $\alpha(z)$, we find

$$\alpha(z) = \frac{\alpha}{1 + \dfrac{\alpha a^2}{3\pi^2} \ln[1 + \exp(-2\gamma_1(z - z_1))]}, \tag{10}$$

We vary the density through the interface in the following way: Far from the interface, in the bulk solid, we have $\alpha(z) \to \alpha$ and $\mu_0(z) \to \mu_0$. Let d denote the spacing between bulk-solid lattice planes parallel to the interface. Upon approaching the interface, the local density drops to

$$\rho_0[1 + \mu_0(z)].$$

We allow the lattice to expand only in the z direction so that

$$d(z) = d[1 + \mu_0(z)]. \tag{11}$$

Starting with a plane far into the bulk solid, with z-coordinate $z(N)$, we determine the positions of planes nearer the interface using

$$z(i) = z(N) - \sum_{j=i+1}^{N} d(j). \tag{12}$$

Finally, hard spheres associated with the general ith lattice plane are distributed about their lattice sites according to

$$\rho_{ij}(\mathbf{r}) = (\alpha/\pi)^{3/2} \exp[-\alpha_i(\mathbf{r} - \mathbf{R}_j)^2], \tag{13}$$

where

$$\alpha_i = \alpha(d_i), \tag{14}$$

and j refers to an atom within the plane.

The ansatz just outlined preserves the Gaussian character of the density about each site, and simplifies greatly the calculation of the nonlocal integral in Eq. (2),

$$I = \iint d\mathbf{r}_1 d\mathbf{r}_2 \Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2)c(r_{12}). \tag{15}$$

If we use the Percus-Yevick direct correlation function for hard spheres, this integral can be expressed analytically in terms of repeated integrals of the error function[5] summed over lattice sites. The ideal entropy functional in Eq. (2),

$$I' = \int d\mathbf{r}_1 \rho(\mathbf{r}_1) \ln \frac{\rho(\mathbf{r}_1)}{\rho_0} \tag{16}$$

is evaluated numerically, while the other two contributions to Eq. (2) are straightforward to evaluate. We then minimize $\beta\Delta\Omega$ with respect to the four parameters γ_0, z_0, γ_1, and z_1 to obtain the approximate surface free energy per unit area, γ_{SL}. Note that the square-gradient approximation has not been invoked in this calculation.

III RESULTS

At coexistence, the hard-sphere freezing parameters are[3]

$$\mu_0 = 0.1436465,$$
$$\alpha = 373.3089,$$

and

$$\eta_0 = \pi/6\rho_0\sigma^3 = 0.515702.$$

As a check on our algebra, we have arrived at the same results using $\alpha(z) = \alpha$ and $\mu_0(z) = \mu_0$. Consider first the one-parameter variation obtained using the constraints $z_1 = z_0 = 0$, and $\gamma_0 = \gamma_1$. For the [111] interface, we find

$$\gamma_0 = 0.782\sigma^{-1}$$

and

$$\gamma_{SL} = 4.34\ kT/\sigma^2.$$

The full four-parameter variation reduces γ_{SL} by only about eight percent and yields:

$$\begin{aligned}\gamma_0 &= 0.872\sigma^{-1},\\ \gamma_1 &= 0.905\sigma^{-1},\\ z_0 &= 0.884\sigma,\\ z_1 &= 0.032\sigma,\end{aligned}$$

and

$$\gamma_{SL} = 4.00\ kT/\sigma^2.$$

The latter value of the surface free energy listed here is almost 2.5 times as large as the best estimate reported in paper I.

IV DISCUSSION

In Figure 1, we plot the averaged density profile,

$$\frac{\rho(z)}{\rho_0} = \frac{1}{A}\int dx\, dy\, \frac{\rho(\mathbf{r})}{\rho_0}, \tag{17}$$

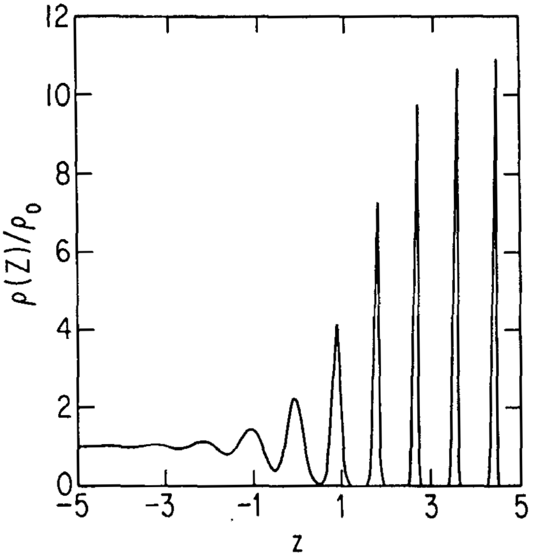

Figure 1 Density profile at the [111] interface based on the four-parameter variation described in the present work.

through the interface. For comparison, in Figure 2, we present a similar plot based on the four-parameter variation of the density in paper I. Interestingly, the profile in Figure 1 looks more reasonable than that of Figure 2. Not only do the oscillations of the former broaden on the liquid side of the interface, but the spacing between widens. Broughton and Abraham[6] have observed such widening in their simulations of the [111] interface of Lennard-Jones atoms.

Nevertheless, as noted above, the paper I trial density, which uses a linear combination of bulk liquid and bulk solid densities, provides the lower estimate of the surface free energy. To facilitate discussion, we restate it here:

$$\rho(\mathbf{r}) = [1 - f_2(z)]\rho_0 + f_1(z)\rho_{\text{solid}}(\mathbf{r}), \tag{18}$$

where

$$f_i(z) = \tfrac{1}{2}[1 + \tanh \gamma_i(z - z_i)]; \quad i = 1, 2.$$

The reasons that Eq. (18) yields the lower γ_{SL} are not entirely clear to us. We note that the ansatz detailed in the present paper allows spheres in the interfacial region to relax from their bulk-solid positions only in the z direction. In the two directions parallel to the interface, the spheres are localized about their solid-phase lattice sites. The present

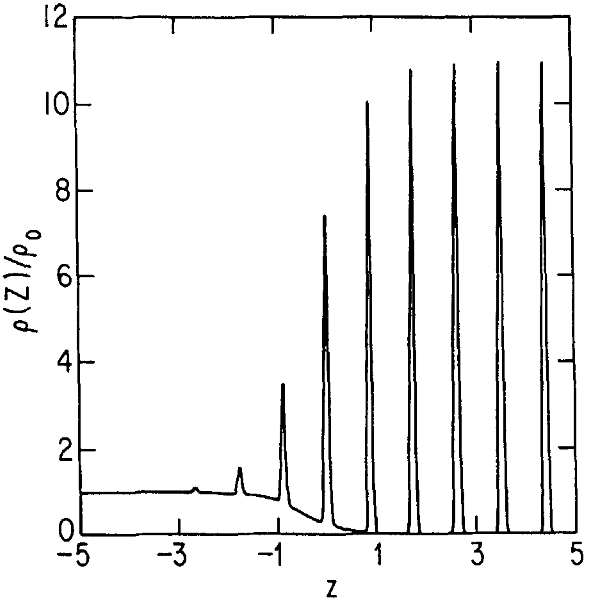

Figure 2 Same as Figure 1 but for the ansatz and four-parameter variation of paper I.

ansatz forces the spheres near the interface to assume an asymmetric structure. Because the equilibrium solid and liquid are both isotropic, we might conjecture that the asymmetry makes rather large local contributions to γ_{SL}. Certainly we would expect relaxation in the x and y directions too, perhaps in a way that mitigates the stretching along z. Accounting for this might reduce γ_{SL} somewhat. Notice that the paper I ansatz does not provide for any relaxation, but it does allow the density to remain isotropic through the interface.

A number of similarities exist between the present results and the previous ones despite their quantitative differences. Most obviously, both treatments result in a rather narrow interface. This suggests that a square-gradient approach to the nonlocal integral, Eq. (15), might not prove reasonable. As in paper I, however, a square-gradient treatment yields good agreement with the results of the full nonlocal integration. Using Eq. (10) for $\alpha(z)$, Eq. (9) for $\mu_{\mathbf{q}}(z)$, and Eq. (6) for the density, but regarding $\alpha(z)$ as a continuous variable, we find $\gamma_0 = 1.70\sigma^{-1}$ and $\gamma_{SL} = 3.74kT/\sigma^2$ at the square-gradient level. This agrees well with the one-parameter results quoted above given that the direct integration assumes discrete values of $\alpha(z)$ instead of continuous ones. As explained in paper I, we cannot relax the constraint $\gamma_0 = \gamma_1$, which limits the accuracy of the square-gradient treatment. A number of other problems may arise when more highly parameterized forms are attempted for the inhomogeneous density. In the present application, it appears that the density profile is not so sharp that the square-gradient theory becomes meaningless, and the method serves as a useful tool for obtaining qualitative information about the interface.

Another noteworthy feature of the present results is that z_0 is significantly more positive than z_1, indicating that the average density change is shifted relative to the structure change. Thus, in moving from bulk liquid toward the interface, one first encounters a structured region with density close to that of the liquid, and only later does the density increase to its bulk solid value. This feature, which was also seen in earlier, more approximate models (see Figures 2 and 3 of Ref. [7]), appears to be a general property of the crystal-melt interface.

After this work was completed, a different but related calculation of the hard-sphere interface was presented by Curtin.[4] This work used a different density functional and a different ansatz for the density variation through the interface. The surface free energies obtained were lower than those in paper I, but the interfacial widths were comparable. Curtin includes a variational parameter ν in his ansatz which, in rough terms, would correspond to a continuous variation from no broadening of peaks ($\nu = 0$), as in our paper I, to quasi-harmonic broadening of peaks ($\nu = 1$), as in the present paper. Curtin finds the lowest free energy near $\nu = 0.25$, a result that is consistent with our observation of a lower free energy in paper I than in this work. It is possible that some variational combination of the ansatz from I and the present one would give a lower surface free energy as well as a more realistic density profile.

V SUMMARY AND CONCLUSIONS

While the surface free energies calculated here are not as low as those presented earlier, we do obtain agreement between the qualitative features of the old and new treatments. The interface consists of only a few monolayers in opposition to the Cahn[8] picture. Despite this finding, we again find that a square-gradient approach to the nonlocal part of the grand potential provides reasonable results.

The profile that we obtain in our four-parameter variation appears quite physical and looks similar to those observed in molecular dynamics simulations of Lennard-Jones atoms. If hard-spheres behave similarly, then we could probably arrive at a lower estimate of γ_{SL} than that determined in paper I by allowing the separation between lattice sites to change in the interfacial region. We conjectured that relaxation in all three directions—not just the direction of the interface—might be important. It appears that the numerical results are quite sensitive to the form of the trial density.

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