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Orientational dependence of the interfacial tension in the adhesive-sphere system

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We examine the orientational dependence of the solid-fluid interfacial free energy γ in the adhesive-sphere system. In the hard-sphere, or infinite temperature, limit the interfacial tension is nearly isotropic with $\gamma\sigma^2/kT \sim 0.66 \pm 0.02$. As the strength of the attractive interaction in this model increases, γ increases and the interface narrows, yet these values show little variation with fcc low-index interface orientation. We also examine the higher-index fcc (211) and (311) interfaces and find that they remain stable over the entire range of attraction strengths investigated, indicating, but not verifying, a nonfaceted structure.

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I. INTRODUCTION

The adhesive-sphere model developed by Baxter [1] has become an important theoretical system for studying the influence of attractive strength on liquid and solid state properties. This is due not only to the relative simplicity of the model, but also to the rich phase behavior it exhibits, including both fluid-fluid [2] and fluid-solid equilibrium [3–6], as well as percolation behavior [7,8] at high concentration. The versatility of this model is evident by its ability to describe the behavior of experimental systems such as colloidal silica grafted with octadecyl groups in a number of nonaqueous solvents [9]. These dispersions can be made to crystallize or gel at very high volume fractions depending on the choice of solvent or temperature. The similarity between the adhesive-sphere and hard-sphere models has led to analytic expressions for the liquid state properties [1,10] as a function of density and strength of attraction. The interaction potential $u(r)$ is described as

$$u(r)/kT = \lim_{\sigma' \to \sigma} \begin{cases} \infty, & 0 < r < \sigma' \\ \ln\left[\frac{12\tau(\sigma-\sigma')}{\sigma}\right], & \sigma' < r < \sigma \\ 0, & \sigma < r, \end{cases} \quad (1)$$

where σ is the hard-sphere diameter and τ is a dimensionless measure of the temperature. This equation reduces to the hard-sphere interaction in the $\tau^{-1} \to 0$ limit.

Since the liquid state properties are available in analytic form, this model is an ideal choice for studies, such as investigations of the interface, that are limited by their computational requirements. We have developed a density-functional approach known as the planar weighted density approximation (PWDA) designed to lower computational requirements for interfacial studies sufficiently to make investigation of model systems such as hard spheres practical [11]. We used the adhesive-sphere model and the PWDA [5] to investigate the influence of interaction strength on both the structure and energy of the interface between crystalline and amorphous phases. In that work we limited ourselves to the densest plane between liquid and equilibrium crystal, the fcc (111) plane. The question arises as to whether the other low-index planes show the same behavior and whether one should expect anisotropy as the temperature is lowered in a model attractive system.

There has been relatively little investigation of the orientational dependence of interfacial properties in solid-fluid model systems because of the tremendous computational requirements of traditional interface approaches. Using density-functional theory and the weighted density approximation (WDA), Curtin [12] examined the hard-sphere solid-fluid interface and found a nearly isotropic surface free energy of $\gamma_{100}^{\mathrm{WDA}}\sigma^2/kT = 0.66 \pm 0.02$ and $\gamma_{111}^{\mathrm{WDA}}\sigma^2/kT = 0.63 \pm 0.02$. Our planar-averaged approach has been applied to another density-functional formulation developed initially as the generalized effective liquid approximation (GELA) [13] and later modified as LGELA [14]. This approach, known as PGELA, when applied to the hard-sphere interface by Kyrlidis and Brown [15], shows significant anisotropy with $\gamma_{100}^{\mathrm{PGELA}}\sigma^2/kT = 0.28$, $\gamma_{111}^{\mathrm{PGELA}}\sigma^2/kT = 0.30$, and $\gamma_{110}^{\mathrm{PGELA}}\sigma^2/kT = 0.25$. Another approach due to Ohnesorge, Löwen, and Wagner [16] begins with the WDA but adds a minimization of the lattice variational parameters. These workers find $\gamma_{100}^{\mathrm{OLW}}\sigma^2/kT = 0.35$, $\gamma_{111}^{\mathrm{OLW}}\sigma^2/kT = 0.26$, and $\gamma_{110}^{\mathrm{OLW}}\sigma^2/kT = 0.30$, also showing large anisotropy but relative magnitudes different than those seen with the PGELA. The only other density-functional study we are aware of is due to McMullen and Oxtoby [17] who found a significantly higher, but isotropic, interfacial free energy of $\gamma\sigma^2/kT = 1.7$. For comparison to these theoretical predictions the only

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simulation study available includes attractions and is the molecular dynamics investigation of Broughton and Gilmer [18]. These authors studied the interfacial free energy in the Lennard-Jones system and found that the crystal-melt interface at the triple point was nearly isotropic with $\gamma^{lj}_{111}\sigma^2_{lj}/\epsilon = 0.35 \pm 0.02$, $\gamma^{lj}_{100}\sigma^2_{lj}/\epsilon = 0.34 \pm 0.02$, and $\gamma^{lj}_{110}\sigma^2_{lj}/\epsilon = 0.36 \pm 0.02$, where ϵ is the well depth and σ_{lj} the separation where the potential equals zero.

One may expect, *a priori*, little orientational dependence of the interfacial tension in hard spheres because of its entropic nature [19]. It is clear from the studies presented above, however, that there is little consensus not only on the variation of the interfacial tension with orientation but also on its absolute magnitude, properties that both strongly influence the equilibrium crystal structure. From the work of Wulff [20] we know that the relative values of the interfacial tension determine the crystal shape, including facet size and stability. The absolute magnitude of the interfacial tension, on the other hand, is closely related to the roughening transition. This transition describes that temperature at which thermal motion overcomes interfacial energetics and induces a formerly faceted crystal structure to roughen; crystals grown at temperatures below the roughening transition are faceted while those grown at higher temperatures are not [21].

It is interesting, at this point, to present a crude estimate of the state of roughening in the hard-sphere system. One can estimate this point in the model of Jackson by equating thermal energy to the energetic cost of creating an isolated lattice as $kT = \gamma a^2$ [22], where a is the lattice constant. Rearranging would suggest $\gamma\sigma^2/kT < (a/\sigma)^2$ as the criterion for the existence of a rough interface ($\gamma\sigma^2/kT < 0.4$ for the hard-sphere system). This crude estimate falls in the center of the various predictions for γ_{hs} and near the experimental estimate of 0.55 [23]. From this, it would appear that in the hard-sphere limit, the system may or may not be roughened.

One additional feature of an interface above the roughening transition is that the interfacial width should diverge [21]. As we have seen in the density-functional work, however, the interfacial free energy in the hard-sphere system has a well-defined minimum, indicating that the hard-sphere system is nonroughened. From this we may therefore expect faceted crystals in both the adhesive-sphere system and its hard-sphere limit; however, the values we predict for γ_{hs} are relatively close to the estimated transition value. One may need to increase the attractive strength significantly, with its corresponding increase in the interfacial tension [5], in order to observe a faceted interface. How, and if, this transition will be manifest in the relative values of the interfacial tension for the various interfaces is the subject of this investigation.

II. THE PWDA

Briefly, the PWDA is a means of estimating the excess free energy in any inhomogeneous system. It is aimed, however, specifically at systems whose bulk density varies in one dimension such as found at the solid-fluid interface. We approximate the excess free energy as the sum of local free energies estimated with the fluid excess free energy per particle ψ_0 evaluated at a planar weighted density $\overline{\rho}$,

$$F_{\mathrm{ex}}^{\mathrm{PWDA}}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\psi_0(\overline{\rho}(z)) \tag{2}$$

with

$$\overline{\rho}(z) \equiv \frac{\int dxdy\rho(\mathbf{r}) \int d\mathbf{r}'\rho(\mathbf{r}')w(\mathbf{r}-\mathbf{r}';\overline{\rho}(z))}{\int dxdy\rho(\mathbf{r})}. \tag{3}$$

Requiring the weighting function to be normalized and the two particle direct correlation function c_0 to be recovered in the homogeneous limit through

$$-c_0(\mathbf{r}-\mathbf{r}';\rho_0) = \lim_{\rho\to\rho_0} \frac{\delta^2 F_{\mathrm{ex}}/kT}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \tag{4}$$

determines the excess free energy. We refer the reader to previous publications [5,11] for solution details. What remains now is a means of expressing the density distribution through the solid-fluid interface. We follow Curtin [12] who defined

$$\rho(\mathbf{r}) = \rho_l + (\rho_s - \rho_l)f_0(z) + \sum_G \rho_s f_G(z) e^{i\mathbf{G}\cdot\mathbf{r} - G^2/4\alpha}, \tag{5}$$

where

$$f_G(z) = \begin{cases} 1, & |z| < z_0 \\ \frac{1}{2}[1+\cos(\pi\frac{z-z_0}{\Delta z_G})], & z_0 < |z| < z_G \\ 0, & z_G < |z|. \end{cases} \tag{6}$$

$\mathbf{G}$ are the reciprocal lattice vectors, z_0 is the position of the solid-fluid interface boundary, Δz is the interface width, α is the particle localization, $f_0(z) = f_{G_1}(z)$, and $\Delta z_G = (G_1/G)^\nu \Delta z$. This allows us to specify an interfacial profile dependent on the width Δz and the Fourier decay parameter ν. The excess grand potential can be expressed as

$$\Delta\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \mu \int d\mathbf{r}\rho(\mathbf{r}) + PV \tag{7}$$

and must be minimized to find the equilibrium interfacial energy and profile. To do this correctly we must minimize $\Delta\Omega$ with respect to both ν and Δz for a given τ.

III. RESULTS AND DISCUSSION

We use the adhesive-sphere model system to study the influence of attractions on interfacial properties by first examining the hard-sphere limit. We then gradually increase the attractive strength and calculate the structure and energy of the resulting equilibrium interfaces. Previous studies [5,24,25] have shown that the fcc lattice is the lowest energy crystal structure and we will therefore look at various interfaces between this lattice and its coexisting equilibrium fluid.

In Fig. 1 we show the results of our calculations for the hard-sphere limit at $\nu = 0.0$. The most apparent feature is the similarity of the minima for the different interfaces despite the difference in their structure. The minima all occur at a value of approximately 0.8 kT/σ^2 and at approximately three lattice planes for the fcc (111) interface and five lattice planes for the fcc (110) interface. Since the distance between planes δ is significantly different for the different interfaces, this suggests that we should renormalize the data by the fcc lattice parameter $a = (4/\rho_s)^{1/3}$ in order to properly compare their behavior. We show the renormalized data in Fig. 2 where the free energies of the various interfaces condense to a single curve. This behavior is observed at all values of ν studied and indicates the strong dependence of the interfacial free energy on interface width and the complete lack of dependence on low-index orientation in the hard-sphere system. In Fig. 3 we show the ν and Δz dependence of the excess grand potential. After minimizing with respect to both Δz and ν we find for the interfacial tension in the hard-sphere ($\tau^{-1} = 0$) system values of $\gamma_{111}\sigma^2/kT = 0.70 \pm 0.01$, $\gamma_{100}\sigma^2/kT = 0.70 \pm 0.01$, and $\gamma_{110}\sigma^2/kT = 0.70 \pm 0.01$.

We save significant computational effort in our calculations by using the MWDA [26] to determine the bulk phase properties required as input in determining interfacial properties. To check the validity of this approach, we have calculated bulk properties in the hard-sphere system using each low-index interface and the PWDA and find that all values for the coexisting densities agree within 0.5%. When these bulk values from the PWDA are now used to determine interfacial energetics we find the slightly different, and predictably lower, values of $\gamma_{111}^{\mathrm{PWDA}}\sigma^2/kT = 0.68 \pm 0.01$, $\gamma_{100}^{\mathrm{PWDA}}\sigma^2/kT = 0.65 \pm 0.01$, and $\gamma_{110}^{\mathrm{PWDA}}\sigma^2/kT = 0.66 \pm 0.01$. The slight anisotropy shown here likely arises from the small differences in the coexisting bulk properties determined for the various orientations; however, the agreement is nonetheless quite good and justifies the use of the MWDA in subsequent calculations.

As we gradually increase the strength of attraction in the system by lowering τ, we observe a broadening in the density gap between coexisting phases. This translates into both an increase in the interfacial free energies and a decrease in the thickness of all the interfaces studied as summarized in Table I. The surface free energies are nearly identical as τ is decreased but begin to show a small amount of anisotropy under conditions of the strongest attractions studied. The origin of this anisotropy remains unclear as it does not appear to directly correlate with the surface density ϱ, where $\varrho_{111} = 4/\sqrt{3}a^2$, $\varrho_{100} = 2/a^2$, and $\varrho_{110} = \sqrt{2}/a^2$. One thing to note is that the lowest tension corresponds to that interface with the highest surface density suggesting the importance of interplanar interactions in determining interfacial tension. Unfortunately, we were unable to extend the calculation to lower τ to determine whether this anisotropy would become more pronounced.

We show in Fig. 4 the calculated interfacial free energies as a function of τ and a prediction due to Turnbull [28], who found that one could correlate γ with the latent heat per unit area. We see that the agreement between our calculated interfacial tensions and the predictions due to this empiricism is quite good, particularly in the hard-sphere limit. As τ decreases, however, this

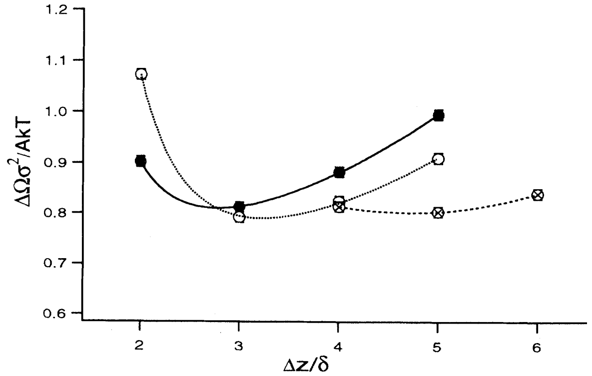

FIG. 1. Excess grand potential as a function of interfacial width at $\tau = \infty$ and $\nu = 0.0$ [●, fcc (111) interface with $\delta_{111} = a/\sqrt{3}$; ○, fcc (100) interface with $\delta_{100} = a/2$; ⊗, fcc (110) interface with $\delta_{110} = a/\sqrt{8}$].

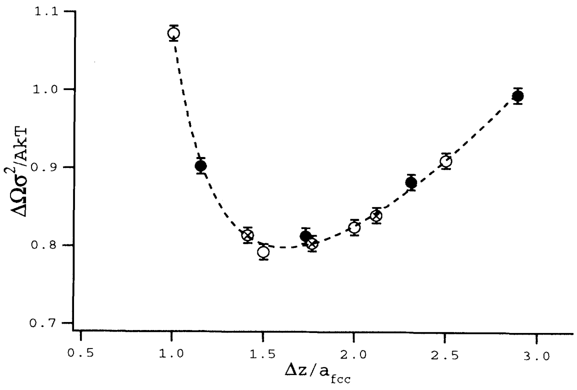

FIG. 2. Data of Fig. 1 now normalized on the fcc lattice parameter a.

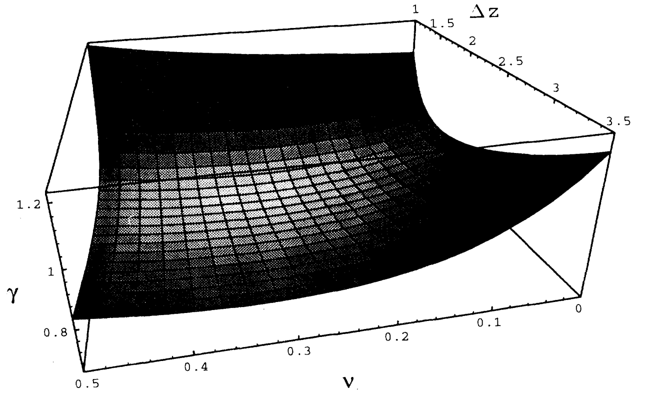

FIG. 3. The excess grand potential shown vs the interface width Δz and the Fourier decay parameter ν in the hard sphere ($\tau \to \infty$) limit. Note the shallow minimum.

TABLE I. Interfacial tensions γ and widths Δz for the low-index crystal face orientations at various adhesive-sphere strengths τ.

τ	$\gamma_{111}^{\rm PWDA}\sigma^2/kT$	$\gamma_{110}^{\rm PWDA}\sigma^2/kT$	$\gamma_{100}^{\rm PWDA}\sigma^2/kT$	$\Delta z/a$	ν
∞	0.70 ±0.01	0.70 ±0.01	0.70 ±0.01	1.95 ±0.05	0.33 ±0.01
3	0.79 ±0.01	0.80 ±0.01	0.79 ±0.01	1.80 ±0.05	0.26 ±0.01
2	0.91 ±0.01	0.92 ±0.01	0.92 ±0.01	1.60 ±0.05	0.21 ±0.01
1.7 [27]	1.01 ±0.01	1.02 ±0.01	1.03 ±0.01	1.43 ±0.05	0.16 ±0.01
1.5 [27]	1.05 ±0.01	1.07 ±0.01	1.09 ±0.01	1.30 ±0.05	0.13 ±0.01

agreement worsens and anisotropy in the interfacial free energy develops as noted above. These both occur at approximately that point in the phase diagram where the differences between the coexisting solid and fluid phase densities begins to grow (see [5]) resulting in a significant growth in the latent heat. This indicates the strong correlation between the interfacial tension and the heat of the solid-fluid transition.

As noted previously, this technique simultaneously determines interfacial structure along with the energetics. As can be seen in Fig. 5, as the interaction strength is increased the width of the interface decreases and, in fact, becomes a bit sharper (the parameter $\nu = 0.33$ at $\tau = \infty$ and decreases to $\nu = 0.13$ at $\tau = 1.5$). An interesting outcome of these calculations is the orientational isotropy in the interfacial width matching that of the interfacial tensions. Though the number of lattice planes varies with interface, the width, when scaled on the particle size, is nearly constant at a given τ.

Ideally, to determine the equilibrium crystal shape we would calculate $\gamma(\theta)$ at all interaction strengths τ. This would allow determination of both the state of faceting and the roughening transition via a Wulff-type construction. Unfortunately, and despite the reduced dimensionality inherent in our approximation, our approach to determining interfacial properties still requires a great deal of computational effort making such a calculation impractical. We can, however, look at higher-index interfaces and test their stability as a function of τ. We know from a Wulff-type construction that the 211 interface will be stable (that is not facet into a combination of 100 and 111 interfaces) if $\gamma_{211} < 0.388\gamma_{100} + 0.672\gamma_{111}$. Similarly for the 311 interface the stability condition is $\gamma_{311} < 0.603\gamma_{100} + 0.522\gamma_{111}$. Since we have seen for the lower-index interfaces no difference in the interfacial thickness Δz and decay parameter ν, we can lower computational requirements significantly by assuming these also hold for the higher-index interfaces. We list in Table II the values we calculate where we see that these

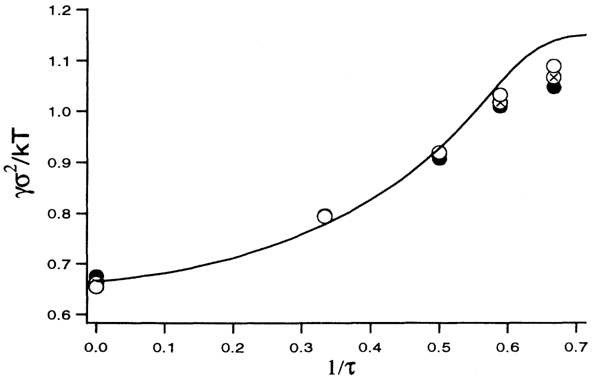

FIG. 4. Interfacial tension shown vs interaction strength τ [●, fcc (111) interface; ○, fcc (100) interface; ⊗, fcc (110) interface]. The line is a prediction based on the calculated bulk phase properties and the empiricism of Turnbull.

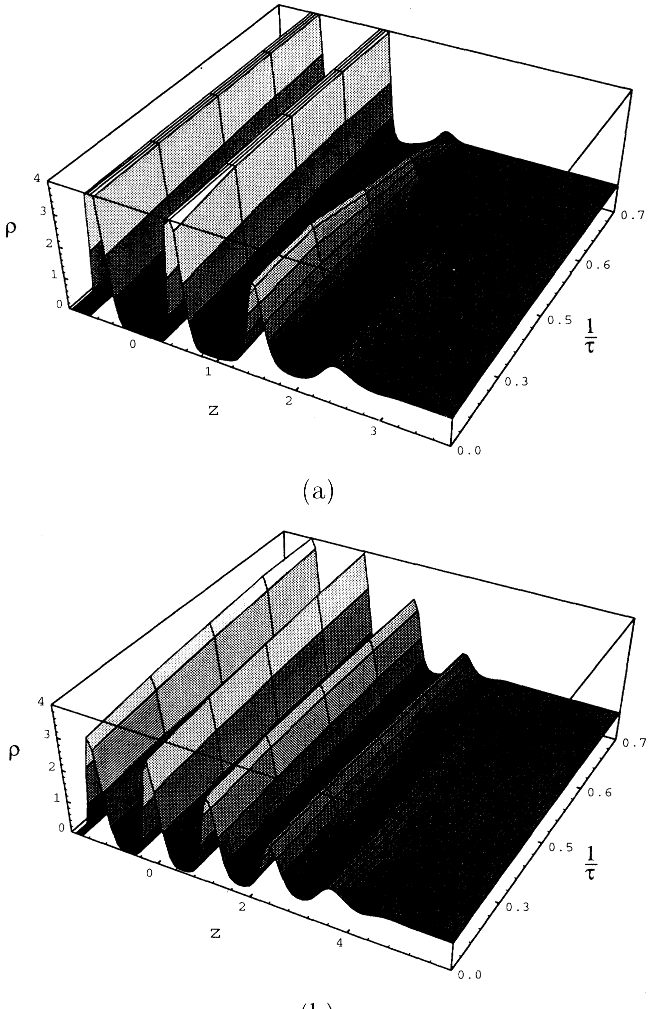

FIG. 5. Planar-averaged structure variation [$\rho(z)\sigma^3$ vs z/δ] of the (a) fcc (111) and (b) fcc (110) interfaces as a function of τ.

TABLE II. Interfacial tensions of the higher-index interfaces.

τ	$\gamma_{211}^{\mathrm{PWDA}}\sigma^2/kT$	$\gamma_{311}^{\mathrm{PWDA}}\sigma^2/kT$
∞	0.70 ±0.01	0.70 ±0.01
3	0.80 ±0.01	0.80 ±0.01
2	0.91 ±0.01	0.91 ±0.01
1.7	0.99 ±0.01	1.01 ±0.01
1.5	1.03 ±0.01	1.04 ±0.01

higher-index surfaces are indeed quite stable for all interaction strengths studied. This indicates that the crystal structure is nonfaceted though, as stated previously, to determine this absolutely would require knowing γ at all orientations and interaction strengths.

This apparent lack of a transition from a spherical to a faceted equilibrium crystal shape as the attractive interactions in this system are increased may suggest that the interaction potential must have range in order to have a nonroughened, faceted equilibrium crystal structure. One must be careful, however, in drawing this conclusion since we are unable to reach attractions stronger than those at a τ of 1.5. Returning to the work of Broughton and Gilmer on the Lennard-Jones system, they obtain nearly isotropic values for the interfacial free energy at the triple point ($T^* = 0.617$). Equating virial coefficients [2] allows us to approximate an equivalent τ via $\tau_{\mathrm{equiv}} = 1 + 2/T^*$, giving $\tau_{\mathrm{equiv}} \sim 0.2$, a value significantly lower than the lowest τ investigated here.

Using density-functional theory and the PWDA we have examined the orientational dependence of the interfacial tension in the adhesive-sphere system. We have investigated both low- and high-index surfaces of the adhesive-sphere crystal and found a small amount of anisotropy in the interfacial tension at the highest attraction strengths. For the interfaces studied here and under the interaction strengths investigated we see no direct evidence of faceting in the adhesive-sphere system. To fully investigate this question will require determining γ at all orientations and a technique that can access a greater range of τ.

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[1] R.J. Baxter, J. Chem. Phys. **49**, 2770 (1968).
[2] B. Barboy, J. Chem. Phys. **61**, 3194 (1974).
[3] S.J. Smithline and A.D.J. Haymet, J. Chem. Phys. **83**, 4103 (1985).
[4] X.C. Zeng and D.W. Oxtoby, J. Chem. Phys. **93**, 2692 (1990).
[5] D.W. Marr and A.P. Gast, J. Chem. Phys. **99**, 2024 (1993).
[6] C.F. Tejero and M. Baus, Phys. Rev. E **48**, 3793 (1993).
[7] Y.C. Chiew and E.D. Glandt, J. Phys. A **16**, 2599 (1983).
[8] N.A. Seaton and E.D. Glandt, J. Chem. Phys. **86**, 4668 (1987).
[9] A. Vrij, M.H.G.M. Penders, P.W. Rouw, C.G. de Kruif, J.K.G. Dhont, C. Smits, and H.N.W. Lekkerkerker, Faraday Discuss. Chem. Soc. **90**, 1 (1990).
[10] C. Regnaut and J.C. Ravey, J. Chem. Phys. **91**, 1211 (1989).
[11] D.W. Marr and A.P. Gast, Phys. Rev. E **47**, 1212 (1993).
[12] W.A. Curtin, Phys. Rev. B **39**, 6775 (1989).
[13] J.F. Lutsko and M. Baus, Phys. Rev. A **41**, 6647 (1990).
[14] A. Kyrlidis and R.A. Brown, Phys. Rev. A **45**, 5654 (1992).
[15] A. Kyrlidis, Ph.D. thesis, MIT (1993).
[16] R. Ohnesorge, H. Löwen, and H. Wagner, Phys. Rev. E **50**, 4801 (1994).
[17] W.E. McMullen and D.W. Oxtoby, J. Chem. Phys. **88**, 1967 (1988).
[18] J.Q. Broughton and G.H. Gilmer, J. Chem. Phys. **84**, 5759 (1986).
[19] E.H. Conrad, Prog. Surf. Sci. **39**, 65 (1992).
[20] G. Wulff, Z. Kristallog. **34**, 449 (1901).
[21] J.D. Weeks, In *Ordering in Strongly Fluctuating Condensed Matter Systems* (Plenum, New York, 1980).
[22] A. Zangwill, in *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).
[23] D.W.M. Marr, J. Chem. Phys. **102**, 8283 (1995).
[24] W.G. Hoover and F.H. Ree, J. Chem. Phys. **49**, 3609 (1968).
[25] B.J. Alder, W.G. Hoover, and D.A. Young, J. Chem. Phys. **49**, 3688 (1968).
[26] A.R. Denton and N.W. Ashcroft, Phys. Rev. A **39**, 4701 (1989).
[27] A small error in the calculation of the ideal contribution to the free energy in [5] has been corrected resulting in lower values for γ at large α.
[28] D. Turnbull, J. Appl. Phys. **21**, 1022 (1950).