Is there Ornstein-Zernike equation in the canonical ensemble?

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A general density-functional formalism using an extended variable-space is presented for classical fluids in the canonical ensemble (CE). An exact equation is derived that plays the role of the Ornstein-Zernike (OZ) equation in the grand canonical ensemble (GCE). When applied to the ideal gas we obtain the exact result for the total correlation function \( h_N \). For a homogeneous fluid with \( N \) particles the new equation only differs from OZ by \( 1/N \) and it allows to obtain an approximate expression for \( h_N \) in terms of its GCE counterpart that agrees with the expansion of \( h_N \) in powers of \( 1/N \).

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The Ornstein-Zernike (OZ) equation is an essential ingredient of any theory of the equilibrium microscopic structure of classical fluids since it provides an exact relation between correlation functions at the two-particle level. In the world of the integral equation theory \([1, 2]\), most integral equations are based on this relation closed with an additional approximate relation between the correlation functions. Closures like the Percus-Yevick approximation, the hypernetted chain approximation, or the mean spherical approximation, together with the OZ relation have led to well-known approximate relations between correlation functions. Closures like the Percus-Yevick approximation, the hypernetted chain approximation, or the mean spherical approximation, together with the OZ relation have led to well-known approximate relations between correlation functions. Closures like the Percus-Yevick approximation, the hypernetted chain approximation, or the mean spherical approximation, together with the OZ relation have led to well-known approximate relations between correlation functions. Closures like the Percus-Yevick approximation, the hypernetted chain approximation, or the mean spherical approximation, together with the OZ relation have led to well-known approximate relations between correlation functions. Closures like the Percus-Yevick approximation, the hypernetted chain approximation, or the mean spherical approximation, together with the OZ relation have led to well-known approximate relations between correlation functions. Closures like the Percus-Yevick approximation, the hypernetted chain approximation, or the mean spherical approximation, together with the OZ relation have led to well-known approximate relations between correlation functions. Closures like the Percus-Yevick approximation, the hypernetted chain approximation, or the mean spherical approximation, together with the OZ relation have led to well-known approximate relations between correlation functions.

When using the OZ equation it is important to notice that it has been formulated for the grand canonical ensemble (GCE) and thus care must be taken when considering it in other statistical mechanics ensembles. Of particular interest is the canonical ensemble (CE), not only from a fundamental point of view but also because of its relevance in the analysis of systems with a fixed, finite number of particles \( N \). The aim of this Letter is to study the possibility of establishing an OZ relation in the CE \([3]\). We shall see how the fixed-\( N \) constraint precludes the direct application of the GCE-OZ relation, this problem will be solved in a DFT context by using an extended variable-space in which, together with the familiar inhomogeneous density, a Lagrange multiplier is considered as a variable.

The OZ equation for a nonuniform system with fixed chemical potential \( \mu \) and temperature \( T \), i.e., in the GCE, in the presence of an external potential \( V_{\text{ext}}(r) \), is usually expressed as the following relation between the total correlation function \( h \) and the direct correlation function \( c^{(2)} \)

\[
h(r_1, r_2) = c^{(2)}(r_1, r_2) + \int \rho(r_3) c^{(2)}(r_1, r_3) h(r_3, r_2) \, dr_3. \quad (1)
\]

where \( \rho(r) \) is the inhomogeneous density, and, in terms of functional derivatives, \( h \) and \( c^{(2)} \) are defined (fixed \( T, \mu \)) by

\[
\beta^{-1} \frac{\delta \rho(r_1)}{\delta V_{\text{ext}}(r_2)} = -\rho(r_1) \rho(r_2) h(r_1, r_2) - \rho(r_1) \delta(r_1 - r_2) \quad (2)
\]

and

\[
\beta \frac{\delta V_{\text{ext}}(r_1)}{\delta \rho(r_2)} = c^{(2)}(r_1, r_2) - \frac{\delta(r_1 - r_2)}{\rho(r_1)}, \quad (3)
\]

with \( \beta = 1/k_B T \). From \([1, 2]\) one easily obtains

\[
\int \frac{\delta \rho(r_1)}{\delta V_{\text{ext}}(r_3)} \frac{\delta V_{\text{ext}}(r_3)}{\delta \rho(r_2)} \, dr_3 = \delta(r_1 - r_2), \quad (4)
\]

which expresses that, via the OZ equation, \( h \) and \( c^{(2)} \) are (essentially) functional inverses. We note that this functional-inversion statement is only possible if there is a one-to-one relation between \( \rho(r) \) and \( V_{\text{ext}}(r) \) (fixed \( T, \mu \)), so that the OZ equation can be viewed as a consequence of this relation. This viewpoint is usual in DFT of classical fluids in the
grand canonical ensemble (GCE) where the one-to-one relation between $\rho(r)$ and $V_{\text{ext}}(r)$ is a key theorem (see, e.g., [3]) and the OZ equation follows as a corollary [4].

We now focus our attention on the canonical ensemble (CE) where the number of particles $N$ is fixed. This means that the CE inhomogeneous density $\rho_N$ is normalized to $N$, i.e.,

$$\int \rho_N(r) dr = N. \tag{5}$$

Furthermore, from the usual definition of the two particle density $\rho_N^{(2)}$ (see, e.g., [1]) it is direct to obtain

$$\int \rho_N^{(2)}(r_1, r_2) dr_2 = (N - 1) \rho_N(r_1),$$

and thus, taking into account that $\rho_N^{(2)}(r_1, r_2) = \rho_N(r_1)\rho_N(r_2) \left(h_N(r_1, r_2) + 1\right)$, the following constraint for $h_N$ arises in the CE:

$$\int \rho_N(r_1) h_N(r_1, r_2) dr_1 = -1, \tag{6}$$

which, as pointed out by Ashcroft [1], in the context of electronic systems leads to the notion of exchange-correlation hole.

We remark that Eq. (6) is a result of considering a system in the CE where the number of particles cannot fluctuate. An important consequence of this equation is that the OZ equation (1) is no longer valid in the CE, since it is inconsistent with (6). Furthermore, since the OZ equation is associated to the one-to-one relation between $\rho(r)$ and $V_{\text{ext}}(r)$ it would seem that there is not a CE counterpart of this one-to-one relation, which would be of serious concern in DFT of the CE. The goal of this Letter is to clarify this point and to introduce a CE-OZ equation similar to (1).

It is clear that, fixed $N$ and $T$, the CE density $\rho_N$ is determined by the external potential $V_{\text{ext}}$, but this potential is not (strictly) unique: any potential that differs from $V_{\text{ext}}$ by an additive constant leads to the same $\rho_N$ and thus the inhomogeneous density is not uniquely determined by the external potential. This does not contradict the first Hohenberg-Kohn theorem for DFT [7] because it allows for this additive constant. However, this (strict) nonuniqueness means that the (Legendre) transform from the functional variable $V_{\text{ext}}$ to the functional variable $\rho_N$ is not invertible and thus $\delta \rho_N(r_1)/\delta V_{\text{ext}}(r_2)$ is a singular matrix, which in turn implies that Eq. (6) cannot hold for the pair $V_{\text{ext}}$, $\rho_N$. We want to stress that this is due to the fixed-$N$ constraint which implies that $0 = \delta N/\delta V_{\text{ext}}(r_2) = \int \delta \rho_N(r_1)/\delta V_{\text{ext}}(r_2) dr_1$, which shows that the matrix is singular [8]. Our proposal for solving this difficulty is to ‘bypass’ the constraint by means of an extended variable space where instead of $V_{\text{ext}}$ alone we consider the set $\{V_{\text{ext}}, N\}$ and, instead of $\rho_N$, the set $\{\rho_N, \lambda_N\}$ where $\lambda_N$ will be defined later and identified with the Lagrange multiplier related to the fixed-$N$ constraint. The role played by the different variables is clarified by rebuilding the main DFT results in this extended space. Our derivation is based on Legendre transform approach of Ref. [4].

The CE Helmholtz free energy $F$ is a functional of the external potential $V_{\text{ext}}$ and a function of the number of particles $N$ and the temperature $T$, i.e., $F = F(T, N, [V_{\text{ext}}])$. The density $\rho_N$ and the ‘chemical potential’ $\lambda_N$ (different from $\mu$!) are functions of $T$ and $N$ and functionals of $V_{\text{ext}}$, and are obtained from the following derivatives:

$$\rho_N(r, [V_{\text{ext}}]) = \left(\frac{\delta F}{\delta V_{\text{ext}}(r)}\right)_N, \tag{7}$$

$$\lambda_N[V_{\text{ext}}] = \left(\frac{\delta F}{\delta N}\right)_{V_{\text{ext}}} \tag{8}$$

where the explicit dependence on $T$ has been been omitted. We next consider the Legendre transform of $F$ to the new variables $\rho_N$ and $\lambda_N$,

$$\hat{F}(\lambda_N, [\rho_N]) = F(\lambda_N, [\rho_N]) - \int \rho_N(r) V_{\text{ext}}(r, \lambda_N, [\rho_N]) dr - \lambda_N \int \rho_N(r) dr, \tag{9}$$

where we have used $N = \int \rho_N(r) dr$ [Eq. (5)] and we define $F(\lambda_N, [\rho_N]) = \hat{F}(\int \rho_N(r) dr, [V_{\text{ext}}(\lambda_N, [\rho_N])])$. In order to introduce a variational principle we ‘revert’ this transform by obtaining a functional that depends on both the new variables $\{\rho_N, \lambda_N\}$ and the old ones $\{V_{\text{ext}}, N\}$:

$$F_{V_{\text{ext}}, N}(\lambda_N, [\rho_N]) = \hat{F}(\lambda_N, [\rho_N]) + \int \rho_N(r) V_{\text{ext}}(r) dr + \lambda_N N. \tag{10}$$
The minimization of this functional w.r.t. \( \{ \rho_N, \lambda_N \} \) leads to

\[
\left( \frac{\delta \tilde{F}(\lambda_N, [\rho_N])}{\delta \rho_N(\mathbf{r})} \right)_{\lambda_N} + V_{\text{ext}}(\mathbf{r}) = 0
\]  

(11)

and

\[
\left( \frac{\partial \tilde{F}(\lambda_N, [\rho_N])}{\partial \lambda_N} \right)_{\rho_N} + N = 0 .
\]

(12)

Substituting (9) into (12) and taking into account Eq. (5) one has that the functional

\[
\tilde{F} \equiv \tilde{F} + \lambda_N \int \rho_N(\mathbf{r}) d\mathbf{r} = F(\lambda_N, [\rho_N]) - \int \rho_N(\mathbf{r}) V_{\text{ext}}(\mathbf{r}, \lambda_N, [\rho_N]) d\mathbf{r}
\]  

(13)

does not depend on \( \lambda_N \), that is \( \tilde{F} = \tilde{F}[\rho_N] \) and thus, from (11) we obtain

\[
\frac{\delta \tilde{F}[\rho_N]}{\delta \rho(\mathbf{r})} \bigg|_{\rho = \rho_{\text{eq}}} + V_{\text{ext}}(\mathbf{r}) = \lambda_N .
\]  

(14)

Comparing this equation with the GCE Euler-Lagrange equation we see that \( \lambda_N \) plays the role of the chemical potential \( \mu \) (see, e.g., Ref. [3]). If on the other hand we compare with the CE Euler-Lagrange equation obtained in Ref. [4] (see also [3]) by means of the Lagrange multiplier technique we can identify \( \lambda_N \) with the Lagrange multiplier associated to the constraint (3) and \( F \) is the intrinsic free energy functional in the CE. Therefore, we see that using the extended variable space one obtains the same Euler-Lagrange equation than in the standard DFT procedure, with a intrinsic free energy functional \( F \) that only depends on the density.

As an example we apply the above expressions to the classical ideal gas. For this system one has \( -\beta F(T, N, [V_{\text{ext}}]) = N \log(\Lambda^3 f \exp[-\beta V_{\text{ext}}(\mathbf{r})]d\mathbf{r}) - \log N! \) where \( \Lambda \) is the thermal wavelength. Using (7) we obtain the familiar barometric result \( \rho_N(\mathbf{r}, [V_{\text{ext}}]) = N \exp[-\beta V_{\text{ext}}(\mathbf{r})]/ \int \exp[-\beta V_{\text{ext}}(\mathbf{r})]d\mathbf{r} \) and from (8) we would trivially obtain the corresponding result for \( -\beta \lambda_N V_{\text{ext}} \). These results can be inverted to obtain \( N[\rho_N] = \int \rho_N(\mathbf{r}) d\mathbf{r} \) and an explicit expression (not shown) for \( V_{\text{ext}} \) in terms of \( \rho_N \) and \( \lambda_N \). Substituting these expressions in (13) we obtain the following result for the intrinsic free energy functional of the ideal gas in the CE:

\[
\beta \mathcal{F}_{\text{id}}[\rho_N] = -\int \rho_N(\mathbf{r}) \left( \log(\Lambda^3 \rho_N(\mathbf{r})) - 1 \right) d\mathbf{r} + \phi \left( \int \rho_N(\mathbf{r}) d\mathbf{r} \right).
\]

(15)

with \( \phi(x) = \log x! - x \log x + x \). We note that this free-energy only differs from the GCE result by the term \( \phi(\int \rho_N(\mathbf{r}) d\mathbf{r}) \), i.e., by \( \phi(N) \). For large \( N \), \( \phi(N) \approx (\log N)/2 \), and, since the mean square fluctuation \( \Delta^2(N) \) of the ideal gas in the GCE is equal to \( N \) we find that (13) agrees with the saddle point approximation of Ref. [10] in which the leading correction to the CE free energy functional is given by \( (\log(\Delta^2(N)))/2 \). Finally, we recall that using (15) in Eqs. (14) we rederive the result for the equilibrium density \( \rho_N \), as we would have done using (13) and (14) with the constraint (3).

An important property of using the extended variable space is that, as we have seen in the example, the set \( \{ \rho_N, \lambda_N \} \) determines completely the set \( \{ V_{\text{ext}}, N \} \), and, since the opposite is also (trivially) true, there is a one-to-one relation between both sets. This means that the Lagrange transform is invertible and the (Hessian) matrix \( \partial(\rho_N, \lambda_N)/\partial(V_{\text{ext}}, N) \) is not singular. Multiplying this matrix by its inverse \( \partial(V_{\text{ext}}, N)/\partial(\rho_N, \lambda_N) \) and equating to the identity matrix in the extended space, we obtain a set of equations that, in the canonical ensemble, correspond to the OZ equation. After some algebra we obtain the exact relations

\[
h_N(\mathbf{r}_1, \mathbf{r}_2) = c_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \int \rho_N(\mathbf{r}_3) c_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3) h_N(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 - \frac{1}{\rho_N(\mathbf{r}_2)} \frac{\partial \rho_N(\mathbf{r}_2)}{\partial N}
\]

(16)

and

\[
\frac{\partial \rho_N(\mathbf{r}_2)}{\partial N} = \frac{\rho_N(\mathbf{r}_2)}{N} \left( 1 + \int \rho_N(\mathbf{r}_1) \frac{\partial \rho_N(\mathbf{r}_3)}{\partial N} \left( c_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3) - c_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \right) d\mathbf{r}_1 d\mathbf{r}_3 \right),
\]

(17)

where in analogy with the GCE we have introduced the CE direct correlation function \( c_N^{(2)} \) as
the first contribution to Eq. (21). In order to evaluate (23) we need an expression (valid to first order) for \( \Delta \) which leads to

\[
c^{(2)}_N(r_1, r_2) = -\beta \frac{\delta^2 (F[\rho_N] - F_{id}[\rho_N])}{\delta \rho_N(r_1) \delta \rho_N(r_2)}
\]

(18)

with \( F_{id} \) given by (15). Eqs. (16)-(18) are the main results of the present work. These equations show that it is possible to derive the CE counterpart of the direct correlation function and the OZ equation. The new OZ equation is consistent with the constraints (5) and (6) as one can readily show by noting that, independently of the functional form of \( c^{(2)}_N \), these constraints lead to identities when used in (16) and (17) (after an appropriate integration).

Given an explicit form for the intrinsic free-energy functional \( F \), one can obtain \( c^{(2)}_N \) via functional differentiation and then \( \partial \rho_N(r_2)/\partial N \) is obtained from (17). Finally, using (16) one obtains the total correlation function \( h_N \). In general, solving these equations is not an easy task and one must resort to self-consistent procedures. There are some cases in which one can obtain the required information by means of simple methods. The simplest situation arises for the ideal gas. In this case \( c^{(2)}_N = 0 \), Eq. (17) implies \( \partial \rho_N(r)/\partial N = \rho_N(r)/N \) and, from (16) we obtain the well-known result \( h_N = -1/N \) for the total correlation function of the ideal gas.

Another simple situation arises in the uniform limit. Considering that in this limit \( \rho_N(r) \to \rho_N \equiv N/V \) (\( V \) is the volume of the system), one has \( \partial \rho_N/\partial N = \rho_N/N \) and thus Eq. (17) becomes

\[
h_N(r_{12}) = c^{(2)}_N(r_{12}) + \rho N \int c^{(2)}_N(r_{13}) h_N(r_{32}) dr_3 - \frac{1}{N}
\]

(19)

where \( |r_i - r_j| \equiv r_{ij} \) and we have taken into account that the uniform fluid is both translationally and rotationally invariant. This equation should be compared with the GCE-OZ equation (1), that, in the uniform limit, \( \rho(r) \to \rho = \rho_N \), reduces to

\[
h(r_{12}) = c^{(2)}(r_{12}) + \rho \int c^{(2)}(r_{13}) h(r_{32}) dr_3.
\]

(20)

Then, for uniform fluids, both equations only differ by the \( 1/N \) term which vanishes in the thermodynamic limit.

It is well-known that the GCE radial distribution function \( g(r) = h(r) + 1 \) can be related to \( g_N(r) = h_N(r) + 1 \) by means of a series expansion in powers of \( 1/N \). Using this expansion one has for the total correlation function (with \( \rho_N = \rho \))

\[
h_N(r) \approx h(r) - \frac{S(0)}{N} - \frac{S(0)}{2N} \frac{\partial^2}{\partial \rho^2} \left( \rho^2 h(r) - \frac{S(0)}{N} \right)
\]

(21)

where \( S(k) = 1 + \rho \delta(k) \) is the structure factor, being \( \delta(h(k)) = \int h(r) \exp(\i k \cdot r) dr \) the Fourier transform of \( h(r) \). In what follows we shall indicate how one can rederive this result by means of the OZ equations (19) and (20) and an approximate expression for \( c^{(2)}_N \) in terms of \( c^{(2)}(r) \) (conversely, Eq. (21) and Eqs. (19)-(20) can be used to obtain an approximate expression for \( c^{(2)}_N \)). Since the OZ equations (17) and (20) involve convolutions it is convenient to work in Fourier space. Subtracting (20) from (19), after some algebra, we obtain the exact relation

\[
\hat{\Delta} \hat{h}(k) = \frac{-8\pi^3 N^{-1} S(k) \delta(k) + \Delta \hat{c}(k) S^2(k)}{1 - \rho S(k) \Delta \hat{c}(k)}
\]

(22)

where \( \hat{\Delta} \hat{h}(k) \equiv \hat{h}_N(k) - \hat{h}(k) \) and \( \hat{\Delta} \hat{c}(k) \equiv \hat{c}^{(2)}_N(k) - \hat{c}^{(2)}(k) \). From this equation [or, alternatively, from Eq. (17)] one easily obtains \( \hat{\Delta} \hat{h}(0) = -S(0)/\rho \), i.e., although \( \Delta h(r) \) is of order \( 1/N \), its integral over the total volume \( V \) does not vanish with increasing \( N \). A simple analysis of Eq. (22) can be done by considering that, since the difference between the CE and the GCE free-energy functionals is of order \( \log N \) (11), one has that \( \Delta \hat{c}^{(2)}(k) \) is of order \( 1/N \), and thus, to first order in \( \Delta \hat{c}^{(2)}(k) \) we obtain

\[
\Delta \hat{h}(k) \approx -\frac{8\pi^3 S(k) \delta(k)}{N} + \left( \frac{S(k)}{\rho} - \frac{8\pi^3 S(k) \delta(k)}{N} \right) \rho S(k) \Delta \hat{c}(k).
\]

(23)

We note that, to zeroth order, this equation reduces to \( \Delta \hat{h}(k) \approx -8\pi^3 S(k) \delta(k)/N \) and thus \( \Delta h(r) \approx -S(0)/N \), i.e., the first contribution to Eq. (21). In order to evaluate (23) we need an expression (valid to first order) for \( \Delta \hat{c}^{(2)}(k) \). This expression can be obtained from the above-mentioned saddle point approximation for the CE free-energy functional (11) which leads to
\[ \Delta c^{(2)}(r_{12}) \approx -\frac{1}{2} \frac{\delta^2}{\delta \rho(r_1) \delta \rho(r_2)} \left( \log \frac{\Delta^2(N)}{N} \right). \] (24)

From this approximation, a rather lengthy calculation shows that Eq. (23) becomes the series expansion result of Eq. (21). This demonstration is not only a proof of the usefulness of the CE-0Z equation but also it gives further support to the saddle point approximation of Ref. [10]. We note that this approximation has been shown [13] to yield results for the inhomogeneous density that are equivalent to first order to those of the series expansion of the CE inhomogeneous density introduced by González et al [14].

In summary, we have seen that the fixed-N constraint of the CE is inconsistent with the standard OZ relation in the GCE. By resorting to DFT methods we have identified the source of this inconsistency with the lack of a strict one-to-one relation between the density and the external potential which leads to a singular Hessian matrix. This problem has been solved by means of an extended variable-space in which we rederive the usual CE Euler-Lagrange equation with the advantage that the new Hessian matrix is no longer singular and allows to introduce a CE-OZ relation. For both the ideal gas and the uniform fluid this CE-OZ relation only differs from GCE-OZ by a $1/N$ term. The presence of this term leads to the exact total correlation function for the ideal gas. For the uniform fluid we recover the result of the standard series expansion of the CE total correlation function.

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