

Modified weighted density-functional approach to the crystal-melt interface

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We present a modified weighted density-functional approach to study the structure and energetics of the crystal-melt interface of hard sphere fluid. Compared to the earlier theories of the solid-liquid interface, computational requirements have been considerably reduced through the newly defined layer-by-layer weighted density. Interfacial width obtained from the present approach is slightly larger than that obtained from earlier weighted density based theories using density parametrization, but is close to the result from similar theories with free minimization as well as the computer simulation result of soft-sphere (r^{-12}) potential, which resembles hard sphere potential. Surface free energy predicted by the present theory is somewhat lower than that obtained from earlier weighted density based approaches with density parametrization but is again close to that of free minimization with respect to the density distribution at the interface. [S1063-651X(98)05302-1]

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I. INTRODUCTION

The study of the interface between a crystal and its melt is of immense importance for the understanding of crystal growth, homogeneous nucleation, and many other important phenomena [1]. Experimental studies of the solid-fluid interface are, however, rather difficult since the interface is confined between two condensed bulk phases. As a result, computer simulation has played the role of a very important and useful technique for the study of solid-fluid interfaces over the years and many simulation studies on the interface have been reported in the literature [2–5]. The simulation studies of (i) Lennard-Jones fcc (111), (100), and (110) interfaces by Broughton and Gilmer [3], (ii) the soft-sphere (r^{-12}) fcc (100) interface by Cape and Woodcock [4] and (iii) the r^{-12} fcc (111) interface by Tallon [5] are some of the works that are of particular relevance in the present context. Since the early simulation [6,7] work for hard spheres in 1968, there has been an upsurge of interest in the theoretical approaches for the study of solid-fluid transition process. An accurate and easy to handle microscopic theory for the freezing as well as crystal-melt interface has, however, still not been fully developed. Recently, density-functional theory [8] (DFT), a computationally simple and versatile approach applicable to many-electron quantum systems [9] as well as many-particle classical systems [10,11] has provided a rather easy means to describe the fluid-solid transition [11] not only for simple fluids but also for complex fluids [12] as well as quantum systems [13]. A wide variety of other problems, involving the equilibrium structure and thermodynamics of nonuniform as well as uniform fluids [10,14,15] can be investigated by DFT with great ease and a sophisticated level of accuracy.

In DFT, the grand potential of a many-particle system is treated as a functional of its single-particle density [16] and this functional assumes a minimum value for the true density. The exact functional form of the grand potential is, however, not known in general for an inhomogeneous density distribution, and therefore it is essential to find a suitable

approximation [17] for this density functional. The unknown part of the functional is, however, universal for a system of prescribed interparticle interaction and is independent of the external potential responsible for the inhomogeneity of the density distribution. For some systems, the exact functional form of this quantity for uniform density is known and this knowledge can be used to obtain approximations for the functionals for the corresponding nonuniform density distribution. The simplest among these approximate procedures is the perturbative approach [11,17,18], which involves a functional Taylor series expansion of the *excess* free energy around the homogeneous bulk density in powers of the density deviation. This expansion, however, involves all the higher-order correlation functions of the fluid and since the correlation functions beyond the two-particle direct correlation function (DCF) are not known in general, a truncation in second order is often necessary to implement this procedure in practical problems. To bypass the problem of truncation associated with the perturbative approach, nonperturbative approaches [19–21] that do not involve truncation but incorporate the two-particle DCF exactly and all the higher order correlation functions in an approximate manner have been developed. These nonperturbative procedures have been widely used for fluids involving short range (such as hard sphere) interactions [19–21] as well as ionic systems [14,15] with long range Coulomb interaction. In this approach, the free energy functional of the actual inhomogeneous system is obtained by evaluating the corresponding homogeneous fluid expression using an effective density. Curtin and Ashcroft [20] define the effective density as the weighted average of the actual density distribution of the inhomogeneous system and this is known as weighted density approximation (WDA), which, however, requires the determination of a spatially varying weighted density $\bar{\rho}(\mathbf{r})$ and hence is a computationally demanding approach. For this reason, its application to more complex systems has been somewhat restricted although it is highly successful in predicting the solid-fluid coexistence for hard sphere systems. To overcome this difficulty, a much simplified approach, known as the

modified weighted density approach (MWDA) has been proposed by Denton and Ashcroft [21]. This approach involves the determination of a spatially invariant weighted density and therefore significantly reduces the computational requirements in contrast to WDA. For the hard sphere bulk fluid-solid transition, predictions of both WDA and MWDA agree quite well with the simulation results.

Though there are several procedures to study the bulk solid-fluid transition, very few approaches to study the solid-melt interface have been reported so far. As in the case of bulk solid-fluid transition, both perturbative and nonperturbative approaches have been used to investigate the solid-melt interface. Earlier works on the solid-melt interface are largely based on the perturbative approach of Haymet and Oxtoby (HO) [18], which involves a functional Taylor series expansion truncated in second order in the density deviation and an additional square-gradient approximation for the variation of $\rho(\mathbf{r})$ through the interface. In this approach, a very broad interface has been predicted by Haymet and Oxtoby [18] that may be a consequence of using the truncated expression and the square-gradient approximation. These difficulties of the perturbative approach have inspired the development of alternative nonperturbative approximations to the *excess* free energy functional $F_{\text{ex}}[\rho(\mathbf{r})]$ and a suitable parametrization of the density distribution bypassing the square-gradient approximation. Curtin [22] was the first to extend their WDA approach for bulk solid-fluid transitions to the crystal-melt interface by a suitable flexible parametrization of the density, predicting the structure and energetics in fairly close agreement with the simulation results. Though this approach overcomes all the drawbacks associated with the HO approach, its computational requirements are very demanding as it involves the calculation of the weighted density $\bar{\rho}(\mathbf{r})$ as a function of \mathbf{r} . Encouraged by the success of MWDA in reducing the computational effort in the case of bulk fluid-solid transition, Marr and Gast [23] have introduced recently a planar weighted density approximation (PWDA) that involves the calculation of a one-dimensional weighted density $\bar{\rho}(z)$ in contrast to the calculation of a three-dimensional weighted density $\bar{\rho}(\mathbf{r})$ in Curtin's approach. This approach yields results quite similar to that of Curtin's WDA approach [22]. In both of these nonperturbative approaches, the calculation of the weight function involves numerical solution of a nonlinear differential equation. To overcome this difficulty and to further simplify the computational requirements we propose in this paper a layerwise MWDA approach, where the weighted density is constant within a layer, but changes from layer to layer i.e., every layer is associated with a constant weighted density. In this approach, the *excess* free energy of each of the layers is obtained by evaluating the homogeneous free energy expression with the weighted density of that layer and the total *excess* free energy of the interface is obtained as the sum of the free energies of all the layers. Thus, this approach involves the evaluation of only a few weighted density quantities in contrast to the PWDA, which requires the weighted density values to be evaluated at each mesh point in the z direction. We have applied the proposed layerwise MWDA based technique to calculate the density profile and the surface free energy of the crystal-melt interface of the hard sphere fluid. This paper is organized as follows. In Sec. II,

we review different nonperturbative weighted density based approaches along with our proposed approach. In Sec. III, the density parametrization and the application of our approach to the hard sphere system are presented. Finally results are discussed in Sec. IV along with a short concluding remark in Sec. V.

II. DENSITY-FUNCTIONAL THEORY

In DFT, the grand potential $\Omega[\rho]$ of a many-particle inhomogeneous system characterized by an external potential $u(\mathbf{r})$ is treated as a unique functional of the density distribution $\rho(\mathbf{r})$ and is expressed as

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r} [u(\mathbf{r}) - \mu] \rho(\mathbf{r}), \quad (1)$$

where μ is the chemical potential and $F[\rho]$, the intrinsic Helmholtz free energy functional, is a universal functional of density consisting of an *ideal-gas* contribution (F_{id}) and an *excess* free energy contribution (F_{ex}), viz.,

$$F[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho]. \quad (2)$$

The ideal-gas free energy functional ($F_{\text{id}}[\rho]$), which represents the free energy of the nonuniform system in the absence of internal interactions, can be explicitly expressed by the exact functional form

$$F_{\text{id}}[\rho] = \beta^{-1} \int d\mathbf{r} \rho(\mathbf{r}) \{ \ln[\rho(\mathbf{r}) \Lambda^3] - 1 \}, \quad (3)$$

where $\beta [= (k_B T)^{-1}]$ (k_B is the Boltzmann constant) represents the inverse temperature, and Λ denotes the thermal de Broglie wavelength. On the other hand, the excess free energy contribution (F_{ex}) arises due to interparticle interactions and the exact form of this functional is not known in general for an inhomogeneous density distribution. Various approximate schemes (perturbative as well as nonperturbative) have therefore been proposed for the calculation of $F_{\text{ex}}[\rho]$ and most of them make use of the knowledge of this functional or its derivative for specific systems of uniform density. The relevant nonperturbative approaches based on an effective weighted density prescription are discussed in the next subsection.

A. Weighted density approximation

Curtin and Ashcroft [20] have approximated the average (per particle) excess free energy of the inhomogeneous system locally by the excess free energy per particle of the corresponding homogeneous fluid (ψ_0) evaluated at some effective liquid density $\bar{\rho}(\mathbf{r})$ and the total excess free energy is then expressed as a sum of the local contributions, viz.,

$$F_{\text{ex}}^{\text{WDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi_0(\bar{\rho}(\mathbf{r})), \quad (4)$$

where the effective weighted density $\bar{\rho}(\mathbf{r})$ is a suitably chosen average of the actual inhomogeneous density distribution, defined as

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}(\mathbf{r})). \quad (5)$$

The weight function $w(|\mathbf{r}-\mathbf{r}'|)$ is normalized to unity to ensure the correct result at the uniform density limit and is uniquely determined by demanding that the approximated $F_{\text{ex}}[\rho]$ yields the correct two-particle direct correlation function in the homogeneous limit (bulk density ρ_0), viz.,

$$-\beta^{-1} c_0^{(2)}(|\mathbf{r}-\mathbf{r}'|; \rho_0) = \lim_{\rho \rightarrow \rho_0} \frac{\delta^2 F_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')}. \quad (6)$$

Using these two conditions, w is solved for readily in Fourier space and one obtains

$$-\beta^{-1} c_0^{(2)}(k; \rho_0) = 2\psi_0' w(k; \rho_0) + \rho_0 \frac{\partial}{\partial \rho_0} [\psi_0' w^2(\mathbf{k}; \rho_0)], \quad (7)$$

where the primes denote derivatives with respect to the density. Clearly, evaluation of $w(k; \rho_0)$ in this approach involves the solution of a nonlinear second order differential equation for each value of k .

B. Modified weighted density approximation

The MWDA of Denton and Ashcroft [21] has simplified and reduced the computational procedure drastically by approximating the global *excess* free energy per particle of the inhomogeneous system by the same for the homogeneous fluid evaluated at a spatially invariant effective density and expressing F_{ex} as

$$F_{\text{ex}}^{\text{MWDA}}[\rho] = N \psi_0(\bar{\rho}), \quad (8)$$

where N is the number of particles and the weighted density $\bar{\rho}$ is defined as

$$\bar{\rho} = \frac{1}{N} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}). \quad (9)$$

Demanding normalization and the condition defined by Eq. (6), w in Fourier space is obtained as

$$w(k; \rho_0) = -\frac{1}{2\psi_0'} [\beta^{-1} c_0^{(2)}(k; \rho_0) + \delta_{k,0} \rho_0 \psi_0'']. \quad (10)$$

The evaluation of $w(k; \rho_0)$ is thus much easier here as compared to the WDA procedure, since the expression is simple and explicit and no differential equation is to be solved.

C. Planar weighted density approximation

Curtin [22] has successfully applied WDA to the interfacial problem but with a significant computational effort as it involves the calculation of a three-dimensional weighted

density distribution $\bar{\rho}(\mathbf{r})$. On the other hand, although MWDA requires the evaluation of only one effective density quantity, and has been quite successful for the bulk solid, use of a single density parameter is unlikely to reproduce the interfacial properties properly. In an attempt to reduce the computational requirement associated with WDA, Marr and Gast [23] proposed a planar weighted density approximation, where they retained WDA only in the perpendicular z direction and employed MWDA in the x - y plane parallel to the interface. Thus, they defined a spatially varying one-dimensional weighted density, $\bar{\rho}(z)$ as

$$\bar{\rho}(z) = \frac{\int \int dx dy \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}(z))}{\int \int dx dy \rho(\mathbf{r})} \quad (11)$$

and proposed to obtain the *excess* free energy as

$$F_{\text{ex}}^{\text{PWDA}}[\rho] = \int d\mathbf{r} \hat{\rho}(z) \psi_0(\bar{\rho}(z)) \quad (12)$$

where the planar-averaged density $\hat{\rho}(z)$ is defined as

$$\hat{\rho}(z) = \frac{1}{A} \int \int dx dy \rho(\mathbf{r}) \quad (13)$$

with A denoting the interfacial area. Here also w is determined from the condition of normalization and the requirement on the limiting behavior [Eq. (6)]. In Fourier space w is obtained as the solution of the differential equation

$$-\beta^{-1} c_0^{(2)}(k; \rho_0) = 2\psi_0' w(k; \rho_0) + \delta_{k,0} \rho_0 \frac{\partial}{\partial \rho_0} [\psi_0' w^2(k; \rho_0)]. \quad (14)$$

In contrast to WDA, PWDA has reduced the computational requirements significantly as this procedure involves calculation of a one-dimensional weighted density instead of a three-dimensional one.

D. Layerwise modified weighted density approximation

Motivated by the success of the PWDA, we propose a method leading to its further simplification. In this approach, we follow PWDA and employ MWDA in the x - y plane but instead of using WDA in the z direction, we employ suitable coarse graining in the z direction. Thus we divide the region of inhomogeneous interface into different atomic layers and instead of only a single weighted density parameter as in the full MWDA, we have one density parameter for each layer and hence a total of n density parameters where n is the number of atomic layers in the interface region. This is considerable simplification as compared to PWDA, which involves $\bar{\rho}(z)$ and hence density parameters equal to the number of mesh points in the z direction. After evaluating a spatially invariant weighted density for each layer, the *excess* free energy contribution for a particular layer is calculated

from this weighted density and finally the total *excess* free energy is obtained as the sum of the individual contributions from all the layers of the interface. Thus, within this layerwise MWDA (LMWDA), the *excess* free energy is given by

$$F_{\text{ex}}^{\text{LMWDA}} = \sum_{i=1}^n N_i \psi_0(\bar{\rho}_i), \quad (15)$$

where N_i is the number of particles in the i th layer and $\bar{\rho}_i$, the weighted density of the i th layer, is defined as

$$\bar{\rho}_i = \frac{\int_{z_i}^{z_f} dz \int \int dx \, dy \, \rho(\mathbf{r}) \int d\mathbf{r}' \, \rho(\mathbf{r}') w(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}_i)}{\int_{z_i}^{z_f} dz \int \int dx \, dy \, \rho(\mathbf{r})}, \quad (16)$$

where z_i and z_f define the range of averaging (coarse graining) for the i th layer in the z direction. Since this scheme is similar to MWDA, we propose to employ the MWDA expression for the weight function.

III APPLICATION TO SOLID-FLUID INTERFACE

The conventional MWDA to DFT has been quite successful in predicting the bulk solid-fluid transition. In this approach, the solid phase with a periodically varying inhomogeneous density distribution is viewed as an effective uniform fluid of density $\bar{\rho}$, which is used in the *excess* free energy expression of the uniform system to obtain the *excess* free energy of the solid phase. Conventionally, the periodic inhomogeneous density distribution $\rho(\mathbf{r})$ of the solid phase is represented as a superposition of normalized Gaussians centered at each lattice site, viz.,

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\mathbf{R}} e^{-\alpha(\mathbf{r}-\mathbf{R})^2}, \quad (17)$$

which can also be rewritten in Fourier space as

$$\rho(\mathbf{r}) = \rho_s + \sum_{\mathbf{G} \neq 0} \rho_G e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (18)$$

where \mathbf{R} and \mathbf{G} represent the Bravais and reciprocal lattice vectors corresponding to the lattice structure of the solid and $\rho_G = \rho_s e^{-G^2/4\alpha}$ with ρ_s denoting the average bulk density of the solid phase. The parameter α is determined so as to minimize the total free energy of the solid phase. The solid-liquid phase coexistence is determined by equating the chemical potential and pressure of the two phases.

For the interface region, the density distribution is modeled by an expression that is a modification of Eq. (18) and has been originally suggested by Curtin [22] and employed by others [23]. Considering the z direction as perpendicular to the interfacial x - y plane, the density profile is assumed to be given by

$$\rho(\mathbf{r}) = \rho_l + (\rho_s - \rho_l) f_0(z) + \sum_{\mathbf{G}} \rho_G f_G(z) e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (19)$$

where

$$f_G(z) = \begin{cases} 1 & |z| < z_0 \\ \frac{1}{2} (1 + \cos[\pi(z-z_0)/\Delta z_G]) & z_0 < |z| < z_G \\ 0 & |z| > z_G, \end{cases} \quad (20)$$

where z_0 denotes the position of the solid-fluid interface boundary, $\Delta z_G = |z_G - z_0| = (G_1/G)^\nu \Delta z$, with G_1 being the magnitude of the smallest nonzero reciprocal lattice vector, Δz is the interface width and ν is a parameter. The function $f_0(z)$ is defined as $f_{G_1}(z)$. Clearly, Eq. (19) becomes identical to Eq. (18) inside the bulk solid phase ($|z| < z_0$) and yields the liquid density ρ_l in the bulk liquid region ($|z| > z_0 + \Delta z$). For the parametrized density given by Eq. (19), the planar averaged density $\hat{\rho}(z)$ as defined by Eq. (13) is given by

$$\hat{\rho}(z) = \rho_l + (\rho_s - \rho_l) f_0(z) + \sum_{\mathbf{G} \neq 0} \rho_G f_G(z) e^{iG_z z} \delta_{G_x,0} \delta_{G_y,0}. \quad (21)$$

Also using Eqs. (19) and (20) into Eq. (16), we obtain the final expression for the layerwise effective density for the interface given by

$$\begin{aligned} \bar{\rho}_i = & \frac{\rho_l}{n_z} \left[\rho_l (z_f - z_i) + (\rho_s - \rho_l) \int_{z_i}^{z_f} dz f_0(z) + \sum_{\mathbf{G} \neq 0} \delta_{G_x,0} \delta_{G_y,0} \rho_G f_G^{\text{res}}(G_z) \right] \\ & + \frac{1}{2\pi n_z} \left[\rho_l (\rho_s - \rho_l) \int dk w(k) f_0(-k) \left\{ \frac{\sin(kz_f) - \sin(kz_i)}{k} \right\} \right. \\ & + (\rho_s - \rho_l)^2 \int dk w(k) f_0(-k) f_0^{\text{res}}(-k) + (\rho_s - \rho_l) \int dk w(k) f_0(-k) \sum_{\mathbf{G} \neq 0} \delta_{G_x,0} \delta_{G_y,0} \rho_G f_G^{\text{res}}(G_z - k) \\ & + \rho_s \int dk w(k) \left\{ \frac{\sin(kz_f) - \sin(kz_i)}{k} \right\} \sum_{\mathbf{G} \neq 0} \delta_{G_x,0} \delta_{G_y,0} \rho_G f_G(G_z + k) \\ & \left. + \sum_{\mathbf{G} \neq 0} \sum_{\mathbf{G}' \neq 0} \delta_{G_x, -G'_x} \delta_{G_y, -G'_y} \rho_G \rho_{G'} \int dk w(\sqrt{G'^2 + k^2}) f_{G'}(k + G'_z) f_G^{\text{res}}(G_z - k) \right], \quad (22) \end{aligned}$$

where

$$n_z = \int_{z_i}^{z_f} dz \frac{1}{A} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \rho(\mathbf{r}), \quad (23)$$

$$f_0^{\text{res}}(k) = \int_{z_i}^{z_f} dz f_0(z) e^{ikz} \quad (24)$$

and

$$f_G^{\text{res}}(k) = \int_{z_i}^{z_f} dz f_G(z) e^{ikz}. \quad (25)$$

The system that we consider here is the hard sphere fluid and the interface chosen is along the (111) plane of fcc structure of the solid phase. The layerwise MWDA that we adopt essentially employs full MWDA in the x - y plane and an effective density is obtained for each layer in the z direction. The parameters z_i and z_f denoting the range of z for integration in Eq. (16) are clearly different for different layers and are chosen such that the layerwise MWDA for layers within the bulk solid phase region yields the same effective density as that obtained by full MWDA for the bulk solid. In view of the nature of the relation between the distance between the planes and the lattice constant for the fcc structure, it is found that for LMWDA corresponding to a particular layer of interest, the z integration range should cover three layers, which includes one adjacent layer on each side in addition to the concerned layer of interest.

The interfacial energy is obtained by calculating the *excess* grand potential $\Delta\Omega$ for various interfacial widths and finding the minimum with respect to Δz . Using the expression

$$\Delta\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \mu \int d\mathbf{r} \rho(\mathbf{r}) + PV \quad (26)$$

along with Eqs. (2) and (3) and LMWDA we obtain

$$\begin{aligned} \Delta\Omega[\rho(\mathbf{r})] = & F_{\text{ex}}^{\text{LMWDA}}[\rho(\mathbf{r})] + PV \\ & + \int d\mathbf{r} \rho(\mathbf{r}) [\beta^{-1} \{ \ln[\rho(\mathbf{r}) \Lambda^3] - 1 \} - \mu], \end{aligned} \quad (27)$$

where P , V , and μ represent pressure, volume, and chemical potential, respectively. Defining

$$(\hat{f}_{\text{id}})_i = \int_{z_i}^{z_f} dz \frac{1}{A} \int \int dx dy \rho(\mathbf{r}) \ln \rho(\mathbf{r}), \quad (28)$$

$$\hat{\mu} = \beta\mu - (\ln \Lambda^3 - 1) \quad (29)$$

and using Eq. (15), Eq. (27) can be written as

$$\frac{\beta\Delta\Omega}{A} = \sum_{i=1}^n n_i \beta\psi_0(\bar{\rho}_i) + \sum_{i=1}^n \hat{\mu} n_i + \sum_{i=1}^n (\hat{f}_{\text{id}})_i + \beta P \Delta z \quad (30)$$

the minimum of which with respect to Δz denotes the interfacial tension, γ , viz.,

$$\gamma = \left. \frac{\beta\Delta\Omega}{A} \right|_{\min}. \quad (31)$$

Here n_i denotes the number of particles per unit area in the i th layer. The chemical potential μ and the pressure P are calculated for the fluid phase using the expressions

$$\mu = \frac{\partial(\rho F[\rho]/N)}{\partial\rho} \quad (32)$$

and

$$P = \rho(\mu - F[\rho]/N) = \rho^2 \frac{\partial(F[\rho]/N)}{\partial\rho}. \quad (33)$$

IV. RESULTS AND DISCUSSION

In the present investigation, we have studied the structure of solid-fluid interface of the hard sphere fluid, with the interface chosen to be parallel to the (111) plane of the fcc lattice. The z coordinate defined in the perpendicular direction has been normalized in terms of the distance between the (111) planes, $\delta (= a/\sqrt{3})$, where $a [= (4/\rho_s)^{1/3}]$ denotes the fcc lattice constant. The density parametrization of Eqs. (19) and (20) used here is the same as that used by Curtin [22] as well as Marr and Gast [23], with the value of the parameter ν chosen to be the same as that used by Marr and Gast [23] and is equal to 0.25. In order to obtain the solid and fluid phase densities corresponding to the bulk fluid-solid transition, we first employ the present method to the bulk phases. Clearly in the solid phase, the density parametrization of Eqs. (19) and (20) becomes the same as Eq. (18). For a chosen value of ρ_s , the exponent α is determined by minimizing the solid phase free energy, where the excess free energy is evaluated through the present LMWDA. By evaluating the derivatives in Eqs. (32) and (33) numerically, the chemical potential μ_s and pressure P_s for the solid phase is obtained for different values of ρ_s . The bulk densities at the phase coexistence are predicted by equating μ_s and P_s with μ_l and P_l , respectively, for the liquid phase. Percus-Yevick expressions for the equation of state and the correlation functions have been employed throughout.

The bulk solid and fluid phase densities (dimensionless, i.e., in units of $1/\sigma^3$, where σ is the hard sphere diameter) obtained in this manner are $\rho_s = 1.033$ and $\rho_l = 0.911$, which are close to those from other WDA and PWDA based studies. The calculated values of P and μ using ρ_l in Eqs. (32) and (33) are 10.8546 and 15.4538, respectively. The layerwise weighted density $\bar{\rho}_i$ for each layer has been calculated for different values of the interfacial width Δz and the corresponding n_i values are also calculated. $\bar{\rho}_i$ clearly runs from the MWDA $\bar{\rho} (= 0.53477)$ in the bulk solid to $\rho_l (= 0.911)$ in the fluid region. The quantity $(\beta\Delta\Omega/A)$ is then calculated using Eq. (30) for different values of Δz and the results are plotted in Fig. 1. It is clear from the figure that the width of the interface as obtained from the minimum value of $(\beta\Delta\Omega/A)$ corresponds to 8–9 layers and the dimensionless surface free energy we obtain is $\gamma = 0.33$. Clearly the value of interfacial width obtained from the present approach is slightly larger than the same obtained from the earlier WDA and PWDA approaches using the same form of parametrized

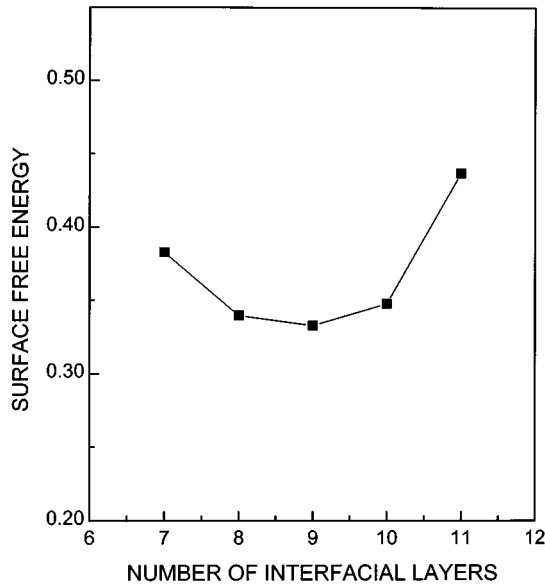


FIG. 1. Plot of calculated surface free energy vs number of interfacial layers for fcc liquid (111) interface of hard sphere fluid.

density. The value of the surface free energy γ is, however, smaller than those obtained by WDA and PWDA procedures (0.63 and 0.60, respectively). It may be noted that in this work we have proposed further simplification of the PWDA approach of Marr and Gast [23] and to have a proper comparison with their results, we have employed the same density parametrization. While alternative procedures involving free minimization using unconstrained density variation numerically as has been proposed recently [24] can also be attempted within the present LMWDA prescription, such a procedure will be highly computationally demanding. We have therefore restricted ourselves to the more simplified treatment using an analytical trial form for the density profile of the interface as has been used earlier [22,23]. It is, however, interesting to note that the predicted interfacial width and surface free energy obtained through the present ap-

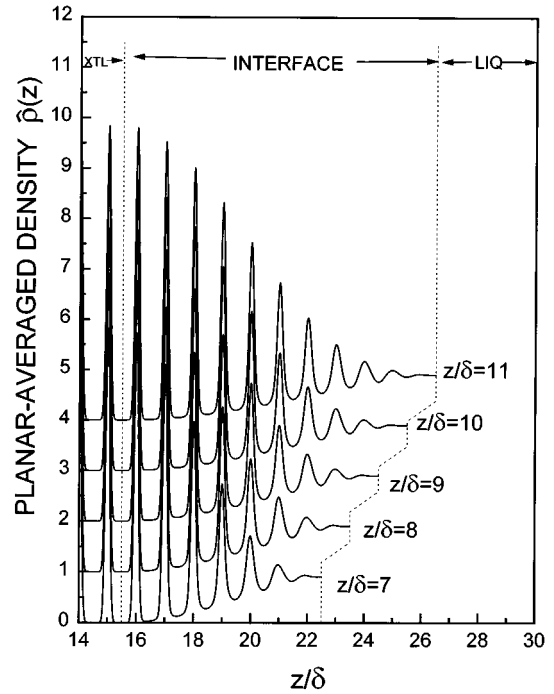


FIG. 2. Plot of planar averaged interfacial density profile $\hat{\rho}(z)$ for the (111) fcc liquid interface of hard sphere fluid for several values of interfacial width.

proach are quite close to the values $\Delta z \approx 8$ layers (7σ) typically and $\gamma = 0.26$ as obtained through the unconstrained *free* minimization. Since there are few complete simulation studies on the hard sphere interface, we are not able to compare our results with simulation. However, simulation results on the system with the r^{-12} potential are available and comparison with this result can be made as it resembles the hard sphere potential because of the steeply repulsive nature of the r^{-12} potential. The r^{-12} (111) interface studied by Tollan [4] consists of six to seven layers and hence our result matches quite well with this.

TABLE I. Layerwise weighted density, particle number, and contribution to excess free energy.

Δz	quantity	Layer number										
		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th
7	$\bar{\rho}_i$	0.5755	0.7458	0.8098	0.8456	0.9241	0.9280	0.9184				
	n_i	0.9381	0.9269	0.9067	0.8814	0.8562	0.8360	0.8236				
	$\psi_0 n_i$	1.8119	2.8112	3.2396	3.4510	4.1028	4.0464	3.8888				
8	$\bar{\rho}_i$	0.5674	0.7090	0.7684	0.8165	0.9193	0.9297	0.9191	0.9176			
	n_i	0.9377	0.9292	0.9133	0.8926	0.8702	0.8494	0.8334	0.8241			
	$\psi_0 n_i$	1.7708	2.5626	2.9355	3.2445	4.1180	4.1302	3.9425	3.8828			
9	$\bar{\rho}_i$	0.5614	0.6796	0.7330	0.7874	0.9085	0.9253	0.9173	0.9213	0.9166		
	n_i	0.9375	0.9307	0.9180	0.9008	0.8814	0.8618	0.8446	0.8317	0.8245		
	$\psi_0 n_i$	1.7407	2.2777	2.6939	3.0399	4.0566	4.1425	3.9766	3.9567	3.8748		
10	$\bar{\rho}_i$	0.5568	0.6563	0.7036	0.7598	0.8925	0.9150	0.9118	0.9255	0.9209	0.9154	
	n_i	0.9373	0.9318	0.9214	0.9071	0.8902	0.8725	0.8556	0.8412	0.8306	0.8247	
	$\psi_0 n_i$	1.7181	2.2392	2.5061	2.8517	3.9309	4.0831	3.9715	4.0456	3.9469	3.8637	
11	$\bar{\rho}_i$	0.5532	0.6379	0.6795	0.7346	0.8725	0.9000	0.9030	0.9277	0.9252	0.9178	0.9148
	n_i	0.9372	0.9327	0.9240	0.9118	0.8972	0.8813	0.8654	0.8508	0.8387	0.8296	0.8249
	$\psi_0 n_i$	1.7009	2.1340	2.3600	2.6868	3.7638	3.9678	3.9262	4.1149	4.0307	3.9115	3.8593

To obtain insight into the nature of the interface, we have plotted in Fig. 2 the planar averaged density $\hat{\rho}(z)$ as a function of Δz and also presented the calculated values of $\bar{\rho}_i$, n_i , and layerwise contribution to the *excess* free energy $n_i\psi_0(\bar{\rho}_i)$ for several values of Δz in Table I. From Fig. 2 it is clear that the structure of the first layer in each case resembles that of the bulk solid phase and becomes more solidlike with an increase in Δz . This is also reflected in the trend of the values of the weighted density $\bar{\rho}_i$ for the first layer, which are close to the effective density of the bulk MWDA result (0.53477) and approaches this result as Δz increases. The value of n_i for the first layer varies very slowly and approaches the bulk solid phase value $\rho_s\delta=0.9365$ with an increase in Δz .

From the plot in Fig. 2 it is clear that the density oscillation is damped as one moves along the interface towards the liquid phase. The values of n_i also decrease monotonically as one passes through the layers and n_i for the last layer is close to the bulk liquid result $\rho_l\delta=0.8259$ and approaches this value with increase in Δz . The values of $\bar{\rho}_i$ for the last layer, which is liquidlike, are close to the bulk liquid density $\rho_l=0.911$. In general, the values of $\bar{\rho}_i$ vary between the solid phase MWDA effective density and the bulk liquid density

across the layers for any particular Δz with minor oscillations in the values in different intermediate layers. It is also interesting to study the contributions of different layers towards the *excess* free energy $[\psi_0(\bar{\rho}_i)n_i]$ as shown in Table I, although no definite conclusion can be reached from its variation.

V. CONCLUDING REMARKS

In this work, we have presented a density-functional approach to study the fluid-solid interface. The approach provides a simplification of the PWDA approach proposed by Marr and Gast [23] recently since the number of the weighted density values to be evaluated has been reduced drastically as compared to the PWDA approach. Also as we are using the MWDA weight function, a solution of any differential equation is not involved for the calculation of the weight function. The results for the hard sphere fluid are quite encouraging and work on application to other systems [25,26] is in progress. Recent studies on the DFT of the crystal-melt interface in the context of nucleation and crystal growth [27] are also of interest.

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