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An *ab initio* density functional for penetrable spheres

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Abstract. We develop a density functional theory for a system of penetrable spheres that interact with a constant pair potential energy if their separation distance is smaller than their diameter. As sufficient input, just the geometrical properties of the particles and the exactly known statistical behaviour of the system under strong confinement are needed. The theory predicts the bulk fluid properties in good agreement with computer simulations and better than liquid integral theories, as well as the freezing transition to a multiply occupied face-centred-cubic lattice. It becomes exact in the limits of strong confinement and high temperature, and coincides with a successful hard-sphere theory for zero temperature.

Classical density functional theory (DFT) is one important theoretical tool for the study of the microscopic structure of liquids [1] and solids [2, 3]. Its power lies in its ability to deal with inhomogeneous situations on a microscopic length scale. There are a large variety of physical situations where a liquid exhibits a spatial structure, ranging over the behaviours near confining walls, in gravitational fields, at interfaces and in capillaries [4]. But DFT can go beyond the description of fluids in contact with their surroundings. It also accounts for self-sustained inhomogeneities that are not being caused by external potentials. This phenomenon can occur if a system 'decides' to freeze and to build up a crystal with an intrinsic broken translational symmetry. As DFT is able to treat solid and fluid phases on an equal footing, it is considered as a major theoretical advance in statistical physics from a fundamental point of view. It is also of great practical importance, as explicit calculations can be done for toy models as well as for realistic systems.

The central quantity of DFT is the Helmholtz excess free energy expressed as a functional of the single-particle density. There are few systems for which this functional is known exactly; one example is a system of one-dimensional hard rods. Through the years, various approximations, like the one given by Ramakrishnan and Yussouff, the weighted-density approximation (WDA) and the modified WDA (see, e.g., reference [3]) have been developed. One common feature of these approaches is the requirement of having information about the homogeneous fluid phase in order to obtain results for inhomogeneous situations. The information about homogeneous fluids, like the equation of state and the pair distribution function, may be taken from the solution of liquid integral equations. The DFT then acts as a container for the knowledge about the homogeneous bulk phase. So it is of great interest to find approximations to the density functional of specific systems that 'stand on their own feet' and do not require input from other theoretical approaches involving further approximations.

There is one class of systems for which one has been able to derive powerful density functionals, namely those exhibiting hard-core interactions such as hard spheres [5–7] and

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cubes [8, 9]. One important property of these fundamental-measure functionals (FMF) is their correct dimensional crossover: the three-dimensional (3D) functional yields a reasonable 2D hard-disc functional, the exact 1D hard-rod functional and the exact statistical properties of the 0D limit represented by a cavity that can hold a single particle. Reversing this line of thought, one has been able to derive the 3D functional by imposing the correct behaviour for 0D [10]. So far, these approaches have been restricted to hard-core interactions, where the temperature scales out of the Boltzmann factor. In this article a systematic extension of the FMF to soft cores is proposed.

Therefore we study a system of penetrable particles. We call particles 'penetrable' if there is no divergence of the pair potential energy if two particles have zero separation. So far, these bounded potentials have attracted less interest than potentials with a divergence at the origin. One example of a penetrable potential is the Gaussian core model introduced by Stillinger *et al* [11, 12]. Graf and Löwen [13] have shown that Gaussian cores arise between the centres of star polymers if the polymeric arms are treated in a harmonic approximation. Although diverging at the origin, an ultra-soft pair potential between star polymers has been proposed [14] and validated [15] with computer simulations.

As the, in a sense, simplest model for a penetrable interaction, we assume a step function:

$$V(r) = \begin{cases} 0 & \text{if } r > \sigma \\ \epsilon & \text{if } r \leqslant \sigma. \end{cases}$$

This was recently studied by Likos *et al* [16] using liquid integral equations for the fluid phase and a cell model for the solid phase as well as computer simulation. Virial coefficients were studied in reference [17]. The model has two thermodynamic parameters, namely the packing fraction $\eta = (\pi/6)N/V_\infty$, where N is the number of particles inside a (large) volume V_∞, and the reduced temperature $k_B T/\epsilon$, where k_B is Boltzmann's constant.

In this work, we derive a functional for a thermal system of penetrable spheres on the same solid footing as was previously only possible for hard-core interactions. We would like to stress that the new functional is not built as a theory of perturbations around some reference hard-sphere system, but has the penetrability of the particles genuinely built in. It incorporates the geometrical shape of the particles and the statistical mechanics of clusters of two or more overlapping particles.

Let us sketch the derivation of the new functional. We first discuss a generic free-energy density functional. Then, the exact solution for the 0D limit for penetrable spheres is presented. This is needed as a situation of extreme confinement for which we require the functional to give the exact result. Then, the freedom in the generic functional is fixed by requiring that this solution comes out from the functional. Explicit expressions for the DF are given.

We start with a generic density functional possessing the Rosenfeld form [5]: it is assumed that the Helmholtz excess free energy in an inhomogeneous situation can be expressed as an integral over all space:

$$F^{\mathrm{exc}}(T, [\rho(\boldsymbol{r})]) = k_B T \int \mathrm{d}\boldsymbol{x}\ \Phi(T, \{n_\alpha(T, \boldsymbol{x})\})$$

where T is the temperature and k_B is Boltzmann's constant. The integrand is a reduced free-energy density Φ depending on T and on a set of weighted densities $\{n_\alpha\}$ indexed by α. Each weighted density is given by a convolution of its temperature-dependent weight function w_α with the density profile:

$$n_\alpha(T, \boldsymbol{x}) = \int \mathrm{d}\boldsymbol{r}\ \rho(\boldsymbol{r}) w_\alpha(T, \boldsymbol{x} - \boldsymbol{r}).$$

This DF is generic in the sense that the dependence on the interaction potential V between the particles is hidden in the as-yet unspecified functions Φ and w_α. Although it is generic, it is of course not the most general form of a density functional. The severe approximation is that Φ is not a functional but only a *function* of the weighted densities n_α. One convenient property is that the weight functions do not depend implicitly on the density profile. However, they may depend on the thermodynamic state point, given by the temperature T. For hard-core interactions the only temperature dependence of the free energy is a trivial linear scaling with T. Hence, in the original work focusing on hard spheres [5], Φ and w_α are temperature independent. In the current work we are interested in soft cores; so we have included the temperature dependence in this way, which we believe is the most general one within the current framework.

Let us now solve for the 0D limit of penetrable spheres. Consider a cavity with volume $V_{0\mathrm{D}}$, small enough that any two particles that are inside overlap. The system will be coupled to a heat bath and to a particle bath. If there are N particles present, the potential energy is proportional to the number of pairs of particles and is given by $\epsilon N(N-1)/2$. The grand partition sum is

$$\Xi(N_{\mathrm{max}}) = \sum_{N=0}^{N_{\mathrm{max}}} b^{N(N-1)/2} z^N / N!$$

with the Boltzmann factor $b = \exp(-\epsilon/k_{\mathrm{B}}T)$ and the scaled fugacity $z = V_{0\mathrm{D}} \exp(\mu/k_{\mathrm{B}}T)$, where μ is the chemical potential, and $V_{0\mathrm{D}}$ is the volume accessible to one particle. In principle, we have to perform the limit $N_{\mathrm{max}} \to \infty$; it is, however convenient to keep this dependence, as no closed form for the free energy for arbitrary N_{max} is obtainable. The grand potential is $\Omega = -k_{\mathrm{B}}T \ln \Xi$. The mean number of particles is $\bar{N} = z\,(\partial/\partial z)\Omega$. Inversion of this relation yields the fugacity as a function of $\bar{N}$. Technically, this inversion is not possible analytically for arbitrary N_{max}, as one has to find the roots of a polynomial of degree N_{max}. From the fugacity we obtain the excess chemical potential as a function of the particle number through $\mu_{0\mathrm{D}}(\bar{N}) = \ln(z(\bar{N})/\bar{N})$. (The excess free energy can be obtained by integrating $\phi_{\mathrm{exc}} = \int_0^N \mathrm{d}\bar{N}\ \mu_{0\mathrm{D}}(\bar{N})$.) It is not possible to find a general solution in the limit $N_{\mathrm{max}} \to \infty$. This is not a serious drawback for our current investigation: one can find general solutions for $N_{\mathrm{max}} \leqslant 4$ that provide excellent approximations for cases of small particle numbers, $N \lesssim N_{\mathrm{max}}/2$, or use numerical methods. For the case of $N_{\mathrm{max}} = 1$ we recover the hard-sphere solution $\mu_{0\mathrm{D}}(T \to 0, N) = -\ln(1-N)$; for $N_{\mathrm{max}} = 2$ we have

$$\begin{aligned}\mu_{0\mathrm{D}}(T, N) &= \epsilon - \ln(2-N) - \ln(N) \\ &\quad + \ln\left(\sqrt{(1-N)^2 + 2N(2-N)\exp(-\epsilon/k_{\mathrm{B}}T)} - (1-N)\right)\end{aligned}$$

which contains the essential contributions for low temperatures.

The idea is to consider a multi-cavity limit [10]. There the confining potential is given by a small set of cavities. Physically, the cavities are hollow and have the shape of one particle. The particles are forced to be inside one of the cavities, so their density distribution vanishes outside. For an integer number C of cavities located at positions $\boldsymbol{c}_i$ we have

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{C} N_i \delta(\boldsymbol{r} - \boldsymbol{c}_i).$$

If the distance between two cavities is larger than the particle diameter, they are decoupled. If the distance is smaller than the diameter all particles overlap and the statistical behaviour is the same as for a single cavity. By considering consecutively the one-, two- and three-cavity cases, $C = 1, 2, 3$, one is able to fix the form of the generic functional. The geometrical analysis follows the hard-sphere case [10], where the strategy leads to the Rosenfeld hard-sphere functional [6, 7].

For penetrable spheres the FMT excess free-energy functional derived in this way is given by $\Phi = \Phi_1 + \Phi_2 + \Phi_3$. The individual contributions are

$$\Phi_1 = n_0 \mu_{0\mathrm{D}}(T, n_3)$$
$$\Phi_2 = (n_1 n_2 - \boldsymbol{n}_{\mathrm{v}1} \cdot \boldsymbol{n}_{\mathrm{v}2}) \mu'_{0\mathrm{D}}(T, n_3)$$
$$\Phi_3 = n_2^3 (1 - (\boldsymbol{n}_{\mathrm{v}2}/n_2)^2)^3 \mu''_{0\mathrm{D}}(T, n_3)/(24\pi)$$

where the prime denotes differentiation with respect to the argument n_3 (in the 0D case, with respect to N) and the index v is a reminder that $\boldsymbol{n}_{\mathrm{v}1}$ and $\boldsymbol{n}_{\mathrm{v}2}$ are vectors. The linearly independent weight functions are given by

$$w_3(T, \boldsymbol{r}) = \Theta(R - r) \qquad w_2(T, \boldsymbol{r}) = \delta(R - r) \qquad \boldsymbol{w}_{\mathrm{v}2}(T, \boldsymbol{r}) = \delta(R - r)\boldsymbol{r}/r$$

where $r = |\boldsymbol{r}|$, and $R = \sigma/2$ is the particle radius. Dependent on the above are the further weights

$$w_1 = w_2/(4\pi R) \qquad w_0 = w_2/(4\pi R^2) \qquad \boldsymbol{w}_{\mathrm{v}1} = \boldsymbol{w}_{\mathrm{v}2}/(4\pi R)$$

where the arguments have been omitted. We find that the free-energy density carries a temperature dependence through $\mu_{0\mathrm{D}}$, but the weight functions remain independent of temperature.

Let us investigate the properties of the functional. For low densities one can expand the free-energy density to find $\mu_{0\mathrm{D}} = (1 - \exp(-\epsilon/k_{\mathrm{B}}T))n_3$; hence the total free-energy density becomes

$$\Phi = (1 - \exp(-\epsilon/k_{\mathrm{B}}T))(n_0 n_3 + n_1 n_2 - n_{\mathrm{v}1} n_{\mathrm{v}2})$$

which is the deconvolution of the Mayer function for the penetrable-sphere interaction, and hence the low-density expansion of the true density functional. The deconvolution is also valid in the limit of high temperature, where we get the mean-field free-energy density $\mu_{0\mathrm{D}} = \epsilon N(N - 1)/2$. The low-temperature limit $k_{\mathrm{B}}T/\epsilon \to \infty$ yields $\mu_{0\mathrm{D}} = -\ln(1 - \eta)$, which gives the well-known Rosenfeld hard-sphere functional including the Percus–Yevick direct correlation function [5], the cell model as the high-density limit of the crystal near close packing [18] and excellent values for the coexisting-liquid-and-solid packing fractions at the freezing transition [6, 7]. We repeat the fact that the functional is, by construction, exact in the zero-dimensional limit.

Having demonstrated the correct behaviour in limiting cases, we are confident in investigating the predictions of the current DFT for physically more interesting regions, namely intermediate temperatures and densities. First, we investigate the liquid structure predicted by the functional. To get the pair correlation function $g(r)$ we impose Percus's test particle limit by minimizing the functional in the presence of an external potential that coincides with the pair potential. The results are shown for packing fraction $\eta = 0.5$ as solid lines in figure 1. The agreement with Monte Carlo simulation data (symbols) is very good outside the core, $r > \sigma$. For $r < \sigma$ and intermediate temperatures, the rise near the origin is overestimated by the DFT. Any thermodynamic integrals over $g(r)$ are robust against this error, because of multiplication with a volume element $4\pi r^2$ which vanishes for $r \to 0$. Recently, $g(0)$ has been used successfully within the framework of liquid integral equations to fulfil a zero-separation theorem [19]. The small wiggles in figure 1, e.g. for $k_{\mathrm{B}}T/\epsilon = 0.2$ near $r/\sigma = 1.5$, are artifacts due to the numerical representation of the functions as cubic splines.

In general, our results are superior to those obtained from standard liquid integral equations, as there is 'an inadequacy of the traditional liquid-state integral theories to describe in a satisfactory way the high-density fluid phase of the system' [16] (see figure 3 therein for the result of the Percus–Yevick closure). We have also used a simpler way to get $g(r)$ via the second functional derivative of the free energy with respect to density together with the Ornstein–Zernicke relation. This result agrees fairly well at low density but the agreement becomes

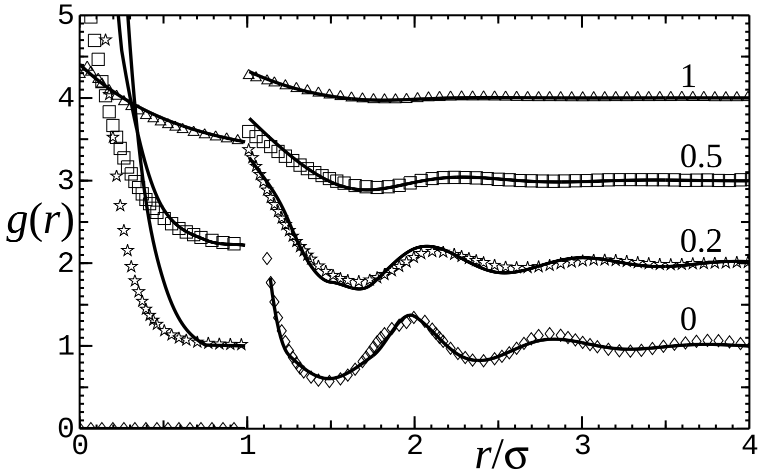


Figure 1. The pair correlation function for penetrable spheres with packing fraction $\eta = 0.5$ at different temperatures such that $k_B T/\epsilon = 0, 0.2, 0.5, 1$. Lines denote theoretical results; symbols indicate simulation data. (For the sake of clarity, the curves are shifted upwards by one unit and the $T = 0$ curve is not drawn near contact, $r/\sigma < 1.14$.)

worse upon increasing the density beyond $\eta > 0.3$. One encounters negative values inside the core, which are of course unphysical. For the fluid free energy, we take a linear combination of the compressibility and virial expressions with weights 1/3 and 2/3, respectively; this is similar to the Carnahan–Starling procedure [3]. The details will be presented elsewhere [20].

To investigate the solid phase, the density distribution is parametrized with a Gaussian *ansatz*:

$$\rho(\boldsymbol{r}) = \eta_0(\alpha^3/\pi^{3/2}) \sum_{\{\boldsymbol{R}_i\}} \exp(-\alpha^2(\boldsymbol{r} - \boldsymbol{R}_i)^2)$$

where the summation runs over the lattice sites $\{\boldsymbol{R}_i\}$ of a face-centred-cubic (fcc) lattice. This *ansatz* allows for multiply occupied lattice sites through the occupancy number η_0, which may be larger than unity. Upon minimizing the functional with respect to α and η_0, we find the solid phase to be stable. The occupation number grows for increasing density and increasing temperature.

By imposing thermal, mechanical and chemical equilibrium between the fluid and solid phase, we calculate the phase diagram shown in figure 2. There appears a first-order freezing transition into an fcc structure with multiply occupied lattice sites. As expected physically, the solid phase becomes destabilized upon increasing the temperature. The solid–fluid coexistence is shifted towards lower packing fractions compared to those given by the combined integral-equation–cell-model approach of Likos *et al* [16] (e.g., $\eta = 0.8$–1.0 at temperature 0.2). The claimed clustering transitions [16] are not thermodynamic phase transitions, but merely sharp increases in the occupation numbers [21]. In accordance with this result from the cell model, the present DFT yields a single-crystalline phase.

To illustrate the physics of the penetrable-sphere model, we finally show snapshots taken from computer simulation in figure 3. In the fluid phase (figure 3(a)), there are large clusters of overlapping particles. In the solid phase (figure 3(b)), each lattice site can be occupied by more than one particle. Both configurations have the space-filling packing fraction $\eta = 1$, with temperatures such that $k_B T/\epsilon = 1, 0.1$.

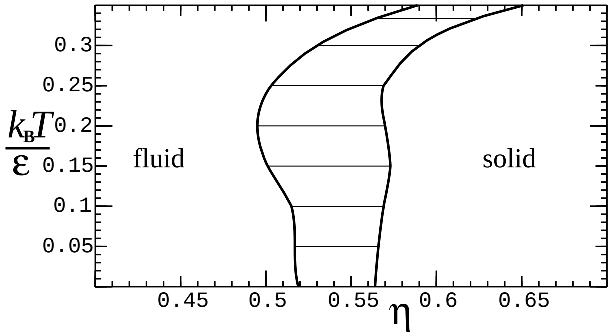
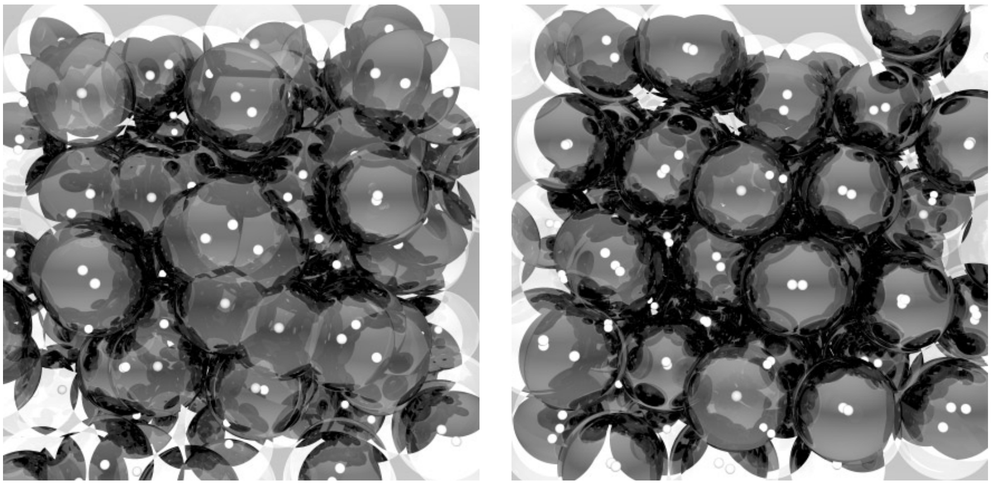


Figure 2. The phase diagram for penetrable spheres depending on the packing fraction and temperature. Coexistence is denoted by thin horizontal tie lines. The simulation results for $T = 0$ are $\eta = 0.494$–0.545 [3].



(a) (b)

Figure 3. Snapshots from computer simulation of the fluid phase (a) and the solid phase (b) at packing fraction $\eta = 1$. The particles are rendered as transparent bubbles with small white balls indicating their centres.

In this work we have demonstrated that a very successful theory of hard-body fluids and solids, the so-called fundamental-measure density functional theory, can be generalized to penetrable particles, while retaining its simplicity and accuracy. The major advance is the systematic introduction of an internal energy scale into a hitherto purely entropic theory. We have considered a model of penetrable spheres, interacting with a step-function potential which is ϵ inside the core and zero outside. The functional is derived by considering both the geometric properties of the spherical particles and the so-called zero-dimensional limit, consisting of a hard cavity of the size of a single particle. To our knowledge, it is the first non-perturbative functional of the Rosenfeld type derived for a thermal system. We have considered the fluid structure derived using the functional, finding good agreement with simulations. Describing the solid as a superposition of Gaussian peaks, the theory predicts a freezing transition into a multiply occupied fcc lattice. Finally, we note that it is highly desirable to apply the current approach to more general pair potentials. Work along these lines is in progress.

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