# Density Functional Theory for Small Systems: Hard Spheres in a Closed Spherical Cavity

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(Received 14 July 1997)

We present a new approach to determining the equilibrium structure of a closed (canonical) inhomogeneous fluid which combines grand canonical density functional theory and a series expansion of the distribution functions in powers of $(1/\bar{N})$, where $\bar{N}$ is the average number of particles. For hard spheres in a hard spherical cavity, comparison with canonical Monte Carlo results shows that the method is rather accurate, even for small values of $\bar{N}$. In certain (high packing) situations the density profile develops a pronounced peak in the center of the cavity. Accounting properly for such peaks provides a severe test of any density functional approximation. [S0031-9007(97)04188-4]

PACS numbers: 61.20.Gy, 68.45.–v

Understanding the properties of fluids confined in narrow capillaries or micropores is important for several branches of surface physics and chemistry. Microporous and mesoporous solids are widely used in separation processes and as materials for catalyst supports while zeolites, clathrates, and fullerenes are molecular sieves, structures with cavities which can hold only a few adsorbed molecules. In all such systems the fluid is extremely spatially inhomogeneous and its thermodynamical [1] and dynamical [2] properties are very different from those in bulk. Developing a statistical mechanics of small systems is a challenging problem [3]. In this Letter we focus on the equilibrium structure (the average density profile) for a simple model, a hard-sphere fluid confined in a hard spherical cavity, and show that this can be described accurately by density functional theory (DFT) even for cases of very strong confinement where the packing constraints are very pronounced.

Previous approaches to such problems include virial expansions of the grand potential [3–5], integral equation theories [6], and computer simulation [7]. Direct calculation of the partition functions can be made for cavities containing up to about six molecules [5]. For larger systems alternative (approximate) methods are required and DFT is a natural candidate as it has been applied successfully to other types of confinement, e.g., fluids in slit and cylindrical pores where it has provided much insight into the structure and phase behavior [8]. Recent DFT approximations are designed to deal with confining geometries which reduce the effective dimensionality below that of the bulk fluid. In the most extreme situation one considers a very small spherical cavity which cannot hold more than one particle, and then one speaks of *zero dimension* (0D) cavities [9,10]. Investigating this dimensional crossover has provided a much deeper understanding of the analytical structure of the free-energy functionals required for accurate DFT of fluids of hard spheres and hard disks [9–11] and of parallel hard cubes [12]. In particular, obtaining the correct 0D limit of the free-energy functional appears to be important for a good description of the freezing transition [9].

The usual procedure in studying adsorption of confined fluids is to assume that there is a particle reservoir so that one is working at a fixed chemical potential $\mu$; the grand canonical ensemble is the appropriate one. In the present situation we are dealing with a finite, inhomogeneous, closed system (with a fixed, finite number of particles $N$), and a conventional DFT approach (at fixed temperature $T$ and $\mu$) is inadequate. One way of overcoming this problem would be to construct a canonical ensemble DFT in which a free-energy variational principle is established instead of the usual minimum grand-potential principle [13], but then it is not clear how to modify a standard DFT recipe in order to account for the minimum free-energy principle which comes from the fixed $N$ constraint. Here we suggest an alternative approach which first performs a grand canonical DFT treatment of the problem and then uses the solution to obtain an approximate profile for the canonical ensemble. The first step requires a reliable DFT recipe (see, e.g., Ref. [8]), utilized in such a way that it gives rise to a predetermined average number of particles for a given confining box or cavity. This procedure is equivalent to determining an appropriate chemical potential, as we shall see below. The second step is based on an early idea of Lebowitz and Percus [14] which relates the canonical pair correlation function $g_N(r)$ to its grand canonical counterpart. This idea has been used recently in analyzing finite size effects in the calculation of the structure factor by canonical molecular dynamics simulations [15]. The present application provides a demanding test for the proposed method which can be generalized easily to other situations. Moreover, by making comparison with canonical Monte Carlo simulation results we examine the performance of the recently proposed free-energy functionals [9] in dealing with extremely confined fluids.

The grand canonical density profile $\rho(\mathbf{r})$ of an *open* system subject to an external potential $V_{\text{ext}}(\mathbf{r})$ is obtained by minimizing the grand potential functional $\Omega[\rho] = \mathcal{F}[\rho] + \int d\mathbf{r}\, \rho(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - \mu]$ at a given chemical potential $\mu$. A DFT recipe provides a prescription for the intrinsic Helmholtz free-energy functional $\mathcal{F}[\rho]$ (see, e.g., Ref. [8]). In this Letter we employ the fundamental measure theory (FMT) of Rosenfeld [16] which appears to be one of the most successful theories for the study of hard spheres in highly inhomogeneous situations [17]. Furthermore, the original FMT of Rosenfeld has recently been modified in order to account for the correct dimensional crossover, giving rise to new functionals with the appropriate 0D behavior [9,10]. Below we give a brief account of the FMT; more details can be found in the original papers [9,10,16,17]. The main assumption of the FMT is that the excess contribution $\mathcal{F}_{\text{ex}}[\rho]$ to the free-energy functional of a one-component system of hard spheres can be expressed as

$$\beta\mathcal{F}_{\text{ex}}[\rho] = \beta\mathcal{F}[\rho] - \beta\mathcal{F}_{\text{id}}[\rho] = \int d\mathbf{r}\, \Phi[\{n_\alpha(\mathbf{r})\}], \tag{1}$$

where $\beta = 1/k_B T$, and $\beta\mathcal{F}_{\text{id}}[\rho]$ is the ideal-gas contribution, i.e., the excess free-energy density $\beta^{-1}\Phi$ is expressed as a function of a set of weighted densities $n_\alpha(\mathbf{r})$ which are defined by $n_\alpha(\mathbf{r}) = \int \rho(\mathbf{r}')\omega^{(\alpha)}(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}'$. The weight functions $\omega^{(\alpha)}$, based on the fundamental geometric measures of a three dimensional sphere of radius $R$, consist of four scalar and two vector quantities and are given in [16,17]. In order to account for the dimensional crossover in the FMT it is useful to express $\Phi$ as $\Phi = \Phi_1 + \Phi_2 + \Phi_3$ where $\Phi_1 = -n_0 \log(1 - n_3)$, $\Phi_2 = (n_1 n_2 - \mathbf{n}_1 \cdot \mathbf{n}_2)/(1 - n_3)$ and $\Phi_3 = [\frac{1}{3}n_2^3 - n_2(\mathbf{n}_2 \cdot \mathbf{n}_2)]/8\pi(1 - n_3)^2$ (ROS) where the dot denotes scalar product. In the uniform limit the vector weighted densities $\mathbf{n}_1 = \mathbf{n}_2 = 0$ and $\Phi$ is the scaled-particle or Percus-Yevick (PY) approximation to the excess free energy. In the same limit the pair direct correlation functions obtained by functional differentiation are identical to those of PY; $n_3$ is simply the packing fraction. If one eliminates $\Phi_3$, the remainder $\Phi_1 + \Phi_2$ yields the exact free-energy and pair direct correlation function for a uniform hard rod fluid in the limit of a one dimensional density distribution.

Such considerations lead Rosenfeld *et al.* [9] to investigate the 0D limit and to propose modifications for $\Phi_3$. The antisymmetrized form $\Phi_{3,\text{asym}} = n_2^3(1 - \xi^2)^3/24\pi(1 - n_3)^2$ (RSLT1) preserves the favorable features of the original functional for three dimensional situations (it yields PY pair correlation functions) but vanishes in the 0D limit and $\Phi$ then reduces to the exact free energy [9]. Note that $\xi(\mathbf{r}) = |\mathbf{n}_2(\mathbf{r})/n_2(\mathbf{r})|$. We have also investigated the form $\Phi_{3,\text{int}} = n_2^3(1 - 3\xi^2 + 2\xi^3)/24\pi(1 - n_3)^2$ (RSLT2) which interpolates between $\Phi_3$ in (ROS) and $\Phi_{3,\text{exact}-0\text{D}}$ presented in [9]. One might expect that the density profiles obtained from minimization of the functionals with different choices of $\Phi_3$ would be very similar except for those cases where a quasi-0D situation arises.

So far we have described the DFT used to calculate the density profile for an open system. This grand canonical profile will be used below to obtain the canonical one. One subtlety should be pointed out. We require grand canonical profiles with a fixed integer average number of particles. For a given choice of chemical potential $\mu$, we have no way to ensure *a priori* that this choice will take us to the final desired value of the average number of particles. The method of tackling this problem is to vary $\mu$ slowly in the iterative process of solving the Euler-Lagrange equations which arise from the minimization of the grand potential. $\mu$ is varied in order to obtain a density profile whose integral over the volume considered yields the desired average number of particles. Since $\mu$ acts as a parameter in the iterative solution of the Euler-Lagrange equations and at the end of this process remains unchanged, this procedure is equivalent to knowing in advance the (correct) chemical potential $\mu_{\text{final}}$.

As the final step in our method we use the following relation between the canonical one-particle density $\rho_{\bar{N}}(\mathbf{r})$ and the grand canonical one $\rho(\mathbf{r})$, the latter associated with average number of particles $\bar{N}$.

$$\rho_{\bar{N}}(\mathbf{r}) = \rho(\mathbf{r}) + f_1(\mathbf{r}, \bar{N}) + f_2(\mathbf{r}, \bar{N}) + O\left(\frac{1}{\bar{N}^3}\right), \tag{2}$$

where

$$f_1(\mathbf{r}, \bar{N}) = -\frac{1}{2} \frac{\partial \bar{N}}{\partial(\beta\mu)} \frac{\partial^2}{\partial \bar{N}^2} \rho(\mathbf{r}) \tag{3}$$

and

$$\begin{aligned} f_2(\mathbf{r}, \bar{N}) = &-\frac{1}{2} \frac{\partial \bar{N}}{\partial(\beta\mu)} \frac{\partial^2}{\partial \bar{N}^2} f_1(\mathbf{r}, \bar{N}) \\ &- \frac{1}{6} \frac{\partial^2 \bar{N}}{\partial(\beta\mu)^2} \frac{\partial^3}{\partial \bar{N}^3} \rho(\mathbf{r}) \end{aligned} \tag{4}$$

are corrections of order $1/\bar{N}$ and $1/\bar{N}^2$, respectively. Equations (2)–(4) provide us with the required link between the canonical and the grand canonical density profiles and can be derived following a procedure similar to that used in [15]. Note that the correction terms $f_1$ and $f_2$ depend upon the fluctuations in the number of particles in the cavity and on the variations of the GC profile with respect to $\bar{N}$ (or $\mu$). For large $\bar{N}$ one can expect these corrections to be small but for small values of $\bar{N}$ it is not obvious that the expansion is convergent. These correction terms should be sensitive to packing constraints and their values should reflect the choice of DFT. One advantage of (2), however, is that the integrals of $f_1$ and $f_2$ over the confining volume must both be zero. This provides a useful check on the numerics. Since higher-order terms are complicated and difficult to calculate, the usefulness of (2) rests on the ability of the leading terms to capture the essential physics.

The object of our study is the three dimensional hard-sphere fluid confined to a hard spherical cavity of radius $R_{\text{cav}}$ by means of the following external potential $V_{\text{ext}}(r) = 0$ if $r < R_{\text{cav}}$ and $V_{\text{ext}}(r) = \infty$ if $r > R_{\text{cav}}$ where $r$ is the distance to the center of the cavity. This means that the farthest distance the center of the hard sphere can access is $R_{\text{cav}} - \sigma/2$ where $\sigma$ is the hard-sphere diameter. In this case, because of the symmetry of the problem, the density profile depends on $r$ only, and the Euler-Lagrange equations for obtaining the grand canonical profile can be solved by means of 1D fast Fourier transforms. In order to obtain a canonical density profile one must use Eqs. (2)–(4) for a given $R_{\text{cav}}$ and average number of particles $\bar{N}$. All the derivatives in (3) and (4) are performed numerically.

Clearly the most demanding situations arise for cases with few particles. As a preliminary test of the $1/\bar{N}$ expansion (truncated to second order) we have considered several cases with $\bar{N} \leq 10$ at low average density where any respectable density functional theory should provide good grand canonical results. For these low density cases all the DFT's we considered gave very accurate canonical results when compared with our canonical MC simulations. Although the grand canonical results are significantly different from MC the first two corrections in (2) are sufficient to account for the differences.

The situation is more interesting for high packings. There one needs a good theory and, as argued above, when using the FMT one should see differences between the results of the various prescriptions for $\Phi_3$. In Fig. 1 we present the results of canonical MC simulations for a cavity of radius $R_{\text{cav}} = 1.85\sigma$ and $\bar{N} = 8$, and 10. These simulation data are compared with the results of the present method using the original prescription ROS and RSLT2 for $\Phi_3$: We show the grand canonical profiles (zeroth order results), the results of the first order approximation [neglecting $f_2(\mathbf{r}, \bar{N})$ in (2)] as well as the second order results. The most remarkable feature of Fig. 1 is the peak in the center of the cavity ($r$ near 0) which grows very rapidly as $\bar{N}$ increases. It is here where the main differences between the theories appear. This behavior is a symptom of a quasi-0D situation in the center of the cavity, where there is a zone of strong localization arising from the packing constraints. The grand canonical density profile $\rho(\mathbf{r})$ is always significantly higher than the canonical results in the central zone. Contributions from values of $N$ different from $\bar{N}$ are substantial, especially for higher packings. Also in this zone the convergence of the $1/\bar{N}$ expansion is much slower than in other regions of the profile. For values of $\bar{N} < 7$ all the prescriptions for $\Phi_3$ yield similar results and the convergence is good. For $\bar{N} = 8$ RSLT2 appears to be performing slightly better than ROS but by $\bar{N} = 9$ (not plotted) ROS fails to converge, and for $\bar{N} = 10$ the first order result is very poor in the central zone and the second order is completely unphysical—see Fig. 1(b). The new modifications RSLT1 and RSLT2 yield very similar profiles so we do not plot the former. Both seem to converge for $\bar{N} = 10$ and yield results in good agreement with the simulation for the full range of $r$. Note that all three prescriptions give similar second order profiles for $r \geq 0.4\sigma$, for $\bar{N} \leq 9$.

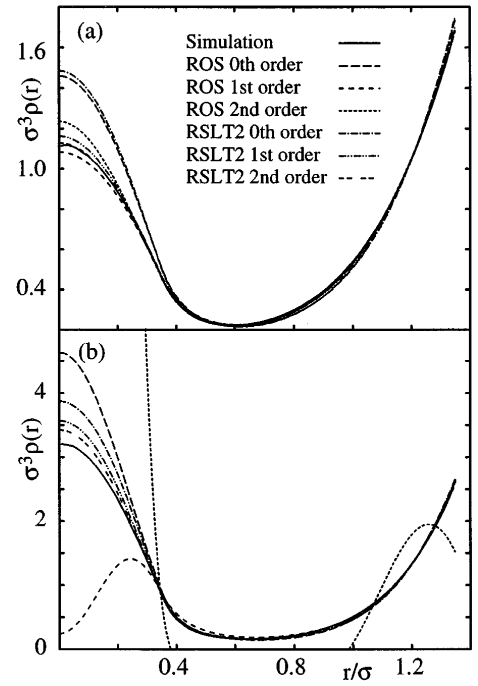

FIG. 1. Density profiles of hard spheres of diameter $\sigma$ in a spherical cavity of radius $R_{\text{cav}} = 1.85\sigma$ (maximum radius available to the center of the hard sphere is $R_{\text{cav}} - \sigma/2$). (a) $\bar{N} = 8$ and (b) $\bar{N} = 10$ particles. The solid lines are the results of canonical MC simulations. Other lines represent zeroth (grand canonical), first, and second order results of ROS and RSLT2 theories (see text). Note the difference in vertical scales.

The differences between the canonical and the grand canonical profiles in the center of the cavity remain even when the number of particles is large enough to give negligible differences in other regions of the profile. This happens, e.g., when one considers $\bar{N} = 45$ particles in a cavity of radius $R_{\text{cav}} = 2.8\sigma$. For a different situation (e.g., $\bar{N} = 35$, $R_{\text{cav}} = 2.5\sigma$), where there is no room for the central peak, there are only very small differences between zeroth, first, and second order results for a given theory.

The case $\bar{N} = 2$ is clearly a good test for the accuracy of the $1/\bar{N}$ expansion; moreover, this case has the advantage that the density profile is known exactly (the solution is given in terms of the volume available for one particle once the other is placed in the cavity, and is essentially the convolution of two spheres, one of radius $\sigma$ and the other of radius $R_{\text{cav}} - \sigma/2$). In Fig. 2 we compare the exact

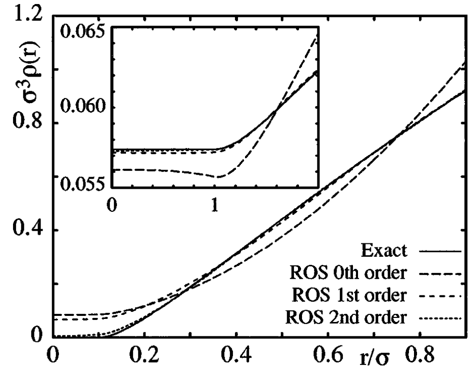

FIG. 2. Density profiles of hard spheres in a spherical cavity of radius $R_{\mathrm{cav}} = 1.4\sigma$ for $\bar{N} = 2$. The solid line is the exact canonical result for $N = 2$ (see text). Other lines represent zeroth (grand canonical), first, and second order results of ROS (see text). The inset displays the low density case ($\bar{N} = 2$, $R_{\mathrm{cav}} = 2.5\sigma$). Note the difference in vertical scales.

density profile for 2 particles in a cavity of radius $R_{\mathrm{cav}} = 1.4\sigma$ with the results of ROS (the other prescriptions give very similar profiles). For this demanding case the second order results remain good even where the exact density is zero, $r < 0.1\sigma$. The inset shows results for the low density case $\bar{N} = 2$, $R_{\mathrm{cav}} = 2.5\sigma$ for which the first order correction already yields very good results while the second order correction gives a nearly exact density profile. For very small cavities, $R_{\mathrm{cav}} \leq 1.3\sigma$, the second order profiles are (slightly) negative in the excluded central region but still capture the main features of the exact results.

In summary, we have presented a new method for dealing with highly inhomogeneous fluids in the canonical ensemble by combining a FMT (density functional) approach with Eq. (2) relating the grand canonical density profile to the canonical one. This method has been applied to a hard-sphere fluid confined in a spherical cavity. In most situations all versions of the FMT theory yield results in good agreement with simulation. However, for high packings and certain radii of the cavity the density profile in the center of the cavity is strongly peaked and is very sensitive to the choice of the FMT theory. In such circumstances the new modifications RSLT1 and RSLT2 (which are designed to achieve the correct dimensional crossover to quasi-0D behavior) fare much better than the original ROS. It would be interesting to examine the performance of other DFT's for this particular problem. It would also be worthwhile to perform grand canonical MC simulations in order to (a) test DFT directly and (b) provide an independent test of the $(1/\bar{N})$ expansion.

A. G., J. A. W., F. L. R., and S. V. acknowledge financial support from the Dirección General de Investigación Científica y Técnica (DGICYT) of Spain under Grant No. PB 95-0934 and by Junta de Castilla y León (Spain) under Grant No. SA78/96. A. G. thanks a fellowship from the Ministerio de Educación y Cultura of Spain. We thank J. A. Cuesta, Y. Rosenfeld, and P. Tarazona for communicating their results before publication. R. E. has benefited from valuable conversations with B. Götzelmann and from the hospitality of S. Dietrich in Wuppertal.

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