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Geometrically based density functional theory of liquids

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Abstract. The geometrically based fundamental-measure free-energy density functional for hard spheres is briefly reviewed. The corresponding bridge functional can be successfully applied for a large variety of quite disparate systems, including classical plasmas. The application of the Gauss–Bonnet theorem enables one to generalize the theory to molecular fluids.

The density functional formalism is a successful and widely applicable approach to a variety of interfacial phenomena such as adsorption, wetting, and freezing, and enables one to investigate confined fluids with all sorts of inhomogeneities [1, 2]. Spatial confinements drastically affect structural and dynamical quantities as well as the location of phase transitions. The exact free-energy functional of the average one-body density, $\rho(\mathbf{r})$, should be able to provide a unifying description of all such confined situations within density functional theory. The central quantity is the excess free energy (over the exactly known ‘ideal-gas’ contributions), $F_{ex}[\rho(\mathbf{r})]$, which originates in interparticle interactions, and is generally unknown! The well studied hard-sphere fluid serves as the almost standard reference system [3] for classical fluids. It provides the starting point, and an important test, for all density functional approximations. This mini-review presents an updated outline of the geometrically based fundamental-measure free-energy density functional [4].

The fundamental-measure excess free-energy functional for a mixture of hard spheres of radii R_i in D dimensions was postulated [5] to have the following form:

$$\frac{F_{ex}[\{\rho_i(\mathbf{r})\}]}{k_B T} = \int d\mathbf{x} \Phi[\{n_\alpha(\mathbf{x})\}]. \quad (1)$$

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

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

The *weight functions* $w_i^{(\alpha)}$ are characteristic functions for the geometry of the particles. This form implies that the n -particle direct correlation functions (dcfs), which are functional derivatives of $F_{ex}[\{\rho_i(\mathbf{r})\}]$, are given by convolutions of the weight functions in the form that (a) is required by the scaled-field-particle [6] geometric analysis, and (b) incorporates the basic idea of *interpolating* between the ‘ideal-liquid’ [7] (high-density) and ideal-gas limits. The ideal-liquid pair dcf is dominated by convolutions of single-particle geometries, i.e. overlap volume and overlap surface area, and the low-density dcf is given by the pair

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exclusion volume. This interpolation is realized through the convolution decomposition of the excluded volume for a pair of convex hard bodies in terms of characteristic functions for the geometry of the two individual bodies. A *unique* solution was found for the special case of spheres with a *convolution decomposition* involving a minimal number of different weight functions [5]:

$$-f_{ij}(\mathbf{r}_{ij}) = w_i^{(0)} \otimes w_j^{(3)} + w_j^{(0)} \otimes w_i^{(3)} + w_i^{(1)} \otimes w_j^{(2)} + w_j^{(1)} \otimes w_i^{(2)} - w_i^{(V1)} \otimes w_j^{(V2)} - w_j^{(V1)} \otimes w_i^{(V2)} \quad (2)$$

where the Mayer function for a pair of spheres is minus the Heaviside step function, $f_{ij}(\mathbf{r}_{ij}) = -\Theta(R_i + R_j - r)$, and where the convolution product,

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

also implies the scalar product between vectors. The minimal weight-function space for $D \geq 1$ 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, $w_i^{(D)}(\mathbf{r}) = \Theta(R_i - r)$; $w_i^{(D-1)}(\mathbf{r}) = \delta(R_i - r)$; $w_i^{(V(D-1))}(\mathbf{r}) = (\mathbf{r}/r)\delta(R_i - r)$. The other weight functions in 3D are proportional to these three, and are given by

$$w_i^{(0)}(\mathbf{r}) = \frac{w_i^{(2)}(\mathbf{r})}{4\pi R_i^2} \quad w_i^{(1)}(\mathbf{r}) = \frac{w_i^{(2)}(\mathbf{r})}{4\pi R_i} \quad w_i^{(V,1)}(\mathbf{r}) = \frac{w_i^{(V2)}(\mathbf{r})}{4\pi R_i}.$$

The weighted densities $n_\alpha(\mathbf{x})$ are *dimensional* quantities with dimensions $[n_\alpha] = (\text{volume})^{(\alpha-D)/D}$ where $0 \leq \alpha \leq D$, and provide a functional basis set, $\{\phi_j\}$, for expanding the function, $\Phi = \sum_i A_i(n_D)\phi_i$, of dimension $(\text{volume})^{-1}$. The coefficients, $A_i(n_D)$, as functions of the dimensionless n_D are determined from the scaled-particle differential equation

$$-\Phi + \sum_\alpha n_\alpha \frac{\partial \Phi}{\partial n_\alpha} + n_0 = \frac{\partial \Phi}{\partial n_D}$$

and the constants of integration can be fixed by known limits or desirable properties. By including only the simplest positive power combinations of the weighted densities, $\{\phi_j\} = n_0, n_1 n_2, \mathbf{n}_{V1} \cdot \mathbf{n}_{V2}, n_2^3, n_2(\mathbf{n}_{V2} \cdot \mathbf{n}_{V2})$, the following excess free-energy density was derived [5]:

$$\Phi^{(D=3)}[\{n_\alpha\}] = \Phi_1^{(3)} + \Phi_2^{(3)} + \Phi_3^{(3)}$$

$$\Phi_1^{(3)} = -n_0 \ln(1 - n_3) \quad \Phi_2^{(3)} = \frac{n_1 n_2 - \mathbf{n}_{V1} \cdot \mathbf{n}_{V2}}{1 - n_3} \quad \Phi_3^{(3)} = \frac{\frac{1}{3}n_2^3 - n_2(\mathbf{n}_{V2} \cdot \mathbf{n}_{V2})}{8\pi(1 - n_3)^2}. \quad (3)$$

This free-energy model provides [8, 9] the first unified derivation of the Percus–Yevick (PY) [10] and scaled-particle-theory (SPT) [11] results for hard spheres. The PY-SPT theory is the most comprehensive available analytic description of the bulk hard-sphere thermodynamics and structure, that serves as the standard input for other *weighted-density* models. Functional differentiation of the functional (3) yields a bulk dcf which is identical to the analytic solution of the PY equation, in its geometric form [6]. It was subsequently found [12, 13] that in the special case of 3D spheres, the functional (3) is unique in the sense that a completely equivalent [14] functional can be derived which contains only scalar weight functions. This result is also important for checking numerical calculations: the calculations using this so-called ‘simplified’ version are completely equivalent to using the original functional (3). The bulk three-particle dcf was calculated in k -space [5, 12, 14] with

good agreement with simulations. The same procedure, that led to (3) in 3D, when applied [5, 8] to 1D spheres leads to the exact functional [15] for hard rods. The 2D functional [9] features an accurate bulk free energy for hard discs, and provides accurate analytic structure factors [9]. The solution of the density profile equations (i.e. the Euler–Lagrange equations for minimizing the grand potential) using the functional (3), in the special case when the external potential is generated by a *test particle* at the origin of coordinates, yields [16, 17] bulk pair correlation functions, which are generally consistent with the PY dcf obtained from functional differentiation, yet in better agreement with the simulations. The functional (3) yields the PY bulk dcfs, thus predicting that bulk hard-sphere fluid binary mixtures never phase separate. Yet in the test-particle bulk limit it predicts phase separation for large size ratios between the spheres [17]. The functional (3) yields density profiles of hard spheres and hard-sphere binary mixtures [16, 13] in slit-like pores, in very good agreement with the simulations even for narrow slits.

Quasi-2D (fluids between two narrow plates), quasi-1D (fluids inside narrow cylindrical pores), and quasi-0D (a cavity that cannot hold more than one particle) situations, provide important consistency checks of any approximate functional. The geometrically based fundamental-measure theory provides [18] the first *comprehensive* free-energy functional for 3D hard spheres with the correct properties of dimensional crossover. The term $\Phi_3^{(3)}$ diverges, however, in the 1D limit and in the 0D limit, which is why the functional (3) cannot stabilize a solid. A simple symmetrized version of $\Phi_3^{(3)}$ was introduced recently [18] in order to overcome these divergences:

$$\Phi_{3,sym}^{(3)} = \left[\frac{\frac{1}{3}(n_2)^3}{8\pi(1-n_3)^2} \right] (1-\xi^2)^3 \quad \text{with } \xi = \left| \frac{n_{V2}(\mathbf{r})}{n_2(\mathbf{r})} \right|$$

and where the form $(1-\xi^2)^3$ was chosen since it recovers $\Phi_3^{(3)}$ by the first two terms, $1-3\xi^2$, in its ξ^2 -expansion, and thus yields the same PY dcfs for the bulk fluid. Modelling the 3D solid by Gaussians at fcc sites, it was found [18] that $\Phi_{3,sym}^{(3)}$ yields better solid–fluid transition parameters [18] than almost all previous functionals when compared with simulations. In the 0D limit the new $\Phi_{3,sym}^{(3)}$ vanishes so that the functional (3) gives the exact 0D free energy. As a result it is the first that can yield the solid, with the correct vacancy concentration (i.e. the normalization of the Gaussians), under completely *free minimization!* The symmetrized form of $\Phi_{3,sym}^{(3)}$, suggested by the 0D limit, also improves the already good performance of the functional near the bulk 3D limit [18]. For the functional (3) to give the exact bulk hard-rod excess free energy, $\Phi_3^{(3)}$ must vanish in the 1D limit. The contribution of the new $\Phi_{3,sym}^{(3)}$ does not strictly vanish in the bulk 1D limit, but it is relatively very small, except near closest packing where it dominates. In the 2D limit it performs about as well as $\Phi_3^{(3)}$: the functional (3) yields the bulk hard-disc excess free energy in good agreement with simulations.

The fundamental-measure functional provides explicit simple expressions [16] for the *bridge functional*, which represents the sum of all terms *beyond second order* in the functional Taylor expansion. The *ansatz* of *universality* of the bridge functional [16], which is approximated by that for the hard spheres, enables one to apply the hard-sphere functional (3) for fluids with arbitrary interactions. With the bridge functional derived from the free-energy density (3), accurate results are obtained for the bulk pair correlation functions for a large variety of potentials, for both one-component systems and mixtures [16, 17, 19, 20], including also a highly accurate solution for the ‘inverse’ scattering problem. The hard-sphere ‘universal’ bridge functional has been tested (directly and implicitly) very successfully also for a variety of inhomogeneous systems of particles, in slab geometry, for hard- and soft-pair interactions and different external potentials [21, 22, 23]. Particularly

striking tests are provided by strong electrolytes near a charged electrode [13, 16], and by the plasma of point charges near a wall [16].

It appears from these many investigations that, by capturing the correct geometrical features, the fundamental-measure hard-sphere functional leads to accurate description of the structure of the inhomogeneous simple fluid. The fundamental-measure weighted densities have quite remarkable properties, but they cannot provide the complete basis set for the exact functional. Yet, they enable comprehensive analysis and systematic improvement of the functional: the new $\Phi_{3,sym}^{(3)}$ already provides the first comprehensive free-energy density functional for 3D hard-sphere fluids with adequate properties of dimensional crossover. The direct extension of the functional equation (3) to molecular ('complex') fluids is made possible by the relation [24] between the convolution decomposition for spheres, equation (2), and the *Gauss–Bonnet theorem* for convex bodies. An interesting application of the fundamental-measure theory [6, 5] to parallel hard cubes was published very recently [25].

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