

Reformulation of nonperturbative density-functional theories of classical nonuniform systems

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It is shown that most nonperturbative density-functional theories of classical systems can be reformulated as second-order truncations of exact perturbative expansions, thus eliminating the *ad hoc* nature of such theories. This reformulation is used as a basis for discussion as to why some theories work better than others when applied to hard spheres, why most theories perform poorly for continuous potentials, and in what direction they might be modified so as to improve their performance.

I. INTRODUCTION

Density-functional theory (DFT) is an attempt to calculate the thermodynamic properties of inhomogeneous fluids (in this case including solids) from the known thermodynamics of the uniform fluid phase (for a review see Ref. 1). Such theories divide naturally into two types: the so-called perturbative and nonperturbative DFT's. Although providing a qualitative understanding of the hard-sphere freezing transition, the perturbative approach has been criticized on the basis of calculations performed by Cutrin² and Baus and Colot³ which seem to indicate that the underlying perturbative expansion is at best slowly convergent. This puts in doubt perturbative calculations which, for reasons of practicality, necessarily truncate the expansion at second order. The nonperturbative theories⁴⁻⁹ are an attempt to circumvent this problem by avoiding the perturbative expansion altogether. To do this, physically motivated *ad hoc* assumptions are introduced to render the exact expressions for the free energy of inhomogeneous systems calculable. Although this approach has met with considerable success in describing hard-sphere freezing, it has recently been shown^{10,11} that most nonperturbative theories fail, to a greater or lesser extent, when applied to more realistic potentials. This is not really surprising, and only serves to exemplify the underlying uncertainty of the nonperturbative approach: since the theories are based on uncontrolled approximations, one has no means to predict when they will work and when they will fail.

A previous paper⁹ attempted to address the related question of why several theories, all with different physical motivations, give more or less equivalently accurate results for hard spheres. The conclusion was that most nonperturbative theories introduce assumptions which in one way or another result in the substitution of the direct correlation function (DCF) of the liquid phase for that of the solid. On the basis of this elementary observation, a new theory was proposed, the generalized effective-liquid approximation GELA, which used this as the only assumption and which was found to reproduce the thermodynamics of the hard-sphere freezing transition to within the uncertainty of the results of simulation.⁹ Some of the

other nonperturbative theories were then shown to be derivable from the GELA given additional assumptions, thus explaining their similarity. In this paper we go further and show that several of the most commonly discussed nonperturbative theories, including the GELA, can be derived as truncations of exact perturbative expansions, thus, in some sense, eliminating the distinction between "perturbative" and "nonperturbative" theories. More importantly, the consideration of higher-order terms in the expansions for the first time provide a basis for discussing why and when a particular theory will work. It must be said, however, that the analysis of these higher-order terms is a nontrivial task, and in this paper we only attempt to draw fairly general conclusions.

In Sec. II we recall the exact density-functional relations on which all theories are based and review, briefly, the assumptions underlying several of the most popular nonperturbative DFT's. In Sec. III we introduce the generalized perturbative expansion and shown how each of the previously described theories fits into this framework. Section IV discusses some general conclusions drawn from these reformulations, including what we see to be the difficulty in applying DFT to continuous potentials and in what way modification of these theories is possible so as to remedy this problem.

II. NONPERTURBATIVE DFT

We consider a classical system enclosed at the inverse temperature $\beta = 1/k_B T$ in a vessel of volume V and corresponding to an (average) number of particles $\rho_S V$, where ρ_S is the average number density resulting from spatially averaging the local number density $\rho(\mathbf{r})$ over the volume V :

$$\rho_S = \frac{1}{V} \int_V d\mathbf{r} \rho(\mathbf{r}). \quad (2.1)$$

Here, any implicit dependence on T and V (of, e.g., the local density) will not be indicated explicitly. The quantity of interest is the (Helmholtz) free energy F of the system. We will also denote the free energy per particle as $\phi = F/(\rho_S V)$.

For a solid, which is our prototype nonuniform system,

the density $\rho(\mathbf{r})$ is nonuniform, and the dependence of ϕ on $\rho(\mathbf{r})$ is thus a functional dependence. We will indicate this by square brackets¹² as $\phi = \phi[\rho]$, indicating thereby that ϕ depends on $\rho(\mathbf{r})$ for all spatial arguments \mathbf{r} belonging to V . It consists of three terms, $\beta\phi = \beta\phi_{\text{id}} + \beta\phi_{\text{ext}} + \beta\phi_{\text{ex}}$: the ideal-gas contribution $\beta\phi_{\text{id}}$,

$$\beta\phi_{\text{id}} = \frac{1}{\rho_S V} \int_V d\mathbf{r} \rho(\mathbf{r}) \ln[\Lambda^3 \rho(\mathbf{r})] - 1, \quad (2.2)$$

with Λ being the thermal wavelength, the contribution $\beta\phi_{\text{ext}}$ from the external field $u(\mathbf{r})$,

$$\beta\phi_{\text{ext}} = \frac{1}{\rho_S V} \int_V d\mathbf{r} \rho(\mathbf{r}) u(\mathbf{r}), \quad (2.3)$$

and the excess term $\beta\phi_{\text{ex}}$, which is due to interatomic interactions. The external field represents the effect of the walls of the vessel and is responsible, e.g., for fixing the orientation of the lattice if $\rho(\mathbf{r})$ represents a crystalline solid. In practice, one assumes that all of the intensive thermodynamic variables are independent of the external

field except through its action on $\rho(\mathbf{r})$. One therefore drops $\beta\phi_{\text{ext}}$ and uses an ansatz for $\rho(\mathbf{r})$ such as $\rho(\mathbf{r}) = \rho_S$ for a uniform liquid or

$$\rho(\mathbf{r}) = \left[\frac{\alpha}{\pi} \right]^{3/2} \sum_i \exp[-\alpha(\mathbf{r} - \mathbf{R}_i)^2] \quad (2.4)$$

for a crystalline solid (see, e.g., Ref. 1). Here \mathbf{R}_i represent the lattice vectors of the solid, and the localization parameter α is subsequently fixed by minimizing the free energy with respect to it. Various asymptotic formulae and numerical results are used to evaluate $\beta\phi_{\text{id}}$ (see, e.g., Ref. 9).

Finally, the excess free energy is related to the hierarchy of direct correlation functions by

$$c_n(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) = - \frac{\delta^n \beta F_{\text{ex}}[\rho]}{\delta\rho(\mathbf{1}) \cdots \delta\rho(\mathbf{n})}, \quad (2.5)$$

where we have introduced the shorthand notation in which $\mathbf{1} \equiv \mathbf{r}_1, \dots, \mathbf{n} \equiv \mathbf{r}_n$. This equation can be functionally integrated to obtain

$$\begin{aligned} \beta\phi_{\text{ex}}[\rho] &= \frac{\rho_L}{\rho_S} \beta\phi_{\text{ex}}(\rho_L) + \left[1 - \frac{\rho_L}{\rho_S} \right] \beta\mu_{\text{ex}}(\rho_L) \\ &\quad - \frac{1}{\rho_S V} \int d\mathbf{1} d\mathbf{2} \int_0^1 d\lambda (1-\lambda) c_2(\mathbf{1}, \mathbf{2}; [\rho_L + \lambda(\rho - \rho_L)]) [\rho(\mathbf{1}) - \rho_L] [\rho(\mathbf{2}) - \rho_L]. \end{aligned} \quad (2.6)$$

In arriving at this result, we have functionally integrated in density-function space along a linear path from a uniform state with $\rho(\mathbf{r}) = \rho_L$ to an arbitrary value of $\rho(\mathbf{r})$. The initial point ρ_L is called the reference liquid density (not to be confused with the density of the coexisting liquid). Equation (2.6) is the starting point used in DFT to develop approximations for the excess free energy of nonuniform states. Equation (2.5) can also be used to express the DCF of an inhomogeneous system in terms of that of a homogeneous system by means of a functional Taylor expansion:

$$c_2(\mathbf{1}, \mathbf{2}; [\rho]) = c_2(\mathbf{1}, \mathbf{2}; \rho_L) + \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int d\mathbf{3} \cdots d\mathbf{n} c_n(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}; \rho_L) [\rho(\mathbf{3}) - \rho_L] \cdots [\rho(\mathbf{n}) - \rho_L], \quad (2.7)$$

where we have explicitly indicated the translational invariance of the DCF of the fluid phase occurring on the right side of this expression. Combining Eqs. (2.5) and (2.6), one can immediately construct the usual perturbative expansion for $\beta\phi_{\text{ex}}$, which is given by

$$\beta\phi_{\text{ex}}[\rho] = \frac{\rho_L}{\rho_S} \beta\phi_{\text{ex}}(\rho_L) + \left[1 - \frac{\rho_L}{\rho_S} \right] \beta\mu_{\text{ex}}(\rho_L) - \frac{1}{\rho_S V} \sum_{n=2}^{\infty} \frac{1}{n!} \int d\mathbf{1} \cdots d\mathbf{n} c_n(\mathbf{1}, \dots, \mathbf{n}; \rho_L) [\rho(\mathbf{1}) - \rho_L] \cdots [\rho(\mathbf{n}) - \rho_L], \quad (2.8)$$

and which was used in the original perturbative theory of Ramakrishnan and Yussouff.¹³ Normally, the reference-liquid density ρ_L is taken to be the same as the ρ_S of the solid, although it has also been proposed¹⁴ that the free energy be minimized with respect to ρ_L . The so-called second-order theory sometimes discussed in the literature is based on Eqs. (2.1) and (2.8). For reasons to become clear below, we will refer to this as the elementary second-order theory (ESO).

Having reviewed the basic DFT relations and sketched the perturbative approach, we turn to a description of some of the most well-known nonperturbative theories.

A. The ELA

The effective-liquid approximation of Baus and Colot⁵ begins by choosing $\rho_L = \rho_S$ in Eq. (2.6). The fundamental approximation introduced is that the unknown DCF for the inhomogeneous phase in Eq. (2.6) can be replaced by that of a liquid at some as yet to be determined density $\hat{\rho}_{\text{ELA}}$:

$$\beta\phi_{\text{ex}}[\rho] = \beta\phi_{\text{ex}}(\rho_L) - \frac{1}{\rho_S V} \int d\mathbf{1} d\mathbf{2} \int_0^1 d\lambda (1-\lambda) c_2(\mathbf{1}, \mathbf{2}; \hat{\rho}_{\text{ELA}}[\rho_S + \lambda(\rho - \rho_S)]) [\rho(\mathbf{1}) - \rho_S] [\rho(\mathbf{2}) - \rho_S]. \quad (2.9)$$

The theory is closed by choosing $\hat{\rho}_{\text{ELA}}$ such that the first peak of the static structure factor corresponding to $c_2(r; \hat{\rho}_{\text{ELA}}[\rho_S + \lambda(\rho - \rho_S)])$ occurs at the smallest reciprocal lattice vector of the solid prescribed by $\rho(\mathbf{r})$. Thus, $\hat{\rho}_{\text{ELA}}$ is independent of λ and the excess free energy is given by

$$\beta\phi_{\text{ex}}[\rho] = \beta\phi_{\text{ex}}(\rho_L) - \frac{1}{2\rho_S V} \int d\mathbf{1} \int d\mathbf{2} c_2(|\mathbf{1}-\mathbf{2}|; \hat{\rho}_{\text{ELA}}[\rho]) [\rho(\mathbf{1}) - \rho_S][\rho(\mathbf{2}) - \rho_S], \quad (2.10)$$

which together with the specification of $\hat{\rho}_{\text{ELA}}$ given above defines the ELA.

B. The MWDA

The modified weighted-density approximation of Denton and Ashcroft⁶ was introduced as a simplification of the weighted-density approximation of Curtin and Ashcroft.⁷ Because of the computational complexity of the latter, it has not been as widely used as the MWDA and we shall not discuss it here.

Although not originally discussed in these terms, let us begin by asking what uniform liquid density $\hat{\rho}_{\text{MWDA}}$ would give rise to the same excess free energy as a given nonuniform density $\rho(\mathbf{r})$ so that

$$\beta\phi_{\text{ex}}[\rho] = \beta\phi_{\text{ex}}(\hat{\rho}_{\text{MWDA}}). \quad (2.11)$$

Using Eq. (2.6) with $\rho_L = 0$, one can express $\hat{\rho}_{\text{MWDA}}$ as a doubly weighted density:

$$\hat{\rho}_{\text{MWDA}} = \frac{1}{\rho_S V} \int d\mathbf{1} \int d\mathbf{2} w(\mathbf{1}, \mathbf{2}; [\rho]) \rho(\mathbf{1}) \rho(\mathbf{2}), \quad (2.12)$$

where the weighting function $w(\mathbf{1}, \mathbf{2}; [\rho])$ is given by

$$w(\mathbf{1}, \mathbf{2}; [\rho]) = \frac{\int_0^1 d\lambda (1-\lambda) c_2(\mathbf{1}, \mathbf{2}; [\lambda\rho])}{\int d\mathbf{r} \int_0^1 d\lambda (1-\lambda) c_2(r; \lambda\hat{\rho}_{\text{MWDA}})}. \quad (2.13)$$

Denton and Ashcroft begin with Eqs. (2.11) and (2.12) but, rather than attempting to evaluate Eq. (2.13), they fix the weighting function by imposing several physically motivated conditions on it. First, it is required to be translationally invariant: $w(\mathbf{1}, \mathbf{2}; [\rho]) = w(|\mathbf{1}-\mathbf{2}|; [\rho])$. Second, it is required to be normalized:

$$1 = \int d\mathbf{r} w(|\mathbf{r}|; [\rho]); \quad (2.14)$$

and, third, it is only to depend on $\rho(\mathbf{r})$ implicitly via $\hat{\rho}_{\text{MWDA}}$:

$$w(|\mathbf{1}-\mathbf{2}|; [\rho]) = w(|\mathbf{1}-\mathbf{2}|; \hat{\rho}_{\text{MWDA}}[\rho]). \quad (2.15)$$

Finally, it is required that Eq. (2.5) hold for $n=2$ in the uniform limit

$$c_2(|\mathbf{1}-\mathbf{2}|, \rho_L) = - \frac{\delta^2 \beta F_{\text{ex}}[\rho]}{\delta\rho(\mathbf{1})\delta\rho(\mathbf{2})} \Big|_{\rho=\rho_L}. \quad (2.16)$$

Together, these conditions are sufficient to determine the weighting function uniquely. The MWDA may then be summarized by the resulting specification of the effective density

$$2\hat{\rho}_{\text{MWDA}}\beta\phi'_{\text{ex}}(\hat{\rho}_{\text{MWDA}}) + \rho_S\hat{\rho}_{\text{MWDA}}\beta\phi''_{\text{ex}}(\hat{\rho}_{\text{MWDA}}) = - \frac{1}{\rho_S V} \int d\mathbf{1} \int d\mathbf{2} \rho(\mathbf{1})\rho(\mathbf{2})c_2(|\mathbf{1}-\mathbf{2}|, \hat{\rho}_{\text{MWDA}}), \quad (2.17)$$

where primes denote differentiation with respect to density, and Eq. (2.11).

C. The GELA

As mentioned in the Introduction, the generalized effective-liquid approximation of Lutsko and Baus⁹ was introduced in the attempt to minimize the number of approximations used to calculate the free energy. This was done within the context of Eqs. (2.11)–(2.13) by introducing the single approximation that the DCF of the inhomogeneous phase is taken to be the same as that of some homogeneous liquid

$$\int d\mathbf{1} \int d\mathbf{2} \rho(\mathbf{1})\rho(\mathbf{2})c_2(|\mathbf{1}, \mathbf{2}|, [\lambda\rho]) = \int d\mathbf{1} \int d\mathbf{2} \rho(\mathbf{1})\rho(\mathbf{2})c_2(|\mathbf{1}-\mathbf{2}|, \hat{\rho}_{\text{GELA}}[\lambda\rho]), \quad (2.18)$$

and where Eq. (2.11) becomes, more generally,

$$\beta\phi_{\text{ex}}[\lambda\rho] = \beta\phi_{\text{ex}}(\hat{\rho}_{\text{GELA}}[\lambda\rho]), \quad (2.19)$$

which is sufficient to completely specify the GELA. A simple method for solving Eq. (2.19) has been given previously⁹ and need not be repeated here. Instead, we conclude with the observation, which shall be used later, that for fixed $\rho(\mathbf{r})$,

Eq. (2.19) only requires knowledge of $\hat{\rho}_{\text{GELA}}$ as a function of λ so that the functional dependence on $\rho(\mathbf{r})$ may be suppressed. Equation (2.19) then becomes an ordinary integral equation for $\hat{\rho}_{\text{GELA}}(\lambda)$.

D. Summary

This completes our brief survey of nonperturbative DFT's. Our aim has not been to criticize these theories or even to discuss at any length their motivations and limitations. For this, we refer the reader to the original literature. As our only comparison, we give in Table I the predictions of these theories regarding the hard-sphere freezing transition as well as the results of the second-order perturbation theory.

III. PERTURBATION THEORY REVISITED

Let us now return to the exact expression for the free energy given in Eq. (2.6). We wish to expand about a uniform state, as is usually done. However, rather than expand about a fixed reference liquid density as in Eq. (2.8), we somewhat more generally write

$$c_2(\mathbf{1}, \mathbf{2}; [\rho_L + \lambda(\rho - \rho_L)]) = c_2(|\mathbf{1} - \mathbf{2}|; \rho_L + \delta\hat{\rho}(\lambda)) + \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int d\mathbf{3} \cdots d\mathbf{n} c_n(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}; \rho_L + \delta\hat{\rho}(\lambda)) \Delta\rho(\mathbf{3}, \lambda) \cdots \Delta\rho(\mathbf{n}, \lambda), \quad (3.1)$$

where

$$\Delta\rho(\mathbf{r}, \lambda) = \lambda[\rho(\mathbf{r}) - \rho_L] - \delta\hat{\rho}(\lambda). \quad (3.2)$$

Note that both ρ_L and $\delta\hat{\rho}(\lambda)$ are as yet completely arbitrary and in general could be functionals of $\rho(\mathbf{r})$. Taking $\delta\hat{\rho}(\lambda) = 0$ we recover the simpler expansion given by Eq. (2.7), and used by Ramakrishnan and Yussouff,¹² as a special case. Substitution of Eq. (3.1) into Eq. (2.6) gives the perturbative expansion of the free energy:

$$\beta\phi_{\text{ex}}[\rho] = \frac{\rho_L}{\rho_S} \beta\phi_{\text{ex}}(\rho_L) + \left[1 - \frac{\rho_L}{\rho_S} \right] \beta\mu_{\text{ex}}(\rho_L) - \frac{1}{\rho_S V} \sum_{n=2}^{\infty} \frac{1}{(n-2)!} \int d\mathbf{1} \cdots d\mathbf{n} \int_0^1 d\lambda (1-\lambda) c_n(\mathbf{1}, \dots, \mathbf{n}; \rho_L + \delta\hat{\rho}(\lambda)) \times [\rho(\mathbf{1}) - \rho_L][\rho(\mathbf{2}) - \rho_L] \Delta\rho(\mathbf{3}, \lambda) \cdots \Delta\rho(\mathbf{n}, \lambda). \quad (3.3)$$

We now show that all of the nonperturbative DFT's discussed in Sec. II can be expressed as truncations at second order of exact perturbative expansions that differ only in their choice of ρ_L and $\delta\hat{\rho}(\lambda)$.

TABLE I. The fluid-fcc solid coexistence data as computed from various density-functional theories of hard-sphere freezing and compared to simulation results. Here $\eta = (\pi/6)\sigma^3\rho$ is the packing fraction of the coexisting solid (S) and liquid (L) phases of hard spheres of diameter σ and density ρ . Further, $\Delta\eta = \eta_S - \eta_L$ is the density change, $\Delta s = s_L - s_S$ the entropy change per particle, $p^* = \beta p \sigma^3$ the reduced pressure at coexistence, and L the corresponding Lindemann parameter [root-mean-squared displacement divided by the nearest-neighbor distance; $L = (3/\alpha a^2)^{1/2}$ for a fcc crystal, with a being the lattice constant $\rho_S = 4/a^3$]. All theories use the Percus-Yevick DCF to describe the solid, while the equation of state used for the fluid is indicated in parentheses [Percus-Yevick (PY) or Carnahan-Starling (CS)].

| | η_L | η_S | $\Delta\eta/\eta_S$ | $\Delta s/k_B$ | p^* | L |
|-----------------------------|----------|----------|---------------------|----------------|-------|-------|
| MC ^a | 0.494 | 0.545 | 0.094 | 1.16 | 11.7 | 0.126 |
| GELA ^b (CS) | 0.495 | 0.545 | 0.092 | 1.15 | 11.9 | 0.100 |
| Eq. (4.1) ^c (CS) | 0.487 | 0.534 | 0.088 | 1.04 | 11.0 | 0.110 |
| MWDA ^d (CS) | 0.476 | 0.542 | 0.122 | 1.35 | 10.1 | 0.097 |
| ELA ^e (PY) | 0.520 | 0.567 | 0.083 | 1.36 | 16.1 | 0.074 |
| ESO ^f (PY) | 0.506 | 0.601 | 0.157 | 2.47 | 15.1 | 0.06 |

^aFrom Hoover and Ree (Ref. 15).

^bFrom Lutsko and Baus (Ref. 9).

^cFrom this work.

^dFrom Denton and Ashcroft (Ref. 6).

^eFrom Baus and Colot (Ref. 5).

^fFrom Barat, Hansen, Pastore, and Waisman (Ref. 11).

A. The ELA

To recover the ELA, we very simply choose

$$\rho_L = \rho_S, \quad \delta\hat{\rho}(\lambda) = \hat{\rho}_{\text{ELA}} - \rho_S, \quad (3.4)$$

with $\hat{\rho}_{\text{ELA}}$ chosen according to the criterion of the ELA given previously. Combining Eqs. (3.3) and (3.4), we then find that

$$\begin{aligned} \beta\phi_{\text{ex}}[\rho] &= \beta\phi_{\text{ex}}[\rho]|_{\text{ELA}} \\ &- \frac{1}{\rho_S V} \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int d\mathbf{1} \cdots d\mathbf{n} \int_0^1 d\lambda (1-\lambda) c_n(\mathbf{1}, \dots, \mathbf{n}; \hat{\rho}_{\text{ELA}}) \\ &\quad \times [\rho(1) - \rho_S][\rho(2) - \rho_S] \Delta\rho_{\text{ELA}}(\mathbf{3}; \lambda) \cdots \Delta\rho_{\text{ELA}}(\mathbf{n}; \lambda), \end{aligned} \quad (3.5)$$

with

$$\Delta\rho_{\text{ELA}}(\mathbf{r}; \lambda) = \lambda[\rho(\mathbf{r}) - \rho_S] - (\hat{\rho}_{\text{ELA}} - \rho_S), \quad (3.6)$$

where the notation used in Eq. (3.5) and the following is that $\beta\phi_{\text{ex}}[\rho]|_{\text{ELA}}$ refers to the free energy *exactly as computed in the ELA*. The remaining terms are therefore the systematic corrections to the ELA.

B. The MWDA

In this case, both ρ_L and $\delta\hat{\rho}(\lambda)$ are specified by nontrivial relations. First, we set

$$\delta\hat{\rho}(\lambda) = \hat{\rho}_{\text{MWDA}} - \rho_L. \quad (3.7)$$

Comparison of Eq. (3.3) with Eq. (2.17) then leads to the condition on ρ_L that

$$\beta\phi_{\text{ex}}(\rho_L) - \rho_L \beta\phi'_{\text{ex}}(\rho_L) - \left[1 - \frac{\rho_L}{2\rho_S} \right] \rho_L^2 \beta\phi''_{\text{ex}}(\rho_L) = \beta\phi_{\text{ex}}(\hat{\rho}_{\text{MWDA}}) - \hat{\rho}_{\text{MWDA}} \beta\phi'_{\text{ex}}(\hat{\rho}_{\text{MWDA}}) - \frac{1}{2} \rho_S \hat{\rho}_{\text{MWDA}} \beta\phi''_{\text{ex}}(\hat{\rho}_{\text{MWDA}}), \quad (3.8)$$

while ρ_{MWDA} is still given by Eq. (2.17). The exact expression for the free energy then becomes

$$\begin{aligned} \beta\phi_{\text{ex}}[\rho] &= \beta\phi_{\text{ex}}[\rho]|_{\text{MWDA}} \\ &- \frac{1}{\rho_S V} \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int d\mathbf{1} \cdots d\mathbf{n} \int_0^1 d\lambda (1-\lambda) c_n(\mathbf{1}, \dots, \mathbf{n}; \hat{\rho}_{\text{MWDA}}) \\ &\quad \times [\rho(1) - \rho_L][\rho(2) - \rho_L] \Delta\rho_{\text{MWDA}}(\mathbf{3}; \lambda) \cdots \Delta\rho_{\text{MWDA}}(\mathbf{n}; \lambda), \end{aligned} \quad (3.9)$$

with

$$\Delta\rho_{\text{MWDA}}(\mathbf{r}; \lambda) = \lambda[\rho(\mathbf{r}) - \rho_L] - (\hat{\rho}_{\text{MWDA}} - \rho_L). \quad (3.10)$$

Although Eqs. (3.7) and (3.8) are deduced by comparing the perturbative expansion, Eq. (3.3), with the equations defining the MWDA, Eqs. (2.11) and (2.17), they could be equally well derived by imposing on the perturbative expansion the physical requirements of the MWDA.

C. The GELA

Like the ELA, the GELA follows very simply from the perturbative framework. We have only to choose

$$\begin{aligned} \rho_L &= 0, \\ \delta\hat{\rho}(\lambda) &= \hat{\rho}_{\text{GELA}}(\lambda) \end{aligned} \quad (3.11)$$

with $\hat{\rho}_{\text{GELA}}$ required to satisfy Eq. (2.19). The complete perturbative expansion is then

$$\begin{aligned} \beta\phi_{\text{ex}}[\rho] &= \beta\phi_{\text{ex}}[\rho]|_{\text{GELA}} \\ &- \frac{1}{\rho_S V} \sum_{n=3}^{\infty} \frac{1}{(n-2)!} \int d\mathbf{1} \cdots d\mathbf{n} \int_0^1 d\lambda (1-\lambda) c_n(\mathbf{1}, \dots, \mathbf{n}; \hat{\rho}_{\text{GELA}}(\lambda)) \\ &\quad \times \rho(1)\rho(2) \Delta\rho_{\text{GELA}}(\mathbf{3}; \lambda) \cdots \Delta\rho_{\text{GELA}}(\mathbf{n}; \lambda), \end{aligned} \quad (3.12)$$

with

$$\Delta\rho_{\text{GELA}}(\mathbf{r};\lambda)=\lambda\rho(\mathbf{r})-\hat{\rho}_{\text{GELA}}(\lambda). \quad (3.13)$$

One notable aspect of this expansion is that the $\Delta\rho(\lambda)$ term is proportional to λ [that $\hat{\rho}_{\text{GELA}}(\lambda)$ is proportional to λ is discussed in Ref. 9]. The n th term in Eq. (3.12) is therefore proportional to $(1-\lambda)\lambda^{n-2}$. Neglecting the other λ dependence in the integral in Eq. (3.12), this gives a factor, upon integration, of $1/n(n-1)$, which may well be responsible for accelerating the convergence of the series, and may account, at least in part, for the accuracy of the GELA when applied to hard spheres (see Table I).

IV. DISCUSSION

We have shown that many of the so-called nonperturbative DFT's can, in fact, be expressed as second-order truncations of exact perturbative expansions. Although they were originally proposed in order to circumvent such an expansion, in reality their success or failure is not qualitatively different from that of the elementary second-order perturbative theory. In the present context, they can all be described as perturbative theories, which, by altering the reference state of the perturbative expansion, attempt to accelerate the convergence of the expansion. This is done by fixing the parameters of the reference state(s) by forcing the truncated expansion to fulfill certain physically motivated conditions. This is, of course, not unusual. For example, Lado¹⁶ improved upon the WCA (Ref. 17) thermodynamic perturbation theory by requiring term-by-term thermodynamic consistency. This also answers a question raised in the Introduction: why do theories with such different physical motivations give such similar results? Clearly, from the present viewpoint, the theories are all just second-order truncations of the same perturbative expansion, albeit beginning with different reference states.

Besides placing the "nonperturbative" theories in a more familiar context, the present interpretation allows us to ask new questions about these theories. For example, why do the GELA and MWDA work as well as they do for hard spheres? In both cases, the effective density at which the direct correlation functions are evaluated (for the fcc solid) is quite low—about half the solid density for the MWDA. In the GELA, the effective density is λ dependent and varies in the integrals from a maximum value of about half the solid density to zero (at $\lambda=0$). (An additional factor in the case of the GELA is its unique λ dependence, as discussed above.) In contrast, the ESO evaluates the correlation functions at the solid density, while the ELA evaluates them at nearly 90% of the solid density. (Indeed, within the perturbative framework presented above, this would lead one to conclude that there is little difference between the ELA and the second-order perturbative theory, at least for the fcc phase.) That this explains the success of these theories is consistent with two other facts. First, correlations are

known to be weak in the hard-sphere solid. In parametrizing the pair distribution function for the hard-sphere solid, Weis¹⁸ found that beyond the nearest-neighbor shell, his data, from computer simulations, could be fit by a product of one-body densities of the form given in Eq. (2.4), thereby indicating a complete lack of correlations. Second, the GELA fails for inverse power potentials, where the effective density turns out to be much larger than for hard spheres. One is tempted to conclude that the underlying idea of the nonperturbative theories is to force the reference density to be relatively small in the solid state. This is not that easy, however, since whatever condition one imposes on the reference-state density must, for a uniform system, give the correct free energy if we are to have any hope of describing liquid-solid coexistence. The ELA, MWDA, and GELA all satisfy this property. There are, obviously, an infinite number of such conditions. For example, consider the condition that

$$b_2\hat{\rho}(\lambda)=\frac{\lambda}{2\rho_S V}\int d\mathbf{1}d\mathbf{2}\rho(\mathbf{1})\rho(\mathbf{2})\times\{1-\exp[-\beta v(|\mathbf{1}-\mathbf{2}|)]\}, \quad (4.1)$$

where b_2 is the second virial coefficient of the liquid and $v(r)$ is the interatomic potential. This is just the low-density limit of Eq. (2.19) and, used in place of Eq. (2.20) of the usual GELA formalism, gives the correct free energy of the liquid phase. (It is also identical to a condition used by Stoessel¹⁹ in a DFT-like theory.) We have recalculated the freezing point using Eq. (4.1), and otherwise following the procedures of Ref. 9 for hard spheres and the results are shown in Table I. Notwithstanding its rather unphysical nature, we see that this condition performs respectably well (and in fact gives a better value for the Lindemann parameter than the other theories).

Notwithstanding its success in the case of the hard-sphere system, DFT is still far from providing a predictive theory of liquid-solid coexistence for arbitrary pair potentials.¹⁰ The present work is an attempt to remove some of the arbitrariness of the most successful theories so as to allow one to identify why they do or do not work and to make possible their extension or modification. It is clear from the proceeding that much of the formalism of these theories is tied to the basic perturbative expansion given in Eqs. (3.1)–(3.3) and, as such, it is difficult to imagine in what way this could be modified systematically. Rather, we believe that attention should be focused on understanding the subsidiary conditions used to fix the parameters of the reference state; conditions which at this point appear as more or less arbitrary.

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