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Density-functional theory for soft interactions by dimensional crossover

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A density-functional theory for spherical particles interacting via an arbitrary soft pair potential is presented. The derivation is solely based on limits, where the behavior is exactly known, namely, a zero-dimensional cavity and the low-density virial expansion. The approach generalizes the fundamental-measure theory for hard bodies and yields the structure and thermodynamics of the homogeneous fluid as an output. We apply the theory to an ultrasoft logarithmic potential that mimics star polymers in a good solvent. The theory, when supplemented by a rescaling procedure, reproduces the peculiar features of the pair correlations in this system that we also find in computer simulations. [S1063-651X(99)50712-5]

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Particles interacting via soft pair potentials build up a general class of statistical systems ranging from the Coulomb interaction of charged bodies, the screened Coulomb or Yukawa potential present in suspensions of charged colloidal particles to inverse-power potentials [1]. Another important example is the Lennard-Jones potential that describes the noble gases accurately. In the context of soft matter one is faced with a zoo of potentials acting on a mesoscopic length scale. Two examples are the depletion potential that acts between large spheres immersed in a suspension of small spheres [2] and the ultrasoft repulsive logarithmic potential between star polymers [3]. These examples clarify that a soft potential is a pairwise interaction that is finite everywhere except for a possible singularity at the origin. The counterpart of soft potentials are hard-body interactions, as in the famous hard sphere system. The interaction in these systems is infinite once two particles overlap. There are elaborate theories dealing with these purely entropic forces.

We propose a generalization of a successful density-functional theory (DFT) for hard bodies, the so-called fundamental-measure theory (FMT), to soft potentials. The FMT approach has proven to describe accurately the structure and thermodynamics of hard bodies, as hard spheres [4,5], or aligned hard cubes [6,7]. It is able to yield the structure of the homogeneous fluid, namely, the pair correlation function as an output rather than needing it as an input as other DFTs do [8]. In the case of hard spheres the resulting fluid structure is the same as the solution of the Percus-Yevick closure relation. Also the freezing transition into a face-centered cubic crystal is captured correctly [4,5].

The FMT has also been used to deal with soft potentials. In these approaches it is used to describe the hard spheres as a reference system for a perturbation theory, e.g., via the assumption of universality of the bridge functional [9]. Concerning non-FMT approaches for soft potentials there is a large literature of successful applications; see the reviews by Singh [10], Evans [8], and Löwen [1]. Recently, Kol and Laird studied the inverse-power potentials [11].

We attempt to find a generalization of the FMT to soft potentials. Let us therefore first outline the major features of the FMT. The FMT is a weighted density approximation (WDA). In this approach a smoothing of the density profile is used to cope with highly inhomogeneous situations, like the density peaks representing the lattice sites in a crystal. In a WDA this smoothing is implemented by a convolution of the one-particle density distribution with appropriate weight functions yielding weighted densities. To construct a WDA one has to define the weight functions. It is worth noting that the FMT uses a set of several weight functions. Another important feature of the FMT opposed to other WDAs is the range of the weight functions. While to our knowledge all other WDAs for hard spheres use weight functions with a range of the particle diameter σ, the FMT weight functions have a range of half the particle diameter, or particle radius $R=\sigma/2$. In this way the non-overlap criterion for hard spheres can be fulfilled exactly. The small range of the weights is not a drawback in cases where a range of nonlocality of the sphere diameter σ is needed, e.g., for the pair correlation function. In this case the arising convolutions of two weights render the functional non-local with range σ.

One essential ingredient of the FMT is a geometrical view of hard particles. The basic statistical objects such as the Mayer function are either zero or unity for hard particles. In the geometrical picture a function value of unity means ‘‘inside the geometrical shape,’’ while a function value of zero means ‘‘outside of the geometrical shape.’’ Using this correspondence one can exploit powerful results from integral geometry like the Gauss-Bonnet theorem [12]. In the case of soft cores the statistically relevant functions take on nontrivial values different from zero and unity.

The main modification of the FMT we present here is a generalization of the weight functions to handle soft cores while keeping their short range. The emerging new weights are built to

(i) deconvolve the Mayer function,
(ii) yield the exact zero-dimensional single cavity limit.
(iii) give a reasonable, albeit not exact, multi-cavity limit.

It turns out that the ‘‘thermodynamic ingredients,’’ namely, the free energy density depending on the weighted densities remain unaffected and keep their hard body form.

Let us start by introducing a generic form of a DF. The excess free energy is expressed as

$$F^{\text{exc}}(T,[\rho(\mathbf{r})])=k_BT\int d\mathbf{x}\,\Phi(T,\{n_\alpha(T,\mathbf{x})\}), \tag{1}$$

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

$$n_\alpha(T,\mathbf{x})=\int d\mathbf{r}\,\rho(\mathbf{r})w_\alpha(T,\mathbf{x}-\mathbf{r}). \tag{2}$$

To summarize, the DF has the following properties:

1. There is a *set* of weighted densities.
2. The free energy density is a function of the weighted densities.
3. The weighted densities are obtained by convolutions of the density profile with appropriate weight functions.
4. The weight functions are explicitly known, i.e., do not implicitly depend on the density distribution.

The task is to give explicit expressions for Φ and $\{n_\alpha\}$ to model the DF for a given pair potential. Let us discuss the range of non-locality of the present functional by considering the direct correlation function which can be obtained by functional differentiation

$$c_2([\rho],\mathbf{r}_1,\mathbf{r}_2)=-(k_BT)^{-1}\left.\frac{\delta^2F^{\text{exc}}}{\delta\rho(\mathbf{r}_1)\,\delta\rho(\mathbf{r}_2)}\right|_{\rho=\rho_0}, \tag{3}$$

where ρ_0 is the equilibrium density. In the framework of the FMT, the differentiation of the generic functional results in

$$c_2([\rho],\mathbf{r}_1,\mathbf{r}_2)=\sum_{\alpha,\gamma}\psi_{\alpha\gamma}n\alpha*n_\gamma, \tag{4}$$

where $\psi_{\alpha\gamma}=\partial^2\Phi/(\partial n_\alpha\partial n_\gamma)$ are numerical coefficients not depending on any spatial coordinate and the convolution of two weights is defined as

$$n_\alpha*n_\gamma=\int d^3x\,n_\alpha(\mathbf{r}_1-\mathbf{x})n_\gamma(\mathbf{r}_2-\mathbf{x}). \tag{5}$$

The crucial point is that c_2 has the double range compared to that of the weight functions w_α. The direct correlation function is only known in the low-density limit $c_2\to f=\exp(-\beta V)-1$, as $\rho\to0$, where f is the Mayer function, and $\beta=1/k_BT$. The requirement to fulfill this limit will be used to find the explicit form of the weight functions.

The second requirement is to reproduce the exact free energy in the zero-dimensional (0D) limit. The 0D limit is defined through the density distribution $\rho_{0\text{d}}=\eta\delta(\vec{r})$. Physically, it describes a small cavity that can hold only one single particle. The 0D limit has proven to be a useful construct for hard spheres [4,5,13]. In this case it can be realized by a spherical cavity with diameter σ with hard walls. It has only two states: Either it is empty, or it holds a single particle. However, the idea is not restricted to hard bodies. We use it to model a cavity for a soft particle. As we assume a divergence to infinity of the soft potential under consideration, it would cost infinite energy to insert a second particle. Hence, the 0D limit for soft cores is the same as for hard bodies! It was shown [13] that a functional that fulfills the 0D limit is given by

$$\Phi_1=-n_0\ln(1-n_3), \tag{6}$$

if the weight functions have the property

$$w_0(r)=-(4\pi r^2)^{-1}\frac{\partial}{\partial r}w_3(r), \tag{7}$$

with boundary conditions $w_3(0)=1$, and $w_3(\infty)=0$. The index $\alpha=0{,}3$ is related to the dimension of the weighted densities, which is $(\text{length})^{\alpha-3}$. The emerging integral can be solved and yields the exact 0d free energy $F^{\text{exc}}=\eta+(1-\eta)\ln(1-\eta)$ [4,5], no matter what the functional dependence of n_3 on r is. The freedom can be used to tune the weight functions to fit a prescribed interaction potential.

We assume that the set of weight functions is related to the ''generating'' weight function w_3 through

$$w_2(r)=-\frac{\partial w_3(r)}{\partial r}=-w_3'(r), \tag{8}$$

$$\mathbf{w}_{v2}(\mathbf{r})=w_2(r)\,\mathbf{r}/r, \tag{9}$$

$$w_1(r)=w_2(r)/(4\pi r), \tag{10}$$

$$\mathbf{w}_{v1}(\mathbf{r})=w_1(r)\,\mathbf{r}/r, \tag{11}$$

$$w_0(r)=w_1(r)/r, \tag{12}$$

where w_2, w_1, and w_0 are scalar quantities and $\mathbf{w}_{v1},\mathbf{w}_{v2}$ are vectors. What remains is to find an explicit expression for the generalized local packing fraction weight $w_3(r)$. Therefore, we consider the low-density limit of the true density functional,

$$F^{\text{exc}}\to-\frac{k_BT}{2}\int d\mathbf{r}_1\,d\mathbf{r}_2\,f(|\mathbf{r}_1-\mathbf{r}_2|)\rho(\mathbf{r}_1)\rho(\mathbf{r}_2), \tag{13}$$

and impose that we recover the Mayer-bond, $f(r)=\exp[-\beta V(r)]-1$, by a sum of convolutions of weight functions

$$-\frac{1}{2}f(r)=w_0*w_3+w_1*w_2-\mathbf{w}_{v1}*\mathbf{w}_{v2}, \tag{14}$$

where the convolution product, denoted by $*$, also implies scalar products between vectors. Inserting the hierarchical relations yields

$$1-\exp[-\beta V(r)]=\frac{2}{4\pi}\left(-\frac{w_3'(r)}{r^2}*w_3(r)+\frac{w_3'(r)}{r}*w_3'(r)-\frac{w_3'(r)}{r^2}\mathbf{r}*\mathbf{r}\frac{w_3'(r)}{r}\right), \tag{15}$$

which is an equation for the determination of the generating weight w_3, once a pair potential $V(r)$ is specified. The dependence of w_3 on temperature has been suppressed in the notation, and the prime denotes differentiation with respect to the argument r.

For the free energy density we take over the hard sphere expression $\Phi=\Phi_1+\Phi_2+\Phi_3$, with the contributions $\Phi_1=-n_0\ln(1-n_3)$, $\Phi_2=(n_1n_2-\mathbf{n_{v1}}\cdot\mathbf{n_{v2}})/(1-n_3)$, $\Phi_3=n_2^3[1-(\mathbf{n_{v2}}/n_2)^2]^3/[24\pi(1-n_3)^2]$. As discussed above, Φ_1 yields the exact single-cavity limit. The additional terms Φ_2 and Φ_3 correctly vanish in this limit. The two-cavity case is not reproduced exactly, but a numerical evaluation shows satisfactory agreement [14].

We want to apply the theory to star polymer solutions that are characterized by an ultra-soft repulsive interaction [15]. This system has two parameters, the functionality or arm number of the stars f and a length scale σ^*, which are used to build a dimensionless density $\eta^*=(\pi/6)\sigma^{*3}N/V$, where N is the particle number inside a volume V. The pair potential [16] consists of a logarithmic potential for small distances and an exponentially decaying Yukawa potential for large distances. In order to keep the present analysis simple we use a modified form for large distances,

$$\beta V(r)=\begin{cases}-2q\ln(r/R)+\ln\binom{2q}{q} & 0\leqslant r<R\\ \phi_q(r)+\ln\binom{2q}{q} & R\leqslant r<2R\\ 0 & 2R\leqslant r,\end{cases}\tag{16}$$

where $\binom{2q}{q}$ is the binomial coefficient. The crossover function between small and large distances is given by

$$\phi_q(r)=-\ln[(1+\xi)^{2q}-\xi^{q+1}B_q\,{}_2F_1(1,1-q;2+q;-\xi)],\tag{17}$$

where $\xi=(r/R)-1$, $B_q=2\Gamma(1+2q)\Gamma^{-1}(q)\Gamma^{-1}(2+q)$, and ${}_2F_1$ is the hypergeometric function. The parameters are related to Ref. [16] via $q=(5/36)f^{3/2}$, and $R/\sigma^*=\exp[(1+\sqrt{f}/2)^{-1}-(2q)^{-1}\ln\binom{2q}{q}]$. It is natural to define a dimensionless density $\eta=(4\pi/3)R^3N/V=8\eta^*(R/\sigma^*)^3$. The potential $V(r)$ given by Eq. (16) is shorter ranged than the original one. It is slightly smoother as it is q times differentiable at $r=R$ and one time differentiable at $r=2R$.

The specific form of the crossover function $\phi_q(r)$ allows us to deconvolve the Mayer function [Eq. (14)] and construct the weight functions analytically. The solution is

$$w_3(r)=\begin{cases}1-(r/R)^q & \text{if } 0\geqslant r\geqslant R\\ 0 & \text{else.}\end{cases}\tag{18}$$

In the limit $q\to\infty$ we recover hard spheres: The weight function approaches a step-function, $w_3(r)\to\Theta(R-r)$ and the potential becomes hard core with range $2R$.

The weighted densities, Eq. (2), when evaluated for the homogeneous fluid are constant in space,

$$n_\alpha=4\pi\rho\int_0^a dr\, r^2 w_\alpha(r),\tag{19}$$

with $a\to\infty$. In particular, n_3 is proportional to ρ. The free energy density Φ, however, is only defined for $n_3<1$, thus implying an unphysical upper limit of densities. To circumvent this problem, we propose to reduce the upper limit of integration in Eq. (19) to the Wigner-Seitz (WS) radius $a=R\eta^{-1/3}$, so that only the density field within a WS cell contributes to the weighted density. As usually $w_3\leqslant 1$ holds, it can be seen that the cutoff ensures $n_3\leqslant 1$. When applied to the hard sphere case no harm is done, as only unphysical states are affected: All $\eta>1$ are mapped onto $\eta=1$. The validity of the procedure will be checked by comparison with simulations.

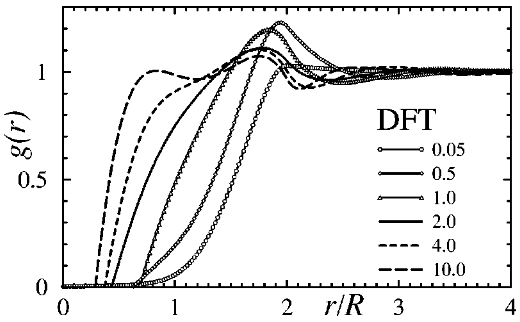

FIG. 1. Pair correlation functions $g(r)$ as a function of the scaled distance r/R obtained from density-functional theory for a solution of star polymers [Eq. (16)]. The variation with density η is shown.

To test the theory, we calculate pair distribution functions $g(r)$ in the fluid phase. We choose the extremely soft case $q=3$, that corresponds to a (noninteger) arm number of roughly 7.75. To perform a severe test, no use of the test-particle limit is made, i.e., no minimizing of the functional with an external field given by the pair potential itself is done. Instead, we use the direct correlation function given by the second functional derivative of the excess free energy functional, Eq. (3). The Ornstein-Zernike relation yields the pair correlation function $g(r)$. In Fig. 1 we show results for a large range of densities, $\eta=0.05-10$, corresponding to $\eta^*=0.007\,97-1.595$. For comparison, Monte Carlo simulation data are shown in Fig. 2. The reasonable agreement is, however, achieved by an empirical modification. We rescale heuristically the direct correlation function, $\lambda * c_2$, where λ is roughly proportional to η^{-1}. The particular values are (η given in parentheses) $\lambda=1$ (0.05), 0.7 (0.5), 0.2 (1.0), 0.05 (2.0), 0.04 (4.0), and 0.02 (10.0). The main effect is a res-

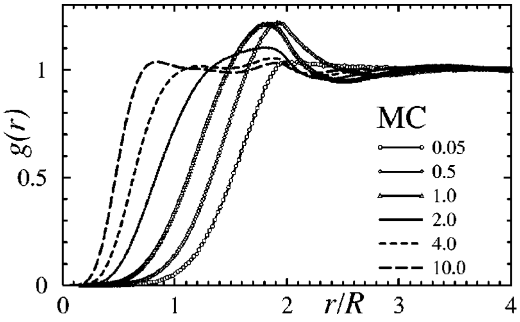

FIG. 2. Same as Fig. 1, but obtained from Monte Carlo computer simulation.

caling of the amplitude of the oscillations in $g(r)$. From a strict point of view, we have introduced one fit parameter per curve. We note, that this is only necessary for the extremely soft case $q=3$. For $q>12$ and $\eta=0.5$ good agreement is found without rescaling (i.e., $\lambda=1$).

The results are fairly good. Wavelength and phase of the oscillations are correct. The peculiar shrinking of the first peak and growing of the second peak upon decreasing the density is reproduced. For small distances, the theory yields unphysical negative values of $g(r)$ (not shown in Fig. 1). The worst case is $g(0)=-1.11$ for $\eta=10$. Apart from this, we find a remarkable agreement between theory and simulation.

In conclusion, we have proposed a systematic way to generalize the fundamental-measure density-functional theory for hard bodies to soft interactions. This ''soft FMT'' is based on the exactly solvable dimensional crossover to a set of zero-dimensional cavities and on the virial expansion. As a test case, we studied the ultrasoft logarithmic potential that mimics the effective interaction between star polymers in solution. Prominent features such as the anomalous pair correlation function are captured qualitatively correct. An empirical modification leads to good quantitative agreement with computer simulation results. Concerning future work, it is highly desirable to apply the soft FMT to the recently found freezing transitions for star polymers [17] and to inhomogeneous liquid situations. Furthermore, the performance for other soft repulsive interactions like the Yukawa or inverse-power potentials should be investigated. It would also be highly interesting to test the current approach for attractive interactions like the Lennard-Jones potential, where preliminary investigations have shown that the numerical deconvolution of the Mayer function is possible.

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