

Equivalence of two free-energy models for the inhomogeneous hard-sphere fluid

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It is shown that the free-energy model for the inhomogeneous hard-sphere fluid introduced by Rosenfeld [Phys. Rev. Lett. **63**, 980 (1989)], which contains both vector and scalar contributions, and the fully scalar expression proposed subsequently by Kierlik and Rosinberg [Phys. Rev. A **42**, 3382 (1990)] represent two equivalent forms of the same functional. This unexpected result was partly obscured by a sign error in the original derivation of the vector part.

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I. INTRODUCTION

Over the past decade, the use of density-functional (DF) methods has considerably improved our understanding of inhomogeneous classical fluids and interfacial phenomena. This success is due to the development of sophisticated approximation schemes for the intrinsic Helmholtz free energy $F[\rho]$, which is a unique functional of the one-body density $\rho(\mathbf{r})$ for a given intermolecular potential $\phi(r)$. For simple (atomic) fluids described by a pairwise potential of Lennard-Jones type, most DF theories are based on the separation of $\phi(r)$ into attractive and repulsive contributions. Attractive forces are usually treated in a mean-field fashion while repulsive forces are modeled by hard spheres. Therefore, a major goal of the theory in recent years has been the development of an accurate free-energy functional for the nonuniform hard-sphere fluid. The most popular theories are the so-called "weighted-density approximations" (WDA), which introduce some coarse-graining procedure whereby $\rho(\mathbf{r})$ is averaged over a local volume. Various versions have been proposed that correspond to different recipes for the averaging procedure (for a comprehensive recent review, see [1]). An appealing approach is the one proposed by Rosenfeld [2], which is an important improvement over other versions in that it makes an optimal use of geometric considerations and is specifically designed for mixtures, while other recipes encounter difficulties when extended to multicomponent fluids. Rosenfeld's theory is intimately related to the scaled particle description of the hard-sphere fluid [3] and, by construction, the Percus-Yevick (PY) pair direct-correlation functions $c_{ij}^{(2)}(r)$ [4] are reproduced in the limit of the uniform fluid. Simple analytic expressions of the n -body direct-correlation functions are also obtained in Fourier space, and the predictions for the triplet function are in good agreement with extensive Monte Carlo simulations [5].

In Rosenfeld's original derivation, the free-energy model contains both scalar and vector contributions, owing to his choice of the set of functions required to decompose the pair-exclusion step function [which is the exact low-density limit of $c_{ij}^{(2)}(r)$] in terms of purely geometrical factors. The possibility that weighted densi-

ties could be vectors was suggested in an earlier work of Percus [6]. However, this choice is not unique and, subsequently, two of us [7] (hereafter noted KR) proposed a simplified version of this approach, using only scalar weight functions. This second version of the theory has been shown to predict very well the density profile of hard-sphere fluids near hard and soft walls [7] and has been used to describe the adsorption of simple fluids at solid surfaces or inside narrow pores [8–10]. Another advantage of this DF theory is that it is numerically much simpler than most other WDA's.

Apart from the introduction of vector weight functions, there seem to be some other differences between the Rosenfeld and KR versions. They do not yield the same $c^{(3)}$ (although numerical results are close) and do not predict the same free energy for the crystal phase (both theories fail to describe the freezing transition, but, apparently, for opposite reasons). However, as shown below, these discrepancies are due to an unfortunate error of sign in Rosenfeld's derivation [2]. In fact, when this error is corrected, it turns out that the two theories become completely equivalent. The object of this report is to give the proof of this unexpected result.

II. TWO VERSIONS OF THE FREE-ENERGY FUNCTIONAL

Both versions of the free-energy functional are based on the assumption that the excess free energy of an n -component hard-sphere fluid mixture can be written as

$$\beta F^{\text{ex}}[\{\rho_i\}] = \int d\mathbf{r} \Phi(\{n_\alpha(\mathbf{r})\}), \quad (1)$$

where Φ is a general function of linear averages or weighted densities,

$$n_\alpha(\mathbf{r}) = \sum_{i=1}^n \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega_i^{(\alpha)}(\mathbf{r}-\mathbf{r}'), \quad (2)$$

$\rho_i(\mathbf{r})$ is the density of particles of species i , and the weights $\omega_i^{(\alpha)}(\mathbf{r})$ are individual-sphere functions that characterize the geometry of the particles and are density independent. This form of the free energy is suggested by the exact result for the one-dimensional hard rods [11] and by the remarkable structure of the PY pair direct-

correlation function, as described by Rosenfeld [12],

$$-c_{ij}^{(2)}(r) = \chi^{(3)} \Delta V_{ij}(r) + \chi^{(2)} \Delta S_{ij}(r) + \chi^{(1)} \Delta R_{ij}(r) + \chi^{(0)} \Theta(R_i + R_j - r), \quad (3)$$

where R_i is the radius of a sphere of species i , ΔV_{ij} and ΔS_{ij} are, respectively, the overlap volume and the overlap surface area of two spheres belonging to species i and j , and $\Theta(r)$ is the Heaviside function [$\Theta(r < 0) = 0$, $\Theta(r > 0) = 1$]. ΔR_{ij} is a further geometrical measure, and the coefficients $\chi^{(k)}$ depend only on the four basic variables of the scaled particle theory [3]

$$\xi^{(k)} = \sum_{i=1}^n \rho_i R_i^{(k)}, \quad k=1,2,3,4, \quad (4)$$

where $R_i^{(0)} = 1$, $R_i^{(1)} = R_i$, $R_i^{(2)} = 4\pi R_i^2$, $R_i^{(3)} = 4\pi R_i^3/3$ are the "fundamental measures" characterizing a particle of species i .

The two versions of the theory differ in their choice of Φ and of the weight functions $\omega_i^{(\alpha)}(\mathbf{r})$ (a more detailed discussion can be found in [1], [2], and [7]). In Rosenfeld's version [2], Φ contains both a scalar and a vector part

$$\bar{\Phi} = \Phi_s(\{\bar{n}_\alpha(\mathbf{r})\}) + \Phi_v(\{\bar{n}_\alpha(\mathbf{r}), \bar{\mathbf{n}}_\beta(\mathbf{r})\}), \quad (5)$$

with

$$\Phi_s(\{n_\alpha(\mathbf{r})\}) = -\bar{n}_0 \ln(1 - \bar{n}_3) + \frac{\bar{n}_1 \bar{n}_2}{1 - \bar{n}_3} + \frac{1}{24\pi} \frac{\bar{n}_2^3}{(1 - \bar{n}_3)^2}, \quad (6)$$

$$\Phi_v(\{\bar{n}_\alpha(\mathbf{r}), \bar{\mathbf{n}}_\beta(\mathbf{r})\}) = -\frac{\bar{\mathbf{n}}_1 \cdot \bar{\mathbf{n}}_2}{1 - \bar{n}_3} - \frac{1}{8\pi} \frac{\bar{n}_2(\bar{\mathbf{n}}_2 \cdot \bar{\mathbf{n}}_2)}{(1 - \bar{n}_3)^2},$$

and the weight functions are

$$\begin{aligned} \bar{\omega}_i^{(3)}(r) &= \Theta(R_i - r), \quad \bar{\omega}_i^{(1)}(r) = \bar{\omega}_i^{(2)}(r)/4\pi R_i, \\ \bar{\omega}_i^{(2)}(r) &= \delta(R_i - r), \quad \bar{\omega}_i^{(0)}(r) = \bar{\omega}_i^{(2)}(r)/4\pi R_i^2, \\ \bar{\omega}_i^{(2)}(\mathbf{r}) &= \frac{\mathbf{r}}{r} \delta(R_i - r), \quad \bar{\omega}_i^{(1)}(\mathbf{r}) = \bar{\omega}_i^{(2)}(\mathbf{r})/4\pi R_i. \end{aligned} \quad (7)$$

In these equations and in the following, we use the overbar to distinguish the functions introduced by Rosenfeld from those used by KR.

Φ_s is just the PY (compressibility) result, expressed in terms of scaled particle variables. Note the minus sign in the vector part Φ_v in Eq. (6), in contrast with Rosenfeld's original expression [2,5]. This was due to an error in the Fourier transform of $c_{ij}^{(2)}(r)$, expressed as a sum of products of weight functions. From Eqs. (1), (2), and (5), one obtains

$$\begin{aligned} -c_{ij}^{(2)}(k) &= \sum_{\alpha, \alpha'} \frac{\partial^2 \bar{\Phi}}{\partial n_\alpha \partial n_{\alpha'}} \bar{\omega}_i^{(\alpha)}(k) \bar{\omega}_j^{(\alpha')}(-k) \\ &+ \sum_{\beta, \beta'} \frac{\partial^2 \bar{\Phi}}{\partial \mathbf{n}_\beta \partial \mathbf{n}_{\beta'}} \bar{\omega}_i^{(\beta)}(\mathbf{k}) \cdot \bar{\omega}_j^{(\beta')}(-\mathbf{k}). \end{aligned} \quad (8)$$

The minus sign in ω_j is irrelevant when the Fourier transforms of the weights are even functions of k , which is the case for the scalar weights. But the vector weights defined by Eq. (7) are odd functions in \mathbf{k} space, and one

has to change the sign of the vector contribution to $\bar{\Phi}$ in [2,5] in order to recover the correct PY result for $c_{ij}^{(2)}(k)$.

In the KR version [7], one has simply

$$\Phi = \Phi_s(\{n_\alpha(\mathbf{r})\}), \quad (9)$$

with four scalar weight functions defined by

$$\begin{aligned} \omega_i^{(3)}(r) &= \bar{\omega}_i^{(3)}(r) = \Theta(R_i - r), \\ \omega_i^{(2)}(r) &= \bar{\omega}_i^{(2)}(r) = \delta(R_i - r), \\ \omega_i^{(1)}(r) &= \frac{1}{8\pi} \delta'(R_i - r), \\ \omega_i^{(0)}(r) &= -\frac{1}{8\pi} \delta''(R_i - r) + \frac{1}{2\pi r} \delta'(R_i - r), \end{aligned} \quad (10)$$

where $\delta'(r)$ and $\delta''(r)$ are the first and second derivatives of $\delta(r)$, respectively. The introduction of the derivatives of the δ function is the price to pay for not using vector functions.

At first sight, the two forms of the free energy look different. However, they are equivalent, as we prove in Sec. III.

III. PROOF OF THE EQUIVALENCE OF THE TWO FORMS

To show the equivalence of the two descriptions, let us consider the quantity $\int d\mathbf{r}(\bar{\Phi} - \Phi)$. Since $n_3(\mathbf{r}) = \bar{n}_3(\mathbf{r})$ and $n_2(\mathbf{r}) = \bar{n}_2(\mathbf{r})$, we find

$$\begin{aligned} \int d\mathbf{r}(\bar{\Phi} - \Phi) &= \int d\mathbf{r} \left[-(\bar{n}_0 - n_0) \ln(1 - n_3) \right. \\ &+ \frac{(\bar{n}_1 - n_1)n_2 - \bar{\mathbf{n}}_1 \cdot \bar{\mathbf{n}}_2}{1 - n_3} \\ &\left. - \frac{1}{8\pi} \frac{n_2(\bar{\mathbf{n}}_2 \cdot \bar{\mathbf{n}}_2)}{(1 - n_3)^2} \right]. \end{aligned} \quad (11)$$

On the other hand, since

$$\bar{\mathbf{n}}_2(\mathbf{r}) = -\nabla n_3(\mathbf{r}), \quad (12)$$

we have

$$\begin{aligned} \int \frac{\bar{\mathbf{n}}_1 \cdot \bar{\mathbf{n}}_2}{1 - n_3} d\mathbf{r} &= \int \bar{\mathbf{n}}_1 \cdot \nabla \ln(1 - n_3) d\mathbf{r} \\ &= -\int \nabla \cdot \bar{\mathbf{n}}_1 \ln(1 - n_3) d\mathbf{r}, \\ \int n_2 \frac{\bar{\mathbf{n}}_2 \cdot \bar{\mathbf{n}}_2}{(1 - n_3)^2} d\mathbf{r} &= -\int n_2 \bar{\mathbf{n}}_2 \cdot \nabla \left[\frac{1}{1 - n_3} \right] d\mathbf{r} \\ &= \int \frac{\nabla \cdot (n_2 \bar{\mathbf{n}}_2)}{1 - n_3} d\mathbf{r} \\ &= -\int (\nabla \cdot \nabla) n_3 \frac{n_2}{1 - n_3} d\mathbf{r} \\ &\quad - \int (\nabla \cdot \nabla) n_2 \ln(1 - n_3) d\mathbf{r}, \end{aligned} \quad (13)$$

where we have used several integrations by parts and neglected the surface terms. Inserting in Eq. (11), we obtain

$$\int d\mathbf{r}(\bar{\Phi}-\Phi)=\int \left\{ \left[-\bar{n}_0+n_0+\nabla\cdot\bar{n}_1+\frac{1}{8\pi}(\nabla\cdot\nabla)n_2 \right] \ln(1-n_3)+\left[\bar{n}_1-n_1+\frac{1}{8\pi}(\nabla\cdot\nabla)n_3 \right] \frac{n_2}{1-n_3} \right\} d\mathbf{r}. \quad (14)$$

Now, from Eqs. (2), (7), and (12), we have

$$\begin{aligned} & -\bar{n}_0(\mathbf{r})+n_0(\mathbf{r})+\nabla\cdot\bar{n}_1(\mathbf{r})+\frac{1}{8\pi}(\nabla\cdot\nabla)n_2(\mathbf{r}) \\ &= \sum_{i=1}^n \rho_i(\mathbf{r}) \circ \left[-\frac{\omega_i^{(2)}(\mathbf{r})}{4\pi R_i^2} + \omega_i^{(0)}(\mathbf{r}) \right. \\ & \quad \left. -\frac{(\nabla\cdot\nabla)\omega_i^{(3)}(\mathbf{r})}{4\pi R_i} + \frac{(\nabla\cdot\nabla)\omega_i^{(2)}(\mathbf{r})}{8\pi} \right], \\ & \bar{n}_1(\mathbf{r})-n_1(\mathbf{r})+\frac{1}{8\pi}(\nabla\cdot\nabla)n_3(\mathbf{r}) \\ &= \sum_{i=1}^n \rho_i(\mathbf{r}) \circ \left[\frac{\omega_i^{(2)}(\mathbf{r})}{4\pi R_i} - \omega_i^{(1)}(\mathbf{r}) + \frac{(\nabla\cdot\nabla)\omega_i^{(3)}(\mathbf{r})}{8\pi} \right], \end{aligned} \quad (15)$$

where \circ denotes the convolution. Going to \mathbf{k} space and using the Fourier transforms of the weights $\omega_i^{(\alpha)}$ [7], it is easy to see that the two combinations of the weight functions that appear in Eqs. (15) are identically zero. Thus, we finally obtain

$$\int d\mathbf{r}(\bar{\Phi}-\Phi)=0, \quad (16)$$

which proves the equivalence of the two expressions of the functional.

This demonstration is valid for any type of inhomogeneity. However, as an additional verification, we have checked explicitly that the two different sets of weight functions yield the same result even for extremely inhomogeneous density profiles, as in the two-dimensional (2D) limit considered in Ref. [8], where the density has

the form $\rho(\mathbf{r})=\rho_{2D}\delta(z)$, or for a solidlike density represented by a superposition of Gaussian peaks. In the first case, the free energy is in very good agreement with the simulation data for hard disks [8], and this is the reason why this functional is well suited for applications to adsorption of gas or liquids at planar surfaces or in slit-shaped pores. In the latter case, the free energy decreases extremely rapidly with the Gaussian width and is always lower than that of the liquid; the theory is thus inherently unsuited for applications to freezing (the result in Ref. [2] is erroneous because of the wrong sign in the vector part of $\bar{\Phi}$). Of course, in the uniform three-dimensional fluid, the n -body direct-correlation functions calculated from the two descriptions are all identical. In fact, this could be an alternative proof of the equivalence. In particular, $c^{(3)}$ behaves as shown in Ref. [7].

In summary, we have shown that the free-energy models for the hard-sphere fluid based on Rosenfeld's idea to generalize scaled particle theory to nonuniform situations are more uniquely defined than thought previously [1,7], since the apparent freedom in choosing the weight functions that correspond to the PY theory in the uniform fluid is immaterial. This reinforces the belief that this version of DF theory is better founded than other WDA's.

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