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Fundamental-measure density functional theory study of the crystal-melt interface of the hard sphere system

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Two versions of the fundamental measure density functionals together with a new interfacial density profile parametrization were used to study the hard-sphere crystal-melt interface in the framework of the fundamental measure density functional theory. The equilibrium interfacial density profiles and interfacial free energies were found as a result of minimization of grand canonical potential of system with respect to parameters of density profile. We found that the average interfacial free energy is about 0.78, which is in reasonable agreement with simulation results.

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I. INTRODUCTION

Investigations of the interfaces between a crystal and its melt play an important role for the better understanding of the processes of crystal growth and melting. One of the key quantities of the crystal-melt interface is the interfacial free energy. Experimentally, this quantity can be extracted from nucleation data [1] or from experimentally measured Wulff shape of the crystal-melt system [2]. The former is based upon the classical nucleation theory and only the overall average of interfacial free energy can be obtained. The latter can yield anisotropy of the interfacial free energies, but so far only a few systems have been studied [3]. Thus efficient and accurate theoretical-computational methods will be valuable alternatives to provide reliable information on the crystal-melt interfaces.

The computational methods to study the thermodynamics and structures of the interface which accounts for the microscopic structure are molecular simulations, either Monte Carlo (MC) or molecular dynamics (MD) simulations. There are two main strategies to extract the interfacial free energies from molecular simulations. The first one is the cleaving potential method, which is based on the basic thermodynamic statement that the interfacial free energy is equal to the reversible work to create that interface [4–6]. The second one is the capillary wave method, which is based on the measurements of interfacial fluctuations, which is related to the interfacial stiffness that in turn yields the interfacial free energy [7–10]. These methods have been applied to various model systems, but the computational cost is still quite demanding. For the hard sphere system, it was found that the anisotropy in the interfacial free energies related to the different crystal surface orientations is weak and the average value is ~0.6 [5,10].

For the past two decades a number of density functional theories were developed for the investigation of the properties of the hard sphere system including the interfaces. From these theories, phase diagram, the equilibrium density profile of the interface, and the interfacial free energies have been obtained (see Ref. [11]). Furthermore, the thermodynamic properties of systems with soft interaction can be computed with the help of the hard sphere system together with the appropriate perturbative theories (see, for example, Refs. [12,13]).

For the density functional theory (DFT) study of interfacial properties the choice of interfacial density parametrization is crucial in addition to the choice of various versions of density functionals. The commonly used interfacial density parametrization is the two-parameter one proposed by Curtin [14] (which is based on a earlier form by Haymet *et al.* [15]). As it turns out the Curtin parametrization could become unphysical in some parameter region (see Sec. II). Another parametrization which includes more than 10^5 independent parameters was proposed [16], but the minimization for the interface free energy of such a large parameter space is computational very demanding.

As for the density functionals used, all the studies are based on earlier versions of DFT involving either the truncated expansion of the free energy [15,17,18] or more elaborated nonperturbation types of DFT such as weighted density approximation (WDA), modified weighted density approximation (MWDA), generalized effective liquid approximation (GELA) and their modifications [14,16,19–22]. The results of these works are not consistent with each other where the interfacial free energy falls in the range of 0.25–4.0 (see brief review Ref. [23] and Table II).

Based on some geometrical properties of the hard sphere system, a fundamentally different form of density functional, called fundamental measure (FM) DFT, was proposed [24]. With some modifications this functional is very successful to describe the different properties of hard sphere (HS) liquid, solid phases and their coexistence (for the recent review see Ref. [25]), although up to now the HS solid/liquid interface properties have not been explored yet.

The present work was undertaken to study the interfacial properties of the hard sphere system using the fundamental density functional. We have proposed a more physical parametrization of the interfacial density profile to overcome the drawbacks of previous methods. The resulting interfacial free energy is reasonably in agreement with simulation results.

The article is organized as the following. In Sec. II the fundamental measure DFT is briefly presented to make the paper self-contained. In Sec. III the coexistence properties of the bulk solid and liquid phases are calculated to pave the way for our presentation of interfacial free energy calculations. In Sec. IV the parametrization of the interfacial density profile are described. The results for the equilibrium density profiles and the interfacial free energies at various crystal orientations are obtained in Sec. IV.

II. FUNDAMENTAL MEASURE DENSITY FUNCTIONAL THEORY

In the framework of DFT the free energy F_{HS} of a HS system can be written as a functional of number density profile $\rho(\vec{r})$. It consists of two parts: the ideal gas contribution $F_{\mathrm{id}}[\rho]$ and the excess free energy $F_{\mathrm{ex}}[\rho]$ over the ideal-gas part

$$F_{\mathrm{HS}}[\rho(\vec{r})] = F_{\mathrm{id}}[\rho(\vec{r})] + F_{\mathrm{ex}}[\rho(\vec{r})], \tag{1}$$

where

$$F_{\mathrm{id}}[\rho(\vec{r})] = k_B T \int d\vec{r} \rho(\vec{r}) \{\ln[\rho(\vec{r})\Lambda^3] - 1\}, \tag{2}$$

and k_B is the Boltzmann constant, T temperature, and Λ de Broglie wavelength.

From the above functional the corresponding grand canonical potential functional Ω_{HS} may also be constructed

$$\Omega_{\mathrm{HS}}[\rho(\vec{r})] = F_{\mathrm{HS}}[\rho(\vec{r})] - \int d\vec{r} \mu \rho(\vec{r}) + \int d\vec{r} V_{\mathrm{ext}}(\vec{r}) \rho(\vec{r}), \tag{3}$$

where μ is the chemical potential of the system and $V_{\mathrm{ext}}(\vec{r})$ the potential of the external field acting on the system. The variational principle

$$\left. \frac{\delta \Omega_{\mathrm{HS}}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \right|_{\mu,T} = 0 \tag{4}$$

yields the equation for the equilibrium density profile in an external potential.

In the framework of Rosenfeld Fundamental Measure DFT the excess part of the free energy F_{ex} is expressed as a volume integration on the Rosenfeld functional Φ [24–28]

$$\beta F_{\mathrm{ex}} = \int d\vec{r} \Phi\{n_\alpha(\vec{r})\}. \tag{5}$$

The scalar n_2, n_3, vector $\vec{n}_{v_2}$, and tensor $\hat{n}$ weighted densities in this expression are given by the integral convolutions of the number density $\rho(\vec{r})$ with corresponding weight functions

$$n_\alpha(\vec{r}) = \int d\vec{r}\,' \rho(\vec{r}\,') \omega_\alpha(\vec{r} - \vec{r}\,'). \tag{6}$$

The weight functions ω_α in these expression were defined as

$$\omega_2(y) = \delta\left(\frac{\sigma}{2} - y\right), \quad \omega_3(y) = \Theta\left(\frac{\sigma}{2} - y\right), \tag{7}$$

$$\vec{\omega}_{v_2}(\vec{y}) = \vec{e}_y \delta\left(\frac{\sigma}{2} - y\right), \quad \hat{\omega}_{jk}(\vec{y}) = \vec{e}_j \vec{e}_k \delta\left(\frac{\sigma}{2} - y\right). \tag{8}$$

Here $\vec{e}_y$ is a unit vector along the $\vec{y}$ direction and σ is the diameter of the hard sphere, $\delta(r)$ the Dirac delta-function, $\Theta(r)$ the Heaviside step function, $\vec{\omega}_{v_2}$ and $\hat{\omega}_{jk}$ are the vector and tensor weight functions, respectively.

Among different approximations for the Rosenfeld functional Φ, we chose the two which successfully describe the liquid, solid phases, and their coexistence. The first version [26] (denoted as V2PY version) is independent of the tensor weighted densities

$$\Phi^{(\mathrm{V2PY})} = -\frac{n_2}{\pi\sigma^2}\ln(1-n_3) + \frac{n_2^2 - n_{v_2}^2}{2\pi\sigma(1-n_3)} + \frac{(n_2^2 - n_{v_2}^2)^3}{24\pi n_2^3}\frac{1}{(1-n_3)^2} \tag{9}$$

and in the homogeneous density limit reduces to the Percus-Yevick (PY) free energy expression. Another version (T2CS) [27,28] is also a functional of tensor densities

$$\Phi^{(\mathrm{T2CS})} = -\frac{n_2}{\pi\sigma^2}\ln(1-n_3) + \frac{n_2^2 - n_{v_2}^2}{2\pi\sigma(1-n_3)} + \frac{1}{8\pi n_3^2}\left(\frac{n_3}{(1-n_3)^2} + \ln(1-n_3)\right)\{\vec{n}_{v_2}\hat{n}\vec{n}_{v_2} - n_2\vec{n}_{v_2}^2 - \mathrm{tr}(\hat{n}^3) + n_2\mathrm{tr}(\hat{n}^2)\}, \tag{10}$$

which in the homogeneous density limit gives the Carnahan-Starling (CS) free energy. It is known that the CS expression is more accurate to describe the HS liquid free energy as compared to the Percus-Yevick one, whereas the PY-based FM DFT functionals are more accurate to describe the HS solid properties (see discussion in Ref. [28]).

III. HS SOLID AND LIQUID PHASES COEXISTENCE

To study the interfacial properties, we first need to outline the coexistence conditions under the functionals used. Below we briefly describe the necessary ingredients for the calculation of the coexistence conditions using the functionals given by Eqs. (9) and (10) (more details of the calculations are available in Refs. [13,26–28]).

The fcc solid phase lattice parameter is $a = (4/\rho)^{1/3}$, where ρ is the number density in the bulk solid $\left[\rho = \frac{1}{V}\int_V \rho_s(\vec{r}) dV\right]$. The density profile $\rho_s(\vec{r})$ in the bulk solid can be accurately parametrized by a sum of Gaussian density distributions around the solid lattice sites $\{\vec{R}\}$

$$\rho_s(\vec{r}) = \sum_i \rho_\Delta(\vec{r} - \vec{R}_i) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_i e^{-\alpha(\vec{r} - \vec{R}_i)^2}, \tag{11}$$

where α is the width of the Gaussian distribution. The weighted densities can be written as a sum of the corresponding contributions from different lattice sites

TABLE I. HS fcc solid-liquid coexisting parameters; ρ_l and ρ_s are the liquid and solid densities, $L=(3/\alpha)^{1/2}/a$ the Lindemann ratio, P pressure at coexistence. Results of MC simulation are taken from Ref. [29].

	ρ_l	ρ_s	L	P
T2CS	0.934	1.023	0.133	11.29
V2PY	0.937	1.020	0.113	12.26
MC	0.943	1.041	0.129	11.7

$$n_\alpha(\vec{r}) = \sum_i n_\Delta^{(\alpha)}(\vec{r} - \vec{R}_i). \tag{12}$$

All the weighted densities $n_\Delta^{(\alpha)}(\vec{r})$ can be found in analytical forms [13,30]. For a given bulk density ρ the value of free energy $F[\alpha;\rho]$ can be calculated as a function of the Gaussian parameter α. The minimum of $F[\alpha;\rho]$ with respect to α gives the equilibrium value of free energy $F[\rho]$ and equilibrium value of parameter α. The dependence of the FM DFT solid free energy on the bulk density ρ was found to be in a good agreement with the result of MC simulations. The knowledge of the functional dependence of free energy F on the bulk density ρ in the solid and liquid phases allows to compute the coexisting conditions between the solid and the liquid phases. The results are given in Table I. It is shown that both versions of FM free energy functional agree well with simulation results, except that T2CS version provides slightly better Lindemann ratio (together with the Gaussian parameter α) at coexistence.

IV. HARD SPHERE CRYSTAL/MELT INTERFACE

Now let us consider the interface between the coexisting HS bulk solid and liquid. In the interfacial region the properties of bulk solid are smoothly transformed to the properties of the bulk liquid. The interfacial free energy is defined as

$$\gamma = \frac{\Omega(\mu,T) - \Omega_{\text{bulk}}(\mu,T)}{A} = \frac{\Omega + PV}{A}, \tag{13}$$

where Ω is the grand canonical potential in the system with the interface, $\Omega_{\text{bulk}}=\Omega_{\text{solid}}=\Omega_{\text{liquid}}$ is the grand canonical potential of the equilibrium solid and liquid phases (in the bulk $\Omega=-PV$, P is the coexistence pressure, V the volume of the system), A the area of the interface. To calculate the interfacial grand canonical potential Ω an appropriate interfacial density parametrization is needed.

In the literature, a widely used method to parameterize the density profile of the interface is [14]

$$\rho(\vec{r}) = \rho_l + (\rho_s - \rho_l) f_0(z) + \sum_{G\neq 0} \rho_G f_G(z) e^{i\vec{G}\cdot\vec{r}}, \tag{14}$$

where

TABLE II. The density functional theory results for the hard-sphere solid-liquid interfacial free energy with the interfacial density profile parametrized by Eqs. (14)–(17).

Authors	Year	Method	$\gamma\sigma^2/k_BT$
Curtin [14]	1989	WDA	0.63–66
Marr, Gast [20]	1993	PWDA	0.60
Kyrlidis, Brown [21]	1995	PGELA	0.25–0.37
Choudhury, Ghosh [22]	1998	MWDA	0.33

$$f_G(z) = \begin{cases} 1, & |z| \leq z_0, \\ \frac{1}{2}\left[1 + \cos\left(\pi\frac{(z - z_0)}{\Delta z_G}\right)\right], & z_0 < |z| \leq z_G, \\ 0, & z_G < |z|, \end{cases} \tag{15}$$

$$\Delta z_G = |z_G - z_0| = \left(\frac{G_1}{G}\right)^{\nu} \Delta z \ (\Delta z_0 = \Delta z), \tag{16}$$

$$0 \leq \nu \leq 1, \ G \geq G_1. \tag{17}$$

Here z is the coordinate in the perpendicular direction to the interface, $\vec{G}$ is a reciprocal lattice vector, G its magnitude, G_1 the magnitude of the smallest nonzero reciprocal lattice vector. The parameter Δz is the width of the interface and the parameter ν controls the rate of broadening of the solid density peaks. The interface is located in the region $[z_0;z_0+\Delta z]$; for $z<z_0$ the density profile reduces to the density profile in the bulk solid $\rho_s(\vec{r})=\rho_s+\Sigma_{G\neq 0}\rho_G e^{i\vec{G}\cdot\vec{r}}$ written with reciprocal lattice vectors; for $z>z_g=z_0+\Delta z$ it gives the homogeneous density in the bulk liquid ρ_l. To calculate the interfacial free energy some authors used this parametrization together with the different types of DFT. Table II summarizes these results. It is seen that the results for the interfacial free energy differ from each other for various types of DFT used.

We also started with this interfacial density profile parametrization together with the fundamental measure DFT. All the corresponding weighted densities in the interface n_2, n_3, $\vec{n}_{v_2}$, and $\hat{n}$ were computed analytically (except for the regions $[z_0-\sigma/2;z_0+\sigma/2]$ and $[z_g-\sigma/2;z_g+\sigma/2]$ where the weighted densities were reduced to the one dimensional integrals). For various ν and Δz we did not find the global minimum for the interfacial free energy γ. For example, for every given Δz with increasing ν from $\nu=0$ to $\nu=1$ the γ just gradually decreases even to some negative value for big ν.

There is also another problem with the density parametrization of Eqs. (14)–(17). It is known that an important condition for the HS system is the non-overlapping of hard spheres [16,31–33]. In the integral form this condition can be written as

$$\int d^3r' \Theta\left(\frac{\sigma}{2} - |\vec{r} - \vec{r}'|\right)\rho(\vec{r}') \leq 1, \tag{18}$$

which gives restrictions on the values of the weighted density n_3 [Eqs. (6) and (7)]

$$n_3(r) \leqslant 1. \tag{19}$$

For previous DFT approximations (such as WDA, MWDA, GELA) the condition of Eq. (18) is not intrinsic to the functional, although an attempt to adopt constrained MWDA that satisfies this condition was undertaken [31]. In the framework of the fundamental measure DFT, which is based on some geometrical properties of hard spheres [34], the condition of the nonoverlapping of hard spheres is automatically accounted for by the special form of the free energy functional Φ, where the condition $n_3 \geqslant 1$ leads to divergent functional Φ in Eqs. (9) and (10). We have observed that for some small values of Δz and big values of ν at some points of the interface the local packing fraction n_3 is larger than 1, which indicates the unphysical nature of this density profile parametrization. This unphysical behavior can also been seen from the following argument. For $\nu=0$ the density profile can be shown to be

$$\rho(\vec{r}) = \rho_l[1 - f_0(z)] + f_0(z)\rho_s(\vec{r}). \tag{20}$$

It can be easily seen that the density profile is a mixing of a bulk liquid density ρ_l and a solid density profile $\rho_s(\vec{r})$, which under certain conditions will leads to overlapping hard spheres, i.e., $n_3 \geqslant 1$.

To avoid the abovementioned difficulties with the parametrization Eqs. (14)–(17) we introduced a new parametrization of the density profile. The main feature of this parametrization is that the fcc lattice structure now is spread all over the system and the density profile of the whole system may be written in a similar way to the one in the bulk solid, but with different widths

$$\rho(\vec{r}) = \sum_{\vec{R}} \left(\frac{\alpha(\vec{R})}{\pi} \right)^{3/2} e^{-\alpha(\vec{R})(\vec{r} - \vec{R})^2}, \tag{21}$$

now the Gaussian parameter α depends on the site position $\vec{R}$. Let the interface be in perpendicular to the z direction. For the lattice sites at the bulk solid ($z < z_0$) the Gaussian parameter $\alpha = \alpha(\vec{R})$ equals to α_s, the equilibrium Gaussian width of the coexistence solid phase. For the ones in the bulk liquid ($z > z_0 + \Delta z$) the parameter α should be small enough to provide the sum of the widely overlapping Gaussians to be equal to the uniform density distribution (we chose $\alpha_l = 1$). For the interfacial region between the bulk solid and liquid ($z_0 < z < z_0 + \Delta z$) there are N layers of lattice sites whose equilibrium values of the Gaussian parameters $\{\alpha_i\}_{i=1}^N$ can be found by minimizing the interfacial free energy. The Gaussian parameters $\alpha_i$within the same layer are the same and the parameters change from layer to layer in the interfacial region with the obvious restriction $\alpha_s \geqslant \alpha_1 \geqslant \alpha_2 \geqslant \cdots \geqslant \alpha_N \geqslant \alpha_l$. Thus, the values of α_i and $\alpha(\vec{R})$ are related by

$$\alpha(\vec{R}) = \begin{cases} \alpha_s, & R_{z,i} \leqslant z_0 \\ \alpha_i, & z_0 < R_{z,i} < z_0 + \Delta z, \\ \alpha_l = 1, & R_{z,i} < z_0 + \Delta z, \end{cases}$$

where $R_{z,i}$ is projection of the lattice vector of the i shell on the z axis.

In addition, the fcc solid lattice spacing a_s in the plane of the interface (i.e., along the x and y axis) is fixed to be

$$a_{x,i} = a_{y,i} = a_s = (4/\rho_s)^{1/3}, \tag{22}$$

whereas in the perpendicular direction to the interface (along the z-axis direction) it increases from $a_s = (4/\rho_s)^{1/3}$ at $z < z_0$ to $a_l = 4/(\rho_l a_s^2)$ at $z > z_0 + \Delta z$. Such choice of a_l provides the value of the homogeneous density at $z > z_0 + \Delta z$ to be equal to the coexisting liquid density ρ_l. The lattice parameter in the transition area is chosen to be equal to

$$a_{z,i}(\vec{R}) = 4/[\rho_{sm}(\vec{R})a_s^2], \tag{23}$$

where $\rho_{sm}(z)$ is some smoothed density profile in the interface region which may be parametrized by an expression with hyperbolic tangent (other reasonable function forms give the same results)

$$\rho_{sm}(z) = \rho_l + (\rho_s - \rho_l)\begin{cases} 1, & |z| \leqslant z_0, \\ \frac{1}{2}\left[1 - \tanh\left(\frac{6(z - z_0 - \Delta z/2)}{\Delta z}\right)\right], & z_0 < |z| \leqslant z_0 + \Delta z. \\ 0, & z_0 + \Delta z < z. \end{cases} \tag{24}$$

In the bulk fcc crystal lattice the distance d between layers along different crystal orientations are $d_{110} = a/2\sqrt{2}$, $d_{100} = a/2$, $d_{111} = a/\sqrt{3}$ ($d_{110} < d_{100} < d_{111}$). In this lattice (110) is more densely packed, but the most densely packed plane is (111). Extending this to the whole system (bulk solid +interfacial region+bulk liquid) we can write the interlayer spacing d_i along the normal direction to the interface (along the z axis) as

$$d_i^{(100)} = \frac{a_{z,i}}{2},\ d_i^{(110)} = \frac{a_{z,i}}{2\sqrt{2}},\ d_i^{(111)} = \frac{a_{z,i}}{\sqrt{3}}. \tag{25}$$

For a given crystal direction the distance between layers, $\Delta R_{z,i} = d_i$, increases with the increasing z from the bulk solid ($z < z_0$) to bulk liquid ($z > z_0 + \Delta z$). The width of the transition region Δz is

TABLE III. The results for the HS solid-liquid surface tension (in the units of k_BT/σ^2) for the different crystal interface orientations obtained by MD (Davidchak and Laird [5]), MC (Mu, Houk and Song [10]) simulations, WDA DFT (Ohnesorge, Lowen, Wagner [16]) and also the results of the present work with T2CS and V2PY versions of FM free energy density functional.

	MD	MC	DFT	T2CS	V2PY
γ_{100}	0.62±0.01	0.64±0.02	0.35	0.79	0.68
γ_{110}	0.64±0.01	0.62±0.02	0.30	0.89	0.84
γ_{111}	0.58±0.01	0.61±0.02	0.26	0.87	0.82
γ	0.61±0.01	0.62±0.02	0.30	0.85	0.78

$$\Delta z = \sum_{i=1}^{N} d_i. \tag{26}$$

Finally, to find the values of lattice parameter $a_{z,i}$ in the transition region a set of Eqs. (23)–(26) are solved by the iterations.

With the above interfacial density parametrization, all weighted densities can be written conveniently a sums of the contributions from different lattice sites. Moreover every contribution can be given by an analytical expression.

To find the grand canonical potential Ω [Eq. (3)] incorporated into the expression for the interfacial free energy γ [Eq. (13)] the three-dimensional volume integral can be calculated numerically. To reduce the volume of integration a simplex of the integration volume can be found by taking into account the symmetry of the system. This simplex is chosen to be a prism with its rib along the z direction and its base being a triangle in the x-y plane. The equation of this triangle is for (100) orientation $0 \leqslant x \leqslant \frac{a_s}{4}$, $y < x$ and $\frac{a_s}{4} \leqslant x \leqslant \frac{a_s}{2}$, $y < \frac{a_s}{2} - x$, and its area $A = \frac{a_s^2}{16}$; for (110) orientation: $0 \leqslant x \leqslant \frac{a_s}{2\sqrt{2}}$ and $0 \leqslant y \leqslant \frac{a_s}{2}$, $A = \frac{a_s^2}{4\sqrt{2}}$; for (111) orientation: $0 \leqslant x \leqslant \frac{a_s}{2\sqrt{2}}$ and $-\frac{x}{\sqrt{3}} \leqslant y \leqslant \frac{x}{\sqrt{3}}$, $A = \frac{a_s^2}{8\sqrt{3}}$.

Now for a given crystal orientation, the number of variational parameters N and every set of Gaussian parameters in transition region $\{\alpha_i\}_{i=1}^{N}$, $\gamma(\alpha_1, \ldots, \alpha_N)$ can be calculated numerically. To minimize γ with respect to $\{\alpha_i\}$s we used the numerical downhill simplex method in multidimensions [35].

We performed the minimization of functional γ with different numbers of layers $N \geqslant 2$. It was found that with the increasing of the number N the equilibrium γ decreases until it reaches a limiting value for $N \gtrsim 17$. The obtained results of the interfacial free energy for T2CS and V2PY versions of FM free energy functional are compared in Table III with the results of MD [5] and MC [10] simulations and also DFT of Ref. [16]. Reference [16] used the WDA functional but with the interfacial density profile parametrized by almost 1 million independent parameters and at the same time, the condition Eq. (18) was taken into account. It can be seen that the average interfacial energy γ obtained in Ref. [16] is two times smaller than the one obtained from simulations, whereas the γ obtained at the present study overestimates by 37% (T2CS version) or 26% (V2PY version).

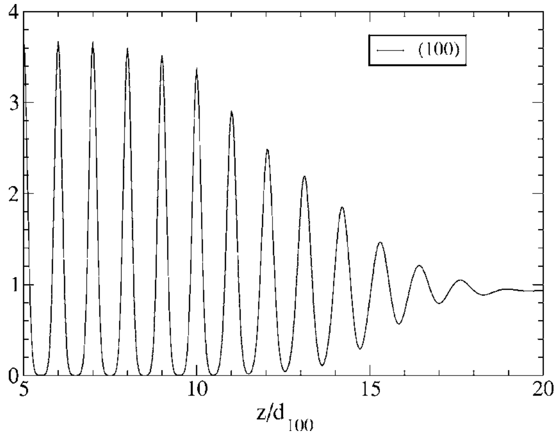

FIG. 1. The interfacial density profile $\rho(z)$ as a function of z/d_{100} for the (100) direction. As a small change in the initial part of the interfacial density profile will be accumulated over the whole profile, thus a direct comparison with simulation results is not illuminating. We did compare the overall features of our density profile with simulations [37] and they are consistent with each other for the three directions computed here.

It should be noted that γ_{100} overestimates the simulation results by only 10% (V2PY version). The reason that the V2PY version of FM DFT provides better agreement with the simulation results than the T2CS version may be explained as the following. From the discussion in Ref. [28] it may be concluded that the versions of FM DFT based on the PY approximation provides a better description of the HS crystal, whereas the ones based on CS approximation are more accurate for the HS fluid. In our model solid/liquid interfacial system, all the system is considered to be the solidlike, with the atoms located at the sites of model solid lattice. The density profile in such solidlike system has the form of a sum of Gaussian distributions around these solid lattice sites, with the Gaussian parameter α decreases and lattice parameter a increases toward the bulk liquid side. It seems that according to the discussions in Ref. [28] a PY version will be indeed a better choice than the CS one for such system. In Ref. [28] the tensor version of Rosenfeld functional T2PY is provided, which gives rather crude coexisting densities $\rho_s = 0.985$ and $\rho_l = 0.892$. So it seems that the vector version V2PY of Ref. [24] provides the best choice for the calculation of the interfacial free energy in the framework of the present solidlike model.

The result for the equilibrium interfacial planar averaged density profile $\rho(z) = \frac{1}{A}\int\int dx dy \rho(\vec{r})$ are shown in Fig. 1 for the 100 crystal orientation. The obtained width of interface may be estimated as approximately 7–9 interfacial layers for all the orientations, which is in line with the results of MC [21], MD simulations [36,37], although the WDA DFT [16] provides slightly narrower interface. The other crystal orientations gives similar agreements between our calculation and the simulations.

V. CONCLUSIONS

We applied the fundamental measure density functional theory to study the interface between coexisting hard sphere liquid and its fcc solid. The minimization of the interfacial free energy using earlier interfacial parametrization of the density profile [14] was found to give nonphysical configurations of the interfacial density.

As a result a more physical parametrization of the density profile was introduced and the minimization of the interfacial free energy provides good equilibrium density profile in the interfacial region. The resulting interfacial free energy has an average value of $\gamma = 0.78$ (V2PY version). The interfacial free energies along different crystal directions are also calculated. We found 26% difference between the interfacial free energy obtained in the present study and the one obtained by the MC and MD simulations [5,10]; it seems that the anisotropy could not be resolved reliably from the current density function formulation.

The fact that the obtained values for the interfacial free energy γ overestimate the simulation ones means that there is enough "room" to continue the minimization. Indeed it seems that for more flexible parametrization or for larger number of the minimization parameters the minimization of the grand canonical functional may decrease the result for γ further. The increasing the number of minimization parameters may be achieved with introducing the tensor values of parameter $\{\alpha\}$s in the interface rather the scalar ones. Another possibility is to utilize as the minimization parameters the values of the interlayer interfacial distances $\{a_z\}$s rather than using the parametrization (23) and (24). However, it should be noted here that the increasing of the numbers of minimization parameters makes the numerical computation more extensive.

Applications of the present strategy to various model systems where simulation results are known [9,38] should be interesting. From such calculations we may have a better error estimate of the density functional approach to interfacial free energies. The power of the present approach may lie in the applications to the interfaces of multicomponent systems, where computer simulations are much more computational intensive.

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