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Closure-based perturbative density-functional theory of hard-sphere freezing: Properties of the bridge functional

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The study of freezing using perturbative classical density-functional theory is revisited, using a bridge functional approach to resum all terms beyond second order in the free energy expansion. More precisely, the first-order direct correlation function of the solid phase is written as a functional expansion about the homogeneous liquid phase, and the sum of all higher-order terms is represented as a functional of the second-order term. Information about the shape and uniqueness of this bridge functional for the case of hard spheres is obtained via an inversion procedure that employs Monte Carlo fluid-solid coexistence data from the literature. The parametric plots obtained from the inversion procedure show very little scatter in certain regions, suggesting a unique functional dependence, but large scatter in other regions. The scatter is related to the anisotropy of the solid lattice at the particle scale. Interestingly, the thermodynamic properties of the phase transition are quite insensitive to the regions where the scatter is large, and several simple closures (i.e., analytical forms of the bridge function) reproduce exactly the liquid-solid coexistence densities and Lindemann parameter from simulation. The form of these closures is significantly different from the usual closures employed in liquid-state integral equation theory.

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I. INTRODUCTION

Classical density-functional theory (DFT), rooted in the functional dependence of free energy on density profile [1], has been a popular tool to study liquid-solid transitions in classical systems [2]. The solid phase is represented by a density distribution within a lattice structure imposed through an order parameter, while the liquid phase is assumed homogeneous with certain characteristic correlation functions. Two categories of theory emerge that differ in the manner of implementation of the above concept. Perturbative DFT, pioneered by Ramakrishnan and Yussouff [3], expresses the excess Helmholtz free energy of the solid in a functional expansion about the excess Helmholtz free energy of the coexisting liquid. This approach was pursued by Haymet and Oxtoby [4,5] and Bagchi *et al.* [6] and yielded remarkably good predictions of the coexistence properties of the hard-sphere system. However, progress in this area then slowed due to issues with the convergence of the functional expansion [7] and the Fourier transform methodology employed in the calculations [8]. Nonperturbative DFT focuses on models for the excess Helmholtz free energy density [2], constructed so as to reproduce the direct correlation function of the liquid phase upon functional differentiation, e.g., the weighted density approximation (WDA) and its extensions [9–12], or by mapping free energy density and structural correlation function of a solid onto those of an effective liquid, e.g., the effective liquid approximation (ELA) and its extensions [13–15]. The hard-sphere coexistence property predictions of these theories were in much closer agreement with the molecular simulation results. However, such thermodynamic and structural mapping is argued [16] to be applicable only when large density changes occur at freezing transitions, which limits their applicability to soft interparticle interactions [17]. Furthermore, nonperturbative DFTs tend to become computationally costly as each pair of phase points involves evaluating equilibrium structure of solid and then searching for a coexisting liquid. Therefore it is worthwhile to consider if the traditional limitations of perturbative DFT can be overcome.

In the present study, we apply an idea first developed in the DFT of inhomogeneous fluids [18] to improve the accuracy of perturbative DFT of liquid-solid phase transitions. We propose that it is possible to resum the higher-order terms in the free energy functional expansion and represent them as a bridge functional, which in turn may be represented in terms of certain structure functions. We explore this idea in the context of freezing of the hard-sphere fluid. In Sec. II we present a general overview of the theory of phase transition and our *ansatz* regarding the bridge functional resummation. In Sec. III we use an inverse procedure to extract the bridge functional from Monte Carlo (MC) simulation data on hard-sphere freezing; we explore issues of uniqueness of the bridge functional and show how it may be represented as a simple polynomial function of a structural correlation function. Sec. IV provides conclusions.

II. THEORY

A. Some exact thermodynamic relationships

First consider a single thermodynamic phase comprising one particle species at fixed temperature T, volume V, and chemical potential μ. No external fields are present. The grand potential energy of the phase [2,19] can be written as $\Omega = F - \mu\int d1\rho(1)$, where F is the Helmholtz free energy and $\rho(1)$ is the number density of particles at position $\mathbf{R}_1$, which is denoted by the shorthand notation 1. Both Ω and F are functionals of $\rho(1)$. For fluid phases with no external fields

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the density will be simply a constant, but this will not be true for the solid phase model so we keep the more general functional notation. At equilibrium the grand potential is minimized with respect to the density function so that

$$\left.\frac{\delta\Omega[\rho]}{\delta\rho(1)}\right|_{\rho_{eq}} = 0. \tag{1}$$

Splitting the Helmholtz free energy into ideal and excess parts as $F = F_{id} + F_{ex}$ and applying Eq. (1) gives

$$\beta\mu = \ln[\rho(1)\lambda^3] - c^{(1)}[\rho(1)], \tag{2}$$

where λ is the thermal de Broglie wavelength of the particles, $\beta = 1/kT$ with k the Boltzmann constant, and $c^{(1)}[\rho(1)] = -\delta\beta F_{ex}[\rho]/\delta\rho(1)$ is the first-order direct correlation function (dcf).

Next we assume the conventional starting point for the perturbative DFT of solid-liquid equilibrium. The liquid is homogeneous with constant number density $\rho_0 = N_0/V$. The solid is constrained to a lattice such that the density field is $\rho_s(1) = \frac{1}{v_l}\sum_{i=1}^{N_s} e^{-(\mathbf{R}_1 - \mathbf{r}_i)^2/l^2}$, where $v_l = \pi^{3/2} l^3$ with l the Gaussian width parameter, and the $\mathbf{r}_i$ are the Bravais lattice vectors. Note that $\int d1 \rho_s(1) = N_s$. For the two phases to be in equilibrium the following conditions must be met

$$\Omega_s[\rho_s] - \Omega_0[\rho_0] \equiv \Delta\Omega = 0, \tag{3}$$

$$\mu_s - \mu_0 \equiv \Delta\mu = 0, \tag{4}$$

$$\partial\Delta\Omega/\partial l = 0. \tag{5}$$

The first two equations represent the conditions of mechanical and chemical stability, respectively. The introduction of the parameter l imposes a symmetric distribution of each particle center about its lattice point [20], and we require an additional condition of stability for that parameter as given by Eq. (5). The chemical potential equality of Eq. (4) combined with Eq. (2) leads immediately to a useful relationship between the dcf's of the two coexisting phases

$$c_s^{(1)}[\rho_s(1)] - c_0^{(1)}(\rho_0) = \ln\left(\frac{\rho_s(1)}{\rho_0}\right), \tag{6}$$

which we will use later.

The goal is to employ an accurate model of the free energy functional $F[\rho]$, or more to the point the free energy difference $\Delta F = F[\rho_s] - F[\rho_0]$, to predict the values of ρ_0, $\bar{\rho}_s \equiv N_s/V$, and l that satisfy Eqs. (3)–(5).

B. Perturbative DFT and our bridge functional ansatz

The free energy difference between the solid and liquid phases can be written as the sum of ideal and excess contributions, $\Delta F = \Delta F_{id} + \Delta F_{ex}$, where

$$\beta\Delta F_{id} = \int d1 \rho_s(1)\ln[\rho_s(1)\lambda^3/e] - \int d1 \rho_0 \ln[\rho_0\lambda^3/e], \tag{7}$$

and

$$\beta\Delta F_{ex} = -\int d1 \int_{\rho_0}^{\rho_s(1)} \delta\rho(1) c^{(1)}[\rho(1)]. \tag{8}$$

The excess contribution is given by a functional integration of $c^{(1)}$ as the density distribution changes from the homogeneous liquid state ρ_0 to the structured solid state $\rho_s(1)$. A perturbative approach makes this functional integration tractable by employing an expansion about the liquid state

$$\begin{aligned} c^{(1)}[\rho(1)] &= c_0^{(1)}(\rho_0) + \int d2 c_0^{(2)}(1,2;\rho_0)(\rho(2) - \rho_0) \\ &\quad + \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \int \cdots \int d2d3 \ldots d(n) \\ &\quad \times \prod_{m=2}^{n} (\rho(m) - \rho_0) c_0^{(n)}(1,2,\ldots,n;\rho_0). \end{aligned} \tag{9}$$

The coefficients in the expansion are the hierarchy of direct correlation functions of the homogeneous liquid phase. In principle these functions are amenable to numerical computation, but in practice only $c_0^{(2)}$ is readily accessible. The earliest work on DFT of freezing was based on truncation of this series at $n=2$, which gave fairly accurate results for hard spheres [6,5]. Curtin later estimated the third-order term by differentiating the WDA free energy functional three times; it was found to be of the same order of magnitude as the second-order term, leading to the conclusion that convergence of the expansion is not rapid enough to justify a truncation at $n=2$ and there must be some fortuitous cancellations in the sum of higher-order terms [7]. Understandably, little progress has been made on perturbative DFT of freezing since that time.

More recently an important observation was made by Zhou and Ruckenstein [18] while working on the related problem of perturbative DFT of inhomogeneous fluids. In such problems there is only one thermodynamic phase but its spatial density profile is inhomogeneous due to the presence of an external field. Equation (9) then relates the properties of the fluid in the field to those of the homogenous fluid. Zhou and Ruckenstein showed that the $n \geq 3$ terms in the expansion could be resummed and represented as a bridge functional, based on the universality principle of the free energy functional (i.e., the functional form of the free energy expansion is independent of the specific nature of the inhomogeneity). Equation (9) thus becomes

$$c^{(1)}[\rho(1)] = c_0^{(1)}(\rho_0) + \gamma(1) + B[\vartheta(1)], \tag{10}$$

where $\gamma(1) \equiv \int d2 c_0^{(2)}(1,2;\rho_0)(\rho(2) - \rho_0)$ and $\vartheta(1)$ is some suitable choice of a structural distribution function. This formulation has much in common with Ornstein-Zernike (OZ) integral equation theory and in fact yields the OZ equation when the Percus identity is invoked [18]. The function $\gamma(1)$ is similar to the OZ indirect correlation function in that it represents a convolution of the local density difference with the bulk dcf. If B is represented as a functional of γ, viz. $B[\gamma(1)]$, then closure relations in the typical OZ form, such as hypernetted-chain (HNC, $B=0$) or Percus-Yevick (PY, $B = \ln[1+\gamma] - \gamma$), may be applied. Closures of this type were found to be quite accurate for predicting the structure of various model fluids at solid interfaces [18,21].

The main purpose of the current paper is to explore the extension of the bridge functional representation to the liquid-solid transition of homogeneous systems. Our primary *ansatz* is that Eq. (10) may be applied to the liquid- solid transition such that

$$c_s^{(1)}[\rho_s(1)] = c_0^{(1)}(\rho_0) + \gamma(1) + B[\gamma(1)], \qquad (11)$$

with

$$\gamma(1) \equiv \int d2 c_0^{(2)}(1,2;\rho_0)(\rho_s(2) - \rho_0). \qquad (12)$$

There are significant differences between the present problem of solid-fluid equilibrium and that of inhomogeneous fluids. Here the inhomogeneity is imposed through a Gaussian field structure on the solid density, rather than some external potential acting mechanically on the particles. Furthermore, the present problem involves a thermodynamic phase transition while the other (usually) does not. Since the structure and free energy in the liquid state are being used to predict the same quantities in a completely different thermodynamic state, there is no *a priori* guarantee that the same closures, or indeed the bridge functional approach of Eq. (11), will be useful in predicting fluid-solid equilibrium.

III. RESULTS

A. Extracting the bridge function from Monte Carlo simulation data

The usual forward calculation procedure would be to assume a model for B, thus yielding a model for ΔF_{ex} and allowing Eqs. (3)–(5) to be solved for ρ_0, $\bar{\rho}_s$, and l at liquid-solid equilibrium. Conversely, we can take advantage of the fact that these three coexistence properties are known from independent Monte Carlo simulation work and use them to discover the underlying form of the bridge function. We proceed in this direction by combining Eqs. (6) and (11) to find the following exact relationship:

$$B = \ln(\rho_s(1)/\rho_0) - \gamma(1). \qquad (13)$$

Taking the coexistence properties $\rho_0 = 0.943\,47$, $\bar{\rho}_s = 1.040\,87$, and $l = 0.113\,98$ from the MC simulation study of Hoover and Ree [22], and employing for $c_0^{(2)}(1,2,\rho_0)$ in Eq. (12) the highly accurate analytical expression from PY-OZ theory [19], we see that all terms on the right-hand-side of Eq. (13) are known for any location $\mathbf{R}_1$ in the lattice. Thus the local value of the bridge functional is also known exactly. The only approximations are any uncertainties in the MC simulation data and any inaccuracies inherent in the PY-OZ dcf for the homogeneous fluid phase. (We explored the effects of the latter issue by trying different forms of the dcf, such as those obtained from other closures at the OZ level. Only slight quantitative differences were observed; the qualitative behavior was identical to that presented below.) We started the numerical evaluation by considering the smallest repeating volumetric unit of the fcc lattice as shown in the inset of Fig. 2. A $50 \times 50 \times 50$ grid of points was laid uniformly over this volume, and the values of γ and B were calculated at each grid point using Eqs. (12) and (13). The integral in Eq. (12) was evaluated in real space using methods presented previously [23]. The large set of points in Fig. 1 represents a parametric plot of (γ, B) values obtained at the grid points.

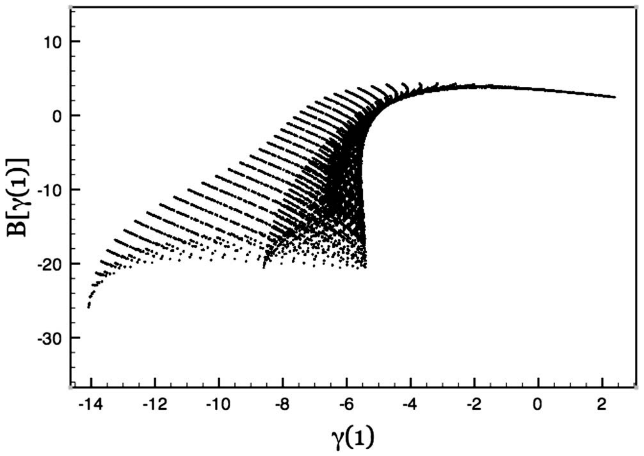

FIG. 1. Parametric representation of the bridge function of Eq. (13) as extracted from MC simulation data.

As a general guide, the region $\gamma(1) > -2$ corresponds to locations $\mathbf{R}_1$ that are within 0.25σ or $2.2l$ of a lattice site $\mathbf{r}_i$, where σ is the hard-sphere diameter and l is the Gaussian width parameter used to describe solid density. A unique functional dependence of B on γ is evident in this region. However, the points scatter widely at lower values of γ, indicating no unique functional relationship, before pinching together again at $\gamma \approx -14$. Clearly, in regions outside the Gaussian core, there are many locations that have identical values of γ but very different values of B. It is interesting that a regular striped pattern appears in this region of the data. The number of stripes, and the density of points along a given stripe, increases with the number of grid points used, but the basic pattern is maintained. Each stripe represents a trace as we move from a point on one edge to corresponding point on a parallel edge of the smallest volumetric unit. These stripes usually end up in the dense region ($-8 \leq \gamma \leq -5$) of Fig. 1 as strands or loops. All stripes (and consequently the entire data set of Fig. 1) are thus bounded on the left side by the points lying along an edge of the volumetric unit.

Equation (13) and the behavior in Fig. 1 also imply that γ is not everywhere a unique function of ρ_s. A parametric plot of these two functions, as given in Fig. 2, provides more insight. The small brushlike features that appear for $\gamma < -2$ indicate the source of the nonuniqueness that is reflected more dramatically in Fig. 1, namely, that there are locations in the lattice with the same value of density but different values of the convolution integral γ. This is a consequence of the anisotropy of the lattice at the particle scale. Near each lattice site the density distribution is dominated by the particle associated with that site; this density will have a high degree of spherical symmetry due to the assumed isotropic Gaussian form, yielding many locations with nearly identical densities. However, the value of $\gamma(1)$ from the volume inte-

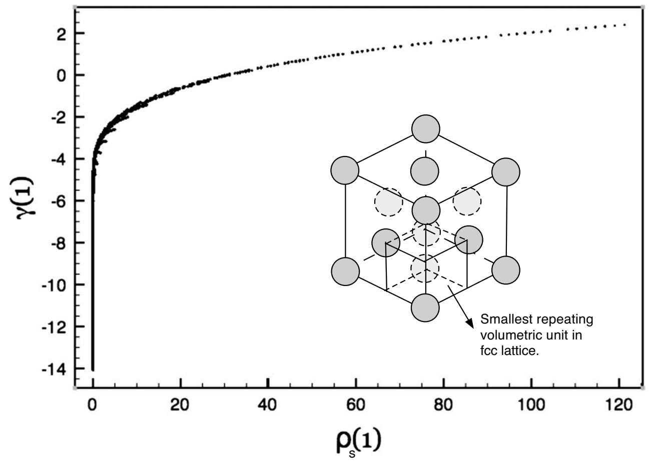

FIG. 2. Parametric plot of $\gamma(1)$ vs $\rho_s(1)$ from unique points in the lattice. The highest $\rho_s(1)$ values occur near lattice sites.

gral of Eq. (12) will obviously depend on the distribution of other particles (lattice sites) around location $\mathbf{R}_1$. The sensitivity of $\gamma(1)$ to the surrounding structure is weak for $\mathbf{R}_1$ very close to a lattice site, since the range of the integral is limited by the dcf and its value will be dominated by the density of the particle associated with that site. Thus $\gamma(1)$ is nearly a unique function of $\rho_s(1)$ at high densities. The sensitivity of $\gamma(1)$ to the surrounding structure will become stronger for $\mathbf{R}_1$ that are farther from a lattice site, leading to the nonuniqueness at lower densities. The regular patterns seen in the scatter plot of Fig. 1 reflect patterns in the directional anisotropy of the fcc lattice at the particle scale. Baus commented on the limitations of using isotropic Gaussians to parameterize a solid lattice [20]; it would be interesting to see how a more general parameterization would affect the results in Figs. 1 and 2.

B. Simple polynomial forms for the bridge function

Figure 1 shows that there are regions where B is a unique function of γ but other regions where it certainly is not. This begs the question of whether a function that at least approximately describes the behavior of the bridge functional can be useful in predicting the thermodynamics of the phase transition. We consider the case of OZ theory, where inversion of data from the MC simulation of a fluid is used to generate scatter plots analogous to Fig. 1. (In OZ theory, γ is the indirect correlation function and the plots are commonly referred to as Duh-Haymet plots [24].) Recent work on hard-sphere fluids shows that uniqueness is not strictly satisfied, with violations especially seen outside the hard core region, and yet closures based on the assumption of uniqueness can still yield accurate predictions of structure and thermodynamics [25]. We explore this possibility here by postulating a low-order polynomial functionality for $B[\gamma]$ and fitting the coefficients to the thermodynamic properties known from MC simulation. More specifically, we assume that B is a polynomial in γ having exactly three unknown coefficients and iteratively solve Eqs. (3)–(5) until we find the set of coefficient values that yield the known ρ_0, $\bar{\rho}_s$, and l from MC simulation. We solve Eqs. (3)–(5) using a real-space method presented previously [8,23]. The only difference is that our free energy model now includes the higher-order terms via the bridge functional. In the Appendix we derive the new form of the free energy.

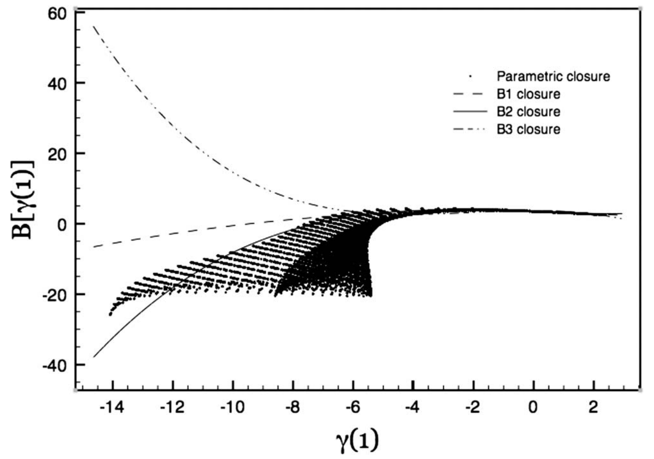

FIG. 3. Comparative plot of B with simple polynomial functions fit to the coexistence properties. Note that all of these functions reproduce the exact MC freezing results for hard spheres.

Since the extracted $B[\gamma]$ data shown in the previous section do not pass through origin, we can say that there must be a constant term in the polynomial model. Following are a few of the polynomic forms that we tried, written with the fitted values of the coefficients:

$$B_1[\gamma] = -0.0609\gamma^2 - 0.2047\gamma + 3.4766, \tag{14}$$

$$B_2[\gamma] = 0.0146\gamma^3 - 0.3073\gamma + 3.3692, \tag{15}$$

$$B_3[\gamma] = -0.0291\gamma^3 - 0.1825\gamma^2 + 3.6906. \tag{16}$$

Figure 3 provides a comparative plot between the exact and polynomial bridge functions.

Interestingly, all of the polynomial models match the extracted B data at higher γ values where a unique functionality is indicated. However, there is a considerable divergence among the various models at lower γ where the extracted data are scattered and no unique functionality is indicated. We emphasize that *all* of the polynomial models presented yield the exact results for ρ_0, $\bar{\rho}_s$, and l as obtained by MC. This leads us to conclude that the behavior of the bridge functional at lower values of γ does not have a significant impact on the thermodynamic properties predicted. It is remarkable that similar observations were made by Fantoni and Pastore [25] in their MC study of liquid-state OZ theory bridge functionals in hard-sphere systems. They found that outside the hard core region B is multivalued and the traditional closures do not track the data in a quantitative way, especially at higher density, and yet this situation has little effect on the accuracy of the radial distribution functions and thermodynamic properties predicted by the closures.

Returning to the present study, one could rule out certain closures based on other physical insight. For example, from Eqs. (2) and (11) it is clear that $\gamma(1)+B[\gamma(1)]$ represents the excess chemical potential difference between the solid and liquid phases at location $\mathbf{R}_1$. This difference should be negative at low density locations, and the polynomial form B_3 could be discarded as it does not satisfy this criterion. We note that in the thermodynamically relevant region where all models agree with the data, the values of B are on the order of unity and never rise above ~ 4.5; these moderate values are consistent with the fact that setting $B=0$ [truncating Eq. (9) at $n=2$] gives reasonable results for the coexistence properties [5,6].

Finally, we note that traditional OZ closures (other than HNC, $B=0$) are not appropriate as bridge functions for the liquid-solid transition. Consider the PY closure, $B=\ln[1+\gamma]-\gamma$, as an example. This function diverges to $-\infty$ as γ approaches -1, passes through the origin, and never achieves positive values. Such properties, which are common to most traditional OZ closures and are not problematic in that context, are not consistent with the behavior of the bridge functional observed in the current work. Since the problems of single-phase fluid structure and solid-liquid phase coexistence are physically quite different, it is not surprising that the bridge functional behavior is qualitatively different.

IV. CONCLUSION

Employing MC simulation data on the coexistence densities and Gaussian order parameter for hard-sphere freezing, we have constructed parametric plots of the bridge functional $B[\gamma]$ that represents the sum of terms beyond second order in the DFT free energy difference expansion. Distinct regions of uniqueness and nonuniqueness of the $B[\gamma]$ functionality are strongly indicated by the data; the existence of these different regions can be understood through the anisotropy of the solid fcc lattice at the particle scale. Forward DFT calculations using simple closures, i.e., low-order polynomial representations of $B[\gamma]$, demonstrate that the coexistence properties are insensitive to the region of nonuniqueness. There are strong parallel themes between our results and those from recent MC simulation studies on liquid-state OZ theory closures, although the quantitative behavior of the closures is quite different.

In summary we find that the known fluid-solid coexistence properties of hard spheres, within the context of an order-parameter-based perturbative DFT, can be exactly reproduced using a low-order polynomial closure $B[\gamma]$ that is accurate in the high-density regions of the solid lattice. Our findings indicate that there is merit to further exploration of closure-based approaches to the perturbative DFT of freezing. One could anticipate development that parallels that of OZ theory for the liquid state, with an appropriate set of closures that describe the solid-liquid transitions in various potential models.

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APPENDIX A

In this section we derive the equation for the excess free energy functional that corresponds to our bridge function model of the direct correlation function. Applying the charging approach [2] to the functional integration in Eq. (8) gives

$$\beta\Delta F_{ex} = -\int d1 \int_0^1 d\alpha \Delta\rho(1) c^{(1)}[\rho_\alpha(1)], \qquad \text{(A1)}$$

where $\Delta\rho(1) \equiv (\rho_s(1)-\rho_0)$ and $\rho_\alpha(1)=\rho_0+\alpha\Delta\rho(1)$. Our model for the direct correlation function yields

$$c^{(1)}[\rho_\alpha(1)] = c_0^{(1)}[\rho_0] + \gamma(1;\rho_\alpha) + B[\gamma(1;\rho_\alpha)], \qquad \text{(A2)}$$

where the functional dependence of γ on ρ has been explicitly noted. By the definition of γ we have

$$\begin{aligned}\gamma(1;\rho_\alpha) &= \int d2(\rho_\alpha(2)-\rho_0)c_0^{(2)}(1,2;\rho_0)\\ &= \int d2\,\alpha(\rho_s(2)-\rho_0)c_0^{(2)}(1,2;\rho_0) = \alpha\gamma(1),\end{aligned}$$

where $\gamma(1)$ is defined in Eq. (12). Now Eq. (A2) becomes

$$c^{(1)}[\rho_\alpha(1)] = c_0^{(1)}[\rho_0] + \alpha\gamma(1) + B[\alpha\gamma(1)]. \qquad \text{(A3)}$$

Substituting the result of Eq. (A3) into Eq. (A1) and integrating with respect to α yields

$$\beta\Delta F_{ex} = -\int d1 \Delta\rho(1)\left\{ c_0^{(1)}[\rho_0] + \frac{\gamma(1)}{2} + \frac{I[\gamma(1)]}{\gamma(1)}\right\} \qquad \text{(A4)}$$

where $I[\gamma(1)]=\int_0^{\gamma(1)} dt B[t]$.

Equation (A4) is the excess free energy model employed in the present work. It can be evaluated using standard numerical techniques, given an analytical form for $B[\gamma]$. Clearly if $B=0$ then $I=0$, and ΔF_{ex} reduces to the usual result from truncation at second order.

We further note that Eq. (A4) is similar in form to a weighted DFT, with the quantity in braces acting as a free energy per particle that is a function of the weighted density $\gamma(1)$. However, Eq. (A4) has been developed explicitly for the free energy *difference*.

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