

## Generalized density-functional theory: Extended weighted density approaches

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(Received 24 December 1998)

A third-order density-functional theory is introduced by an approach that may be used to find density-functional theories to any higher-order accuracy provided only that known homogeneous state correlation functions are utilized as input. It is constructed from the required knowledge of a single weight function at each order. By way of application results are presented for the melting of classical hard spheres using functionals accurate to a third-order functional Taylor series in the homogeneous limit. Within the framework of the modified weighted density approximation, there is a uniform improvement in the solid phase-free energies, pressures and melting parameters, and further improvement also results when these functionals are optimized in a way that utilizes the close packing limit. The sensitivity of the results to existing and proposed models of the third-order direct correlation function is discussed. [S1063-651X(99)10908-5]

PACS number(s): 61.20.Gy, 71.15.Mb

### I. INTRODUCTION

A primary goal of classical density-functional theory has been the accurate description of the structural and thermodynamic properties of inhomogeneous interacting many-particle systems [1]. For these the Helmholtz free energy is a unique functional of the single-particle density [2] and in modeling this free energy the first step is usually to partition it into the sum of a known ideal part, exact in the limit of vanishing particle interactions but arbitrary external potential, and an excess free energy arising from particle interactions. Early attempts to obtain the excess free energy were made by the perturbative approach of Ramakrishnan and Yusouff (RY), later reformulated in functional terms by Haymet and Oxtoby [3]. Here the excess contribution is approximated by a functional Taylor series in density nonuniformity about the homogeneous liquid phase but truncated at second-order. Because the excess free energy of the fluid state and the second-order direct correlation function (DCF) are both known functions for corresponding homogeneous phases, this approach yields a free-energy functional of the inhomogeneous phase, which can be subsequently minimized with respect to density variations. Though the RY method does yield a stable solid when applied to the hard-sphere system it was later shown that the addition of third-order terms considerably worsen the results [4]. In some contrast the RY theory does *not* lead to a stable solid for the one-component plasma (OCP), the central problem being traced to the fact that the strong density inhomogeneity in the solid phase does not give rise to a correspondingly small density difference for the functional expansion. There is little reason to believe, therefore, that the theory can be truncated at second-order in systems possessing large density inhomogeneities, though it may be satisfactory for weaker variations.

Recognizing that the excess free energy is a highly nonlocal functional, a particularly successful class of nonpertur-

bative density-functional theories have also appeared, most being formulated not only to reproduce the functional Taylor series about the liquid state to second-order in the homogeneous limit, but also to include, at least approximately, contributions from all higher-order terms [5,6]. One of the simplest theories to implement in practice is the modified weighted density approximation (MWDA) that establishes an equivalence between the unknown excess free energy per particle functional of the inhomogeneous system at density  $\rho(\mathbf{r})$  and a fictitious homogeneous system at a density  $\hat{\rho}$  [5]. In so doing, the inherent nonlocal functional dependence in the excess free energy is entirely subsumed in the definition of the effective density  $\hat{\rho}$ . Although the MWDA has been successful in its application to classical bulk hard-sphere systems, it also is unable to predict the freezing of the classical OCP. However, it was later shown that if the MWDA is extended to include third-order accuracy in its functional Taylor expansion about the homogeneous limit, then a stable OCP crystalline phase could indeed ensue [7]. This observation motivates, in part, the present paper.

In a recent paper [8], we showed that the second-order MWDA theory is but a single limit of a much broader functional approach permitting considerable freedom both in the choice of mapping functional as well as in the definition of the effective density. It was also shown that the general scaling functions defined in these mappings may be used to further optimize the excess free-energy functional by enforcing its known value in an additional physical limit, for example the close-packed limit for a hard-sphere system. Despite the inherent functional freedom now introduced, the weight function defining the effective density nevertheless remains proportional to the second order DCF and the theory therefore remains dominated by the second-order input. Because of this, a functionally optimized theory based on the MWDA functional faces the inevitable limitations of a second-order theory and a need clearly arises to formulate the theory based on at least third-order input. Furthermore, even in the case of the freezing of bulk hard spheres, there continues to be considerable room for improvement of the second-order theory free energy, pressure, localization and melting parameters, and in particular, the excess entropy and the Lindemann pa-

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parameter. This provides a further motivation behind the work to follow: here we shall describe a method by which the theory can be extended to third-order accuracy, and we will suggest that such approaches may in a sense be a *required* minimalist construction to density-functional theories for inhomogeneous systems [9] if the important consequences of nonlocality are to be included, at least in part. As will be seen even for the particular limit of the MWDA functional, our approach differs from the earlier theory of Likos and Ashcroft [7] in that only a *single* weight function is now required to define the effective density functional and, significantly, the application of the method to a more general theory accurate to any order is also straightforwardly defined. In fact, it leads to the formal possibility of defining a density-functional theory accurate to *any* order in the functional Taylor expansion.

The outline of the paper is as follows: In Sec. II we briefly review the MWDA and in Sec. III we present the theory of its generalization and extension to third-order. For hard spheres a prescription is given for optimizing density-functional calculations by enforcing the known value of the excess free energy in the limiting case of close packing. In Sec. IV we present results for the freezing of the classical three-dimensional hard-sphere crystal where results are now given for both optimized (via the close-packed limit) and unoptimized functionals. The latter gives considerable insight on the effect of replicating the functional Taylor expansion of the excess free energy to third order, while the former describes the effect of further optimization of the third-order functional. We then summarize and conclude in Sec. V. Finally, in Appendix A we provide a method for calculating the form of the effective density but in a way that ensures the proper limiting form of the excess free energy. Also given there is a discussion of the results based on three methods for calculating the third-order direct correlation function. The first is the Denton-Ashcroft model introduced some years ago [10], and the others are analytic theories (Ref. [11] and Appendix B) that *exactly* satisfy the well-known sum rule [see Eq. (11)] relating the triplet DCF to the second derivative of the second-order DCF. In what follows we adopt the notation of Ref. [11] and simply denote these two analytic models as AT1 and AT2.

## II. REVIEW OF THE MWDA

By way of introduction to generalized mappings, we briefly review the basic concepts of the MWDA. The thermodynamic and structural properties of classical inhomogeneous interacting many-body systems are characterized by a Helmholtz free-energy functional that is generally unknown except, as noted, when interparticle interactions are absent. Density-functional theory provides a rigorous framework within which the contributions to the free energy arising from correlations between particles may be modeled as non-local density functionals. For an inhomogeneous system with one-particle density  $\rho(\mathbf{r})$ , the unknown free-energy functional may be separated in the form,

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

where  $\Lambda$  is the thermal de Broglie wavelength. The first term in Eq. (1) is exact in the limit of vanishing interparticle interactions (but arbitrary external potential) while the second, referred to as the excess free energy of the system, is a generally unknown density functional.

In the MWDA, the excess free energy per particle of the inhomogeneous system at density  $\rho(\mathbf{r})$  is mapped onto a homogeneous system at density  $\hat{\rho}$ . In establishing the required equality,  $F_{\text{ex}}[\rho] = Nf(\hat{\rho})$ , where  $f(\hat{\rho})$  is the known excess free energy of the homogeneous phase at density  $\hat{\rho}$ , it is implied that the effective density is itself an unknown functional of the density through the formal statement  $\hat{\rho} = f^{-1}(F_{\text{ex}}[\rho])$ . Because we will be comparing third-order methods to second-order equivalents, it will be convenient to first rewrite the generally unknown functional  $\hat{\rho}[\rho]$  as a double integral over density, namely,

$$\hat{\rho} = \frac{1}{N} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'; [\rho]), \quad (2)$$

where  $W(\mathbf{r}, \mathbf{r}'; [\rho])$  is an unknown weighting function that is highly nonlocal and also carries a density-functional dependence, also generally unknown. It is possible to obtain the value of this weight function functional in the *homogeneous* density limit (necessarily suppressing, thereby, its *full* functional dependence) by forcing the model excess free-energy functional to reproduce the functional expansion of the excess free energy, that is, by writing

$$\begin{aligned} \beta F_{\text{ex}}[\rho] &= N\beta f(\rho) - \frac{1}{2} \int d\mathbf{r} \Delta\rho(\mathbf{r}) \int d\mathbf{r}' \Delta\rho(\mathbf{r}') \\ &\times c_0^{(2)}(\mathbf{r} - \mathbf{r}'; \rho) - \frac{1}{6} \int d\mathbf{r} \Delta\rho(\mathbf{r}) \int d\mathbf{r}' \Delta\rho(\mathbf{r}') \\ &\times \int d\mathbf{r}'' \Delta\rho(\mathbf{r}'') c_0^{(3)}(\mathbf{r} - \mathbf{r}', \mathbf{r} - \mathbf{r}''; \rho) + \dots, \quad (3) \end{aligned}$$

where the direct correlation functions are defined through repeated functional derivatives (here  $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho$ ,  $\rho = N/V$ , and  $\beta = 1/k_B T$ ), i.e.,

$$c_0^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; \rho) = - \lim_{\rho(\mathbf{r}) \rightarrow \rho} \beta \frac{\delta F_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r}_1), \dots, \delta \rho(\mathbf{r}_n)}. \quad (4)$$

The weight function that emerges from reproducing the functional expansion about the homogeneous limit to second-order is a *function* of the density and thus, as noted, carries little information on nonlocality. In practice, this deficiency is accounted for, but only partially, by making the definition of the effective density *self-consistent* within the MWDA, i.e.,

$$\hat{\rho} = \frac{1}{N} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') W(\mathbf{r} - \mathbf{r}'; \hat{\rho}). \quad (5)$$

As we shall see, in the case of a third-order theory the effective weight function as given in Eq. (2) becomes a truly *nonlocal* functional of the density. Because of the high degree of correlation present in most classical inhomogeneous

systems, a successful excess free-energy functional must include, at least approximately, all of the higher-order terms in its functional expansion, which, therefore, in turn necessitates a self-consistent definition of the effective density.

### III. GENERALIZED DENSITY FUNCTIONALS

#### A. Theory

We shall now formulate a generalized theory that reproduces the functional expansion of Eq. (3) and is, therefore, accurate to third-order in the limit of small density fluctuations but nevertheless continues to retain all higher-order contributions, at least approximately. A quite general free-energy functional for an  $N$  particle system in a volume  $V$  that gives a mapping to a homogeneous system can be defined by

$$F_{\text{ex}}[\rho] = Nf(\rho)\phi(x, y), \quad (6)$$

where  $\rho = N/V$ ,  $x \equiv \hat{\rho}/\rho$ , and  $y \equiv f(\hat{\rho})/f(\rho)$ . Here  $\phi(x, y)$  is a scaling function and for the moment is arbitrary, but from dimensional arguments it can only be a function of dimensionless parameters such as  $x$  and  $y$ , and in the homogeneous limit it must also satisfy  $\phi(1, 1) = 1$ . Various choices of the scaling function  $\phi$  can be seen to give rise to different mapping functionals. For example, if we choose  $\phi(x, y) = y$ , we recover the MWDA functional  $F_{\text{ex}} = Nf(\hat{\rho})$ , which has the clear physical interpretation of a mapping of the unknown excess free energy per particle of the inhomogeneous system onto a homogeneous system at density  $\hat{\rho}$ . On the other hand,  $\phi(x, y) = x$  has the interpretation of a mapping onto a homogeneous system at the same mean density as the inhomogeneous system but with fewer ( $\hat{N} = V\hat{\rho}$ ) particles [8]. Consequently, each of the many choices possible for the form of the scaling function can give rise to an independent density-functional theory. In the following we focus on the MWDA functional and we refer the reader to Ref. [8] for second-order results based on other forms of  $\phi$ .

The effective density is defined in a similar way but with the introduction of yet another scaling function  $\theta$ ; it is given by

$$\begin{aligned} \rho^2 \theta(x, y) &= \frac{1}{N} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') \int d\mathbf{r}'' \rho(\mathbf{r}'') \\ &\times M(\mathbf{r} - \mathbf{r}', \mathbf{r} - \mathbf{r}''; \hat{\rho}), \end{aligned} \quad (7)$$

where  $M(\mathbf{r} - \mathbf{r}', \mathbf{r} - \mathbf{r}''; \hat{\rho})$  is a yet to be specified weight function, and  $\theta(x, y)$  is the new arbitrary scaling function satisfying  $\theta(1, 1) = 1$  [12]. Note that the choice  $\theta = x$  recovers the usual form defining  $\hat{\rho}$  analogous to Eq. (5). Equation (7) is, therefore, a natural extension of Eq. (2) in Ref. [8] and is also the natural form for obtaining a definition of an effective density of a third-order theory. Comparing Eq. (7) to Eq. (2), we see that the *effective* weight function is given by

$$W(\mathbf{r}, \mathbf{r}'; [\rho]) = (1/\rho) \int d\mathbf{r}'' \rho(\mathbf{r}'') M[\mathbf{r} - \mathbf{r}', \mathbf{r} - \mathbf{r}''; \hat{\rho}]. \quad (8)$$

Evidently the third-order approach is the minimalist form of theory that quite straightforwardly gives rise to the incorporation of *nonlocality* into the weight function, one which is

not only an explicit *functional* of the inhomogeneous density but also generally departs from the pure radial function characteristic [Eq. (5)] of the second-order weight function (which depends only on coordinate differences). By requiring the approximate functional to reproduce the functional Taylor series to *third-order* in the homogeneous limit [or equivalently to satisfy Eq. (4) for  $n = 2, 3$ ], the weight function is again uniquely specified. In this case the result is

$$\begin{aligned} &-c_0^{(3)}(\mathbf{r} - \mathbf{r}', \mathbf{r} - \mathbf{r}''; \rho)/\beta \\ &= \frac{6f(\rho)}{\rho^2} \frac{K_1(\phi; \rho)}{K_1(\theta; \rho)} \left( M(\mathbf{r} - \mathbf{r}', \mathbf{r} - \mathbf{r}''; \rho) \right. \\ &\quad \left. + \frac{\rho}{V} \mathcal{P}[W'] - \frac{1}{V^2} \right) + \frac{1}{V^2} (\rho f(\rho))''' \\ &\quad + \frac{6}{V} H(K_1, K_2; \rho) \mathcal{P}[W - 1/V], \end{aligned} \quad (9)$$

where  $\mathcal{P}$  denotes permutations of  $\mathbf{r}$ ,  $\mathbf{r}'$ , and  $\mathbf{r}''$ , i.e.,

$$\mathcal{P}[W] \equiv W(\mathbf{r} - \mathbf{r}'; \rho) + W(\mathbf{r} - \mathbf{r}''; \rho) + W(\mathbf{r}' - \mathbf{r}''; \rho).$$

In Eq. (9)

$$\begin{aligned} H(K_1, K_2; \rho) &\equiv [K_1(\phi; \rho) \{(\rho f(\rho))' - f(\rho)\} \\ &\quad \times [3 + K_2(\theta; \rho)/K_1(\theta; \rho)]] \\ &\quad + f(\rho) K_2(\phi; \rho) / [\rho^2 K_1(\theta; \rho)] \end{aligned}$$

and

$$\begin{aligned} W(\mathbf{r} - \mathbf{r}'; \rho) &\equiv \int d\mathbf{r}'' M(\mathbf{r} - \mathbf{r}', \mathbf{r}''; \rho) \\ &= -\frac{K_1(\theta; \rho)}{K_1(\phi; \rho)} \frac{[c_0^{(2)}(\mathbf{r} - \mathbf{r}'; \rho) - c_0^{(2)}(\rho)/V]/\beta}{6f(\rho)/\rho} \\ &\quad + \frac{1}{V}. \end{aligned} \quad (10)$$

Here we also define the functions  $K_1(\theta; \rho) = \theta_x + \theta_y \rho f'(\rho)/f(\rho)$  and  $K_2(\theta; \rho) = -\theta_x + \theta_y \rho^2 (f'(\rho)/f(\rho))'$ . The primes denote derivatives with respect to density and the subscripts on the scaling functions denote differentiation and subsequent evaluation at  $x = y = 1$ .

The volume dependent terms in Eqs. (9) and (10) serve to ensure that the weight functions are properly normalized and that the sum rule

$$c_0^{(3)}(\mathbf{q}, \mathbf{q}' = 0; \rho) = c_0^{(3)}(\mathbf{q}, -\mathbf{q}; \rho) = \frac{\partial c_0^{(2)}(\mathbf{q}; \rho)}{\partial \rho} \quad (11)$$

is satisfied as well as the Fourier transform condition  $M(\mathbf{q}, \mathbf{q}' = 0; \rho) = W(\mathbf{q}; \rho)$ . The key property of Eqs. (9) and (10) is that after Fourier transformation to  $W(\mathbf{q}; \rho)$  and  $M(\mathbf{q}, \mathbf{q}')$ , the weight functions take on quite simple forms, namely,

$$M(\mathbf{q}, \mathbf{q}'; \rho) = \begin{cases} -\frac{1}{6f(\rho)} \frac{K_1(\theta; \rho)}{K_1(\phi; \rho)} \rho^2 c_0^{(3)}(\mathbf{q}; \mathbf{q}'; \rho), & \mathbf{q}, \mathbf{q}' \neq 0, \mathbf{q} \neq -\mathbf{q}' \\ W(\mathbf{q}; \rho), & \mathbf{q}' = 0, -\mathbf{q} \\ W(\mathbf{q}'; \rho), & \mathbf{q} = 0, -\mathbf{q}' \\ 1, & \mathbf{q} = \mathbf{q}' = 0, \end{cases} \quad (12)$$

where

$$W(\mathbf{q}; \rho) = \begin{cases} -\frac{1}{6f(\rho)} \frac{K_1(\theta; \rho)}{K_1(\phi; \rho)} \rho c_0^{(2)}(\mathbf{q}; \rho), & \mathbf{q} \neq 0 \\ 1, & \mathbf{q} = 0. \end{cases} \quad (13)$$

It is, therefore, evident that  $W$  and  $M$  are simply proportional to the second- and third-order DCF's, respectively. All of the functional freedom embodied in the definition of the scaling functions then collapses into the definition of the density prefactor function  $K_1$ . This function is in turn defined by the scaling functions and their derivatives at  $x=y=1$  (the homogeneous limit). It follows that the scaling functions are seen to affect the *density dependence* of the weight function but *not* its spatial form, a fact evident in the second-order version of the theory as well [8]. Furthermore, the weight functions are defined by the value of the *derivatives* of the scaling functions at  $x=y=1$ . However, it is important to note that the free energy [Eq. (6)] is dependent on the specific form of the scaling functions away from  $x=y=1$  since it is evaluated for  $\hat{\rho} \neq \rho$ .

In contrast to previous approaches to third-order mappings [7], we define here only a single (and unique) weight function  $M(\mathbf{q}, \mathbf{q}'; \rho)$  from which all other necessary functions are then derived. For this reason it can also be seen that the principle behind the method is easily extended to higher-order theories. For example, we see that in a third-order theory, the function  $W(\mathbf{q}; \rho)$  responsible for ensuring that the functional is accurate to second-order, is itself defined by the original weight function  $M(\mathbf{q}, \mathbf{q}'; \rho)$ . In a similar way, therefore, a general theory accurate to an  $n$ th-order functional expansion may be defined as

$$\rho^{n-1} \theta(x, y) = \frac{1}{N} \int d\mathbf{r}_1 \rho(\mathbf{r}_1), \dots, \int d\mathbf{r}_n \rho(\mathbf{r}_n) K(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_1 - \mathbf{r}_3, \dots, \mathbf{r}_1 - \mathbf{r}_n; \hat{\rho}), \quad (14)$$

and other weight functions necessary to ensure the proper value of the  $n$  terms in the functional expansion are defined from integrals over the main weight function  $K$ .

The required effective density  $\hat{\rho}$  is most simply expressed in reciprocal space by transforming Eq. (7) and substituting Eqs. (12) and (13). The resulting expression for the effective density is then

$$\theta(x, y) = 1 - \frac{K_1(\theta; \hat{\rho})}{K_1(\phi; \hat{\rho})} \frac{1}{\beta f(\hat{\rho})} \Phi(\hat{\rho}, \alpha), \quad (15)$$

where all of the structural information about the inhomogeneous system is contained in the function

$$\begin{aligned} \Phi\{\hat{\rho}, [\mu(\mathbf{q})]\} &= \frac{1}{2} \sum_{\mathbf{q} \neq 0} \mu(\mathbf{q})^2 \hat{\rho} c_0^{(2)}(\mathbf{q}; \hat{\rho}) + \frac{1}{6} \hat{\rho}^2 \\ &\times \sum_{\substack{\mathbf{q} \neq 0 \\ \mathbf{q}' \neq -\mathbf{q}}} c_0^{(3)}(\mathbf{q}, \mathbf{q}'; \hat{\rho}) \mu(\mathbf{q}) \mu(\mathbf{q}') \\ &\times \mu(\mathbf{q} + \mathbf{q}'), \end{aligned} \quad (16)$$

and where  $\mu(\mathbf{q}) = \rho(\mathbf{q})/N$  is the normalized [ $\mu(\mathbf{q}=\mathbf{0})=1$ ] Fourier component of the density at a reciprocal lattice vector  $\mathbf{q}$ . It is important to note that since  $x = \hat{\rho}/\rho$ , Eq. (16) gives rise to a *self-consistent* definition of the effective density  $\hat{\rho}$  (as in the original MWDA). The form of Eq. (16) suggests an even more general expansion of  $\Phi$  in terms of homogeneous system correlation functions, based on Eq. (14). (No such calculation has been performed but it is evidently possible to embark on such a procedure.) For the structured systems we consider, for example, the inhomogeneity encountered in a near-harmonic crystal, the density is conveniently approximated in terms of Gaussian sums, namely,

$$\rho(\mathbf{r}) = (\alpha/\pi)^{3/2} \sum_{\mathbf{R}} \exp(-\alpha|\mathbf{r} - \mathbf{R}|^2) \quad (17)$$

with Fourier coefficients  $\mu(\mathbf{q}) = \exp(-q^2/4\alpha)$ , where  $q = |\mathbf{q}|$  is the magnitude of a reciprocal lattice vector.

## B. Method of calculation

An immediate consequence of the formalism presented above is that different choices of scaling functions can now give rise to independent density-functional theories, all of which lead to a correct functional Taylor expansion about the liquid state in the homogeneous limit. The role of the scaling functions is simply to optimize the contribution to the functional from *higher-order* correlation functions (now fourth-order and higher) as implied in the self-consistent definition of the effective density, Eq. (15). We shall give a specific example of optimization of the functional by proposing a particular form for the scaling function. It is known that in the close-packed limit of a hard-sphere system, each lattice site is singly occupied with unit probability. In the same limit, it can be shown that the excess free energy approaches the limiting value of  $\beta F_{\text{ex}}[\rho]/N = 1$  [13]. The importance that this condition places on the selection of a form for the excess free energy was recently pointed out by Rosenfeld [14] in the context of a quite different theory. To the best of our knowledge, until now there has not been a method that permitted approaches such as the MWDA or the weighted density approximation [1] to reproduce this limit. Within the present framework several paths open up that actually

achieve this goal. For example, we may choose to fix the definition of the effective density (a fixed form of  $\theta$ ) and consider different functionals (i.e., choose various forms for  $\phi$ ). Alternatively there is the intuitive notion that for a fixed choice of functional, there should be an effective density, functional  $\hat{\rho}[\rho]$  that will optimize the mapping. We adopt the latter approach and confine our discussion to the MWDA functional. We shall carry out the optimization within the quite general definition of the effective density by choosing the scaling function  $\theta$  in a way that always ensures  $\beta F_{\text{ex}}[\rho]/N=1$  in the limit that the density becomes a set of delta functions on lattice sites.

Since we have a single condition on the excess free energy, we may choose a single parameter form, for example,

$$\theta(x) = ax + (1-a)x^2, \quad (18)$$

where  $\alpha$  is the unknown [15]. Note that this form satisfies the necessary condition  $\theta(x=1)=1$ . The details for establishing the value of  $a$  are given in Appendix A, but given a form for  $\theta$ , the total free-energy functional is then well defined, and it may subsequently be minimized with respect to the localization parameter  $\alpha$  of the Gaussian density. It is the high degree of localization that allows the ideal part of the free energy to be approximated by its value for nonoverlapping Gaussians, namely,

$$\beta F_{\text{id}}/N \approx \frac{3}{2} \ln\left(\frac{\alpha}{\pi}\right) + 3 \ln(\Lambda) - \frac{5}{2}. \quad (19)$$

Evidently the ideal contribution to the total free energy is a monotonically increasing function of  $\alpha$ . By contrast, the excess free energy is a decreasing function of  $\alpha$  and it favors localization. When the sum of the two contributions yields a free-energy minimum, say, at a nonzero value of  $\alpha$  below the  $\alpha=0$  (the homogeneous liquid) value, a stable crystalline state is predicted. The effective density  $\hat{\rho}$  is a decreasing function of localization and is smaller in magnitude than the average density ( $\rho=N/V$ ) of the crystalline state. To then locate the melting parameters of the hard-sphere system, we must minimize the total free energy with respect to  $\alpha$  at a given average density of the inhomogeneous solid. Having therefore determined the free energy per unit volume of the solid, we perform a common tangent construction utilizing the known free energy of the liquid state.

In what follows we focus on applications of the MWDA functional for the excess free energy although as already pointed out there are other well-defined choices. Because the present method differs from earlier work at third-order [7] (which was limited only to the MWDA functional), and because we now have access to new analytic triplet DCF's that *exactly* obey Eq. (11) (see below), we first present results for the unoptimized [ $\theta(x)=x$ ] theory. This will enable us to ascertain, rather directly, the physical consequences that arise from working with a third-order accuracy functional when compared to the corresponding second-order approach. Calculations are subsequently performed for the melting parameters and thermodynamic properties of the hard-sphere system for several model triplet DCF's. In particular we present results for two factorization ansatz models we have recently introduced [11]. Both have the advantage of being very simple to implement since they are analytic in recipro-

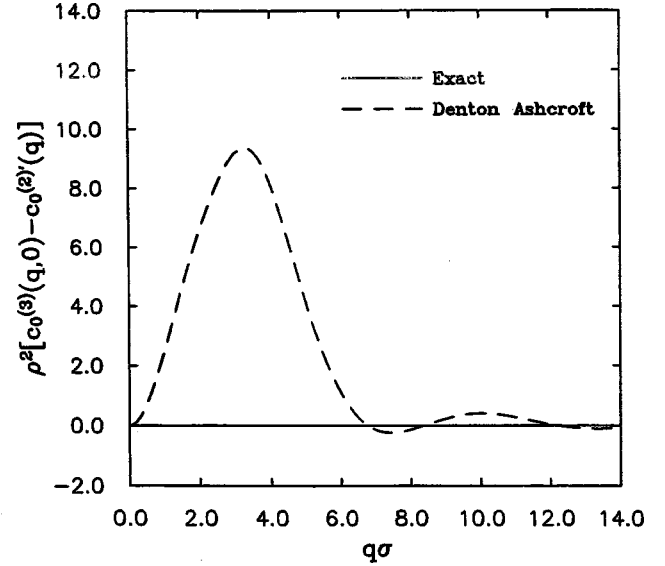


FIG. 1. Deviation of the Denton-Ashcroft model triplet direct correlation function from the exact sum rule. The solid curve is the exact result (zero). Note that for simple structures (e.g., FCC) the first reciprocal lattice vector occurs at  $q\rho_0 \approx 6.52$  and here the deviation is quite small.

cal space, but they nevertheless *exactly* satisfy the sum rule of Eq. (11) for all wave vectors. As noted above, in what follows we shall refer to these two analytic theories for the DCF as AT1 and AT2, respectively [11]; they are briefly summarized in Appendix B. The AT1 and AT2 theories are representative of simple analytic theories for the DCF and may be considered similar to results anticipated through the use of the weighted density approximation for the triplet DCF.

The final triplet theory we investigate here derives from the weighted density approximation (WDA) approximation to the first-order DCF as introduced by Denton and Ashcroft (DA) [10]. This model also has an advantage in that it flows

TABLE I. Melting parameters for hard spheres with and without functional optimization, for various triplet functionals. For comparison, MWDA results using only a second-order DCF are included as well. Simulation data is denoted by ‘‘Sim’’ and optimized functional calculations are denoted by a yes in the ‘‘opt’’ column and the parameter  $a$  is the corresponding value in Eq. (18). The quantities  $\rho_s$  and  $\rho_l$  are the coexisting solid and liquid densities,  $\Delta\rho$  is their difference, and  $\sigma$  is the hard-sphere diameter. The quantity  $\Delta s/k_B$  is the entropy change per particle and  $L$  is the Lindemann parameter.

Functional	Opt	$\theta$	$\rho_s\sigma^3$	$\rho_l\sigma^3$	$\Delta\rho\sigma^3$	$\Delta s/k_B$	$L$
Sim <sup>a</sup>			1.04	0.94	0.10	1.16	0.126
DA	no	$\alpha=1.0000$	1.005	0.882	0.122	1.24	0.124
DA	yes	$a=1.1019$	1.021	0.902	0.119	1.26	0.121
AT1	no	$a=1.0000$	1.029	0.922	0.107	1.21	0.120
AT2	no	$a=1.0000$	1.029	0.918	0.111	1.23	0.119
AT2	yes	$a=1.1847$	1.060	0.954	0.106	1.29	0.114
2nd order <sup>b</sup>	no	$a=1.0000$	1.030	0.880	0.150	1.47	0.107

<sup>a</sup>Reference [18].

<sup>b</sup>Reference [8].

TABLE II. Free energies  $\beta F/N$  for hard spheres as calculated using various triplet DCF's as input. Simulation data is denoted by "Sim." The subscript "opt" indicates that the calculation was performed using an optimized functional. The quantity  $\rho_s$  is the coexisting solid density and  $\sigma$  is the hard-sphere diameter. The column labeled MWDA<sub>2</sub> gives second-order results for comparison.

$\rho_s \sigma^3$	DA	DA <sub>opt</sub>	AT1	AT2	AT2 <sub>opt</sub>	MWDA <sub>2</sub>	Sim <sup>a</sup>
1.000	4.238	4.345	4.444	4.425	4.612	4.240	4.661
1.025	4.462	4.576	4.688	4.665	4.866	4.441	4.868
1.050	4.697	4.817	4.945	4.918	5.131	4.652	5.099
1.075	4.945	5.071	5.216	5.183	5.408	4.875	5.354
1.100	5.209	5.340	5.502	5.465	5.699	5.112	5.663

<sup>a</sup>Reference [19].

from a well-defined functional mapping; nevertheless, it does not exactly satisfy the sum rule on the triplet DCF. This is illustrated in Fig. 1, which shows the deviation of the DA triplet DCF from the exact sum rule. It is important to note that the discrepancy in the sum rule is mostly at wave vectors whose magnitudes fall *below* the smallest wave vector of the chosen lattice (here face-centered cubic) and consequently the DA model remains useful in its application to the calculation of the melting properties of solids [5,16]. For example, for an FCC lattice the smallest nonzero wave vector is  $|\mathbf{q}_0\sigma| = 2\pi\sqrt{3}(\rho\sigma^3/4)^{1/3}$ ; at the density of Fig. 1,  $\eta = \pi\rho\sigma^3/6 = 0.45$  and we get  $|\mathbf{q}_0\sigma| = 6.52$ , which is just beyond the region of greatest discrepancy. The discrepancy in satisfying the sum-rule condition is, therefore, of limited (but not insignificant—see Sec. IV) numerical consequence when the model is implemented.

We have also explored the triplet DCF predicted by the hybrid weighted density approximation (HWDA), recently developed by Leidl and Wagner [16]; since this theory gives an analytic representation of the DCF. Interestingly enough, we find that the DCF predicted by the theory (not the HWDA method itself) does not predict a melting transition within the global mapping DFT we develop here, except at unphysically high densities and thus it cannot be utilized in the present paper. Following a comparison of the unoptimized triplet theory to its second-order counterpart, we examine the effects of optimizing the functional in order to reproduce the limiting value of the excess free energy at close packing, in particular, to determine whether this leads to an improvement over the unoptimized triplet DCF theory. All of the calculations to be reported below are performed using the Carnahan Starling equation of state  $f(\rho) = \eta(4 - 3\eta)/(1 - \eta)^2$ , and the Verlet-Weiss DCF as parameterized by Henderson and Grundke [17].

## IV. RESULTS AND DISCUSSION

### A. Unoptimized functional

In Table I we give the melting parameters resulting from our calculations using both optimized and unoptimized functionals; crystalline free energies and pressures are given in Tables II and III, respectively. The errors in the melting parameters relative to simulation for the unoptimized functional are summarized graphically in Fig. 2 along with the second-order MWDA calculation results for comparison [8].

TABLE III. Pressures  $\beta P/\rho_s$  for hard spheres calculated using various triplet DCF's as input. Simulation data is denoted by "Sim" and optimized functional calculations by the subscript "opt." The quantity  $\rho_s$  is the coexisting solid density and  $\sigma$  is the hard-sphere diameter. The column labeled MWDA<sub>2</sub> gives second-order results for comparison.

$\rho_s \sigma^3$	DA	DA <sub>opt</sub>	AT1	AT2	AT2 <sub>opt</sub>	MWDA <sub>2</sub>	Sim <sup>a</sup>
1.000	8.76	9.04	9.56	9.40	10.00	7.89	10.25
1.025	9.40	9.66	10.26	10.08	10.62	8.45	10.81
1.050	10.14	10.38	11.06	10.87	11.35	9.10	11.49
1.075	10.99	11.22	11.96	11.75	12.21	9.87	12.30
1.100	11.96	12.18	12.98	12.75	13.18	10.78	13.26

<sup>a</sup>Reference [20].

As can be seen, the triplet DCF calculations preserve the earlier results for the liquid and solid-state transition densities, which are already satisfactory but they now significantly improve the Lindemann parameter and the excess entropy (latent heat) of the transition. The analytic theories AT1 and AT2 are seen to give very similar results for all of the melting parameters. The crystalline free energy is also shown in Fig. 3 along with second-order MWDA results for comparison [8]. Here the AT1 and AT2 DCF's give significantly better results for the free energy than previously found in the DA model itself leading to a smaller but significant improvement over the second-order data. The most striking difference between the second- and third-order approaches is seen in Fig. 4, which displays results for the pressure (equation of state) of the system. Here *all* of the triplet theories lead to significantly improved results when compared with the second-order theory, and again there is even further improvement for the AT1 and AT2 triplet DCF theories. For the

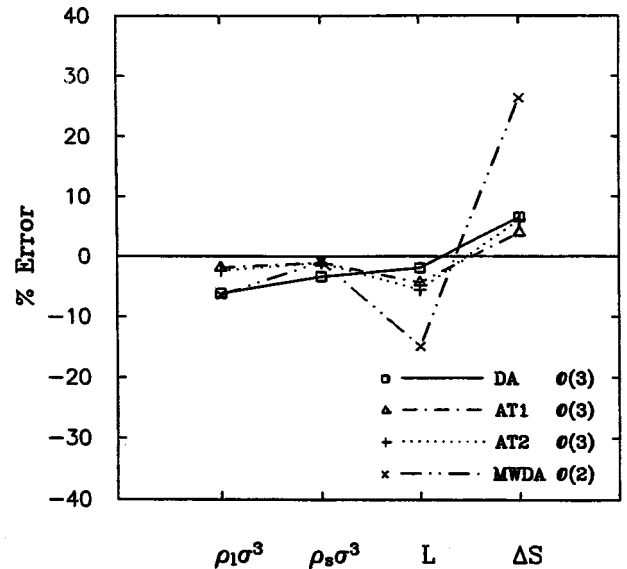


FIG. 2. Relative errors in the melting parameters for hard spheres using unoptimized functionals. Squares, triangles, and plus signs denote, respectively, the DA and the analytic theories AT1 and AT2 models for the triplet direct correlation functions. The crosses give data for the second-order theory for comparison. This data is represented numerically in Table I. The lines connecting the symbols are to guide the eye.

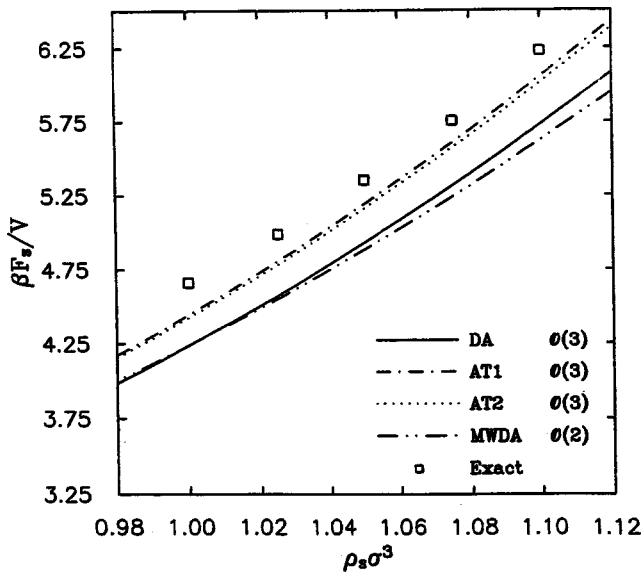


FIG. 3. Free energy of the hard-sphere solid versus average density of the solid state as predicted by the various unoptimized triplet functionals. Second-order MWDA data is included for comparison. The solid line denotes the DA model while the dash dot and dotted lines represent the analytic theories AT1 and AT2, respectively. The dash dot dot line denotes the second order MWDA results. This data is represented numerically in Table II.

pressures, it may be noted that the curvature is also reproduced correctly by all of the theories. Finally, Fig. 5 shows the value of the Gaussian localization parameter  $\alpha_0$  that minimizes the free energy at a given value of average solid density  $\rho_s = N/V$ . Here it is again evident that all of the triplet theories yield an improvement over the second-order results, the AT1 and AT2 giving slightly better results than the DA model. However, the second-order data appears to lead to somewhat better curvature in the pressure curve than the third-order results, even though the absolute error is significantly larger.

Because it bears a direct link to the mean-square displacement of the particles about their lattice sites, the localization

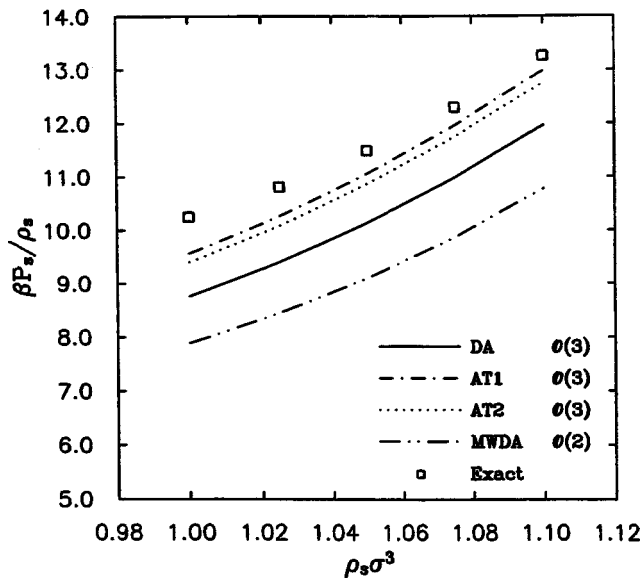


FIG. 4. As in Fig. 3 but for the pressure of the hard-sphere solid.

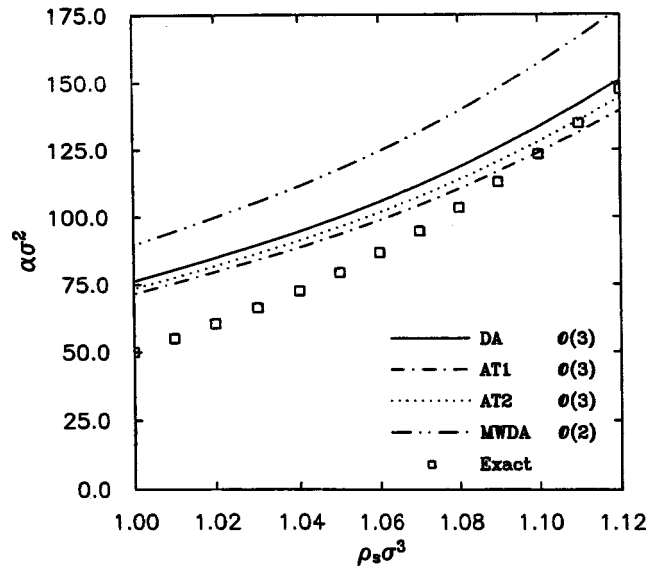


FIG. 5. As in Fig. 3 but for the density localization parameter of the hard-sphere solid.

function  $\alpha_0(\rho_s)$  provides a corresponding link to the microscopic motion of the particles (mean-square displacement) predicted by the theory. Despite its importance, this function is often ignored in similar calculations, even though it directly affects other critical melting parameters such as  $L$ , the Lindemann parameter. It is important to consider both the localization curve and the value of the crystalline transition density when considering results for the Lindemann parameter because the two functions enter as ratios into the calculation of  $L$  and may, therefore, cancel their own errors to yield a reasonable value even though the underlying microscopic mean-square displacements may be incorrect. In the second-order MWDA calculation, it is the overly large value of the localization parameter that is responsible for the small value of the Lindemann parameter, despite a satisfactory prediction for the crystalline transition density. The third-order theories yield improvements for  $L$  simply because they preserve the already satisfactory results for the crystalline transition density while continuing to improve upon the localization parameter.

By way of summary to this point, we see a clear improvement in the melting parameters and thermodynamic properties of the hard-sphere system when a third-order theory including a measure of nonlocality is implemented. Further improvement ensues when either the AT1 or AT2 theory is used for the DCF instead of the DA model, and this appears to stem from the fact that the local DCF's satisfy the exact sum-rule condition. However, as we shall now see in the optimized functional case, the DA approximation may also have other advantages, particularly at low densities.

### B. Optimized functional

Having established that the use of the triplet DCF's leads to a considerable improvement over the second-order theory, we turn to a utilization of the functional freedom in the choice of scaling functions to further improve upon the excess free-energy functional. The unoptimized functional introduced in the previous section was calculated using the

usual MWDA type of definition of the effective density, which corresponds to the choice  $\theta(x) = x = \hat{\rho}/\rho$  [see Eq. (15)]. In this section we report the results that emerge from the use of an extended definition of  $\theta$ , as given by Eq. (18). To fix the value of  $a$  in Eq. (18) we simply impose the condition that in the limit of perfect localization (where the density becomes a sum of delta functions) the excess free energy tends to the known value  $\beta F_{\text{ex}}/N = 1$  [13]. (The details are outlined in Appendix A.) We next give representative results for the analytic theories AT1, AT2 and for the DA model. A similar procedure for the form of  $\theta$  given in Eq. (18) may also be invoked for second-order theories (we have reported results for that system already [8]). When the DA model is optimized using the method of Appendix A, the resulting functional yields  $a = 1.1019$ , which is quite close to the optimized second-order theory result of  $a = 1.1847$  [8]. The proximity of agreement is to be expected, since the second-order theory already predicts the melting transition reasonably well, although as noted there remains considerable room for improvement in the thermodynamic properties of the system. In addition, the values of  $a$  are consistent with the general notion that there should be a universal density functional and that even at the low order at which the functional reproduces its homogeneous functional Taylor expansion, the self-consistent inclusion of all higher-order terms does indeed yield an accurate functional.

As a representative calculation we also optimized the AT2 theory DCF; this does not yield a value of  $a$  consistent with the DA result, nor to the second-order value, despite the fact that the AT2 triplet DCF remains quite accurate when compared to simulation results and also the fact that it gives very similar results to the DA model DCF. The reason for this discrepancy may be traced to the fact that in the calculation of  $a$  (given in Appendix A), a key factor affecting the calculation is the value of the  $\mathbf{r} = \mathbf{r}' = 0$  limit of the triplet DCF determined at the effective density that solves  $\beta F_{\text{ex}}/N = 1$ . For the MWDA this corresponds to a value of  $\hat{\rho}\sigma^3 = 0.36475$ . Thus, although the AT2 model DCF gives very good results for the actual direct correlation function for the higher densities encountered in the calculation of the effective density (typical values for the calculation are  $\rho\sigma^3 = 0.65 - 0.68$ ), it does *not* necessarily yield a satisfactory integrated result for very low densities (in the sense that the  $\mathbf{r} = \mathbf{r}' = 0$  value of  $c_0^{(3)}$  is the double reciprocal space integral of the triplet DCF). This evidently poses no problem for the DA model. Because, however, the values of  $a$  are nearly equal for the DA model optimization and the second-order optimization, it remains a satisfactory physical approximation to optimize the local functional using the second-order value of  $a = 1.1847$ .

Because models of third order DCF's depend on three variables, and are generally unknown except in certain wave-vector geometries (such as those satisfying the sum-rule conditions), it may well be more advisable to use the second-order values for the optimization of future triplet theories. The fact that the DA model yields an accurate value of  $a$  is already evidence that although there may be discrepancies in local structure between the DA model and simulation, it is likely that the integrated Fourier-space contribution remains correct. As we shall see below, the optimization of both the DA model and using the second-order value of  $a$  for the AT2

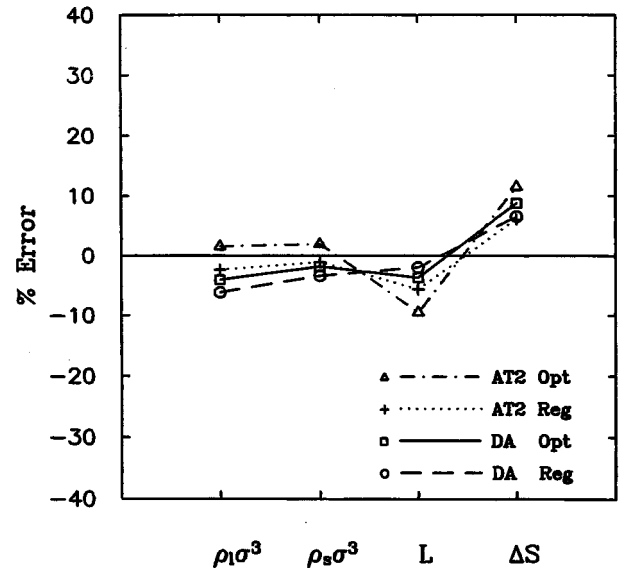


FIG. 6. Relative errors in the melting parameters for hard spheres using optimized functionals. Squares and triangles denote, respectively, the optimized DA and the analytic theory AT2 models for the triplet direct correlation function. Circles and plus signs denote, respectively, the corresponding quantities without optimization. This data is represented numerically in Table I. The lines connecting the symbols are to guide the eye. The melting parameters on the horizontal axis are the same as Table I.

theory both yield uniform improvements in both melting parameters and thermodynamic properties of the system.

Values of the melting parameters for the optimized functional are given in Table I along with unoptimized functional values for comparison. Corresponding crystalline free energies and pressures are given in Tables II and III, respectively. The errors in the melting parameters relative to simulation for the DA model and AT2 model functionals are given in Fig. 6 and as can be seen, the general trend is to increase the values of the solid and liquid transition densities; this is particularly encouraging since both continue to be underestimated in the unoptimized triplet theory. The AT2 model DCF slightly overestimates the correction while the DA model slightly underestimates the required shift. In general, there is a balance between the improvement of the melting parameters and the behavior of the thermodynamic variables. For example, the discrepancy in the excess entropy grows slightly but the transition densities are improved. The crystalline state free energy is given in Fig. 7 and again as can be seen, the optimized functional yields improvement for both the optimized DA and the AT2 functionals, with the latter in almost perfect agreement with simulation. Each value of the crystalline state free energy is the result of a separate minimization procedure so that improvement in the free energy is *not* merely the result of a simple shift in the curve but indicates that the functional itself has been improved. Similar results are found for the pressure, which is also given in Fig. 8. As can be seen, there is a uniform improvement in the pressures for both functionals and again it is evident that the optimized AT2 functional yields results that are almost in perfect agreement with simulation. Finally, Fig. 9 shows the localization parameter for the optimized functionals. Again there is a uniform improvement in the results with the local



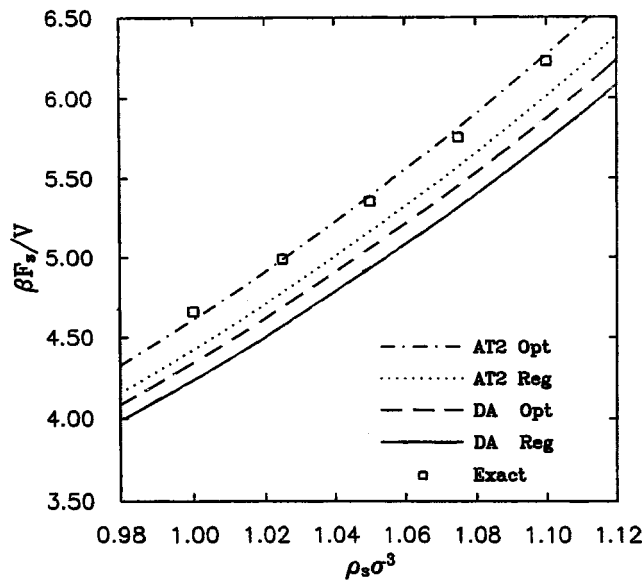


FIG. 7. Free energy of the hard-sphere solid versus average density of the solid state as predicted by the various optimized triplet functionals. The solid and dash dot lines denote, respectively, the optimized DA model and the analytic theory AT2. The dashed and dotted curves, respectively, denote the same quantities without optimization. This data is represented numerically in Table II.

functional giving a further improvement over the DA model. In summary, therefore, optimization is seen to preserve the already satisfactory results for the melting parameters of the unoptimized theory and a uniform improvement is also seen for the crystalline free energies, pressures, and localization parameters.

### V. CONCLUSION

Much detailed physics is embedded in the primary functional [2] and one of the principal aims of weighted density and related approaches has been to extract it, in part, through the successive functional derivatives constituting the direct

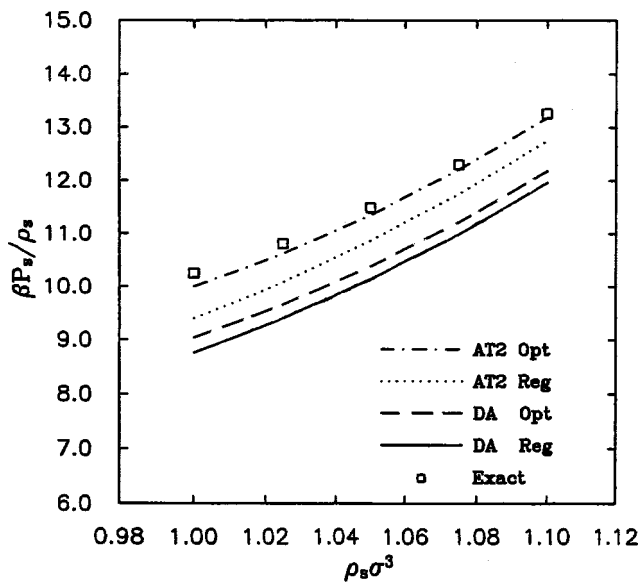


FIG. 8. As in Fig. 7 but for the pressure of the hard-sphere solid.

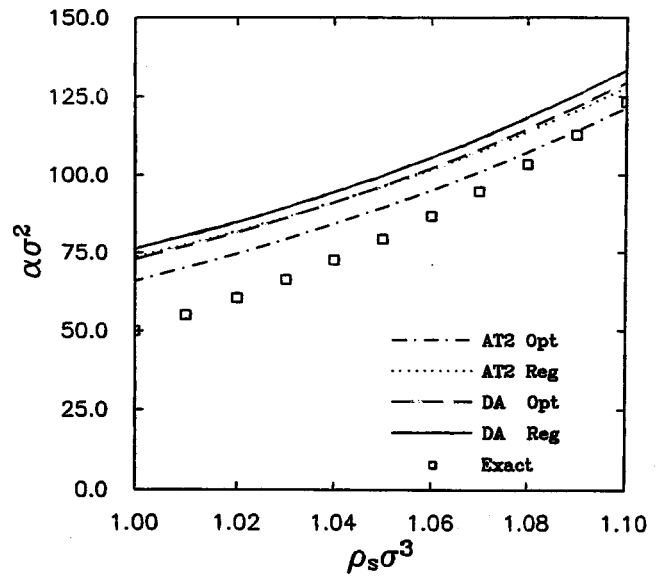


FIG. 9. As in Fig. 7 but for the density localization parameter of the hard-sphere solid.

correlation functions. Because of the subtlety of the initiating functional it is difficult to say *a priori* why some physical properties significantly improve upon inclusion of nonlocality while others fare less well (the latent heat, for example). Nevertheless, the inclusion of nonlocality into the weighted density approach seems overall to have improved the aggregate of physical properties, and therefore, by way of recapitulation we may state that what has been achieved is the following: a generalized density-functional theory is introduced, which embodies considerable functional freedom. The apparent advantage of the approach is that the functional freedom implied in the scaling functions may be systematically exploited to create functionals that are accurate to second, third, or indeed any higher order in their functional Taylor expansion about the homogeneous state. In addition they may be constrained to satisfy other known conditions on the functional. Because the formalism is easily extended to higher order, it is seen that a general  $n$ th-order theory may be formulated from a single weight function with  $n-1$  variables. Application of the method to third-order accuracy functionals yields a uniform improvement for the hard-sphere system in the melting parameters and thermodynamic functions such as free energies, pressures, and localization parameters. When the functionals are optimized to reproduce known limiting forms of the excess free energy (for hard spheres), a further improvement is again observed in the thermodynamic functions.

The two theories (AT1 and AT2) pursued in the foregoing lead to triplet correlation functions that still differ a little from the simulation results; yet as noted, their use generally leads to an overall improvement in the calculated physical properties. One factor contributing to this is the observation that when their wave-vector arguments are varied oscillatory behavior ensues. Because, however, this behavior is sampled at discrete points in lattices, the net contribution can itself be a quite notable function of the phase of the oscillatory structure (the dependence on the form of the functions away from lattice points being weaker). What this now suggests is that further effects of nonlocality may be probed in principle

through the comparison of simulation results carried out for different (but relatively simple) lattices.

### ACKNOWLEDGMENT

This work has been supported by the National Science Foundation through Grant No. DMR 9619854.

### APPENDIX A: SCALING FUNCTION DETERMINATION

In this appendix we describe a simple method for determining the form of the scaling functions based on the limiting value of the excess free energy in the close-packed limit. In this limit, the localization parameter in the Gaussian density becomes infinite and the inhomogeneous particle density is then given by a sum of delta functions on lattice sites, i.e.,  $\rho(\mathbf{r}) = \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R})$ . The corresponding Fourier-space components approach  $\mu(\mathbf{q}) = 1$  since  $\mu(\mathbf{q}) \equiv \rho(\mathbf{q})/N = \exp(-q^2/4\alpha)$ . Here  $\rho(\mathbf{q})$  is the Fourier-space transform of the density [note that  $\rho(\mathbf{q}=\mathbf{0})=N$ ]. The expression for the effective density, Eqs. (15) and (16), then becomes

$$\theta(x,y) = 1 - \frac{K_1(\theta, \hat{\rho})}{K_1(\phi, \hat{\rho})} \frac{1}{\beta f(\hat{\rho})/\hat{\rho}} \left( \frac{1}{2} \sum_{\mathbf{q} \neq \mathbf{0}} c_0^{(2)}(\mathbf{q}; \hat{\rho}) + \frac{1}{6} \hat{\rho} \sum_{\substack{\mathbf{q} \neq \mathbf{0} \\ \mathbf{q}' \neq -\mathbf{q}}} c_0^{(3)}(\mathbf{q}, \mathbf{q}'; \hat{\rho}) \right). \quad (\text{A1})$$

Our goal is to re-express all of the terms in Eq. (A1) in terms of known functions so that at close packing the only unknown is the variable  $a$  defining the scaling function in Eq. (18). We then select  $a$  such that Eq. (A1) becomes an equality. To evaluate the sums on the right-hand side of Eq. (A1) we use Parseval's theorem; starting with the equality

$$\frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') c_0^{(2)}(\mathbf{r} - \mathbf{r}'; \hat{\rho}) = \frac{1}{NV} \sum_{\mathbf{q}} \rho(\mathbf{q})^2 c_0^{(2)}(\mathbf{q}; \hat{\rho}), \quad (\text{A2})$$

and taking the close-packed limit the left-hand side becomes  $\sum_{\mathbf{R}} c_0^{(2)}(\mathbf{R}; \hat{\rho}) \approx c_0^{(2)}(\mathbf{R}=\mathbf{0}; \hat{\rho})$ . Note that the real-space DCF for hard spheres is nearly zero outside a radius  $\sigma$  and that on an FCC lattice the smallest nonzero lattice vector at close packing is greater than the hard-sphere diameter. On the right-hand side of Eq. (A2),  $\rho(\mathbf{q}) \rightarrow N$ . Factoring out the zero wave-vector component of the sum on the right side Eq. (A2) we obtain the desired result, namely,

$$\sum_{\mathbf{q} \neq \mathbf{0}} c_0^{(2)}(\mathbf{q}; \hat{\rho}) = [c_0^{(2)}(\mathbf{r}=\mathbf{0}; \hat{\rho}) - \rho c_0^{(2)}(\mathbf{q}=\mathbf{0}; \hat{\rho})]/\rho, \quad (\text{A3})$$

where the arguments of  $c_0^{(2)}$  simply signify whether we are referring to the real-space function or its Fourier transform.

The evaluation of the second sum in Eq. (A1) on the third-order DCF proceeds in a similar manner. Taking the close-packed limit of the equality,

$$\int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') \int d\mathbf{r}'' \rho(\mathbf{r}'') c_0^{(3)}(\mathbf{r} - \mathbf{r}', \mathbf{r} - \mathbf{r}''; \hat{\rho}) = \frac{1}{V^2} \sum_{\substack{\mathbf{q}, \mathbf{q}' \\ \mathbf{q} \neq \mathbf{0}}} \rho(\mathbf{q}) \rho(\mathbf{q}') \rho(\mathbf{q} + \mathbf{q}') c_0^{(3)}(\mathbf{q}, \mathbf{q}'; \hat{\rho}), \quad (\text{A4})$$

the left-hand side becomes  $N \sum_{\mathbf{R}, \mathbf{R}'} c_0^{(3)}(\mathbf{R}, \mathbf{R}'; \hat{\rho}) \approx N c_0^{(3)}(\mathbf{R}=\mathbf{0}, \mathbf{R}'=\mathbf{0}; \hat{\rho})$ . Factoring the double Fourier summation in Eq. (A4) we find

$$\begin{aligned} \sum_{\substack{\mathbf{q} \neq \mathbf{0} \\ \mathbf{q}' \neq -\mathbf{q}}} c_0^{(3)}(\mathbf{q}, \mathbf{q}'; \hat{\rho}) &= \frac{1}{\rho^2} c_0^{(3)}(\mathbf{r}=\mathbf{0}, \mathbf{r}'=\mathbf{0}; \hat{\rho}) - c_0^{(3)}(\mathbf{q}=\mathbf{0}, \mathbf{q}' \\ &= \mathbf{0}; \hat{\rho}) - \sum_{\mathbf{q} \neq \mathbf{0}} c_0^{(3)}(\mathbf{0}, \mathbf{q}; \hat{\rho}) \\ &\quad - \sum_{\mathbf{q} \neq \mathbf{0}} c_0^{(3)}(-\mathbf{q}, \mathbf{q}; \hat{\rho}). \end{aligned} \quad (\text{A5})$$

Imposing Eq. (11) for the density derivative of the second-order direct correlation function we now obtain

$$\begin{aligned} \sum_{\substack{\mathbf{q} \neq \mathbf{0} \\ \mathbf{q}' \neq -\mathbf{q}}} c_0^{(3)}(\mathbf{q}, \mathbf{q}'; \hat{\rho}) &= \frac{1}{\rho^2} c_0^{(3)}(\mathbf{r}=\mathbf{0}, \mathbf{r}'=\mathbf{0}; \hat{\rho}) \\ &\quad - c_0^{(3)}(\mathbf{q}=\mathbf{0}, \mathbf{q}'=\mathbf{0}; \hat{\rho}) \\ &\quad - \frac{2}{\rho} \left( \frac{\partial c_0^{(2)}(\mathbf{r}=\mathbf{0}; \hat{\rho})}{\partial \hat{\rho}} \right. \\ &\quad \left. - \rho \frac{\partial c_0^{(2)}(\mathbf{q}=\mathbf{0}, \hat{\rho})}{\partial \hat{\rho}} \right). \end{aligned} \quad (\text{A6})$$

The equation for the effective density at close packing becomes

$$\begin{aligned} \theta(x,y) &= 1 - \frac{K_1(\theta; \hat{\rho})}{K_1(\phi; \hat{\rho})} \frac{\hat{\rho}}{\beta f(\hat{\rho})} \left[ \frac{1}{2\rho} [c_0^{(2)}(\mathbf{r}=\mathbf{0}; \hat{\rho}) \right. \\ &\quad - \rho c_0^{(2)}(\mathbf{q}=\mathbf{0}; \hat{\rho})] + \frac{\hat{\rho}}{6} \left( \frac{c_0^{(3)}(\mathbf{r}=\mathbf{0}; \mathbf{r}'=\mathbf{0}; \hat{\rho})}{\rho^2} \right. \\ &\quad - c_0^{(3)}(\mathbf{q}=\mathbf{0}; \mathbf{q}'=\mathbf{0}; \hat{\rho}) \left. \right) - \frac{\hat{\rho}}{3\rho} [c_0^{(2)'}(\mathbf{r}=\mathbf{0}; \hat{\rho}) \\ &\quad \left. - \rho c_0^{(2)'}(\mathbf{q}=\mathbf{0}; \hat{\rho}) \right]. \end{aligned} \quad (\text{A7})$$

At this point we use the Carnahan-Starling excess free energy and the Henderson-Grudke result for the Verlet-Weiss second-order DCF [17] (both sufficiently accurate). Thus

$$c_0^{(2)}(\mathbf{r}=\mathbf{0}; \eta) = - \frac{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4}{(1 - \eta)^4}, \quad (\text{A8})$$

where  $\eta = \pi\rho\sigma^3/6$  is the packing fraction. Other functions are also simple to evaluate, e.g.,  $c_0^{(3)}(\mathbf{q}=\mathbf{0}, \mathbf{q}'=\mathbf{0}; \rho) = c_0^{(2)'}(\mathbf{q}=\mathbf{0}; \rho)$  where  $-c_0^{(2)}(\mathbf{q}=\mathbf{0})/\beta = (\rho f(\rho))'$  (primes denote density derivatives) and  $f(\eta) = \eta(4 - 3\eta)/(1 - \eta)^2$ . Evaluation of the triplet DCF at  $\mathbf{r}, \mathbf{r}' = \mathbf{0}$  is model dependent; for example, examination of the DA model yields

$$c_0^{(3)}(\mathbf{r}=\mathbf{0};\mathbf{r}'=\mathbf{0};\rho)=\frac{1}{c_0^{(1)'}(\rho)}[2c_0^{(2)}(\mathbf{r}=\mathbf{0};\rho)c_0^{(2)'}(\mathbf{r}=\mathbf{0};\rho)] - \frac{c_0^{(1)''}(\rho)}{[c_0^{(1)'}(\rho)]^2}c_0^{(2)}(\mathbf{r}=\mathbf{0};\rho)^2, \quad (\text{A9})$$

where again the primes denote (1) derivatives and  $c_0^{(1)'}(\rho) = c_0^{(2)}(\mathbf{q}=\mathbf{0};\rho)$ . Evidently, Eq. (A9) is simple to evaluate using the known second-order information. If instead we use the AT2 model DCF then we find

$$c_0^{(3)}(\mathbf{r}=\mathbf{0};\mathbf{r}'=\mathbf{0};\rho)=c_0^{(2)'}(\mathbf{r}=\mathbf{0};\rho)W(\mathbf{r}=\mathbf{0};\rho). \quad (\text{A10})$$

The value of the weight function is found from a single one-dimensional integration in Fourier space of the function in Eq. (10) of Ref. [11]. Note that at close packing on the FCC lattice,  $\rho\sigma^3=\sqrt{2}$ , and also note that the excess free energy per particle  $\beta F_{\text{ex}}/N=1$  as required in this limit [13]. Using the chosen excess free-energy functional, it is a simple matter to solve for the effective density  $\hat{\rho}$  at close packing. For example, in the MWDA, we merely solve  $\beta F_{\text{ex}}/N = \beta f(\hat{\rho})=1$  with the solution  $\hat{\eta}=(3-\sqrt{5})/4$  so  $\hat{\rho}\sigma^3=0.36475$ . Finally, having chosen the single parameter form for the scaling function  $\theta(x)=ax+(1-a)x^2$ , where  $x = \hat{\rho}/\rho$ . Equation (A7) then fixes  $a$ .

## APPENDIX B: TRIPLET DIRECT CORRELATION FUNCTIONS

In Ref. [11] arguments are presented to support a symmetry-based ansatz for the triplet correlation  $c^{(3)}$ , an extension of a proposal originally made by Barrat, Hansen, and Pastore [21], namely,

$$c_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2; \rho) = t(\mathbf{r}_1)t(\mathbf{r}_2)t(\mathbf{r}_3), \quad (\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 = \mathbf{0}), \quad (\text{B1})$$

which has a symmetric structure in real space. Key to any proposed form for  $c^{(3)}$  is the requirement that it satisfy the real-space sum rule

$$\int d\mathbf{r}_3 c_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \rho) = \frac{\partial}{\partial \rho} c_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \rho) \quad (\text{B2})$$

which, in terms of Fourier transforms, is the statement

$$c_0^{(3)}(\mathbf{q}_1, \mathbf{q}_2, 0; \rho) = \frac{\partial}{\partial \rho} c_0^{(2)}(\mathbf{q}_1, \mathbf{q}_2; 0). \quad (\text{B3})$$

Because of the simplicity of the latter, the idea introduced in Ref. [11] is to propose a *symmetric* algebraic ansatz for  $c_0^{(3)}$  through its Fourier transform, directly. A quite simple example is the doublet form

$$3c_0^{(3)}(\mathbf{q}_1, \mathbf{q}_2) = A(\rho)[W(\mathbf{q}_1)W(\mathbf{q}_2) + W(\mathbf{q}_2)W(\mathbf{q}_3) + W(\mathbf{q}_3)W(\mathbf{q}_1)],$$

where the sum rule gives  $A(\rho) = c_0^{(2)}(\mathbf{q}=\mathbf{0})$  and

$$W(\mathbf{q}; \rho) = -1 + \sqrt{1 + 3C'(\mathbf{q}; \rho)}$$

with  $C'(\mathbf{q}; \rho) = c_0^{(2)'}(\mathbf{q}; \rho)/c_0^{(2)}(\mathbf{0}; \rho)$ . Note that Eq. (B3) is obeyed exactly. This approximation for  $c_0^{(3)}$  has been identified as AT1 in the text.

As discussed in Ref. [11], a further symmetrized ansatz for the triplet direct correlation function, which incorporates nonlocality on an approximate basis, is to write

$$6c_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \rho) = c_0^{(2)'}(\vec{\mathbf{r}}_1)[W(\mathbf{r}_2) + W(\mathbf{r}_3)] + c_0^{(2)'}(\mathbf{r}_2) \times [W(\mathbf{r}_3) + W(\mathbf{r}_1)] + c_0^{(2)'}(\vec{\mathbf{r}}_3)[W(\mathbf{r}_1) + W(\mathbf{r}_2)]. \quad (\text{B4})$$

In arriving at this form the second-order direct correlation function in an inhomogeneous system is written:

$$c^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho]) = \{c_0^{(2)}[\mathbf{r}-\mathbf{r}'; \bar{\rho}(r)] + c_0^{(2)}[\mathbf{r}-\mathbf{r}'; \bar{\rho}(\bar{r}')]\}/2.$$

By defining  $W(\mathbf{r}-\mathbf{r}') = \delta\bar{\rho}(\mathbf{r})/\delta\rho(\mathbf{r}')$  we then find

$$c_0^{(3)}(\mathbf{r}-\mathbf{r}', \mathbf{r}'-\mathbf{r}''; \rho) = c_0^{(2)'}(\mathbf{r}-\mathbf{r}') [W(\mathbf{r}-\mathbf{r}'') + W(\mathbf{r}'-\mathbf{r}'')]/2.$$

The direct product form of Eq. (B4) is preserved under Fourier transformation with the result

$$6c_0^{(3)}(\mathbf{q}_1, \mathbf{q}_2; \rho) = W(\mathbf{q}_1)[c_0^{(2)'}(\mathbf{q}_2) + c_0^{(2)'}(\mathbf{q}_3)] + W(\mathbf{q}_2) \times [c_0^{(2)'}(\mathbf{q}_3) + c_0^{(2)'}(\mathbf{q}_1)] + W(\mathbf{q}_3) \times [c_0^{(2)'}(\mathbf{q}_1) + c_0^{(2)'}(\mathbf{q}_2)]. \quad (\text{B5})$$

Application of sum rule (B3) now leads to the weight function, namely [11],

$$W(\mathbf{q}; \rho) = 2c_0^{(2)'}(\mathbf{q}; \rho) / \{c_0^{(2)'}(\mathbf{q}; \rho) + [c_0^{(2)'}(\mathbf{q}=\mathbf{0}; \rho)]\}. \quad (\text{B6})$$

It is approximation (B5) for  $c_0^{(3)}$  that has been identified as AT2 in the text.

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