

Local thermodynamic mapping for effective liquid density-functional theory

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The structural-mapping approximation introduced by Lutsko and Baus [Phys. Rev. A **41**, 6647 (1990)] in the generalized effective-liquid approximation is extended to include a local thermodynamic mapping based on a spatially dependent effective density for approximating the solid phase in terms of the uniform liquid. This latter approximation, called the local generalized effective-liquid approximation (LGELA) yields excellent predictions for the free energy of hard-sphere solids and for the conditions of coexistence of a hard-sphere fcc solid with a liquid. Moreover, the predicted free energy remains single valued for calculations with more loosely packed crystalline structures, such as the diamond lattice. The spatial dependence of the weighted density makes the LGELA useful in the study of inhomogeneous solids.

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I. INTRODUCTION

The accurate description of the structure and the thermodynamic properties of inhomogeneous liquids and solids has been the goal of density-functional methods of classical systems that have been developed in the last decade. The progress made by this research and its application to the study of a variety of systems has been described in several review articles [1–3].

The most recent developments are approximations to the local or global excess free energy constructed from a thermodynamic mapping of the excess free energy per particle of the inhomogeneous system to that of a uniform liquid with an effective *weighted* density. Spatially uniform or *global* thermodynamic-mapping methods have been introduced in the modified weighted-density approximation (MWDA) of Denton and Ashcroft [4] and the generalized effective-liquid approximation (GELA) of Lutsko and Baus [5], and provide computationally efficient and accurate descriptions of uniformly spatially periodic hard-sphere solids. The application of the MWDA and the GELA to systems with more realistic interatomic potentials is hindered by shortcomings of the global thermodynamic mapping, which are discussed in detail in Ref. [6]. It is not clear, however, how useful these methods are in the description of inhomogeneous solid regions, such as the melt-solid interface, where the system's symmetries vary from the periodic solid structure to the uniform liquid. These details of the interfacial region are lost with the *global* thermodynamic mapping. The need is evident for accurate spatially dependent or *local* thermodynamic-mapping approximations.

The most recent class of local thermodynamic-mapping approximations is based on nonlocal density approximations for the excess free energy formed by introducing spatially varying weighted densities. The approximation of Tarazona [7] and the weighted-density approximation (WDA) of Curtin and Ashcroft [8] are widely known, and have yielded accurate predictions in the study of wetting transitions near hard walls [9] and the

melt-solid interfaces of hard-sphere and Lennard-Jones systems [10].

In this paper, we present an extension of the GELA of Lutsko and Baus [5] that incorporates a spatially varying weighted density. This extension, called the local generalized effective-liquid approximation (LGELA), is demonstrated to predict very accurately the free energies of hard-sphere solids. This is not surprising, since it reproduces the structural mapping of GELA. Our aim is to study the melt-solid interface of diamond crystal materials like silicon. Therefore, the effect of this lattice structure on the weighted density is also investigated. An accurate description of the structure of the melt-solid interface requires a flexible, multiparameter functional approximation of the density variation. It is important that this functional predict a *unique* value of free energy as a function of the weighted density. It is shown that LGELA has this property but that WDA does not.

II. LOCAL GENERALIZED EFFECTIVE-LIQUID APPROXIMATION

The objective of density-functional theories of inhomogeneous liquids is to predict the Helmholtz free energy F of the system at an inverse temperature $\beta \equiv 1/kT$ and density $\rho \equiv N/V$. The free energy is decomposed as

$$F \equiv F_{\text{id}} + F_{\text{ex}} + F_{\text{ext}}, \quad (1)$$

where F_{id} is the ideal-gas free energy, F_{ex} is the excess free energy, and F_{ext} is the contribution due to the presence of an external potential. For uniform systems, each contribution is a *function* of the density ρ . For inhomogeneous systems there is a functional dependence on the spatially varying density $\rho(\mathbf{r})$, as is evident in the expression for the ideal-gas contribution

$$F_{\text{id}}[\rho] = \beta^{-1} \int d\mathbf{r} \rho(\mathbf{r}) [\ln \Lambda^3 \rho(\mathbf{r}) - 1], \quad (2)$$

where Λ is the thermal wavelength.

The excess free energy is easily found, for a uniform

liquid, from an equation of state. For inhomogeneous systems the excess free energy has to be approximated, and this is typically done by assuming that

$$F_{\text{ex}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi(\mathbf{r}; [\rho]), \quad (3)$$

where $\psi(\mathbf{r}; [\rho])$ is an as yet unspecified functional of the density $\rho(\mathbf{r})$. In most approaches for the description of solids, the effects of the external field are assumed to be incorporated in the symmetries that are inherent in the functional representation of $\rho(\mathbf{r})$, and are neglected in the thermodynamic limit [5].

Typically, the unknown functional $\psi(\mathbf{r}; [\rho])$ is approximated by a *local* thermodynamic mapping of the form

$$\psi(\mathbf{r}; [\rho]) = f_0(\bar{\rho}(\mathbf{r}; [\rho])) \quad (4)$$

that transforms the approximate free energy per particle of the inhomogeneous system to the excess free energy per particle f_0 of a uniform system with an effective *weighted* density $\bar{\rho}(\mathbf{r})$. The excess free energy of the inhomogeneous system is

$$F_{\text{ex}} = \int d\mathbf{r} \rho(\mathbf{r}) f_0(\bar{\rho}(\mathbf{r}; [\rho])). \quad (5)$$

A closure approximation is necessary for the evaluation of the unknown local effective density $\bar{\rho}(\mathbf{r})$. Several approximations have been used that have varying degrees of complexity [7,8]. The most accurate closure approximation has been the WDA, introduced by Curtin and Ashcroft [8]. In the WDA the weighted density $\bar{\rho}(\mathbf{r})$ is computed by requiring that the structure of a uniform liquid be represented exactly by the theory in the limit of this uniform state. This requires

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

where $c^{(2)}(r)$ is the direct-correlation function of a uniform liquid.

Lutsko and Baus have shown recently [5] that because $F_{\text{ex}}[\rho]$ is the generating functional of the successive direct-correlation functions, an exact expression for $F_{\text{ex}}[\rho]$ may be derived by functional integration in density space of the two-body direct-correlation function (DCF). This approach is valuable because the two-body DCF is relatively well characterized. Because of the uniqueness of the free-energy functional [11], any path in density space should yield the same result. Using a linear path linking the inhomogeneous system to a reference system of zero density, Lutsko and Baus derived the expression

$$\beta F_{\text{ex},s} = - \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda (1-\lambda) \rho(\mathbf{r}) \rho(\mathbf{r}') \times c^{(2)}(\mathbf{r}, \mathbf{r}'; [\lambda \rho]), \quad (7)$$

where $c^{(2)}(\mathbf{r}, \mathbf{r}')$ is the unknown DCF of the inhomogeneous system. In the GELA, Lutsko and Baus approximated the density-weighted DCF of the inhomogeneous sys-

tem by the density-weighted DCF of a homogeneous system with effective density $\hat{\rho}$. They also later assumed that $\hat{\rho}$ was the same effective density required by the global thermodynamic mapping. We adopt the approach of Lutsko and Baus and introduce the same closure approximation for the spatially varying weighted density $\bar{\rho}(\mathbf{r})$:

$$\int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') c^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho]) = \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') c_0^{(2)}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}(\mathbf{r})). \quad (8)$$

Using Eq. (8), Eq. (7) is reduced to

$$\beta F_{\text{ex},s} = - \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda (1-\lambda) \rho(\mathbf{r}) \rho(\mathbf{r}') \times c^{(2)}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}(\mathbf{r}; [\lambda \rho])). \quad (9)$$

Comparing Eq. (9) to the local thermodynamic-mapping expression, Eq. (5) leads to the integral equation for the local effective density $\bar{\rho}(\mathbf{r})$

$$\beta f_0(\bar{\rho}(\mathbf{r}; [\rho])) = - \int d\mathbf{r}' \int_0^1 d\lambda (1-\lambda) \rho(\mathbf{r}') \times c^{(2)}(|\mathbf{r}-\mathbf{r}'|; \bar{\rho}(\mathbf{r}; [\lambda \rho])). \quad (10)$$

Equation (10) is the spatially varying extension of GELA that we refer to as LGELA.

LGELA is more flexible than GELA because it can be applied to both homogeneous and inhomogeneous solid systems. However, for the study of idealized solids it is computationally more demanding because Eq. (10) must be solved many times within the unit cell of the crystalline lattice.

III. RESULTS

A. Application to solids

The solid is described as a sum of Gaussian functions centered on the lattice sites

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi} \right)^{3/2} \sum_{\mathbf{R}} \exp[-\alpha |\mathbf{r}-\mathbf{R}|^2], \quad (11)$$

where α is the inverse width of the Gaussian function and is a measure of the localization of the solid structure. The density is conveniently written in the Fourier-series representation

$$\rho(\mathbf{r}) = \frac{\rho}{2} \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) [1 + \exp(-i\mathbf{k} \cdot \mathbf{t})], \quad (12)$$

where $\{\mathbf{k}\}$ is the set of reciprocal-lattice vectors (RLV's) of the fcc crystal lattice, and $\hat{\rho}_{\mathbf{k}} \equiv \exp(-k^2/4\alpha)$. The parametrization (12) is convenient because it describes both the fcc and the diamond lattice. For the fcc lattice $\mathbf{t}=\mathbf{0}$. The diamond lattice is a superposition of two interpenetrating fcc lattices separated by $\mathbf{t}=(a/4)(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})$, where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are the unit vectors and a is the side of the cubic unit cell. Substituting Eq. (12) into Eq. (10) yields the residual equation for LGELA,

$$\mathcal{R}(\bar{\rho}(\mathbf{r})) = 0 = \beta f_0(\bar{\rho}(\mathbf{r})) - \frac{\rho}{2} \sum_{\mathbf{k}} e^{-(k^2/4\alpha)} \exp(i\mathbf{k} \cdot \mathbf{r}) [1 + \exp(-i\mathbf{k} \cdot \mathbf{t})] \int_0^1 d\lambda (1-\lambda) c^{(2)}(k; \bar{\rho}(\mathbf{r}; [\lambda \rho])). \quad (13)$$

TABLE I. Comparison of fcc hard-sphere solid free energies per particle predicted by several density-functional approximations to MC results at various solid densities.

$\rho\sigma^3$	WDA [10]	MWDA [4]	GELA [5]	LGELA (PY)	LGELA (CS)	MC [8]
1.000	4.449	4.412	4.544	4.599	4.572	4.661
1.025	4.674	4.629	4.809	4.865	4.840	4.868
1.050	4.908	4.853	5.083	5.139	5.115	5.099
1.075	5.155	5.090	5.368	5.425	5.401	5.354
1.100	5.422	5.347	5.666	5.724	5.701	5.663

Calculations are performed using a total of 1067 RLV's. The properties of the uniform hard-sphere liquid are evaluated using the Percus-Yevick (PY) approximation [12]. In some computations the Carnahan-Starling (CS) equation of state [12] and a direct-correlation function based on it [13] are applied. All uniform-liquid free energies are calculated from the CS equation of state [12].

The nonlinear integral equation (13) is solved using the technique described by Lutsko and Baus [5] to transform it to a set of algebraic equations, and using Newton's method, at a given solid density ρ and degree of localization α . The derivatives of the residual equations with respect to $\bar{\rho}(\mathbf{r})$ required at each Newton's iteration are computed by finite differences. Convergence is usually obtained within 3 to 5 iterations.

All integrals over the unit cell have been computed using Gaussian quadrature. For the fcc lattice, symmetry arguments allow us to truncate the domain of integration as $0 \leq x \leq a/2$, $0 \leq y \leq a/2$, and $0 \leq z \leq a/2$. Between 12 and 16 Gauss points per spatial dimension are necessary for convergence of the integrals in the fcc lattice. For the diamond lattice these symmetry arguments do not hold, and integration over the entire unit cell is required; in the cases studied here, 25 Gauss points per dimension were used.

The spatial variations of the weighted densities predicted by the LGELA and the WDA along the [100] direction of a unit cell of a hard-sphere solid with density $\rho\sigma^3 = 1.0$ are compared in Fig. 1 for various localizations. Both calculations exhibit the same behavior: lower values occur at the lattice sites, and higher values occur in the interstitial regions. The LGELA predicts larger values of $\bar{\rho}(\mathbf{r})$ than the WDA in the interstitial regions, but this has no effect on the accuracy of the free-energy predictions because the local free energies per particle in Eq. (5) are weighted by the density.

At each density ρ the total free energy is computed from Eq. (1) and is minimized with respect to the locali-

zation parameter α . The free energies per particle predicted from the LGELA for fcc hard-sphere solids with density in the range $1.0 \leq \rho\sigma^3 \leq 1.1$ are listed in Table I. Results are shown for the LGELA using both the Percus-Yevick and the Carnahan-Starling equations of state. These results are compared to the predictions of WDA, MWDA, and GELA and to the results of Monte Carlo (MC) simulations. Overall, the LGELA (CS) yields the best predictions over this range of densities. The maximum deviation between the LGELA (CS) and the MC calculations is about -2% at the density $\rho\sigma^3 = 1.0$. Both the WDA and the MWDA underpredict the solid free energies by approximately 5%. It is interesting to note that both approximations (WDA and LGELA) based on a local thermodynamic mapping predict higher free energies than the methods (MWDA and GELA) that are based on a global thermodynamic mapping.

B. Solid-liquid coexistence

The free energies of both phases as a function of density are given by the canonical-ensemble calculations described in the previous section. The variation with density of the fcc solid free energy per unit volume predicted by the LGELA and the GELA is compared to the variation for a hard-sphere liquid in Fig. 2. The solid becomes stable with respect to the liquid at densities $\rho_s\sigma^3 > 1.0$. The conditions of thermodynamic coexistence of a fcc hard-sphere solid and a hard-sphere liquid are

$$\mu_{\text{sol}}(\rho_s) = \mu_{\text{liq}}(\rho_l), \quad (14a)$$

$$\omega_{\text{sol}}(\rho_s) = \omega_{\text{liq}}(\rho_l), \quad (14b)$$

where μ is the chemical potential and ω is the grand po-

TABLE II. Comparison of coexistence properties predicted by the LGELA and GELA to MC simulations [5], where $\Delta\rho = \rho_s - \rho_l$, $L = (3/\alpha a^2)^{1/2}$ is the Lindemann factor, $P = \beta p \sigma^3$ is the pressure, and $\Delta s_f = (s_l - s_s)/k$ is the entropy change per particle.

Model	$\rho_s\sigma^3$	$\rho_l\sigma^3$	$\Delta\rho/\rho_s$	L	P	Δs_f
MC [5]	1.04	0.94	0.094	0.126	11.7	1.16
LGELA (PY)	1.054	0.956	0.093	0.091	12.5	1.21
LGELA (CS)	1.047	0.952	0.091	0.097	12.2	1.17
GELA [5]	1.041	0.945	0.092	0.100	11.9	1.15

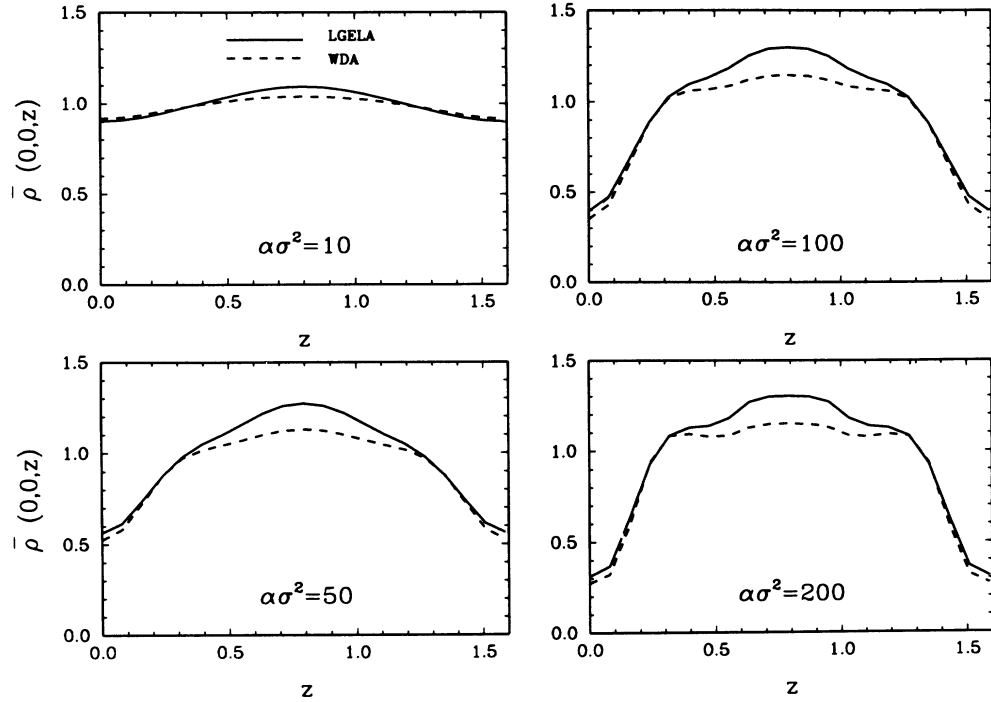


FIG. 1. Comparison of LGELA (—) and WDA (---) weighted density profiles along the [100] direction in the unit cell of fcc hard spheres ($\rho\sigma^3=1.0$) at various degrees of localization $\alpha\sigma^2$.

tential per unit volume.

The study of coexistence is performed in terms of the grand canonical ensemble, where the chemical potential and the grand potential are computed from the free energies as

$$\mu(\rho) = \frac{\partial}{\partial \rho} \left[\frac{F}{V} \right], \quad (15a)$$

$$\omega(\rho) = \frac{F}{V} - \rho\mu. \quad (15b)$$

The conditions of fcc solid-liquid coexistence predicted by the LGELA and the GELA are presented in Table II and compared to MC-simulation predictions. The LGELA does not perform as well as the GELA in this comparison. It overpredicts the solid and liquid densities at coexistence, the pressure P , and the entropy change per particle Δs_f . Also, it underpredicts the value of the Lindemann parameter L . Introducing the CS equation of state significantly improves the predictions. Moreover, the overall performance of the LGELA is a dramatic improvement over the WDA, which was the most accurate approximation based on a local thermodynamic mapping.

C. Diamond-lattice predictions

As we discussed in Ref. [6], the hard-sphere system can be used as a reference state in thermodynamic perturbation expansion for materials modeled by more realistic potentials. These materials do not necessarily crystallize in the densely packed fcc structure. In particular, silicon crystallizes in the diamond lattice. Even though we do not expect the diamond lattice to be either a relatively or globally stable structure for hard spheres, it is important

to be able to predict values of the “free energy” at solid-like values of the localization parameter α in a variational calculation. In this context the values of the functional $F[\rho]$ are not global minima and hence are not true free energies [11]. We demonstrated in [6] using computational nonlinear analysis techniques that MWDA introduces folds in the values of $F[\rho]$ in parameter space, which lead to loss of existence of the weighted density for loosely packed hard-sphere solids.

The variations of the LGELA and the WDA weighted-densities along the [100] direction of the unit

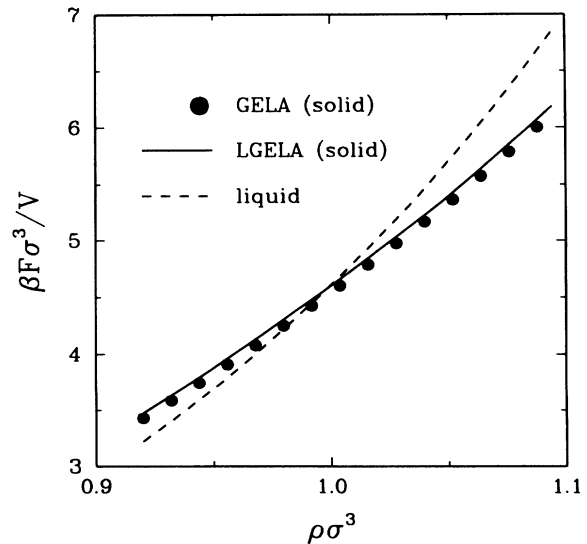


FIG. 2. Helmholtz free energy per unit volume ($\beta F\sigma^3/V$) vs density ($\rho\sigma^3$) for locally stable solid and liquid hard spheres.

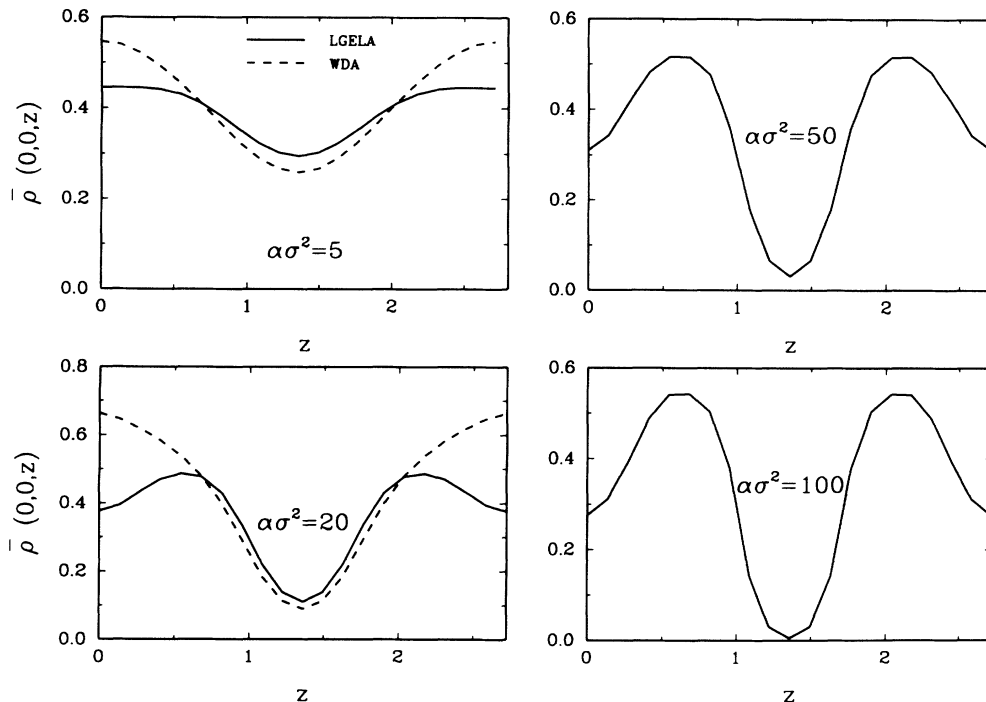


FIG. 3. Comparison of LGELA (—) and WDA (---) weighted density profiles along the [100] direction in the unit cell of diamond-lattice hard spheres ($\rho\sigma^3=0.4$) at various degrees of localization $\alpha\sigma^2$.

cell of the diamond lattice are presented in Fig. 3 for various values of the localization parameter α . In contrast with the results for the fcc lattice, the predictions of the two approximations for the diamond structure differ dramatically. In particular, for $\alpha\sigma^2 > 20$ the WDA does not predict bounded values for $\bar{\rho}(\mathbf{r})$. The LGELA continues to predict single-valued and bounded results for $\bar{\rho}(\mathbf{r})$, even for very localized solid structures. The predictions of the “free energy” of a diamond-lattice hard-sphere solid with density $\rho\sigma^3=0.4$ given by the GELA and the LGELA are compared in Fig. 4 to the “free energies” of an fcc crystal at the same density. Both approximations yield similar predictions that are consistently higher than the fcc free energies. Of course, at this low density, the entropic cost of the solid structure is very large, and the uniform liquid is always the stable state. Unfortunately, the accuracy of these predictions cannot be tested because there are no known MC simulations for diamond-lattice hard spheres. Even if such simulations were available, it would be very hard to compute free energies since there is no locally stable hard-sphere solid with the diamond-lattice structure. The accuracy of the predictions will be tested indirectly when they are used to predict solid free energies for silicon in a thermodynamic perturbation calculation.

IV. SUMMARY

Excellent predictions for the free energy of hard-sphere solids have been obtained by implementing the structural mapping introduced by Lutsko and Baus [5] in a local thermodynamic-mapping density-functional approximation. The predictions of the LGELA free energy of uni-

form hard-sphere solids approximately reproduce MC predictions over a broad range of densities. The LGELA extension of the GELA provides a framework for the study of inhomogeneous solids, where hopefully the functional will retain its accuracy. The LGELA functional is an improvement over the WDA, since it remains single valued and well behaved in all cases studied, particularly in the case of loosely packed crystalline structures such as the diamond lattice. These calculations are reference

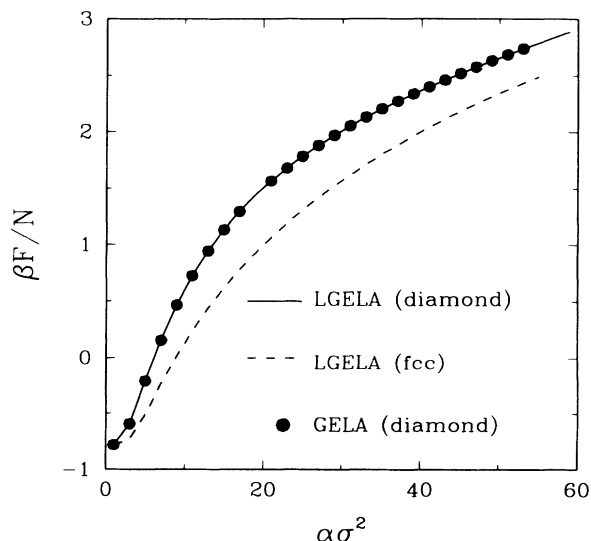


FIG. 4. Comparison of predictions of the GELA and the LGELA for the “free energy” per particle of a diamond-lattice hard-sphere solid of density $\rho\sigma^3=0.4$ as a function of $\alpha\sigma^2$. The dashed line corresponds to the LGELA predictions for fcc hard spheres at the same density.

states for thermodynamic perturbation expansions used to predict the free energies of other solids with more realistic potentials. This good behavior makes the LGELA a promising free-energy functional for the investigation of generalized inhomogeneous solid parametrizations.

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