Density Functional for Hard Sphere Crystals: A Fundamental Measure Approach

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(Received 28 July 1999)

A new free energy density functional for hard spheres is presented, along the lines of the fundamental measure theory, which reproduces the Percus-Yevick equation of state and direct correlation function for the fluid, with a tensor weighted density. The functional, based on the zero-dimension limit, is exact for any one-dimensional density distribution of the spheres. The application to the hard sphere crystals gives excellent results, solving all of the qualitative problems of previous density functional approximations, including the unit cell anisotropy in the fcc lattice and the description of the metastable bcc lattice.

The hard sphere (HS) model is central to the study of molecular packing effects in fluids [1]. The Percus-Yevick (PY) approximation for the correlation structure in the HS fluid [2] is a keystone in the theory of liquids, and the development of density functional (DF) approximations for the Helmholtz free energy of inhomogeneous HS systems, $\mathcal{F}[\rho]$, opened the study of fluids near walls or inside pores [3]. The transition from the dense HS fluid to the fcc crystal has been studied since the 1980s with nonlocal approximations for $\mathcal{F}[\rho]$, based on the previous knowledge of the thermodynamics and the direct correlation function, $c(r, \rho)$, in the bulk fluid [4,5]. The solid phase is treated as a self-maintained inhomogeneous fluid, corresponding to a local minimum of the grand potential, $\Omega = \mathcal{F}[\rho] - \mu N$, which is compared with that for the homogeneous fluid in the same approximation. The results for the coexisting fluid and solid densities and for the properties of the solid phase at higher density are quite good with different types of nonlocal DF, such as the weighted density (WDA) [6,7], the effective liquid [8] approximations (ELA) and their modified forms (MWDA, GELA) [9–11].

However, this general success has limitations: a good description of the solid phase is obtained only within a variational minimization of Ω restricted to normalized Gaussian peaks centered at the lattice positions; the relaxation of the normalization of each peak produces unphysical values of the unit cell occupancy and spoils the good results for the equation of state. Also there is a small but rather systematic error predicting too low values for the Lindemann ratio (the mean square deviation of the molecules from the lattice positions); attempts to remove this problem by relaxing the isotropic Gaussian unit cell density distributions gave qualitatively bad results, with the wrong sign for the anisotropy [12]. A new problem appears when the DF are used to describe less packed crystal structures, such as the bcc lattice which is never the equilibrium state for hard spheres but still may be useful when the HS are a reference system for softer interactions. Constrained computer simulations have been used to describe the hard sphere bcc crystal as a metastable state [13] and it is also possible to find local minima of the WDA free energy when the density is restricted to normalized peaks at the bcc lattice [13,14], but the results of the later are fully unphysical, with the Lindemann ratio increasing with the density and very high compressibility even at the close-packed density, when the molecules should be fixed at their lattice positions.

To understand the reasons for both the remarkable success of the DF theories of crystallization, within the restricted minimization of normalized isotropic peaks in the fcc lattice, and their qualitative failure when the restrictions are removed, we have to look at the way in which the DF approximations are built. The nonlocal forms for $\mathcal{F}[\rho]$ reproduce, through its second order functional derivative, a given approximation (PY usually) for $c(r, \rho)$ in the fluid. In the fcc crystal, with twelve nearest neighbor normalized Gaussian peaks around each particle, the short-range molecular correlations are similar to those in a dense homogeneous fluid, so that any $\mathcal{F}[\rho]$ built to reproduce the latter may give a good description of the crystal-free energy. However, the molecular distribution in a bcc lattice is very different from that in a fluid and the same approximations for $\mathcal{F}[\rho]$ lack the information needed to describe it [15]. Moreover, the information given by $c(r, \rho)$ and used to build $\mathcal{F}[\rho]$ includes only the linear response of the homogeneous bulk to weak external fields. Wise combinations of this information and the equation of state of the fluid have been shown to also give good descriptions of highly inhomogeneous fluids, but they still lack any direct information about the individual molecules contributing to build up the density distribution $\rho(\mathbf{r})$, so that they cannot reproduce the details of unit cell density distribution in the crystal (normalization, Lindemann ratio, and anisotropy). These problems may be avoided by the restricted minimization of Ω for the solid phase but the practical use of the theories to study the crystal interfaces is severely limited.

The fundamental measure theory (FMT) was proposed [16–18] as a different way to build approximations for $\mathcal{F}[\rho]$ which reproduce the PY equation of state and $c(r, \rho)$ for the HS fluid. The first FMT versions had a mixed flavor with excellent results in some cases (wall-fluid interfaces,

etc.) but with complete failure in the description of the HS crystal. The reason was that the nonlocality of $\mathcal{F}[\rho]$ is described through a set of *geometrical basis functions* with delta-function shells at the molecular radius distance. $\mathcal{F}[\rho]$ has convolutions of these delta-function shells to describe the sharp nonlocal dependence on $\rho(\mathbf{r})$, but the overlap of concentrical shells produced divergences which fully invalidate the use of $\mathcal{F}[\rho]$ for density distributions with narrow peaks. An empirical correction [19] opened the possibility of using the FMT for the crystal phase, but a systematic way to avoid the spurious divergences was produced only in a later work [20].

The approach is based on the *zero-dimension* (0D) limit: the free energy in a narrow cavity which cannot hold more than one molecule. For hard molecules of radius R in any dimension D, the functional form to recover this limit is [20]

$$\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + k_B T \sum_{\nu=1}^{D} \Phi_\nu^D[\rho], \tag{1}$$

where $\mathcal{F}_{id}[\rho]$ is the ideal gas-free energy. The excess is given by D terms (three for HS) with the form

$$\Phi_\nu^D[\rho] = \int d\mathbf{r}\, \varphi_\nu[\eta(\mathbf{r})] \prod_{i=1}^{\nu}$$
$$\times \int d\mathbf{R}_i w(\mathbf{R}_i)\rho(\mathbf{r} + \mathbf{R}_i) K_\nu^D, \tag{2}$$

where $\eta(\mathbf{r}) = \int_{|\mathbf{r}'| \leq R} d\mathbf{r}'\, \rho(\mathbf{r} + \mathbf{r}')$ is the local packing fraction, $\varphi_\nu(\eta)$ is the ν's order derivative of the 0D excess free energy $\varphi_0(\eta) = (1 - \eta)\log(1 - \eta) + \eta$; $w(\mathbf{R}_i)$ is a normalized delta-function shell for $|\mathbf{R}_i| = R$, and $K_\nu^D(\mathbf{R}_1, \ldots, \mathbf{R}_\nu)$ are kernels which may be fully determined from the 0D exact result for narrow cavities of arbitrary shape, with $K_1^D = 1$. For hard spheres ($D = 3$) the second kernel is $K_2^{(3)}(\mathbf{R}_1, \mathbf{R}_2) = 4\pi R(R^2 - \mathbf{R}_1 \cdot \mathbf{R}_2)$, which inserted in (2) reproduces precisely the same forms as used in the original FMT. The third kernel $K_3^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ has a complex form, defined in geometrical terms [20], and it differs from the previous empirical trials in the property that it vanishes whenever any two vectors, out of $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$, become identical. This property makes *regular* the FMT, i.e., without the spurious divergences created by the overlap of the delta-function shells, and gives a unique feature: when (1),(2) are used to evaluate the free energy of any one-dimensional (1D) density distribution, embedded in the higher molecular dimension D, the third term Φ_3^D becomes null [21], while $\Phi_1^D + \Phi_2^D$ recovers the exact 1D density functional for hard rods as given by Percus [22].

This approach may be used to build $\mathcal{F}[\rho]$ fully on the basis of the exact 0D limit, so that the equation of state and the correlation structure of the homogeneous fluid are particular outputs rather than inputs to the DF. However, and as a consequence of the *lost cases* (0D cavities with peculiar shapes which cannot be described within the FMT),

the accuracy of the results decays with increasing embedding dimension, and the purely 0D-based FMT form may be regarded as a low D expansion for $\mathcal{F}[\rho]$. On the other hand, a workable approximation for $\Phi_\nu^D[\rho]$ requires a kernel function which might be factorized in terms of one-center convolutions of $\rho(\mathbf{r})$, as it can be done with $\Phi_2^{(3)}[\rho]$ in terms of the scalar and vector weighted densities,

$$n(\mathbf{r}) = \int d\mathbf{R}\, w(\mathbf{R})\rho(\mathbf{r} + \mathbf{R}),$$

$$\mathbf{v}(\mathbf{r}) = \int d\mathbf{R}\, w(\mathbf{R})\rho(\mathbf{r} + \mathbf{R})\hat{\mathbf{R}},$$

with the unit vector $\hat{\mathbf{R}} \equiv (\hat{R}_x, \hat{R}_y, \hat{R}_z) = \mathbf{R}/R$. This is not possible with the full geometrical definition of $K_3^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$, and as a compromise it was proposed [20,23] to take $K_3^{(3)} = 12\pi^2[\mathbf{R}_1 \cdot (\mathbf{R}_2 \times \mathbf{R}_3)]^2$, which gives the PY equation of state and vanishes when the two vectors become equal. However, this kernel does not reproduce the PY correlation because it fails to give the exact first order term in the density expansion of $c(r, \rho)$ (i.e., the triangle diagram [1]).

The DF structure (1),(2), as emanated from the 0D limit, is such that if the kernel $K_3^{(3)}$ gives the exact triangle contribution to $c(r, \rho)$, it reproduces its full PY form for the bulk fluid. This is done by the new *regular form* proposed here [24]:

$$K_3^{(3)} = 4\pi^2 \left(\prod_{(ij)} [R^2 - \mathbf{R}_i \cdot \mathbf{R}_j] - [\mathbf{R}_1 \cdot (\mathbf{R}_2 \times \mathbf{R}_3)]^2 \right) \tag{3}$$

[where (ij) runs over (1 2), (2 3) and (3 1)], which allows the calculation of $\Phi_3^{(3)}[\rho]$ in terms of $n(\mathbf{r})$, $\mathbf{v}(\mathbf{r})$, and a tensor weighted density $\mathcal{T}(\mathbf{r})$, with components

$$t_{\alpha,\beta}(\mathbf{r}) = \int d\mathbf{R}\, w(\mathbf{R})\rho(\mathbf{r} + \mathbf{R})\hat{R}_\alpha \hat{R}_\beta, \tag{4}$$

where α, β run over x, y, z. The final DF form is

$$\Phi_3^{(3)}[\rho] = 12\pi^2 R^6 \int d\mathbf{r}\, \frac{f_3(\mathbf{r})}{[1 - \eta(\mathbf{r})]^2}, \tag{5}$$

with $f_3 \equiv \mathbf{v} \cdot \mathcal{T} \cdot \mathbf{v} - n\mathbf{v} \cdot \mathbf{v} - \text{Tr}[\mathcal{T}^3] + n\,\text{Tr}[\mathcal{T}^2]$, in terms of the trace of the powers of $\mathcal{T}$, with $\text{Tr}[\mathcal{T}] = n$.

This DF, together with $\Phi_1^{(3)}$ and $\Phi_2^{(3)}$, in their well-established forms [16], give the new approximation which captures all of the good properties of any previous version: it reproduces the PY correlation in the fluid (as done by the old WDA, ELA, ..., density functionals), but does it as a *dimensional interpolation* within the FMT, from the exact 0D and 1D limits to the exact zeroth and first order terms in the expansion $c(r, \rho) = c_0(r) + \rho c_1(r) + \ldots$ for the bulk fluid. This DF is completely free of the divergences present in the earlier FMT versions but still it may be used with a similar computing effort, due to the factorization in terms of the scalar, vector and tensor weighted densities.

The application to the HS crystal is done here through a variational minimization with

$$\rho(\mathbf{r}) = \eta_0 \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\mathbf{G}} e^{-\alpha(\mathbf{r}-\mathbf{G})^2}[1 + \tau\alpha^2 f_a(\mathbf{r} - \mathbf{G})], \tag{6}$$

where $\mathbf{G}$ runs over the lattice vectors and $f_a(\mathbf{r}) = x^4 + y^4 + z^4 - 3r^4/5$ is the leading term for the unit cell anisotropy in cubic lattices. The free variational parameters are the lattice size, the Gaussian parameter α, the anisotropy τ, and the unit cell occupancy η_0.

The correct 0D limit leads always to values of η_0, very close to the perfect normalization $(1 - \eta_0 < 10^{-8})$ without the constraints of previous theories. The computer simulation results for the parameter α, shown in Fig. 1, have some scatter due to the different methods used to extract the information, but the previous DF theories predicted clearly too narrow Gaussians (i.e., too large α and too low Lindemann ratio). In contrast, the present results go well within the simulation data, showing that with a better description of the correlations the molecules are allowed to wander further from their lattice sites. As the mean packing fraction η approaches its close-packing limit $(\eta_c \cong 0.74)$ the Gaussian parameter goes like $\alpha \approx C(\eta_c - \eta)^{-2}$; the exponent of this divergence was correctly given by some previous theories, but the present DF gives also the correct prefactor. The equation of state and the free energy results in Fig. 2, also show the quasiexact
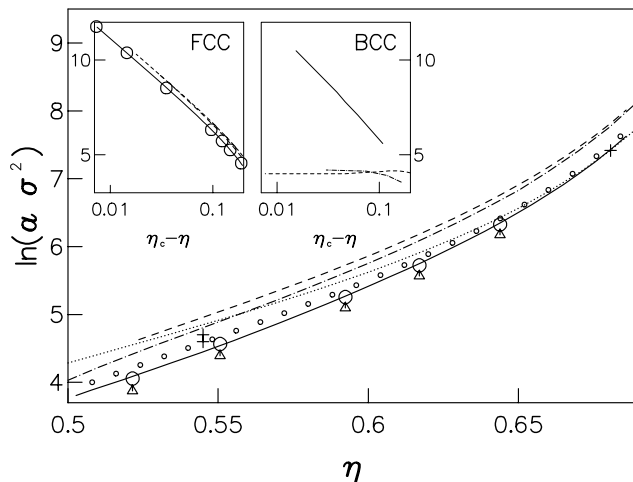
character of the present DF for the fcc crystal: the pressure is in excellent agreement with the molecular dynamics data [25] in the full range of densities and the free energy follows; in the close-packing limit, the form $F/(kTN) = 3 \ln(\eta_c - \eta) + \gamma$ with the correct value for the constant γ.

The anisotropy parameter τ is always small and nearly irrelevant for the equation of state; using the pure Gaussian parametrization $(\tau = 0)$ would raise the free energy per particle in less than $10^{-3}kT$. The information from computer simulations is reduced to a Monte Carlo (MC) study [12] for two density values, and its main interest was showing the qualitative failure of the WDA and MWDA in the description of the unit cell density structure. These DF give broader peaks in the [110] direction than in the [100] direction, by as much as 40%. In contrast, the MC distributions show densities elongated in the interstitial directions ([100] and [111]), with anisotropies in the order of 10% or less. The variational minimization (6) used here is more restrictive than that used in Ref. [12], but it is enough to give good qualitative agreement with the MC data: for $\eta = 0.54$ the minimum is obtained for $\tau \approx 0.02$, with the correct sign to represent the spreading of the density in the interstitial directions, in the order of 10%–15% with respect to the nearest neighbor direction [110] (the WDA and MWDA would give negative τ).

The thermodynamics and the structure of the HS crystal may also be explored with (6) for the bcc lattice. This crystal structure is unstable with respect to the shear deformations for a pure HS system, but it may be stable in systems with other interactions which could be described by means of a reference HS crystal [27]. Computer simulations for this crystal are obtained with a pinning external

FIG. 1. The logarithm of the Gaussian parameter α (in units of the HS diameter σ) vs the mean packing fraction η for the fcc crystal. The computer simulation results include the data [25] (large circles for $N = 500$ and triangles for their extrapolation to infinite N), from [26] as interpreted in [27] (small circles), and from [12] (crosses). The DF approximations are: the WDA [6] (dashed line), the MWDA [9,11] (dotted line), the GELA [11] (dash-dotted line) and the present FMT (full line). The insets show, with horizontal log-scale, the approach to the close-packing density for the fcc and bcc lattices. The GELA and WDA results for the bcc lattice are taken from [10] and [14], respectively.
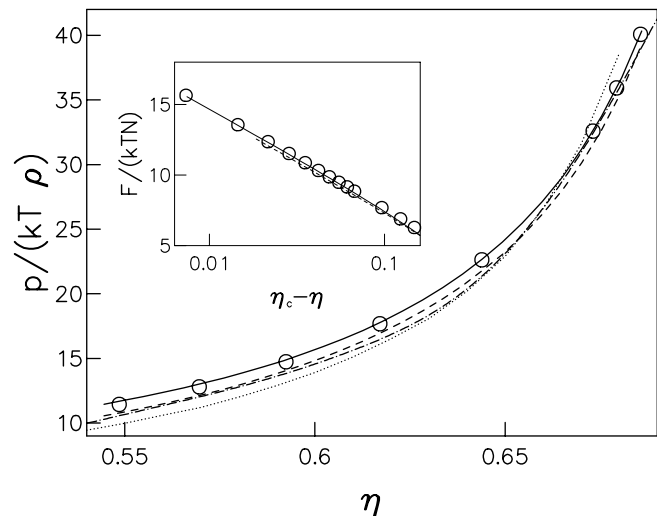

FIG. 2. The equation of state for the fcc crystal. The MD results [25] (circles) are compared with the present results and with other DF theories, with the same notation as in Fig. 1. The inset presents the free energy per particle in the approach to the close-packing limit.

potential [13], although the results are scarce and limited to low η. When the WDA or the MWDA [13,14]) are used to study the bcc crystal they give fully unphysical results in the approach to the close-packing limit (which is now at $\eta_c \cong 0.68$): α has a maximum around $\eta = 0.6$ so that the Gaussian peaks become wider as η approaches η_c and the free energy has no signature of divergences at η_c. Similar problems appear with the GELA [10], although at higher packing fractions. In contrast, the present DF produces the correct qualitative behavior with $\alpha = C(\eta_c - \eta)^{-2}$ (see the inset in Fig. 1) and $F/(kTN) = 3 \ln(\eta_c - \eta) + \gamma$, although there are not computer simulation results to compare with the values of the constants.

In summary, the density functional for hard spheres proposed here solves the qualitative limitations of previous theories: it may be minimized without artificial constraints giving the correct unit cell normalization, anisotropy and Gaussian width; with the exact close-packing behavior in any lattice structure. This is achieved because the new DF is not (as the WDA or the ELA) an extrapolation from the homogeneous fluid towards inhomogeneous systems, but rather a functional interpolation between the exact 0D limit (i.e., the extreme inhomogeneous density distributions) and the 3D bulk fluid (up to the first two orders in the density expansion). Moreover, the quantitative agreement with all the available computer simulation data for the HS crystals is excellent, improving over the already rather good results of other theories. The accuracy obtained for the thermodynamics and the structure of the fcc crystal is even better than that of the PY approximation in the description of the homogeneous fluid, as a consequence of the dimensional interpolation character of the DF approximation.

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