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Density-Functional Theory of Inhomogeneous Fluids in the Canonical Ensemble

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We present a density-functional approach for dealing with inhomogeneous fluids in the canonical ensemble. A general relation is proposed between the free-energy functionals in the canonical and the grand canonical ensembles. The minimization of the canonical-ensemble free-energy functional gives rise to Euler-Lagrange equations which involve averaged Ornstein-Zernike equations of second and third order. The theory is especially appropriate for systems with a small, fixed number of particles. As an example of application we obtain accurate results for the density profile of a hard-sphere fluid in a closed spherical cavity that contains only a few particles.

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Density-functional theory (DFT) has become a fundamental technique for the study of classical fluids [1]. Highly developed approximations for the Helmholtz free-energy functional have led to an accurate description of the equilibrium microscopic properties of inhomogeneous fluids. Although DFT can be formulated in the different statistical-mechanics ensembles [2], these advanced approximations have been obtained in the grand canonical ensemble (GCE). This means that the results of all the existing DFT prescriptions correspond to *open* systems, that is, in contact with a particle reservoir at fixed chemical potential μ. Therefore, as recently pointed out by Evans [3], there is, as yet, no classical DFT approach which works with a fixed number of particles. Usually this is not a problem since the ensembles are equivalent in the thermodynamic limit. However, for (small) systems of finite size this equivalence does not hold and, according to the external conditions, one must choose the appropriate ensemble for the description of the system.

In this Letter we will consider the DFT treatment of *closed* systems, with a fixed number of particles N, which are described by the canonical ensemble (CE)—of course, for N large a GCE-DFT approach is equivalent, and therefore we will focus our attention on very small values of N. In particular, we will show how to use the existing accurate GCE functionals to implement a CE-DFT of similar accuracy, valid for a few particles. Apart from its intrinsic interest, the availability of a CE-DFT is of great importance for comparing with computer simulation results which are commonly obtained for systems with a fixed number of particles. The necessity of a CE functional has been recently pointed out in a time-dependent DFT approach to the relaxation dynamics of a system of interacting particles [4]. Comparison of the time-dependent (GCE) DFT results with Langevin simulations (carried with a fixed number of particles) showed the importance of the fluctuation in the number of particles in the relaxation. Earlier work for (inhomogeneous) fluids in the canonical ensemble has been carried out by Schlijper and co-workers [5] by using an approach inspired by the cluster variation method for lattice systems. We note that, in contrast to the present approach, these authors were interested in obtaining integral equations for the distribution functions of fluids in the thermodynamic limit and thus a delicate asymptotic analysis of the results was required.

In the density-functional theory of the canonical ensemble, the equilibrium density profile $\rho_c(\mathbf{r})$ of a closed system with N particles and intrinsic free energy functional $\mathcal{F}_c[\rho]$ is obtained by minimizing the functional

$$\mathcal{F}_c[\rho] + \int d\mathbf{r}\,\rho(\mathbf{r})V_{\text{ext}}(\mathbf{r}) \tag{1}$$

over all densities that can be associated with the external potential V_{ext} and that are normalized to the (integer) number of particles N. This constraint must be taken into account in the minimization, but, as pointed out in [2], in principle we cannot directly use the Lagrange multiplier technique since the constraint-free variation $\delta\{\mathcal{F}_c[\rho] + \int d\mathbf{r}\,\rho(\mathbf{r})V_{\text{ext}}(\mathbf{r}) - \lambda[\int \rho(\mathbf{r})\,d\mathbf{r} - N]\}$ would require the functional (1) to be defined for noninteger values of the number of particles N. We can assume, however, that (1) can be extended to noninteger values of N (e.g., by means of an adequate interpolation) and then we obtain

$$\left.\frac{\delta\mathcal{F}_c[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_c} + V_{\text{ext}}(\mathbf{r}) = \lambda\,, \tag{2}$$

where $\rho_c(\mathbf{r})$ denotes the equilibrium density of the fluid in the CE and the Lagrange multiplier λ must be calculated from the constraint

$$\int \rho_c(\mathbf{r})\,d\mathbf{r} = N\,. \tag{3}$$

At this point, if we compare Eq. (2) with the usual Euler-Lagrange equation in the grand canonical ensemble $\delta\mathcal{F}_{\text{gc}}[\rho]/\delta\rho(\mathbf{r})|_{\rho=\rho_{\text{gc}}} + V_{\text{ext}}(\mathbf{r}) = \mu$, where $\rho_{\text{gc}}(\mathbf{r})$ is the equilibrium GCE density, we see that λ plays the role of the chemical potential. Furthermore, it is clear that any minimizing scheme developed for the GCE can be applied in the CE by replacing $\mathcal{F}_{\text{gc}}[\rho]$ by $\mathcal{F}_c[\rho]$ and choosing the chemical potential μ so that the density profile integrates to N, i.e., so that the constraint (3) holds. In [6,7] the density profile of a finite system with an average number of particles $\langle N\rangle$ in the GCE was derived. Following the same route for the CE we obtain

$$\rho_c(\mathbf{r}) = N\exp\left[-\beta V_{\text{ext}}(\mathbf{r}) - \beta\,\frac{\delta\mathcal{F}_{\text{gc}-\text{ex}}[\rho]}{\delta\rho(\mathbf{r})}\bigg|_{\rho=\rho_c} + \xi(\mathbf{r};[\rho_c])\right]\bigg/\int d\mathbf{r} \times \exp\left[-\beta V_{\text{ext}}(\mathbf{r}) - \beta\,\frac{\delta\mathcal{F}_{\text{gc}-\text{ex}}[\rho]}{\delta\rho(\mathbf{r})}\bigg|_{\rho=\rho_c} + \xi(\mathbf{r};[\rho_c])\right], \tag{4}$$

where $\beta = 1/k_BT$ is the inverse temperature, $\mathcal{F}_{\text{gc}-\text{ex}}$ is the usual excess (over the ideal-gas) free-energy functional in the *grand* canonical ensemble, and

$$\xi(\mathbf{r};[\rho]) \equiv -\beta\,\frac{\delta(\mathcal{F}_c[\rho] - \mathcal{F}_{\text{gc}}[\rho])}{\delta\rho(\mathbf{r})}. \tag{5}$$

We note that the key difference between the DFT solution for the density profile of a closed system with N particles and that for an open system with average number of particles $\langle N\rangle = N$ is the presence of the term $\xi(\mathbf{r};[\rho_c])$—see Eq. (3.27) in [7]. In order to evaluate $\xi(\mathbf{r};[\rho_c])$ we require an approximation for the difference $\mathcal{F}_c - \mathcal{F}_{\text{gc}}$. We propose

$$\beta\mathcal{F}_c[\rho] - \beta\mathcal{F}_{\text{gc}}[\rho] \approx \frac{1}{2}\log 2\pi\Delta^2(N;[\rho]), \tag{6}$$

where we have made explicit the functional dependence of the mean square fluctuation of the number of particles in the GCE, $\Delta^2(N) \equiv \langle N^2\rangle - \langle N\rangle^2$. In Eq. (6), the chemical potential is adjusted in $\mathcal{F}_{\text{gc}}$ so that it gives rise to the correct (integer) value for the average number of particles. Equation (6) is proposed on the basis of the following standard relation between the CE Helmholtz free energy $F_c(N)$ and the grand potential $\Omega_{\text{gc}}(\mu)$, obtained via a saddle point approximation valid for large N [8]:

$$-\beta\Omega_{\text{gc}}(\mu) \approx -\beta F_c(\langle N\rangle) + \beta\mu\langle N\rangle + \frac{1}{2}\log 2\pi\Delta^2(N). \tag{7}$$

Therefore, in Eq. (6) we are assuming that (7), which is valid for the equilibrium free energies of a homogeneous fluid, is also a good approximation for the functionals of fluids with arbitrary inhomogeneous distributions, and this is the key assumption in our present work.

From (6) and (5) we obtain

$$\xi(\mathbf{r};[\rho_c]) \approx -\frac{1}{2}\,\frac{1}{\Delta^2(N;[\rho_c])}\,\frac{\delta\Delta^2(N;[\rho])}{\delta\rho(\mathbf{r})}\bigg|_{\rho=\rho_c}. \tag{8}$$

The next step in our derivation is to express the mean square fluctuation $\Delta^2(N;[\rho])$ as a functional of the density. This can be done by considering the density-density correlation function $\mathcal{G}$ which in terms of the two particle density $\rho^{(2)}$ can be expressed as [1,9]

$$\mathcal{G}(\mathbf{r}_1,\mathbf{r}_2) = \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) + \rho^{(1)}(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{9}$$

and hence it normalizes to the mean square fluctuation

$$\Delta^2(N) = \iint \mathcal{G}(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,. \tag{10}$$

Moreover, defining the functional inverse $\mathcal{G}^{-1}$ as

$$\int d\mathbf{r}_2\,\mathcal{G}(\mathbf{r}_1,\mathbf{r}_2)\mathcal{G}^{-1}(\mathbf{r}_2,\mathbf{r}_3) = \delta(\mathbf{r}_1 - \mathbf{r}_3), \tag{11}$$

one has that $\mathcal{G}^{-1}$ is essentially the two particle direct correlation function $c^{(2)}$ [1,9],

$$\mathcal{G}^{-1}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)}\,\delta(\mathbf{r}_1 - \mathbf{r}_1) - c^{(2)}(\mathbf{r}_1,\mathbf{r}_1), \tag{12}$$

and Eq. (11) is the Ornstein-Zernike equation [10] written in compact form [1,9]. If we now introduce the auxiliary function

$$\Gamma(\mathbf{r}) \equiv \int \mathcal{G}(\mathbf{r},\mathbf{r}')\,d\mathbf{r}', \tag{13}$$

performing an integration in Eq. (11) and using (12) and (13) we obtain

$$\Gamma(\mathbf{r}) = \rho(\mathbf{r}) + \rho(\mathbf{r})\int d\mathbf{r}'\,\Gamma(\mathbf{r}')c^{(2)}(\mathbf{r},\mathbf{r}'), \tag{14}$$

which is nothing more than an averaged Ornstein-Zernike relation. This equation allows us to obtain $\Gamma(\mathbf{r})$ [and hence $\Delta^2(N) = \int\Gamma(\mathbf{r})\,d\mathbf{r}$] in terms of $\rho(\mathbf{r})$ and $c^{(2)}$ which is itself a functional of $\rho(\mathbf{r})$—recall that

$$c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = -\beta\,\frac{\delta^n\mathcal{F}_{\text{gc}-\text{ex}}[\rho]}{\delta\rho(\mathbf{r}_1)\cdots\delta\rho(\mathbf{r}_n)}. \tag{15}$$

We remark that, following the above procedure, the mean square fluctuation $\Delta^2(N;[\rho])$ expressed as a functional of an arbitrary density $\rho(\mathbf{r})$ is obtained from the GCE functional and using relations valid in the GCE. This is consistent with the fact that the fluctuations in the number of particles arise in the GCE. Finally, we require an appropriate expression for the functional derivative of $\Delta^2(N)$. Performing the functional derivative of the Ornstein-Zernike relation (11) with respect to $\rho(\mathbf{r})$ and exploiting the fact that $\mathcal{G}$ and $\mathcal{G}^{-1}$ are functional inverses, after some integrations we obtain

$$\frac{\delta}{\delta\rho(\mathbf{r})}\Delta^2(N;[\rho]) = \left(\frac{\Gamma(\mathbf{r})}{\rho(\mathbf{r})}\right)^2 + \iint \Gamma(\mathbf{r}_1)\Gamma(\mathbf{r}_2)c^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r})\,d\mathbf{r}_1\,d\mathbf{r}_2\,. \tag{16}$$

Note that Eq. (16) is essentially an averaged Ornstein-Zernike relation for correlation functions of third order [11].

Given a prescription for the free-energy functional of a system in the GCE, Eq. (6) provides an approximate expression for its CE counterpart, and Eq. (4) together with (14) and (16) is the Euler-Lagrange equation for the equilibrium density profile in the CE.

As an application of the theory developed in this work we consider a hard-sphere fluid confined to a hard spherical cavity of radius $R_{\rm cav}$ so that, for hard spheres of diameter σ, the confining potential is given by

$$V_{\rm ext}(r) = \begin{cases} 0, & r < R_{\rm cav} - \sigma/2\,, \\ \infty, & r > R_{\rm cav} - \sigma/2\,, \end{cases} \tag{17}$$

where r is the distance to the center of the cavity. This is an ideal example to test the present CE-DFT. If one considers a closed cavity, the system cannot exchange particles with an external reservoir and the appropriate ensemble is the canonical one. For very small cavities that can hold only a few particles, significant differences from the GCE results arise for the density. In addition, for these small cavities and high packings the situation becomes highly inhomogeneous, providing a demanding test for any DFT. This model fluid was used in Refs. [6,7] to analyze the ensemble dependence of the structure of a confined fluid using an explicit expansion of the CE density profiles in terms of GCE profiles. By contrast our present approach evaluates the CE profiles directly from the CE-DFT. The quality of the new theory is tested by comparison with the simulation and theoretical results in Refs. [6,7].

Although we perform a CE-DFT study, we need the GCE free-energy functional $\mathcal{F}_{\rm gc}$ as input. For hard spheres the exact form of $\mathcal{F}_{\rm gc}$ is not known and one must resort to one of the approximations available in the literature [1]. Among these approximate theories an excellent choice is provided by the fundamental measure theory (FMT) of Rosenfeld which has been shown to give accurate results for a large variety of inhomogeneous situations [12], including a hard-sphere fluid in a spherical cavity treated in GCE [6,7]. Furthermore, the direct correlation functions $c^{(1)}$, $c^{(2)}$, and $c^{(3)}$ required by the CE-DFT are readily calculated from functional differentiation [Eq. (15)] of the FMT functional. In this work we have used the Kierlik and Rosinberg version of the FMT [13] which is completely equivalent to the original FMT [14] and yields very simple expressions for the direct correlation functions.

In this particular example of a hard-sphere fluid in a spherical cavity, the spherical symmetry reduces the problem to dealing with quantities that depend only on the radial coordinate r. The solution of Eq. (4) for the density profile $\rho_c(r)$ requires the simultaneous calculation of $\Gamma(r)$ via the averaged Ornstein-Zernike relation (14). This is done by means of the usual iterative procedure employed in GCE-DFT calculations. Since the direct correlation functions can be expressed in terms of convolutions [13], and (14) and (16) also involve convolutions, all the calculations for each iteration can be performed by means of fast Fourier transform techniques.

In Fig. 1 we consider a cavity of radius $R_{\rm cav} = 1.85\sigma$ with $N = 6$, 8, and 10 particles. This choice of $R_{\rm cav}$ permits the development of a peak of the density profile in the center of the cavity (r near 0); in this zone important differences between ensembles may arise. We present DFT results for the density profile both in the CE and in the GCE (for consistency, in this case we also use the FMT

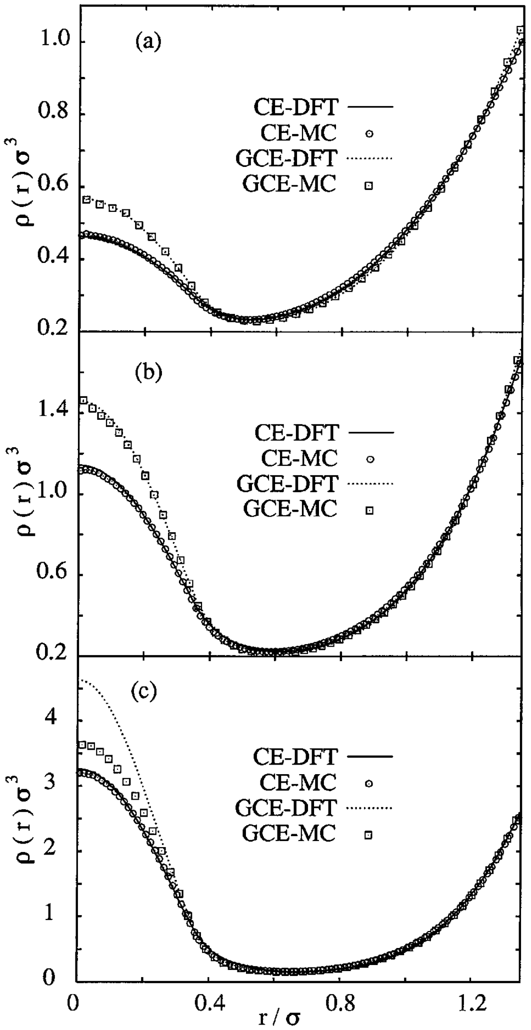

FIG. 1. Density profiles of hard spheres in a spherical cavity of radius $R_{\rm cav} = 1.85\sigma$. (a) $N = 6$, (b) $N = 8$, and (c) $N = 10$ particles. The lines represent the results of the CE-DFT (solid line) and the GCE-DFT (dotted line). The symbols are CE (circles) and GCE (squares) MC data from Refs. [6,7]. Note the different vertical scales in the three figures.

of Rosenfeld). For the purpose of comparison we also plot simulation data of Refs. [6,7]. At moderate packings [Fig. 1(a), $N = 6$], where the GCE-DFT yields very good agreement with simulation, we observe that the results of the CE-DFT are equally good, in spite of the reduced number of particles. Both GCE- and CE-DFT show the same features with an accurate description of the contact zone ($r \gtrsim 1$) and a very slight underestimation of the simulation data in the zone $0.6 \lesssim r \lesssim 0.8$. The only difference arises in the central peak where the CE-DFT slightly underestimates the simulation data. For $N = 8$ [Fig. 1(b)] the results of GCE- and CE-DFT are still very close to simulation data. However, for $N = 10$ [Fig. 1(c)], the results of the GCE-DFT overestimate the central peak to a large extent. This is due to the failure of the original FMT of Rosenfeld to deal with the highly inhomogeneous (quasi-zero-dimensional) situation that arises in the center of the cavity. Recent modifications of Rosenfeld's FMT [15] are more successful for these 0D situations [7] but are not used here since the calculations for the CE-DFT become much more complicated. If we now turn our attention to the CE-DFT result for this case of $N = 10$, surprisingly, it remains accurate even in the central peak. The explanation for this striking fact is that the central peak is less pronounced in the CE than in the GCE and, for $N = 10$ the FMT is still able to handle the inhomogeneity in the CE but not in the GCE. Note that the profile is higher in the peak in the GCE due to contributions from other values of N. In more extreme inhomogeneous situations the CE-FMT also fails, for instance, for $N = 11$ (not shown) it grossly underestimates the central peak in the simulation data.

It is remarkable that, in general, where differences arise between DFT and simulation, these show the same features in both ensembles. This indicates that the present approximation scheme for a DFT of the canonical ensemble has essentially the same strengths and weaknesses as its GCE counterpart, i.e., the accuracy of the CE-DFT depends on the accuracy of the GCE free-energy functional. Exceptions will occur for cases with a very low number of particles ($N = 1$ or 2) where one should take into account that the CE free-energy functional has been obtained from an approximation valid to order $0(\log N)$ and some deviations are expected. In particular, one obtains good results for low and moderate packings but these results become worse (although still reasonable) for higher packings.

In summary, we have shown that given a GCE free-energy functional one can obtain an approximation for the corresponding CE functional so that it is possible to perform DFT calculations in the canonical ensemble of the structure of fluids with a few particles. As an application of the CE-DFT we have considered a hard-sphere fluid confined in a closed spherical cavity. We have found that, except for a few extreme situations, this CE-DFT exhibits the same good quality of performance as the corresponding GCE theory.

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