Close-packed configurations, `symmetry breaking', and the freezing transition in density functional theory

LETTER TO THE EDITOR

Close-packed configurations, 'symmetry breaking', and the freezing transition in density functional theory

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Abstract. It is shown that the density functional theory for the non-uniform hard-sphere fluid, which employs the geometrically based fundamental-measure free-energy functional, (1) has the mechanism to locate situations of hard-sphere closest packing, (2) features 'symmetry breaking' that separates the solid-like and liquid-like solutions for the density profile equation, and (3) contains the free-volume cell theory as a special limit case.

The density functional theory has been the object of intensive development in recent years as a most successful and widely applicable approach to non-uniform classical fluids [1, 2]. The well studied hard spheres serve as the almost standard reference system, and provide an important test for all model functionals [3]. Configurations of densely packed hard spheres, in different effective dimensionalities D, provide the ultimate test for any free-energy model for the inhomogeneous hard-sphere fluid, and are of particular importance for addressing the phase diagram of hard spheres in confined geometries. Very recent Monte Carlo simulations of hard spheres confined between narrow plates in quasi-2D situations located both a fluid–solid transition and solid–solid transitions between buckled, layered, and rhombic crystals [4]. Colloidal dispersions confined between two glass plates have been the object of recent intensive experimental investigations [5, 6], and these predicted transitions should be observable. As already demonstrated in the pioneering works [7], such solid–solid transitions are dictated by considerations of the close-packed density for each different configuration. This provides the *a priori* justification for applying the free-volume cell model [8, 9], which was indeed found [4] to give reliable results for the topology of the phase diagram of confined hard-sphere systems.

In order to provide a *unifying* description of the fluid *and* solids in all such confined situations within density functional theory, we need to construct a comprehensive free-energy functional $F[\rho(\boldsymbol{r})]$ of the average one-body density, $\rho(\boldsymbol{r})$. This functional must have built-in mechanisms to locate close-packed configurations for arbitrary effective dimensionality, and to have correct properties of dimensional crossover. For correct description of densely packed hard spheres, in particular, when each particle can be viewed as confined in a fluctuating cage of its nearest neighbours, this free-energy functional should provide reliable results for the '0D limit' corresponding to a cavity that cannot hold more than one particle. Finally, the density functional description of a solid near closest packing raises the issue of symmetry change between the solid and the fluid: when the solid free energy rises sharply

near closest packing, it becomes *larger* than that for the uniform fluid at the same average density. Thus, the free-energy functional must contain a mechanism of 'symmetry breaking' that will separate the solid-like and liquid-like solutions for the density profile equation.

On the basis of the density expansion [10] or the smoothed-density approximation [11], many functionals were developed [3] which found reasonably good agreement with simulations, for the melting and freezing densities, and for the fcc crystal equation of state at densities considerably below closest packing [12, 13]. But these functionals, which are built upon the 3D bulk fluid data as essentially numerical input, do not contain the appropriate building blocks in order to incorporate the 0D limit and the dimensional crossover, and they do not have mechanisms for locating closest packing and for 'symmetry breaking'. These kind of functionals cannot be expected to give physically reliable results for the phase diagram of confined hard spheres.

The geometrically based fundamental-measure functional (FMF) [14] was the first to derive the uniform (bulk) fluid properties as a special case, rather than employing them as input, and to contain the correct dimensional crossover. It was recently shown [15] that when adjusted to reproduce the exact 0D limit, the FMF gives accurate results for the 3D fluid–solid transition (predicting the correct vacancy concentration of the solid) and for the equation of state of both the fcc and bcc crystals all the way from freezing to near closest packing, and becomes generally reliable in situations of extreme confinements. In this letter I show that the FMF has the desirable properties mentioned above to make it applicable to densely packed confined hard spheres. (i) The free-volume cell theory is *contained* in the density functional theory that employs the FMF. (ii) The FMF has the mechanism to locate situations of hard-sphere closest packing. (iii) The FMF features a 'symmetry breaking' that separates the solid-like and liquid-like solutions for the density profile equation. These results are obtained as general properties of the FMF, independent of further fine optimizations of the functional.

The density profile $\rho(\boldsymbol{r})$ subject to an external potential $u(\boldsymbol{r})$ is obtained by solving the Euler–Lagrange equations $\delta\Omega[\rho(\boldsymbol{r})]/\delta\rho(\boldsymbol{r}) = 0$ which correspond to the minimization of the grand potential, $\Omega[\rho(\boldsymbol{r})] = F_{id}[\rho(\boldsymbol{r})] + F_{ex}[\rho(\boldsymbol{r})] + \int \mathrm{d}\boldsymbol{r}\ \rho(\boldsymbol{r})[u(\boldsymbol{r}) - \mu]$, where μ is the chemical potential. The ideal-gas free energy is given by the exact relation

$$F_{id}[\rho(\boldsymbol{r})] = k_B T \int \mathrm{d}\boldsymbol{r}\ \rho(\boldsymbol{r})\{\ln(\rho(\boldsymbol{r})\lambda^3) - 1\} \tag{1}$$

where $\lambda = (h^2/2\pi m k_B T)^{1/2}$ is the de Broglie wavelength. The central (and generally unknown!) quantity in density functional theory is the excess free energy, $F_{ex}[\rho(\boldsymbol{r})]$, which originates in interparticle interactions. In the special case of the single-component system of 3D hard spheres of radius R, the FMF has the following form [14]:

$$\frac{F_{ex}[\{\rho(\boldsymbol{r})\}]}{k_B T} = \int \mathrm{d}\boldsymbol{x}\ \Phi[\{n_\alpha(\boldsymbol{x})\}] \tag{2}$$

where Φ is a function of the following three weighted densities: $n_\alpha(\boldsymbol{x}) = \int \rho(\boldsymbol{x}')w^{(\alpha)}(\boldsymbol{x} - \boldsymbol{x}')\,\mathrm{d}\boldsymbol{x}'$, which are *dimensional* quantities. The weight functions $w^{(\alpha)}$, $\alpha = 3, 2, V2$, are [14] characteristic functions for the geometry of the sphere: two scalar functions, representing the characteristic functions for the volume and the surface of a particle, $w^{(3)}(r) = \Theta(R-r)$, $w^{(2)}(r) = \delta(R - r)$, and a surface vector function $\boldsymbol{w}^{(V2)}(\boldsymbol{r}) = (\boldsymbol{r}/r)\delta(R - r)$. In particular, $n_3(\boldsymbol{x})$ is a local packing fraction which, for the uniform (bulk) fluid of density $\bar{\rho}$, is equal to the total packing fraction $\eta = \bar{\rho}(4\pi/3)R^3$. Using the dimensionless vector $\boldsymbol{\xi}(\boldsymbol{r}) \equiv \boldsymbol{n}_{V2}(\boldsymbol{r})/n_2(\boldsymbol{r})$, $\xi = |\boldsymbol{\xi}|$, the following excess free-energy density was

simple geometrical considerations the shell contributions of two nearest neighbours will give rise to a singularity $n_3(\boldsymbol{x}) = 1$ only when $a \to 0$ and $\Delta \to 0$ simultaneously: when the big sphere of radius R is at distance R from the small sphere of radius Δ, then as long as R is finite, i.e. $\Delta/R \neq 0$, the overlap volume is smaller than half the small-sphere volume. This is the geometry that enables the $(1 - n_3(\boldsymbol{x}))$ singularities of the FMF to 'detect' touching spheres in close-packed arrangements. Tedious but straightforward calculation shows that setting $a = 0$ for $\delta = \Delta/R \ll 1$ leads to a non-integrable singularity in the terms Φ_2 and Φ_3, while Φ_1 is integrable (i.e. one needs stronger-than-logarithmic singularity for $D = 2, 3$). It is found that the Δ dependence of the excess free energy is only through the ratio Δ/a. All of the singularities are integrable if one sets $\Delta \propto a$, before letting $a \to 0$. Each of the three contributions to the FMF has a different Δ/a dependence, and the total integral behaves like $(\Delta/a)^s$ with exponent s of the order of unity. Minimizing the total free energy one gets the optimal value $\Delta_{MIN}/a \approx \mathrm{O}(1)$, while F_{ex}/Nk_BT is nearly constant, of order unity. The divergence of the equation of state at closest packing, and the free-volume cell picture, are thus obtained for the FMF by minimizing the total free energy with respect to Δ. Unlike in previous density functional approaches to the equation of state of hard-sphere crystals [12, 13], the FMF pressure is dominated by the *ideal-gas* contribution *all* the way from melting to closest packing. It is interesting to note that the variational property with respect to the width parameter makes the pressure equal to the 'standard' density derivative of the *excess* free energy at constant width $\Delta = \Delta_{MIN}$ [19]. This useful relation [19] cannot, however, be treated [13] as a detailed model for the pressure of the solid. Previous density functionals [3, 12, 13] did not contain the mechanism to exclude the unphysical density fields with overlapping hard spheres, namely situations that correspond to $n_3(\boldsymbol{x}) > 1$, and these had to be excluded by imposing $n_3(\boldsymbol{x}) \leqslant 1$ as an extra constraint on the density profile equations. This issue was discussed [20] in the context of surface melting and the crystal–fluid interfaces, but it was not raised in the context of the stability of the solid *versus* the fluid, and the 'symmetry breaking'.

In order to discuss the 'symmetry breaking', namely the division of the solutions of the density profile equations into solid-like and liquid-like forms, consider specifically the density functional description of the phase transition between the fluid and the fcc solid. The modelling of the 3D solid by Gaussians, $\rho_\Delta(x) = \rho_\Delta^{Gauss}(x) = (\alpha/\pi)^{3/2}\mathrm{e}^{-\alpha x^2}$, proves highly accurate [21], the high-density results which were obtained above for a general case do hold with $\Delta \approx 1/\sqrt{\alpha}$, and the pressure of the solid is dominated by the free-volume result [15]. Thus, instead of a general unconstrained search for the optimal density profile as a function of the average density of the spheres, we follow the standard procedure [11, 12] and seek the optimal values of α, for Gaussian peaks located at fcc lattice sites. Like for many other functionals [12], the FMF minimization at low densities leads to a single solution describing a fluid ($\alpha = 0$), while at higher densities, a second minimum appears, describing a solid ($\alpha R^2 \approx \mathrm{O}(25)$). This second minimum is initially *above* the fluid minimum, but at still higher densities (and correspondingly larger values of α) it becomes the global minimum, *below* the fluid free energy. Unlike the FMF, the earlier functionals [12, 13] do not have a true correct divergence of the equation of state at closest packing, but they still feature a very steep (yet finite!) rise in the region of closest fcc packing. At these high densities, the solid-type minimum ($\alpha R^2 \gg 1$) is again *above* the fluid minimum ($\alpha = 0$). Since at these high densities the solid-type solution should be more stable, this result represents a physical inconsistency of the functional, *unless* the two types of minimum belong to two *distinct branches* of the solution, separated by some kind of 'symmetry breaking'. It is interesting to note that this physical consistency problem has not been brought up before. In all calculations of this type (i.e. locating the freezing transition by describing the solid

with localized Gaussians) with previous functionals [12, 13], the constraint $n_3(x) \leqslant 1$ was not imposed, and it was possible to change α, at any fixed density, continuously from the fluid minimum ($\alpha = 0$) to the solid minimum ($\alpha R^2 \gg 1$), and yet the above physical consistency problem (of the 'solid' minimum above the 'fluid' minimum) has never been raised. The FMF, on the other hand, canonically excludes unphysical density fields with overlapping spheres by automatically incorporating the constraint $n_3(x) \leqslant 1$. As a result it features the required 'symmetry breaking' which separates between the solid-like and fluid-like solutions of the density profile equations. That separation makes its physically correct high-density solutions (which behave like the free-volume theory) also physically consistent from the point of view of the logic of the density functional approach, even though the 'solid' minimum is above the 'fluid' minimum.

While the analysis of the behaviour near closest packing involves only a pair of nearest neighbours (the two closest to the lens-shaped shell-overlap region described above), the 'symmetry-breaking' mechanism arises from contributions of a whole environment of neighbouring density peaks which characterize the density distribution $\rho(x)$. Consider again the Gaussian representation, as above, and recall the definition of the total packing fraction, $\eta = (4\pi/3)\bar{\rho}R^3$, where $\bar{\rho}$ is the average density, and some relevant densities for fcc hard spheres are: closest packing: $\eta = \eta_{fcc}^{CP} = \pi\sqrt{2}/6 \cong 0.74$; melting: $\eta_S = 0.545$; and freezing: $\eta_F = 0.494$. Consider a high density, well above the melting density, say $\eta \approx 0.68$, for which the FMF solid minimum is at the Gaussian parameter $(\alpha R^2)_{MIN} \approx \mathrm{O}(1000)$ (i.e. the width $\Delta/R \approx \mathrm{O}(1/30)$). Monitor the local packing fraction, $n_3(x)$, as $\rho(x)$ is modified by changing the value of α (i.e. of the width Δ), and the relative position of the centres of the Gaussians in some neighbourhood around one of the fcc sites chosen as the origin. For simplicity we take into account only the contributions of the Gaussians at this site and its 12 nearest neighbours (NN), $n_3(x) \geqslant n_3(0) \geqslant n_3(0)_{NN} = n_\Delta^{(3)}(0) + 12 n_\Delta^{(3)}(d)$, with $d/R \approx 2(0.74/0.68)^{1/3} \approx 2.06$. Initially, at very small values of $\delta = \Delta/R$, we have $n_3(0)_{NN} = n_\Delta^{(3)}(0) = 1$, and the 12 nearest neighbours essentially do not contribute. As δ gradually increases, and as the 12 neighbours still do not contribute, then at some value of δ around 0.5 the value of $n_\Delta^{(3)}(0)$ starts to decrease below 1, and further decreases as δ is increased. If the distance to the centres of the nearest Gaussians is reduced for $\delta \approx 1/30$ then $n_3(0)_{NN}$ crosses 1 from below for $d/R \approx 1.05$. For $d/R \approx 1.85$ then $n_3(0)_{NN}$ crosses 1 from below when δ increases to ≈ 0.5. This simple calculation provides examples for local 'clusters' of Gaussians that give rise to $n_3(x) > 1$. We expect that a random distribution of the centres of the Gaussians will give rise to many situations with the forbidden $n_3(x) > 1$. For values of the width δ which are relevant for describing the solid with Gaussians, only configurations of relatively high symmetry can exclude forbidden situations with $n_3(x) > 1$. Thus, the FMF result for the stable fcc solid obtained using the Gaussian representation for the density profile (i.e. obtained as the free-energy minimum as a function of the Gaussian width), represents a 'solid' branch of the solution of the density profile equations, separated from the 'fluid' branch by a region of 'forbidden' configurations of the centres of the Gaussians.

In all situations where $n_3(x)$ approaches 1 from below, at $\delta > 0$, the singularities in the FMF occur at points x_0 where $n_3(x)$ is maximal, and thus $1 - n_3(x) \approx \mathrm{O}(x - x_0)^2$. As a result, the first two terms of the FMF are integrable, while the third term is usually not integrable. In any case, the logarithmic term, $\ln(1 - n_3(x))$, signals that the FMF does not admit $1 - n_3(x) < 0$. The space of density profiles composed of Gaussian distributions is divided into solid-like and fluid-like profiles, as two distinct types of solution to the density profile equation. All of the cases for which the maximal value of $n_3(x)$ crosses unity from below to yield $(n_3(x))_{MAX} > 1$ represent physically forbidden situations from

the point of view of the FMF, separating solutions for the density profile equation, of two types of spatial symmetry. This feature is not limited to fcc symmetry or to Gaussians, and represents a general feature of the FMF functional that will emerge as various types of density profile will be studied. It will be especially illuminating to use the FMF in *free-minimization* density functional calculations of the crystal–fluid interfaces and surface melting [20].

The present study sheds new light on the role played by the local packing fraction, $n_3(x)$, as defined by the fundamental-measure theory [14], and on the singularities of the FMF at $n_3(x) = 1$. These singularities locate close-packing configurations, and also provide the 'symmetry breaking' that prevents the FMF functional from reaching unphysical situations. In particular, the corresponding singularity of the bulk fluid equation of state at the unphysical packing fraction $\eta = 1$, as if the spheres fill all of the volume (way above $\eta_{fcc}^{CP} \cong 0.74$ and the random close packing [22] $\eta_{random}^{CP} \approx 0.64$), is *pre-empted* by the freezing transition, and is never reached. This $\eta = 1$ singularity was shown [23] to be a universal asymptotic high-density singularity of the integral equation for the bulk fluid pair structure, and was offered [23] as an 'ideal-liquid' starting point for describing dense fluids. The present discussion offers a new way by which this singularity at an unphysical bulk packing fraction dominates the physical properties of the system.

Finally, note that the discussion in this letter is generally valid also for the 2D version of the FMF which applies to hard discs [14]. In 1D (hard rods) the FMF is identical [14] to the exact functional [24], the free-volume equation of state is exact for all densities, and the only singular situation occurs at the 1D closest packing.

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