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Equivalence of two approaches for the inhomogeneous density in the canonical ensemble

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In this Brief Report we show that the inhomogeneous density obtained from a density-functional theory of classical fluids in the canonical ensemble (CE), recently presented by White *et al.* [Phys. Rev. Lett. **84**, 1220 (2000)], is equivalent to first order to the result of the series expansion of the CE inhomogeneous density introduced by González *et al.* [Phys. Rev. Lett. **79**, 2466 (1997)].

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A statistical mechanics ensemble is a collection of identical systems under the same external conditions. Although the choice of a particular ensemble for studying a concrete system should be guided by the conditions in which the system is found, one can choose—due to mathematical or computational convenience—any ensemble for analyzing the equilibrium properties of the system. This way of proceeding, based on the equivalence of the ensembles in the thermodynamic limit, is only justified for systems with a very large number of particles. For small systems, however, the ensembles are no longer equivalent and the external conditions must determine the choice of ensemble.

In this context, the use of density-functional theory (DFT) for the study of classical inhomogeneous fluids has usually been limited to the grand canonical ensemble (GCE), where the temperature T and the chemical potential μ are fixed by an external reservoir. A large variety of inhomogeneous situations has been successfully studied by means of DFT in the GCE [1–3]. These situations include fluids confined in narrow pores or capillaries [4], or even spherical cavities [5–7], which are implicitly assumed to be open, i.e., allowing exchange of particles with a reservoir. This assumption is crucial for situations with a small number of particles where, depending on the choice of ensemble, important differences may arise in the equilibrium microscopic structure of the system [7,8]. If one wishes to investigate the properties of a small *closed* system at temperature T, the study must be performed in such a way that one obtains results in the canonical ensemble (CE) because the number of particles N is fixed. In DFT this goal can be achieved by means of two different approaches. On the one hand, the DFT could be formulated in the canonical ensemble [9], with a minimum free-energy principle with fixed T and N, and an appropriate CE functional. Very recently, this approach has been explicitly realized [10] by considering an approximate expression for the CE functional. On the other hand, one can perform a conventional DFT study in the GCE and then relate the obtained properties to those of the CE. This approach was followed in Refs. [7,8] where the CE density profile of a hard-sphere fluid in a small spherical cavity was calculated by means of a series expansion in terms of the corresponding GCE profile. The aim of the present paper is to show that these two approaches yield equivalent results to order $1/N$. For clarity we start with a brief summary of the main results of the two approaches.

The first approach is based on the following series expansion of the CE density profile $\rho_{\mathrm{C}}(\mathbf{r})$ in terms of its corresponding GCE density profile $\rho_{\mathrm{GC}}(\mathbf{r})$:

$$\rho_{\mathrm{C}}(\mathbf{r})=\rho_{\mathrm{GC}}(\mathbf{r})-\frac{1}{2}\,\Delta^2(N)\frac{\partial^2}{\partial\langle N\rangle^2}\,\rho_{\mathrm{GC}}(\mathbf{r})+O\left(\frac{1}{\langle N\rangle^2}\right), \tag{1}$$

where the grand canonical profile is obtained for a chemical potential μ that leads to an average number of particles $\langle N\rangle$ equal to N—the fixed integer number of particles in the CE, and $\Delta^2(N)\equiv\langle N^2\rangle-\langle N\rangle^2$ is the mean square fluctuation of the number of particles in the GCE. Higher-order terms in the above expansion also depend on fluctuations and on variations of the GCE profile with repect to $\langle N\rangle$ [7,8]. In DFT, the grand canonical profile ρ_{GC} is the solution of the usual GCE Euler-Lagrange equation with chemical potential μ and external potential $V_{\mathrm{ext}}(\mathbf{r})$,

$$\left.\frac{\delta\mathcal{F}_{\mathrm{GC}}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\mathrm{GC}}}+V_{\mathrm{ext}}(\mathbf{r})=\mu, \tag{2}$$

where $\mathcal{F}_{\mathrm{GC}}[\rho]$ is the GCE free-energy functional. For a chemical potential leading to a given $\langle N\rangle$, Eq. (2) can be rewritten as [7]

$$\rho_{\mathrm{GC}}(\mathbf{r})=\langle N\rangle\exp[-\beta V_{\mathrm{ext}}(\mathbf{r})+c^{(1)}(\mathbf{r};[\rho_{\mathrm{GC}}])]\Big/\int d\mathbf{r}\times\exp[-\beta V_{\mathrm{ext}}(\mathbf{r})+c^{(1)}(\mathbf{r};[\rho_{\mathrm{GC}}])], \tag{3}$$

where $\beta=1/k_BT$ is the inverse temperature and $c^{(1)}$ is the one-body direct correlation function

$$c^{(1)}(\mathbf{r};[\rho])=-\beta\,\frac{\delta(\mathcal{F}_{\mathrm{GC}}[\rho]-\mathcal{F}_{\mathrm{GCID}}[\rho])}{\delta\rho(\mathbf{r})}, \tag{4}$$

$\mathcal{F}_{\mathrm{GCID}}$ being the usual ideal-gas free energy. This correlation function is the first member of the direct correlation hierarchy

$$c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;[\rho])=-\beta\,\frac{\delta^n(\mathcal{F}_{\mathrm{GC}}[\rho]-\mathcal{F}_{\mathrm{GCID}}[\rho])}{\delta\rho(\mathbf{r}_1)\cdots\delta\rho(\mathbf{r}_n)}. \tag{5}$$

From Eq. (3), in DFT it is possible to obtain density profiles normalized for a given $\langle N\rangle$. This allows for obtaining approximate CE profiles using Eq. (1) where the derivatives with respect to $\langle N\rangle$ are calculated numerically. [We note that, using the thermodynamic identity $\Delta^2(N)=\partial\langle N\rangle/\partial(\beta\mu)$, the mean square fluctuation can also be expressed as a derivative with respect to $\langle N\rangle$.] This procedure was used in [7,8] to obtain the CE density profile of a hard-sphere fluid confined in a hard spherical cavity.

The second approach consists of an approximate expression for the free-energy functional in the CE. On the basis of the standard saddle-point relation between the CE Helmholtz free energy and the GCE grand potential [11], the following approximation for the CE free-energy functional $\mathcal{F}_{\mathrm{C}}$ was proposed in Ref. [10]:

$$\beta\mathcal{F}_{\mathrm{C}}[\rho]\approx\beta\mathcal{F}_{\mathrm{GC}}[\rho]+\frac{1}{2}\ln 2\pi\Delta^2(N;[\rho]),\tag{6}$$

where the functional dependence of the GCE mean square fluctuation $\Delta^2(N)$ is made explicit. Since we are now working in the canonical ensemble, the equilibrium density profile $\rho_{\mathrm{C}}(\mathbf{r})$ is obtained by minimizing the functional $\mathcal{F}_{\mathrm{C}}[\rho]+\int d\mathbf{r}\rho(\mathbf{r})V_{\mathrm{ext}}(\mathbf{r})$ subject to the constraint

$$\int d\mathbf{r}\rho_{\mathrm{C}}(\mathbf{r})=N.\tag{7}$$

Using the Lagrange multiplier technique one obtains [10]

$$\left.\frac{\delta\mathcal{F}_{\mathrm{C}}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\mathrm{C}}}+V_{\mathrm{ext}}(\mathbf{r})=\lambda,\tag{8}$$

where the Lagrange multiplier λ must be calculated from the constraint (7). This equation can be re-expressed as

$$\begin{aligned}\rho_{\mathrm{c}}(\mathbf{r})=N\exp[-\beta V_{\mathrm{ext}}(\mathbf{r})+c^{(1)}(\mathbf{r};[\rho_{\mathrm{C}}])\\+\xi(\mathbf{r};[\rho_{\mathrm{C}}])]\Big/\int d\mathbf{r}\exp[-\beta V_{\mathrm{ext}}(\mathbf{r})\\+c^{(1)}(\mathbf{r};[\rho_{\mathrm{C}}])+\xi(\mathbf{r};[\rho_{\mathrm{C}}])],\end{aligned}\tag{9}$$

where

$$\xi(\mathbf{r};[\rho])\equiv-\beta\,\frac{\delta(\mathcal{F}_{\mathrm{C}}[\rho]-\mathcal{F}_{\mathrm{GC}}[\rho])}{\delta\rho(\mathbf{r})},\tag{10}$$

which, for the saddle-point (SP) approximation (6), becomes

$$\xi(\mathbf{r};[\rho])\approx\xi_{\mathrm{SP}}(\mathbf{r};[\rho])=-\frac{1}{2}\,\frac{1}{\Delta^2(N;[\rho])}\,\frac{\delta\Delta^2(N;[\rho])}{\delta\rho(\mathbf{r})}.\tag{11}$$

In order to calculate $\xi_{\mathrm{SP}}(\mathbf{r};[\rho])$ it is important to express the mean square fluctuation $\Delta^2(N;[\rho])$ as a functional of the density. This can be done conveniently in the GCE by means of the density-density correlation function [2,12]

$$\mathcal{G}(\mathbf{r}_1,\mathbf{r}_2)=\beta^{-1}\frac{\delta\rho(\mathbf{r}_1)}{\delta(\mu-V_{\mathrm{ext}}(\mathbf{r}_2))},\tag{12}$$

since this function normalizes to the mean square fluctuation, i.e.,

$$\Delta^2(N)=\int\int d\mathbf{r}_1 d\mathbf{r}_2\mathcal{G}(\mathbf{r}_1,\mathbf{r}_2).\tag{13}$$

In addition, taking into account that $\mathcal{G}$ is the functional inverse of the second derivative of the GCE free-energy

$$\begin{aligned}\mathcal{G}^{-1}(\mathbf{r}_1,\mathbf{r}_2)&=\beta\frac{\delta(\mu-V_{\mathrm{ext}}(\mathbf{r}_1))}{\delta\rho(\mathbf{r}_2)}\\&=\beta\frac{\delta^2\mathcal{F}_{\mathrm{GC}}[\rho]}{\delta\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}\\&=\frac{1}{\rho(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2)-c^{(2)}(\mathbf{r}_1,\mathbf{r}_2),\end{aligned}\tag{14}$$

and satisfies the Ornstein-Zernike relation [2,12]

$$\int d\mathbf{r}_2\mathcal{G}^{-1}(\mathbf{r}_1,\mathbf{r}_2)\mathcal{G}(\mathbf{r}_2,\mathbf{r}_3)=\delta(\mathbf{r}_1-\mathbf{r}_3),\tag{15}$$

one obtains [10]

$$\Delta^2(N;[\rho])=\int d\mathbf{r}\Gamma(\mathbf{r}),\tag{16}$$

$$\begin{aligned}\frac{\delta}{\delta\rho(\mathbf{r})}\Delta^2(N;[\rho])\\&=\int\int d\mathbf{r}_1 d\mathbf{r}_2\frac{\delta\mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)}\Gamma(\mathbf{r}_1)\Gamma(\mathbf{r}_2)\qquad(17)\\&=\left(\frac{\Gamma(\mathbf{r})}{\rho(\mathbf{r})}\right)^2+\int\int d\mathbf{r}_1 d\mathbf{r}_2 c^{(3)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\Gamma(\mathbf{r}_1)\Gamma(\mathbf{r}_2),\qquad(18)\end{aligned}$$

where

$$\Gamma(\mathbf{r})\equiv\int d\mathbf{r}_1\mathcal{G}(\mathbf{r},\mathbf{r}_1),\tag{19}$$

is obtained from the following averaged Ornstein-Zernike relation

$$\Gamma(\mathbf{r})=\rho(\mathbf{r})+\rho(\mathbf{r})\int d\mathbf{r}_1\Gamma(\mathbf{r}_1)c^{(2)}(\mathbf{r},\mathbf{r}_1).\tag{20}$$

In deriving Eq. (17) we have considered the functional derivative with respect to the density of the Ornstein-Zernike relation (15) and exploited the fact that $\mathcal{G}$ and $\mathcal{G}^{-1}$ are functional inverses. We note that the key difference between the GCE result (3) and the CE density (9) is the term $\xi(\mathbf{r};[\rho_{\mathrm{C}}])$. We also note that, in this approach, using Eq. (9) one directly obtains the CE profile while, in the previous approach, the result (3) of GCE-DFT had to be inserted into Eq. (1) in order to obtain an approximation for the CE equilibrium density. In what follows we shall show that both approaches agree to first order, though they yield different results due to higher-order contributions in the saddle-point approach. We first derive some useful relations and then we show the equivalence to first order of the approaches.

Our starting point is the well-known result of GCE density-functional theory that, for given intermolecular potential, chemical potential μ, and temperature T, only one external potential can determine a specified equilibrium density profile [1,2]. Thus there must exist an external potential $\overline{V}_{\rm ext}(\mathbf{r})$ so that its corresponding GCE equilibrium density $\rho_{\rm GC}(\mathbf{r};[\overline{V}_{\rm ext}])$ (here the functional dependence of $\rho_{\rm GC}$ is made explicit) is equal to the CE result $\rho_{\rm C}$. Performing a functional expansion of $\rho_{\rm GC}(\mathbf{r};[\overline{V}_{\rm ext}])$ about $V_{\rm ext}$ and using definition (12) we obtain

$$\begin{aligned}\beta^{-1}\Delta\rho(\mathbf{r}) = {} & \int d\mathbf{r}_1 \mathcal{G}(\mathbf{r},\mathbf{r}_1)\Delta V_{\rm ext}(\mathbf{r}_1) \\ & + \frac{1}{2!}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta\mathcal{G}(\mathbf{r},\mathbf{r}_1)}{\delta(\mu - V_{\rm ext}(\mathbf{r}_2))} \\ & \times \Delta V_{\rm ext}(\mathbf{r}_1)\Delta V_{\rm ext}(\mathbf{r}_2) + \dots, \end{aligned} \tag{21}$$

where

$$\Delta\rho(\mathbf{r}) = \rho_{\rm GC}(\mathbf{r};[\overline{V}_{\rm ext}]) - \rho_{\rm GC}(\mathbf{r};[V_{\rm ext}]) = \rho_{\rm C}(\mathbf{r}) - \rho_{\rm GC}(\mathbf{r}) \tag{22}$$

and

$$\Delta V_{\rm ext}(\mathbf{r}) = V_{\rm ext}(\mathbf{r}) - \overline{V}_{\rm ext}(\mathbf{r}). \tag{23}$$

Therefore, Eq. (21) provides a link between $\Delta\rho$ and $\Delta V_{\rm ext}$ via a functional expansion where the coefficients belong to the standard distribution function hierarchy.

At this point we would like to emphasize the role played by $\overline{V}_{\rm ext}$ in the present work. $\overline{V}_{\rm ext}$ is the external potential that, at chemical potential μ, yields the canonical profile $\rho_{\rm C}$ *in a GCE approach* and this implies that $\rho_{\rm C}$ is the solution of the following GCE Euler-Lagrange equation

$$\left.\frac{\delta\mathcal{F}_{\rm GC}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\rm C}} + \overline{V}_{\rm ext}(\mathbf{r}) = \mu. \tag{24}$$

This fact makes meaningful the use of functionals of $\rho_{\rm C}$ like $\mathcal{G}^{-1}(\mathbf{r}_1,\mathbf{r}_2;[\rho_{\rm C}]) = \beta\delta(\mu - \overline{V}_{\rm ext}(\mathbf{r}_1))/\delta\rho_{\rm C}(\mathbf{r}_2)$, its inverse, $\mathcal{G}(\mathbf{r}_1,\mathbf{r}_2;[\rho_{\rm C}]) = \mathcal{G}(\mathbf{r}_1,\mathbf{r}_2;[\overline{V}_{\rm ext}[\rho_{\rm C}]]) = \beta^{-1}\delta\rho_{\rm c}(\mathbf{r}_1)/\delta(\mu - \overline{V}_{\rm ext}(\mathbf{r}_2))$, or the mean square fluctuation $\Delta^2(N;[\rho_{\rm C}])$. On the other hand, since $\rho_{\rm C}(\mathbf{r})$ is the equilibrium density profile in the canonical ensemble, it is the solution of the CE Euler-Lagrange equation (8) where, in comparison with this GCE equation, the free energy is $\mathcal{F}_{\rm c}$ —the CE functional, the external potential is $V_{\rm ext}$, and the Lagrange multiplier λ is used in the place of the chemical potential μ. From Eqs. (8) and (24) and definition (10) we obtain

$$\Delta V_{\rm ext}(\mathbf{r}) = \lambda - \mu + \beta^{-1}\xi(\mathbf{r};[\rho_{\rm C}]). \tag{25}$$

In the uniform limit, where $\rho_{\rm GC}(\mathbf{r}) \to \rho_0 \equiv \langle N\rangle/V = N/V$ and also $\rho_{\rm C}(\mathbf{r}) \to \rho_0$, from Eqs. (2) and (24) one has $\Delta V_{\rm ext}(\mathbf{r}) = 0$ and thus

$$\mu - \lambda = \beta^{-1}\xi(\rho_0), \tag{26}$$

and Eq. (25) can be rewritten as

$$\beta\Delta V_{\rm ext}(\mathbf{r}) = \xi(\mathbf{r};[\rho_{\rm C}]) - \xi(\rho_0). \tag{27}$$

Using the saddle-point approximation $\xi_{\rm SP}$ [Eq. (11)], this expression could be employed in Eq. (21) to obtain an approximation for the difference $\Delta\rho$. Conversely, since Eq. (1) gives an approximation for $\Delta\rho$, an expansion inverse to Eq. (21) would provide a way to obtain ξ. This inverse expression can be easily derived by substituting the functional expansion of $\delta\mathcal{F}_{\rm GC}[\rho]/\delta\rho(\mathbf{r})$ about $\rho_{\rm GC}$ in Eq. (24). Using definition (14), we obtain

$$\begin{aligned}\beta\Delta V_{\rm ext}(\mathbf{r}) = {} & \int d\mathbf{r}_1 \mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)\Delta\rho(\mathbf{r}_1) \\ & + \frac{1}{2!}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta\mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)}{\delta\rho_{\rm GC}(\mathbf{r}_2)}\Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2) \\ & + \dots, \end{aligned} \tag{28}$$

where we have exploited the fact that $\rho_{\rm GC}(\mathbf{r})$ is the solution of the usual GCE Euler-Lagrange equation (2).

Expansions (21) and (28) are asymptotically exact relations linking $\Delta\rho$ and $\Delta V_{\rm ext}$. However, these expansions need to be truncated in order to become suitable for practical applications. In particular, to first order, Eq. (21) becomes

$$\beta^{-1}\Delta\rho(\mathbf{r}) \approx \int d\mathbf{r}_1 \mathcal{G}(\mathbf{r},\mathbf{r}_1)\Delta V_{\rm ext}(\mathbf{r}_1), \tag{29}$$

and Eq. (28) reduces to

$$\beta\Delta V_{\rm ext}(\mathbf{r}) \approx \int d\mathbf{r}_1 \mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)\Delta\rho(\mathbf{r}_1). \tag{30}$$

Approximations (29) and (30) are, by virtue of Eq. (15), equivalent equations; this fact shows the consistency of the truncation of the expansions. Either Eq. (29) or Eq. (30) will provide a simple (first order) relation between the differences $\Delta\rho$ and $\Delta V_{\rm ext}$. Using these equations, we shall show that the approximation (1) for $\Delta\rho$ is equivalent to first order to the saddle-point approximation $\xi_{\rm SP}$ [Eq. (11)]. By considering the derivative of the GCE Euler-Lagrange equation (2) with respect to $\langle N\rangle$ at fixed $V_{\rm ext}$, one obtains the exact relation

$$\int d\mathbf{r}_1 \mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)\frac{\partial\rho_{\rm GC}(\mathbf{r}_1)}{\partial\langle N\rangle} = \frac{1}{\Delta^2(N)}, \tag{31}$$

where the chain rule for functional differentiation together with definition (14) and the identity $\partial\langle N\rangle/\partial(\beta\mu) = \Delta^2(N)$ have been used. This equation can be rewritten, via Eqs. (15) and (19), as

$$\frac{\partial\rho_{\rm GC}(\mathbf{r})}{\partial\langle N\rangle} = \frac{\Gamma(\mathbf{r})}{\Delta^2(N)}. \tag{32}$$

Differentiating this equation with respect to $\langle N\rangle$ and using Eq. (1), we obtain

$$\Delta\rho(\mathbf{r}) \approx -\frac{1}{2}\left(\frac{\partial\Gamma(\mathbf{r})}{\partial\langle N\rangle} - \frac{\Gamma(\mathbf{r})}{\Delta^2(N)}\frac{\partial\Delta^2(N)}{\partial\langle N\rangle}\right), \tag{33}$$

which inserted into Eq. (30) yields the following approximation for ΔV_{ext}:

$$\beta\Delta V_{\mathrm{ext}}(\mathbf{r})\approx\frac{1}{2\Delta^2(N)}\frac{\partial\Delta^2(N)}{\partial\langle N\rangle}-\frac{1}{2}\int d\mathbf{r}_1\,\mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)\frac{\partial\Gamma(\mathbf{r}_1)}{\partial\langle N\rangle},\tag{34}$$

where we have used the identity

$$\int d\mathbf{r}_1\,\mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)\Gamma(\mathbf{r}_1)=1,\tag{35}$$

which follows from Eqs. (31) and (32) [or, equivalently, from Eqs. (15) and (19)]. Considering the derivative of Eq. (35) with respect to $\langle N\rangle$, and using the chain rule and Eq. (32), Eq. (34) can be re-expressed as

$$\beta\Delta V_{\mathrm{ext}}(\mathbf{r})\approx\frac{1}{2\Delta^2(N)}\left(\frac{\partial\Delta^2(N)}{\partial\langle N\rangle}+\int d\mathbf{r}_1 d\mathbf{r}_2\frac{\delta\mathcal{G}^{-1}(\mathbf{r},\mathbf{r}_1)}{\delta\rho_{\mathrm{GC}}(\mathbf{r}_2)}\Gamma(\mathbf{r}_1)\Gamma(\mathbf{r}_2)\right)\tag{36}$$

$$=\frac{1}{2\Delta^2(N)}\left(\frac{\partial\Delta^2(N)}{\partial\langle N\rangle}-\frac{\delta\Delta^2(N)}{\delta\rho_{\mathrm{GC}}(\mathbf{r})}\right),\tag{37}$$

where in the last equality we have used Eq. (17). Comparing Eq. (37) with Eq. (27) we obtain

$$\xi(\mathbf{r};[\rho_{\mathrm{C}}])\approx-\frac{1}{2\Delta^2(N)}\frac{\delta\Delta^2(N)}{\delta\rho_{\mathrm{GC}}(\mathbf{r})}=\xi_{\mathrm{SP}}(\mathbf{r};[\rho_{\mathrm{GC}}])\tag{38}$$

and

$$\xi(\rho_0)\approx-\frac{1}{2\Delta^2(N)}\frac{\partial\Delta^2(N)}{\partial\langle N\rangle}=\xi_{\mathrm{SP}}(\rho_0),\tag{39}$$

where ξ_{SP} was defined in Eq. (11). Finally, we note that in Eq. (38) it is shown that $\xi[\rho_{\mathrm{C}}]$ is approximately equal to $\xi_{\mathrm{SP}}[\rho_{\mathrm{GC}}]$, i.e., ξ_{SP} evaluated at ρ_{GC} instead of ρ_{C}. This approximate equality also holds for $\xi_{\mathrm{SP}}[\rho_{\mathrm{C}}]$ as we show in what follows. Expanding ξ_{SP} about ρ_{GC} we obtain

$$\xi_{\mathrm{SP}}(\mathbf{r};[\rho_{\mathrm{C}}])=\xi_{\mathrm{SP}}(\mathbf{r};[\rho_{\mathrm{GC}}])+\int d\mathbf{r}_1\frac{\delta\xi_{\mathrm{SP}}(\mathbf{r};[\rho_{\mathrm{GC}}])}{\delta\rho_{\mathrm{GC}}(\mathbf{r}_1)}\Delta\rho+\cdots\tag{40}$$

and, taking into account that ξ is already a $O(\Delta\rho)$ quantity,

$$\xi_{\mathrm{SP}}(\mathbf{r};[\rho_{\mathrm{C}}])\approx\xi_{\mathrm{SP}}(\mathbf{r};[\rho_{\mathrm{GC}}])+O(\Delta\rho)^2.\tag{41}$$

This proves the equivalence to first order of the two approaches for obtaining an approximate density profile in the canonical ensemble.

In summary, we have shown that two different approaches for obtaining the density profile of a fluid in the canonical ensemble are equivalent to first order. The demonstration was based on considering an external potential $\overline{V}_{\mathrm{ext}}$ for which the equilibrium density in the grand canonical ensemble is precisely the canonical ensemble result. Using this external potential we have been able to work in the framework of the grand canonical ensemble where approximations similar to those carried out in this work are commonly encountered.

The proof of the equivalence gives additional support to the saddle-point approximation for the CE free-energy functional introduced in [10]. This approximation allows for a CE-DFT treatment of fluids confined in a closed cavity with excellent agreement with simulation data. However, the SP free-energy functional was proposed on the basis of the well-known SP relation between the equilibrium CE free-energy and the grand potential of a homogeneous fluid, assuming that this relation would also be a good approximation for inhomogeneous fluids. This assumption is thus reinforced by the results of the present paper, which are valid for any inhomogeneous situation. As a final remark, we would like to stress the fact that our demonstration has focused on the approximate CE density rather than on the free-energy functionals, and the equivalence between the two approaches must be understood in this sense.

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