Free-Energy Model for the Inhomogeneous Hard-Sphere Fluid Mixture and Density-Functional Theory of Freezing

Yaakov Rosenfeld
Nuclear Research Center–Negev, P.O. Box 9001, Beer-Sheva, Israel
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A free-energy density functional for the inhomogeneous hard-sphere fluid mixture is derived from general basic considerations and yields explicit analytic expressions for the high-order direct correlation functions of the uniform fluid. It provides the first unified derivation of the most comprehensive available analytic description of the hard-sphere thermodynamics and pair structure as given by the scaled-particle and Percus-Yevick theories. The infinite-order expansion around a uniform reference state does not lead, however, to a stable solid, thus questioning the convergence of the density-functional theory of freezing.

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Density-functional theories of inhomogeneous classical fluids[1] and of freezing[2] have received increasing attention in recent years.[3] Expansions of inhomogeneous fluid or crystal properties around a uniform reference state are generated by the *m*-particle direct correlation functions (DCF's), $c^{(m)}$, which are functional density derivatives of the excess (relative to the ideal gas) Helmholtz free energy $F_{\rm ex}$. The expansions are truncated after second order because very little is known about high-order DCF's, $c^{(n)}$ for $n \geq 3$. Model free-energy functionals, formally equivalent to an infinite-order expansion, always employ weighted (coarse-grained) densities which are *tailored* to reproduce available properties of the homogeneous fluid, notably $c^{(2)}(r)$ and sum rules.[4] Applications to hard spheres (*the* reference system for classical fluids) almost invariably[5] use the analytic solution[6] of the Percus-Yevick (PY) equation[1(a)] for $c^{(2)}$. Only recently significant simulation results for the triplet function $c^{(3)}(r,r')$ of the uniform one-component soft-sphere fluid near freezing were obtained[7] which compare favorably with a factorized *ad hock* form[7] and with the weighted density approximation (WDA) for hard spheres,[8] both gauged by a given $c^{(2)}$. The desirable more comprehensive approach to inhomogeneous fluids should be able to *derive* the uniform fluid properties. In this Letter, I make a step in that direction, and find that (a) general basic constraints on the nature of the free-energy functional fully dictate its complete form, to yield a comprehensive analytic description of the hard-sphere fluid mixture that contains both the PY and scaled-particle[9] theories in a unified way. (b) Applications of this derived free energy raise questions about the convergence of the density-functional theory of freezing.

The lowest-order graph in the diagrammatic (virial) expansion of the excess (relative to the ideal gas) chemical potential corresponds to pair exclusion. For the inhomogeneous fluid mixture of hard spheres characterized by the set of one-particle densities $\{\rho_i(r)\}$, it reads

$$\frac{\delta F_{\rm ex}(\{\rho_i(\mathbf{r})\})/k_BT}{\delta\rho_i(\mathbf{r})} \underset{\rho\to 0}{\longrightarrow} \sum_j \int d^3r'\,\rho_j(\mathbf{r})\,\theta(|\mathbf{r}-\mathbf{r}'|-(R_i+R_j)) = \sum_j \bar{\rho}_j(\mathbf{r})\,, \tag{1}$$

with the unit step function, $\theta(x>0)=0$, $\theta(x\leq 0)=1$, providing an obvious[4] possible weight function for obtaining the coarse-grained densities $\bar{\rho}_j(\mathbf{r})$. Instead, on the basis of previous work on uniform fluids,[10] I seek a description in terms of characteristic functions for the geometry of the individual spheres rather than for the pair exclusion. There is, however, a *unique* decomposition of the pair exclusion function in terms of the individual-sphere functions given by the following identity:

$$\theta(|\mathbf{r}_i-\mathbf{r}_j|-(R_i+R_j)) = \omega_i^{(3)}\otimes\omega_j^{(0)} + \omega_j^{(3)}\otimes\omega_i^{(0)} + \omega_i^{(1)}\otimes\omega_j^{(2)} + \omega_j^{(1)}\otimes\omega_i^{(2)} + \boldsymbol{\omega}_i^{(1)}\otimes\boldsymbol{\omega}_j^{(2)} + \boldsymbol{\omega}_j^{(1)}\otimes\boldsymbol{\omega}_i^{(2)}\,, \tag{2}$$

where

$$\omega_i^{(\alpha)}\otimes\omega_j^{(\gamma)} = \int \omega_i^{(\alpha)}(\mathbf{r}_i-\mathbf{x})\,\omega_j^{(\gamma)}(\mathbf{r}_j-\mathbf{x})\,d^3x\,.$$

I use greek indices to represent both scalar and vector quantities and implied "dot" products when needed to form a scalar. The characteristic (weight) functions for a three-dimensional sphere of radius R_i are defined as follows:

$$\omega_i^{(3)}(\mathbf{r}) = \theta(|\mathbf{r}|-R_i)\,, \quad \boldsymbol{\omega}_i^{(2)}(\mathbf{r}) = \nabla\theta(|\mathbf{r}|-R_i) = (\mathbf{r}/r)\,\delta(|\mathbf{r}|-R_i)\,, \quad \omega_i^{(2)}(\mathbf{r}) = |\nabla\theta(|\mathbf{r}|-R_i)| = \delta(|\mathbf{r}|-R_i)\,.$$

Through these three functions I obtain $\omega_i^{(1)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r})/4\pi R_i$, $\omega_i^{(0)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r})/4\pi R_i^2$, and $\boldsymbol{\omega}_i^{(1)}(\mathbf{r}) = \boldsymbol{\omega}_i^{(2)}(\mathbf{r})/4\pi R_i$. The scalar weights have the property $\omega_i^{(q)}(k=0) = R_i^{(q)} = 1$, R_i, S_i, and V_i for $q=0$, 1, 2, and 3, respectively (S_i and V_i denote the surface area and the volume of the sphere), while the Fourier transforms of the vector-type weights obey $\tilde{\boldsymbol{\omega}}_i^{(q)}(k=0)=0$. Specifically, denoting $t=kR_i$, $\tilde{\omega}_i^{(q)}(k)/R_i^{(q)} = \sin(t)/t$ (for $q=0,1,2$),

$$\tilde{\omega}_i^{(q)}(k)/R_i^{(q)} = 3[\sin(t) - t\cos(t)]/t^3$$

(for $q=3$), and $\tilde{\boldsymbol{\omega}}_i^{(2)}(\mathbf{k}) = -\sqrt{-1}\,\mathbf{k}\tilde{\omega}_i^{(3)}(k)$. Vector-type functions are needed in order to obtain a jump discontinuity expressed as a convolution. Defining the *dimensional* weighted densities that represent either surface or volume-averaged densities

$$n_\alpha(\mathbf{x}) = \sum_i \int \rho_i(\mathbf{x})\omega_i^{(\alpha)}(\mathbf{x}-\mathbf{x}')d^3x',$$

with dimensions $[n_q] = [\mathbf{n}_q] = (\text{volume})^{(q-3)/3}$, then in the limit of uniform densities the scalars obey $n_q(x) \to \xi_q$, where $\xi_q = \sum \rho_i R_i^{(q)}$ are the scaled particle variables,[9,10] while the vectors vanish, $\mathbf{n}_q(x) \to 0$. Using these definitions Eq. (1) takes the form

$$\frac{\delta F_{\text{ex}}/k_BT}{\delta\rho_i(\mathbf{x})} \underset{\rho\to 0}{\longrightarrow} \sum_{\alpha,\gamma} \int n_\alpha(\mathbf{x}')\omega_i^{(\gamma)}(\mathbf{x}-\mathbf{x}')d^3x',$$
$$[n_\alpha] + [\omega^\gamma] = (\text{volume})^{-1}, \tag{3}$$

(with all combinations α,γ yielding a dimensionless integral) implying the following general excess free-energy functional:

$$F_{\text{ex}}(\{\rho_i(\mathbf{r})\})/k_BT = \int d^3x\,\Phi[\{n_m(\mathbf{x}),\mathbf{n}_q(\mathbf{x})\}] \equiv \int d^3x\,\Phi[\{n_\alpha(\mathbf{x})\}]. \tag{4}$$

The sole approximation made, namely that the excess free-energy density, $\Phi[\{n_\alpha\}]$, is a *function* of only the n_α's as defined, has far reaching consequences because the desired function Φ is almost automatically derived.

(i) The excess grand potential, $\Omega_{\text{ex}} = -P_{\text{ex}}V$, is similarly expressed, $\int d^3x\,\Pi(x)$, through the excess pressure function, $\Pi[\{n_\alpha\}]$, related to Φ by $\Pi = -\Phi + \sum_\alpha n_\alpha \partial\Phi/\partial n_\alpha$. The exact relation for the uniform fluid chemical potential,[9-11] $\mu_i \to PV_i$ for $R_i \to \infty$, when imposed on our "fundamental-measure" description yields the following differential equation:

$$\Pi + n_0 = \partial\Phi/\partial n_3. \tag{5}$$

(ii) Note that n_0, n_1n_2, n_2^3, $\mathbf{n}_1\cdot\mathbf{n}_2$, and $n_2(\mathbf{n}_2\cdot\mathbf{n}_2)$ are the *only* five positive power (to yield a virial expansion) combinations of $\{n_\alpha\}$ as defined that are scalars of dimension $[\Phi] = [\Pi] = (\text{volume})^{-1}$, thus providing the basis for expressing Φ and Π with dimensionless, n_3-dependent, coefficients. (iii) Insert this basis function expansion into Eq. (5), solve the resulting five trivial differential equations, and determine the integration constants by requiring that (3) and the third virial coefficient are recovered in the low-density limit. The result is $\Phi = \Phi_S + \Phi_V$, where

$$\Phi_S[\{n_q(\mathbf{x})\}] = -n_0\ln(1-n_3) + \frac{n_1n_2}{1-n_3} + \frac{1}{24\pi}\frac{n_2^3}{(1-n_3)^2}$$

is easily recognized (with $\{n_q\} \to \{\xi_q\}$) as the scaled-particle theory excess free-energy density of the uniform hard-sphere mixture[9-11] and

$$\Phi_V[\{n_m(\mathbf{x}),\mathbf{n}_q(\mathbf{x})\}] = \frac{\mathbf{n}_1\cdot\mathbf{n}_2}{1-n_3} + \frac{1}{8\pi}\frac{n_2(\mathbf{n}_2\cdot\mathbf{n}_2)}{(1-n_3)^2},$$

which vanishes in the limit of uniform densities. The result formally looks like a $Y^{(3)}$ expansion.[12] The exact result[13] is reproduced by our approach when applied to one dimension (1D, inhomogeneous hard rods). In three dimensions it is indeed of the "rank-two representation" type as anticipated by Percus.[3(e)] Previous attempts[14] to generalize the one-dimensional result to three dimensions were mainly based on the first term in Φ_S.

The general expression for the mth order DCF in terms of convolutions of the weight functions is

$$c_{i_1i_2\cdots i_m}^{(m)}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_m) = \frac{-\delta^nF_{\text{ex}}(\{\rho_i(\mathbf{r})\})/k_BT}{\delta\rho_{i_1}(\mathbf{r}_1)\delta\rho_{i_2}(\mathbf{r}_2)\cdots\delta\rho_{i_n}(\mathbf{r}_n)}$$
$$= -\int d^3x' \sum_{\alpha_1,\alpha_2,\ldots,\alpha_m} \Phi_{\alpha_1,\alpha_2,\ldots,\alpha_m}^{(m)}(\mathbf{x}')\omega_{i_1}^{(\alpha_1)}(\mathbf{r}_1-\mathbf{x}')\omega_{i_2}^{(\alpha_2)}(\mathbf{r}_2-\mathbf{x}')\cdots\omega_{i_m}^{(\alpha_m)}(\mathbf{r}_m-\mathbf{x}').$$

Because the weight functions characterize the hard particles, $c^{(m)}$ is nonzero only for tight configurations of the particles when the intersection of all core overlaps is nonzero. Since the derivatives

$$\Phi_{\alpha_1,\alpha_2,\ldots,\alpha_m}^{(m)}(\mathbf{x}) = \left.\frac{\partial^m\Phi}{\partial n_{\alpha_1}\partial n_{\alpha_2}\cdots\partial n_{\alpha_m}}\right|_{\{n_\alpha\}=\{n_\alpha(\mathbf{x})\}}$$

become position independent in the uniform density limit, the Fourier transforms of the homogeneous $c^{(m)}$ are simply a linear combination of products of the weight-function transforms, $\tilde{\omega}_i^{(\alpha)}(k)$. In particular, the triplet function is

$$\tilde{c}_{ijq}^{(3)}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = -\sum_{\alpha,\beta,\gamma} \Phi_{\alpha,\beta,\gamma}^{(3)}[\{\xi_m\}]\omega_i^{(\alpha)}(\mathbf{k}_1)\omega_j^{(\beta)}(\mathbf{k}_2)\omega_q^{(\gamma)}(\mathbf{k}_3)\delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3).$$

Because $\tilde{\omega}_i^{(\alpha)}(k=0)=0$ for the vector-type weight functions, the small-k behavior of all $c^{(m)}$ is mainly determined by Φ_S. The exact sum rule for the uniform fluid,[7] relating the integral of $c^{(m)}$ to the density derivative of $c^{(m-1)}$, as well as Wertheim's relation for the density profile,[1(b)] are obeyed by the present model.

The pair DCF for the homogeneous fluid takes the form ($r=|\mathbf{r}_i-\mathbf{r}_j|$)

$$\begin{aligned}-c_{ij}^{(2)}(r)=\;&\chi^{(3)}[\omega_i^{(3)}\otimes\omega_j^{(3)}]+\chi^{(2)}[\omega_i^{(3)}\otimes\omega_j^{(2)}+\omega_j^{(3)}\otimes\omega_i^{(2)}]\\&+\chi^{(1)}[\omega_i^{(3)}\otimes\omega_j^{(1)}+\omega_j^{(3)}\otimes\omega_i^{(1)}+(1/4\pi)(\omega_i^{(2)}\otimes\omega_j^{(2)}+\boldsymbol{\omega}_j^{(2)}\otimes\boldsymbol{\omega}_i^{(2)})]\\&+\chi^{(0)}[\omega_i^{(3)}\otimes\omega_j^{(0)}+\omega_j^{(3)}\otimes\omega_i^{(0)}+\omega_i^{(1)}\otimes\omega_j^{(2)}+\omega_j^{(1)}\otimes\omega_i^{(2)}+\boldsymbol{\omega}_i^{(1)}\otimes\boldsymbol{\omega}_j^{(2)}+\boldsymbol{\omega}_j^{(1)}\otimes\boldsymbol{\omega}_i^{(2)}]\,,\end{aligned}$$

where

$$\chi^{(q)}=\partial^2\Phi_S/\partial\xi_3\partial\xi_q\,.$$

It is identical, by each $\chi^{(q)}$ term, to the PY DCF written as[10]

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

thus providing a new representation for the exact analytic solution of the PY equation in terms of convolutions of the weight functions. For two spheres R_i and R_j at distance r, $\Delta V_{ij}(r)$ is the overlap volume, $\Delta S_{ij}(r)$ is the overlap surface area,

$$\begin{aligned}\Delta R_{ij}(r)&=\theta(r-(R_i+R_j))\\&=\Delta S_{ij}(r)/4\pi(R_i+R_j)+[R_iR_j/(R_i+R_j)]\theta(r-(R_i+R_j))\,.\end{aligned}$$

(R_i+R_j denotes mean radius of the convex envelope of the union of the two spheres.) Although this $c^{(2)}$ guarantees that the corresponding pair correlations $g^{(2)}$ vanish at core overlap for the uniform fluid, this is unlikely to happen for the general nonuniform fluid.

Figures 1 and 2 compare the present $c^{(3)}(\mathbf{k},\mathbf{k}')$ for the one-component hard-sphere system with the simulation results[7] for soft spheres given only for two particular geometries: (1) Isosceles triangles with $k=k'$ and various angles θ such that $0\le|\mathbf{k}+\mathbf{k}'|\le 2k$; (2) equilateral triangles with various side lengths. I use the packing fraction $\xi_3=0.458$ to yield the value of $c^{(3)}(0,0)$ for the "soft spheres." The overall agreement is very good for case (2), similar to that of Ref. 8. For case (1) the shape and general magnitude agree with the simulation but the hard-sphere peak occurs at smaller $\cos\theta$. Direct and more accurate simulation results for hard spheres are needed in order to check the accuracy of the model.

The fundamental-measure weight functions connect well with the Onsager smearing idea as related to the analytic solution of the mean-spherical-approximation (MSA) integral equations for electrostatic interactions.[15] Interactions between surface-smeared charges satisfy the MSA closure outside the core, while the convolutions appearing in the expression for the PV DCF are the basis functions for the analytic MSA $c_{ij}^{(2)}(r)$, inside the core ($r<R_i+R_j$). Extension of the present model to systems of charged hard particles and to plasmas is currently being investigated.

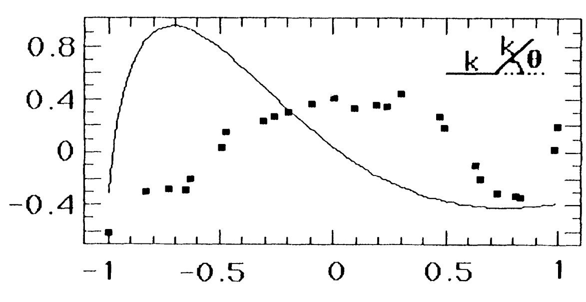

FIG. 1. Triplet DCF $c^{(3)}(k,k')$ for isosceles triangles vs $\cos\theta$ for $ka=k'a=4.3$ [$a=(3/4\pi\rho)^{1/3}$ is the Wigner-Seitz radius]. Dots represent the molecular-dynamics results for soft spheres near freezing (Ref. 7). The line represents our results for hard spheres at packing fraction 0.458.

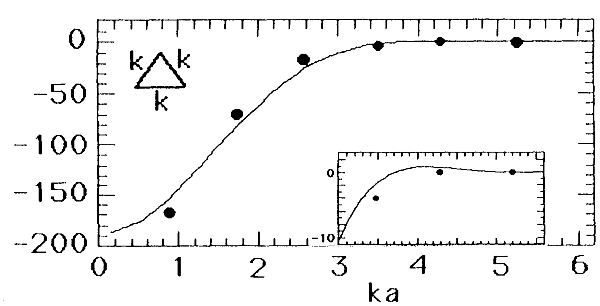

FIG. 2. Triplet DCF $c^{(3)}(k,k,k)$ vs ka for the equilateral triangle geometry. Dots represent the molecular-dynamics results for soft spheres near freezing (Ref. 7). The line represents our results for hard spheres at packing fraction 0.458. Inset: Enlargement of the region $3\le ka\le 5.6$.

The WDA of Curtin and Ashcroft[4] is fitted to the PY $c^{(2)}$ (which is our *derived* second order) and yields $c^{(3)}$ that seems to agree with our result. The results of the present model, when applied in the density-functional theory of freezing truncated at second or third order, are nearly identical to those obtained from the WDA:[16] the third-order term drastically worsening the good second-order predictions for fluid-solid coexistence conditions. The present model supports the conclusion of Curtin[16] that the convergence of the functional expansion is not sufficiently rapid to justify truncation at low orders, and that the success of the second-order theory is apparently fortuitous. Moreover, and now contrary to the WDA,[4,16] the infinite-order result of the present model does not yield a stable solid: Extensive numerical calculations reveal that in the family of one-particle densities that are obtained from Gaussian distributions at lattice sites, the uniform density limit (i.e., infinitely broad Gaussian peaks) always corresponds to minimal free energy—which is a 1D-property. In other words, the present model free energy is never lower for a crystal state than for the uniform liquid state, and thus does not predict freezing for 3D hard spheres. The fundamental-measure weight functions do not provide enough smearing of the Gaussian peaks to enable one to regard the solid as a liquid with an effective density. On the other hand, our fundamental-measure description is not *a priori* limited to small nonuniformity (since it does yield the exact 1D result) and derives the PY scaled-particle theory which is the almost canonical theory for the uniform fluid. The nature and convergence of the functional expansion for solidlike densities are, at present, not well understood and require further systematic analysis.

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