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Density functional theory of molecular fluids: Free-energy model for the inhomogeneous hard-body fluid

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By capturing the correct geometrical features, the *fundamental-measure* free-energy density functional [Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989); J. Chem. Phys. **98**, 8126 (1993)] leads to an accurate description of the general inhomogeneous simple ("atomic") fluid. It is based on the *convolution decomposition* of the excluded volume for a pair of spheres in terms of characteristic functions for the geometry of the individual spheres. By relating that convolution decomposition for spheres with the *Gauss-Bonnet theorem* for general convex bodies, the fundamental-measure functional is made applicable to fluids of asymmetric molecules.

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Density functional methods have received increasing attention in recent years, and achieved a fair amount of success and sophistication in applications to inhomogeneous classical fluids [1]. The idea is to express the free energy as a functional of the average one-body density $\rho(\vec{r})$, from which all the relevant thermodynamic functions can be calculated. The most successful functionals are those based on a coarse-graining procedure whereby weighted densities are constructed as averages of the true density profiles [1]. In contrast to the many developments in density functional theory of simple ("atomic") fluids [1], the corresponding theory for molecular fluids is at a more rudimentary stage [2], as expected in view of the increase in complexity. Ingenious *ad hoc* modifications [3] of the hard-sphere functional were required to make it applicable for hard-body liquid crystals. In turn, an alternative kind of weighted-density functional was derived recently for general inhomogeneous simple fluid mixtures [4–7], which keeps the geometric features to the forefront. Based on the fundamental geometric measures of the particles [8], it was developed *a priori* in the geometrical language applicable to general convex particles, yet derived by using geometric relations which are specific for spheres. The key was the convolution decomposition [4] of the characteristic function for the pair excluded volume of two spheres, in terms of characteristic functions for the individual spheres. The fundamental-measure functional has been tested (directly and also implicitly) very successfully, for a variety of hard and soft pair interactions and external potentials, by comparison with computer simulations of density profiles for a large variety of situations where size or packing effects play an important role [6,7,9–13], and by comparison with experiments on colloids which address the challenging question of phase separation in asymmetric binary hard-sphere mixtures [4]. It appears that by capturing the correct geometrical features, the fundamental-measure hard-sphere functional leads to an accurate description of the inhomogeneous simple fluid. The extension of this functional to molecular ("complex") fluids is now made possible by uncovering the relation between the convolution decomposition for spheres [4] and the Gauss-Bonnet theorem [14] for the geometry of convex bodies. This provides (i) a free-energy functional for hard particles, for which the accurate fundamental-measure functional for hard spheres is just a special case; (ii) a simple geometric test for its expected accuracy; and (iii) makes this powerful general method in density functional theory [6,7] applicable to fluids of asymmetric molecules.

Consider a general fluid of hard convex bodies with one-particle densities $\{\rho_i(\vec{r})\}$. For notational simplicity adopt the discrete representation for polydispersity where an object i is considered distinct from j if they differ in any of their physically relevant characteristics, such as size, shape, or orientation in space. Let $\vec{R}_i(\theta,\varphi)$ be the radius vector from the "center" of particle i to its surface, $R_i=|\vec{R}_i(\theta,\varphi)|$ (= constant for spheres), and let $\vec{r}_i$ denote the radius vector to the "center." The interaction potential $\phi_{ij}(|\vec{r}_{ij}|)$ between two hard bodies i and j is infinite if they overlap and zero otherwise, and the Mayer f function $f_{ij}(|\vec{r}_{ij}|)=\exp[-\phi_{ij}(|\vec{r}_{ij}|)/k_BT]$ characterizes the pair excluded volume,

$$\begin{aligned} f_{ij}(|\vec{r}_{ij}|)&=0 \quad \text{for } i\cap j=\varnothing, \\ f_{ij}(|\vec{r}_{ij}|)&=-1 \quad \text{for } i\cap j\neq\varnothing. \end{aligned} \tag{1}$$

Here $\vec{r}_{ij}=\vec{r}_j-\vec{r}_i$, $i\cap j$ is the intersection of the bodies, and $\varnothing$ denotes the empty set. For spheres, $f_{ij}(|\vec{r}_{ij}|)=-\Theta(|\vec{r}_{ij}|-(R_i+R_j))$, where $\Theta(x)$ is the unit step function, $\Theta(x>0)=0$, $\Theta(x\leq 0)=1$. The motivation for the fundamental-measure description [8] is to interpolate between the low density (near ideal gas) limit described by the pair excluded volume (two-particle diagram) and the ideal liquid asymptotic limit [15] characterized by one-particle geometries. Thus the following general excess (over ideal gas) free-energy functional is postulated [4–6]:

$$\frac{F_{\text{ex}}[\{\rho_i(\vec{r})\}]}{k_BT}=\int d\vec{x}\;\Phi[\{n_\alpha(\vec{x})\}], \tag{2}$$

where it is assumed that the excess free-energy density Φ is a function of only the system averaged fundamental geometric measures of the particles,

$$n_\alpha(\vec{x})=\sum_i \int \rho_i(\vec{x}')w_i^{(\alpha)}(\vec{x}'-\vec{x})d\vec{x}'. \tag{3}$$

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The weighted densities $n_\alpha(\vec{x})$ are dimensional quantities with dimensions $[n_\alpha]=(\text{volume})^{(\alpha-3)/3}$ where $0\leq\alpha\leq 3$, and provide a functional basis set for expanding the function Φ which has dimension $(\text{volume})^{-1}$. The weight functions $w_i^{(\alpha)}$ are characteristic functions for the geometry of the particles, and are determined [4–6] by expanding the Mayer two-particle function in terms of characteristic functions for the individual particles. A unique solution was found for the special case of spheres with a convolution decomposition involving a minimal number of different weight functions [4]:

$$\begin{aligned}-f_{ij}(|\vec{r}_{ij}|)&=w_i^{(0)}\otimes w_j^{(3)}+w_j^{(0)}\otimes w_i^{(3)}\\&\quad+w_i^{(1)}\otimes w_j^{(2)}+w_j^{(1)}\otimes w_j^{(2)}\\&\quad-\vec{w}_i^{(V1)}\otimes\vec{w}_j^{(V2)}-\vec{w}_j^{(V1)}\otimes\vec{w}_i^{(V2)},\end{aligned}\tag{4}$$

where the convolution product

$$w_i^{(\alpha)}\otimes w_j^{(\gamma)}=\int w_i^{(\alpha)}(\vec{x}-\vec{r}_i)\cdot w_j^{(\gamma)}(\vec{x}-\vec{r}_j)d\vec{x}\tag{5}$$

also implies the scalar product between vectors. This minimal weight-function space contains only three functions: two scalar functions representing the characteristic functions for the volume and the surface of a particle and a surface vector function

$$\begin{aligned}w_i^{(3)}(r)&=\Theta(r-R_i),\\w_i^{(2)}(\vec{r})&=|\vec{\nabla}w_i^{(3)}(r)|=\delta(r-R_i),\\\vec{w}_i^{(V2)}(\vec{r})&=\vec{\nabla}w_i^{(3)}(r)=\frac{\vec{r}}{r}\,\delta(r-R_i).\end{aligned}\tag{6}$$

The other weight functions appearing in Eq. (4) are proportional to these three, and are given by

$$\begin{aligned}w_i^{(0)}(\vec{r})&=\frac{w_i^{(2)}(\vec{r})}{4\pi R_i^2},\quad w_i^{(1)}(\vec{r})=\frac{w_i^{(2)}(\vec{r})}{4\pi R_i},\\\vec{w}_i^{(V1)}(\vec{r})&=\frac{\vec{w}_i^{(V2)}(\vec{r})}{4\pi R_i}.\end{aligned}\tag{7}$$

The following excess free-energy density was then derived [4]:

$$\Phi=\Phi_S+\Phi_V,\tag{8}$$

$$\Phi_S=-n_0\ln(1-n_3)+\frac{n_1n_2}{1-n_3}+\frac{n_2^3}{24\pi(1-n_3)^2},\tag{9}$$

$$\Phi_V=-\left(\frac{\vec{n}_{V1}\cdot\vec{n}_{V2}}{1-n_3}+\frac{n_2(\vec{n}_{V1}\cdot\vec{n}_{V2})}{8\pi(1-n_3)^2}\right).\tag{10}$$

As long as the convolution decomposition, Eq. (4), as is but with a suitable generalization of the weight functions (6) and (7), remains a good approximation for the particles composing the fluid, this same $\Phi[\{n_\alpha(x)\}]$ as a function of the fundamental weighted densities applies to the general hard-body fluid. The generalization of Eq. (4) as given below is an approximation, and as such is not limited to convex bodies. However, the mathematical derivation, using methods of differential geometry [14], is restricted to convex bodies.

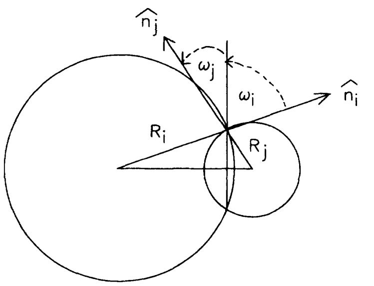

FIG. 1. Intersecting spheres. See the text.

Consider a body i, denote its surface by ∂i, and let $\hat{\mathbf{n}}_i$ be the outward unit normal to that surface. Denote by $\kappa_a^{(i)},\kappa_b^{(i)}$ the principal curvatures of the surface of the body i at any point. The first curvature of the surface of the body, $H_i=\frac{1}{2}(\kappa_a^{(i)}+\kappa_b^{(i)})$, is the mean of the principal curvatures, and the second curvature (also called the Gaussian curvature), $K_i=\kappa_a^{(i)}\kappa_b^{(i)}$, is their product. Consider a curve C drawn on the surface. The circular curvature of the curve C is denoted by κ, and the geodesic curvature of the curve at a given point on the surface is given by $\kappa_g^{(i)}=\kappa\sin\omega_i$. The angle ω_i is the normal angle of the curve, namely, the angle between its principal normal $\hat{\mathbf{n}}$ and the normal of the surface $\hat{\mathbf{n}}_i$ at the same point. $\kappa_g^{(i)}$ is zero when C is a geodesic. For spheres (see also Fig. 1) the curvatures $\kappa_a^{(i)}=\kappa_b^{(i)}=H_i=1/R_i$, $K_i=1/R_i^2$ are constant on the surface. Let S be a simply connected portion of a surface whose boundary is the closed curve C with arc length s. Let κ_g be the geodesic curvature of C and let K be the Gaussian curvature of S, then [14] (Gauss-Bonnet theorem)

$$\int_C\kappa_g ds+\int\int_S K\,dA=2\pi,\tag{11}$$

where dA is the element of area, and ds the element of arc. The integral Gaussian curvature for any convex body i is equal to 4π:

$$G(i)=\int\int_{\partial i}K_i dA_i=4\pi.\tag{12}$$

The intersection of two convex bodies is a single convex body, so that

$$f_{ij}(|\vec{r}_i-\vec{r}_j|)=-G(i\cap j)/4\pi.\tag{13}$$

The intersection $\partial i\cap j$ is the surface of i which is inside j, and the intersection $\partial i\cap\partial j$ consists of closed curves which are shared by the surfaces of i and of j. In the simple case (e.g., the spheres above) when the intersection of i and j produces only one intersection curve connecting the two pieces of $i\cap j$, we apply the Gauss-Bonnet theorem [Eq. (11)] to each piece separately, we then combine the results, and use Eq. (12) to get

$$G(i\cap j)=4\pi=\int\int_{\partial i\cap j}K_i dA_i+\int\int_{\partial j\cap i}K_j dA_j+\int_{\partial i\cap\partial j}(\kappa_g^{(i)}+\kappa_g^{(j)})ds. \qquad (14)$$

With the contributions from all connected pieces of the surface integral of K plus the integral of the geodesic curvatures $(\kappa_g^{(i)}+\kappa_g^{(j)})$ of all the boundary curves, Eq. (14) holds also when there is more than one intersection curve, or when there is no intersection curve (one body is completely inside the other).

The convolution decomposition for spheres [Eq. (4)] turns out to be just a special case of the Gauss-Bonnet theorem [Eq. (14)] for convex bodies. In order to see this, let us rewrite the convolution decomposition for the spheres using the above geometric notations. For overlap configurations of the two spheres, multiply both sides of Eq. (4) by 4π, using (13), and then it reads (term by term)

$$\begin{aligned}G(i\cap j)=4\pi=&\int\int_{\partial i\cap j}K_i dA_i+\int\int_{\partial j\cap i}K_j dA_j\\&+\int_{\partial i\cap\partial j}H_i\frac{ds}{|\hat{\mathbf{n}}_i\times\hat{\mathbf{n}}_j|}+\int_{\partial i\cap\partial j}H_j\frac{ds}{|\hat{\mathbf{n}}_i\times\hat{\mathbf{n}}_j|}\\&-\int_{\partial i\cap\partial j}H_i\frac{\hat{\mathbf{n}}_i\cdot\hat{\mathbf{n}}_j ds}{|\hat{\mathbf{n}}_i\times\hat{\mathbf{n}}_j|}-\int_{\partial i\cap\partial j}H_j\frac{\hat{\mathbf{n}}_i\cdot\hat{\mathbf{n}}_j ds}{|\hat{\mathbf{n}}_i\times\hat{\mathbf{n}}_j|}.\end{aligned} \qquad (15)$$

By using the following relations (Fig. 1): $\hat{\mathbf{n}}_i\cdot\hat{\mathbf{n}}_j=\cos(\omega_i+\omega_j)$, $|\hat{\mathbf{n}}_i\times\hat{\mathbf{n}}_j|=\sin(\omega_i+\omega_j)$, $\kappa^{-1}=R_i\cos\omega_i=R_j\cos\omega_j$, $\kappa_g^{(i)}=(\tan\omega_i)/R_i$, and the identity

$$\sin\omega_i+\sin\omega_j=\frac{1-\cos(\omega_i+\omega_j)}{\sin(\omega_i+\omega_j)}(\cos\omega_i+\cos\omega_j) \qquad (16)$$

in Eq. (15), it becomes identical to Eq. (14). However, Eq. (15) is exact for spheres but not for general convex bodies. This is because the expression [Eq. (14)] for $G(i\cap j)$ for general convex bodies contains an extra term [absent in (15)] which cannot be written in a convolution form. That extra term is exactly zero for spheres [i.e., Eq. (15)], and becomes significant with increasing deviations from sphericity.

We may thus adopt Eq. (15) as an approximation for general hard bodies. It is equivalent to the convolution decomposition Eq. (4) provided that the following set of six distinct weight functions for the general hard body i is employed:

$$\begin{gathered}w_i^{(3)}(\vec{\mathrm{r}})=\Theta(|\vec{\mathrm{r}}-\vec{\mathrm{R}}_i(\theta,\varphi)|),\\ w_i^{(2)}(\vec{\mathrm{r}})=|\vec{\nabla}w_i^{(3)}(\vec{\mathrm{r}})|=\delta(\vec{\mathrm{r}}-\vec{\mathrm{R}}_i(\theta,\varphi)),\\ \vec{\mathrm{w}}_i^{(V2)}(\vec{\mathrm{r}})=\vec{\nabla}w_i^{(3)}(\vec{\mathrm{r}})=\hat{\mathbf{n}}_i\delta(\vec{\mathrm{r}}-\vec{\mathrm{R}}_i(\theta,\varphi)), \qquad (17)\\ w_i^{(0)}(\vec{\mathrm{r}})=\frac{K_i}{4\pi}w_i^{(2)}(\vec{\mathrm{r}}),\quad w_i^{(1)}(\vec{\mathrm{r}})=\frac{H_i}{4\pi}w_i^{(2)}(\vec{\mathrm{r}}),\\ \vec{\mathrm{w}}_i^{(V1)}(\vec{\mathrm{r}})=\frac{H_i}{4\pi}\vec{\mathrm{w}}_i^{(V2)}(\vec{\mathrm{r}}).\end{gathered}$$

For spheres this set reduces to the set given by Eqs. (6) and (7). The mean and Gaussian curvatures, H_i, K_i, are not constant on the surface of the general hard body, and six different weighted densities have to be calculated separately (compared with the three for spheres). Equations (2), (3), (8)–(10), and (17) thus define the fundamental measure (FM) excess free-energy functional for the general hard-body fluid, $f_{\mathrm{FM}}^{\mathrm{ex}}$. When applied to hard spheres, $f_{\mathrm{FM}}^{\mathrm{ex}}$ reduces to the hard-sphere functional [4]. The expected accuracy (relative to that known for spheres) of $f_{\mathrm{FM}}^{\mathrm{ex}}$ can be estimated *a priori* by the extent to which Eq. (15) is a good approximation for the particles $\{i\}$ composing the fluid. It should be noticed that when the number of space dimensions is an even number, then the convolution decomposition of the Mayer f function in terms of geometric weight functions is approximate also for spheres [5]. How the functional works for the general hard-body fluid can be gleaned from the accurate fundamental-measure functional for hard disks [5].

When applied to the homogeneous hard-body fluid $\Phi_V=0$, $f_{\mathrm{FM}}^{\mathrm{ex}}$ is independent of the distribution of orientations and is equal to the form obtained from scaled particle theory [8]. This indicates that although derived for arbitrary inhomogeneous hard-body fluids, $f_{\mathrm{FM}}^{\mathrm{ex}}$ is better suited for isotropic fluids. Indeed, even though Eq. (15) is generally approximate, $f_{\mathrm{FM}}^{\mathrm{ex}}$ yields the exact second virial coefficient, B_{ij} for the isotropic hard convex body bulk fluid [16]. Using (17), integrate (4) to obtain

$$B_{ij}=\tfrac{1}{2}[V(i)+S(i)\bar{R}(j)+\bar{R}(i)S(j)+V(j)], \qquad (18)$$

where $V(i)$, $S(i)$, and $\bar{R}(i)=(1/4\pi)\int_{\partial i}H_i dA_i$ are, respectively, the volume, surface area, and mean radius of the body i. The functional $f_{\mathrm{FM}}^{\mathrm{ex}}$ predicts a third virial coefficient for the one-component isotropic hard spherocylinder bulk fluid which is only 10% smaller than the exact coefficient, even for a large length over width ratio, $L/D=6$. As can be gleaned from related work [8,18], $f_{\mathrm{FM}}^{\mathrm{ex}}$ yields an accurate equation of state for isotropic bulk fluids. Using the scaled field particle diagrammatic representation it was possible to obtain analytic geometric approximations for the direct correlation functions (DCF's) and cavity distribution functions of the general isotropic bulk hard-particle fluid, conformal to those for the hard-sphere fluid mixture [8]. Using the second functional derivatives of $f_{\mathrm{FM}}^{\mathrm{ex}}$ these DCF's are approximately reexpressed in terms of convolutions of the weight functions. Thus, when truncated at second order, $f_{\mathrm{FM}}^{\mathrm{ex}}$ reduces to a version of a recent functional which was employed successfully [2] for the inhomogeneous fluid of hard linear molecules (spherocylinders, ellipsoids). On the basis of these results it is expected that as long as the aspect ratio of the molecules (e.g., the ratio between the longest and shortest distances across the molecule) is not too large (e.g., smaller than about 5), then $f_{\mathrm{FM}}^{\mathrm{ex}}$ for isotropic hard-particle fluids will be of an accuracy comparable to that it demonstrated for the spheres.

The system of parallel hard ellipsoids (PHE's) is related to the hard spheres by an anisotropic mapping [17]. By applying that mapping on the weight functions (6) and (7), to obtain the PHE weight functions, and on Eq. (4) we find that the convolution decomposition holds exactly also for PHE's. Correspondingly, the resulting functional $f_{\mathrm{FM,PHE}}^{\mathrm{ex}}$ yields the exact analytic solution of the Percus-Yevick equations for the DCF's for the PHE fluid, and thus predicts correctly the absence of a smectic phase for the PHE fluid. The PHE's provide a very useful reference system for aligned particles [3]. Comparison with the set (17) shows that it can be improved by treating the H_i and K_i as "free" orientation dependent parameters on the surface, which can be determined by imposing the equality (15) for the bodies in question (i.e., by imposing the exact second virial coefficient for arbitrary distribution of orientations for the homogeneous fluid). Finally, the charge contributions to the direct correlation functions of charged hard-body fluids can also be discussed [15,6] in terms of the fundamental measures. The simple geometric-electrostatic description in the Onsager-bound strong-coupling limit is a good starting point.

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