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LETTER TO THE EDITOR

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Abstract
Density functional theory (DFT), when applied to systems with $T \neq 0$, is based on the grand canonical extension of the Hohenberg–Kohn–Sham theorem due to Mermin (HKSM theorem). While a straightforward canonical ensemble (CE) generalization fails, work in nanopore systems could certainly benefit from a mesoscopic DFT in the CE. We show that, if the asymptotic behaviour of the canonical distribution functions is taken into account, the HKSM theorem can be extended to the CE. We generate N-modified correlation and distribution functions hierarchies, show that their functional relationship is equivalent to the one holding between the more conventional ones and prove that, if they are employed, either a modified external field or the density profiles can be indistinctly used as independent variables. We also write down the N-modified free energy functional and prove that its minimum is reached when the equilibrium values of the new hierarchy are used. This completes the extension of the HKSM theorem.

Density functional theory (DFT) is, undoubtedly, one of the more reliable and established tools in condensed matter theory. It has successfully been used in an ample variety of classical systems [1] as, e.g., uniform and non-uniform systems in simple [2, 3] and general [4] fluids, confined fluids [5, 6], melting and freezing [7], interfaces [8], etc as well as in the calculation of electronic properties in all kinds of systems [9]. This impressive work directly descends from the pioneering work of Hohenberg, Kohn and Sham [10] and its extension to non-zero temperature for systems described in the grand canonical ensemble (GCE) by Mermin [11]. Roughly speaking, the HKSM theorem states that, either the external potential or the density profile can indistinctly be used as independent variables and that the thermodynamic grand potential reaches its minimum when the equilibrium density profile is used. Therefore, it is in the foundation of all sort of variational principles. The failure to implement a straightforward CE extension is already well known, referred to in [6] (where a GCE series expansion was done and an approximate density profile for the CE obtained), and can be traced back to the fixed N constraint (see equation (8)). In fact, years ago, Ramshaw [12] explicitly worked out

the two-body Ornstein-Zernike (OZ) equation for a one-component system in the CE if the pair correlation function $h(r)$ is stripped off of its asymptotic behaviour. As the GCE is an extension of the CE, an obvious question is where the need for such an implementation exists. With respect to that point, we can mention that experiments done in porous glasses (mean pore radius $\approx$ 20–30 Å) [13], simulations [14] and DFT studies [5, 6] show the interest of having a mesoscopic DFT in the CE in order to study the statistical mechanics of finite closed systems like fluids in spherical pores [6]. Although the extension of Ramshaw's work [12] to mixtures is not very complicated, we prefer, in this letter, to focus our attention on a physically far reaching question; i.e. how can his results be used (while keeping the technicalities to the barest minimum) in order to extend the HKSM theorem to the CE? We will prove two main results: (i) that, by stripping the canonical correlation functions off of their asymptotic behaviour, an N-modified set of distribution and correlation function *hierarchies* is generated; (ii) by introducing an N-modified free energy and showing that it is minimized by the N-modified density profile we prove the extension of the HKSM theorem to the CE. In this way, variational principles formulated in the CE have a firm foundation if the N-modified functions are used in them. Specifically, we consider a one-component system with N particles in a box of volume V with a one body external potential $V^{(1)}(x)$. After summarizing Ramshaw's method, we show that his procedure defines (through functional derivatives of the canonical partition function Q_N with respect to a modified external potential (equation (16))) a *hierarchy* of n-body direct and total correlation functions which are related through n-body OZ equations. The physical idea is the same one that shows up in almost every textbook on statistical mechanics when going from the CE to the GCE. There an open subset is considered, here we strip the canonical correlation functions off its asymptotic behaviour. The difference is that, for us, this is the fundamental step, not an intermediate one. We are then able to prove that this step is described, to any n-body order, by functional derivatives with the right formal structure. This proves point (i) and paves the way to the HKSM theorem. Let us emphasize that, as any successful theory of liquids needs to consider all the correlation functions, a valid OZ equation for the pair functions h and c is not good enough to extend DFT to the CE. Therefore, we need to prove that we actually have a set of N-modified *hierarchies* obtained through the same formal scheme of equations (2), (4) and (5) and that they are, indeed, linked by n-body OZ equations.

As usual [1], the distribution functions and full distribution functions, the truncated correlation functions associated to them and direct correlation function hierarchies ($n^{(s)}(\{x\})$, $\hat{n}^{(s)}(\{x\})$, $t^{(s)}(\{x\})$, $\hat{t}^{(s)}(\{x\})$ and $c^{(s)}(\{x\})$ respectively) can be defined by functional derivatives as

$$n^{(s)}(\{x\}) = \frac{\prod_{k=1}^{s} e^{\Phi(x_k)}}{Q_N} \frac{\delta^s Q_N}{\prod_{k=1}^{s} \delta e^{\Phi(x_k)}} \tag{1}$$

$$\hat{n}^{(s)}(\{x\}) = \frac{1}{Q_N} \frac{\delta^s Q_N}{\prod_{k=1}^{s} \delta \Phi(x_k)} \tag{2}$$

$$t^{(s)}(\{x\}) = \prod_{k=1}^{s} e^{\Phi(x_k)} \frac{\delta^s \ln Q_N}{\prod_{k=1}^{s} \delta e^{\Phi(x_k)}} \tag{3}$$

$$\hat{t}^{(s)}(\{x\}) = \frac{\delta^s \ln Q_N}{\prod_{k=1}^{s} \delta \Phi(x_k)} = \frac{\delta \hat{t}^{(s-1)}(\{x_1, \ldots, x_{s-1}\})}{\delta \Phi(x_s)} \tag{4}$$

$$c^{(s)}(\{x\}) = \beta \frac{\delta^s F^{exc}}{\prod_{k=1}^{s} \delta n^{(1)}(x_k)} = \frac{\delta c^{(s-1)}(\{x_1, \ldots, x_{s-1}\})}{\delta n^{(1)}(x_s)} \tag{5}$$

where $\{x\} = (x_1, \ldots, x_s)$ is the coordinate set, $\beta = 1/kT$, F^{exc} the excess free energy and $\Phi(x) = -\beta V^{(1)}(x)$. In the GCE the grand partition function Ξ replaces Q_N. We consider the full distribution and correlation functions $\hat{n}^{(s)}$, $\hat{t}^{(s)}$ as the fundamental quantities (together

with $c^{(s)}$) because they not only pinpoint the problems in the CE, is through these functions that we solve them and no new information can be got from the other functions. Obviously, $n^{(1)} = \hat{n}^{(1)} = t^{(1)} = \hat{t}^{(1)}$ and

$$\delta n^{(1)}(\boldsymbol{x}) = \int \hat{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) \delta \Phi(\boldsymbol{y}) \mathrm{d}\boldsymbol{y}. \tag{6}$$

It is clear that, up to now, the independent variables are the external fields and, in the more usual notation is $\hat{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) = t^{(2)}(\boldsymbol{x}, \boldsymbol{y}) + n^{(1)}(\boldsymbol{x})\delta(\boldsymbol{x} - \boldsymbol{y})$, $t^{(2)}(\boldsymbol{x}, \boldsymbol{y}) = n^{(1)}(\boldsymbol{x})n^{(1)}(\boldsymbol{y})h^{(2)}(\boldsymbol{x}, \boldsymbol{y})$. If the density profile $n^{(1)}$ can also be used as an independent variable, then an inverse kernel $\hat{t}^{(2)-1}(\boldsymbol{z}, \boldsymbol{x}) = \delta \Phi(\boldsymbol{z})/\delta n^{(1)}(\boldsymbol{x})$ must exist such that

$$\int \hat{t}^{(2)^{-1}}(\boldsymbol{z}, \boldsymbol{x})\hat{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y})\mathrm{d}\boldsymbol{x} = \delta(\boldsymbol{z} - \boldsymbol{y}). \tag{7}$$

Using the definition of the pair distribution function in both ensembles [1], the normalization integral is

$$\int \hat{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y})\mathrm{d}\boldsymbol{y} = \begin{cases} 0 & \text{CE} \\ n^{(1)}(\boldsymbol{x})\left[1 + \dfrac{\partial \ln(n^{(1)}(\boldsymbol{x})/z)}{\partial \ln z}\right] & \text{GCE} \end{cases} \tag{8}$$

Eqs. (7) and (8) are obviously incompatible in the CE while, because of the fluctuations, there is no incompatibility in the GCE and the kernel $\hat{t}^{(2)}$ is invertible. Therefore, the OZ equation (obtained when $c^{(2)}(\boldsymbol{z}, \boldsymbol{x})$ is defined by equation (17)) is, mathematically speaking, undefined in the CE and, in that framework, no rigorous DFT is possible.

The irreducible two-body behaviour is exclusively described by $h^{(2)}$ and we will analyse its asymptotic behaviour. The conditional probability of finding a particle in $\boldsymbol{x}$ when another one is fixed in $\boldsymbol{y}$ can be written, when $\boldsymbol{x}$ and $\boldsymbol{y}$ are very far away, as

$$n_\infty(\boldsymbol{x}|\boldsymbol{y}) = n^{(1)}(\boldsymbol{x}) + \frac{\partial n^{(1)}(\boldsymbol{x})}{\partial \rho}\Delta \phi(\boldsymbol{y}). \tag{9}$$

Here $\Delta \phi(\boldsymbol{y})$ is an unknown proportionality factor and, by symmetry

$$h_\infty^{(2)}(\boldsymbol{x}, \boldsymbol{y}) = \Gamma^{(2)} \frac{\partial \ln n^{(1)}(\boldsymbol{x})}{\partial \rho} \frac{\partial \ln n^{(1)}(\boldsymbol{y})}{\partial \rho} \tag{10}$$

$\Gamma^{(2)}$ is an as yet unknown constant and we can define an N-modified correlation function $\tilde{h}^{(2)}$ as the correlation function stripped off of its asymptotic behaviour. More precisely,

$$h^{(2)}(\boldsymbol{x}, \boldsymbol{y}) = \begin{cases} \tilde{h}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) + \Gamma^{(2)} \dfrac{\partial \ln n^{(1)}(\boldsymbol{x})}{\partial \rho} \dfrac{\partial \ln n^{(1)}(\boldsymbol{y})}{\partial \rho} & \boldsymbol{x} \neq \boldsymbol{y} \\ \tilde{h}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) = -1 & \boldsymbol{x} = \boldsymbol{y} \end{cases}. \tag{11}$$

As the stripping is done through a separation of variables the irreducible two-body component is not affected, only the long range behaviour (due to the fixed N constraint) is isolated. As a consequence, $\tilde{h}^{(2)}$ is the correlation function with a truly irreducible two-body behaviour, not $h^{(2)}$, and excluded volume effects are not altered. Therefore, we can define an N-modified full truncated correlation function

$$\tilde{t}_{\alpha\lambda}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) = \begin{cases} \hat{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) - \Gamma^{(2)} \dfrac{\partial \ln n^{(1)}(\boldsymbol{x})}{\partial \rho} \dfrac{\partial \ln n^{(1)}(\boldsymbol{y})}{\partial \rho} & \boldsymbol{x} \neq \boldsymbol{y} \\ \hat{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) & \boldsymbol{x} = \boldsymbol{y} \end{cases} \tag{12}$$

and verify that it satisfies

$$\int \tilde{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) \mathrm{d}\boldsymbol{x} \mathrm{d}\boldsymbol{y} = -\Gamma^{(2)} V^2 \tag{13}$$

This shows that $\tilde{t}^{(2)}$ is indeed invertible. Also, $\Gamma^{(2)}$ can be written as a functional of $\tilde{h}^{(2)}$

$$\Gamma^{(2)} = -\frac{1}{V^2} \int \mathrm{d}\boldsymbol{x} n^{(1)}(\boldsymbol{x}) \left[1 + \int \mathrm{d}\boldsymbol{y} n^{(1)}(\boldsymbol{y}) \tilde{h}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) \right] \tag{14}$$

i.e., like a sort of averaged compressibility and thus recover the classical Lebowitz–Percus results [15]. Replacing equation (12) in (6) and using the chemical potential definition we define a modified external field $\tilde{\Phi}$ and write that

$$\delta n^{(1)}(\boldsymbol{x}) = \int \tilde{t}^{(2)}(\boldsymbol{x}, \boldsymbol{y}) \delta \tilde{\Phi}(\boldsymbol{y}) \mathrm{d}\boldsymbol{y} \tag{15}$$

$$\delta \tilde{\Phi}(\boldsymbol{y}) = \delta \Phi(\boldsymbol{y}) + \beta \delta \mu. \tag{16}$$

If we write that, by definition,

$$\tilde{t}^{(2)-1}(\boldsymbol{z}, \boldsymbol{x}) = \frac{\delta \tilde{\Phi}(\boldsymbol{z})}{\delta \tilde{n}^{(1)}(\boldsymbol{x})} = -\tilde{c}^{(2)}(\boldsymbol{z}, \boldsymbol{x}) + \frac{\delta(\boldsymbol{z} - \boldsymbol{x})}{\tilde{n}^{(1)}(\boldsymbol{x})} \tag{17}$$

the N-modified functions $\tilde{t}^{(2)-1}$, $\tilde{t}^{(2)}$ obey equation (7) and, therefore, $\tilde{h}^{(2)}$ and $\tilde{c}^{(2)}$ are linked by an OZ equation with $\tilde{c}^{(2)}$ playing the role of an N-modified direct correlation function.

These are essentially Ramshaw's results. For the three-body functions we can start from their normalization integrals and repeat the above procedure. However, this does not lead us to easily prove that we have a hierarchy of N-modified functions. On the other hand, the functional differentiation procedure shows very clearly that, if continued, N-modified sets of distribution and correlation functions hierarchically related are generated. That can be seen by analysing the three bodies case. In the GCE we have that both $\hat{t}^{(3)}$ and $\hat{t}^{(3)-1}$ can be obtained by functional differentiation of $\hat{t}^{(2)}$ and $\hat{t}^{(2)-1}$ with respect to Φ and $n^{(1)}$ respectively and, in doing that, $c^{(3)}$ is generated [16]. In general, the procedure for finding the first p OZ eqs. is to perform a Taylor functional expansion of both $n^{(1)}$ and Φ as a functional of each other, substitute one series into the other and equate equal order terms up to order p. In this way, the three-body OZ equation is

$$\hat{t}^{(3)-1}(\boldsymbol{s}, \boldsymbol{u}, \boldsymbol{v}) = -\int \mathrm{d}\boldsymbol{x} \mathrm{d}\boldsymbol{y} \mathrm{d}\boldsymbol{z} \hat{t}^{(2)-1}(\boldsymbol{s}, \boldsymbol{x}) \hat{t}^{(3)}(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{z}) \hat{t}^{(2)-1}(\boldsymbol{y}, \boldsymbol{u}) \hat{t}^{(2)-1}(\boldsymbol{z}, \boldsymbol{v}). \tag{18}$$

If we now turn to the CE, $\delta/\delta \Phi$ is replaced by $\delta/\delta \tilde{\Phi}$, $\hat{t}^{(2)-1}$ by $\tilde{t}^{(2)-1}$ and, as the derivatives are with respect to $\tilde{\Phi}$ it implies that the same must hold for the three-body functions. Therefore, it is (hierarchically) proved that the N-modified hierarchies $\tilde{t}$ and $\tilde{c}$ are generated by functional differentiation (through the operators $\delta/\delta \tilde{\Phi}$ and $\delta/\delta n$) and are linked by n-body OZ equations.

Now we define an N-modified intrinsic free energy functional by

$$\beta \tilde{F} \left[\tilde{n}^{(1)} \right] = \langle \beta (K_N + U_N - \ln P_N) \rangle \tag{19}$$

where K_N, U_N, P_N are the N-body kinetic, potential energy and probability distribution function in the CE and minimize the functional

$$\beta \tilde{\Omega} \left[\tilde{n}^{(1)} \right] = -\int \tilde{n}^{(1)}(\boldsymbol{x}) \tilde{\Phi}(\boldsymbol{x}) \mathrm{d}\boldsymbol{x} + \beta \tilde{F} \left[\tilde{n}^{(1)} \right]. \tag{20}$$

The need for a full hierarchy of correlation functions lies in the entropic term $\ln P_N$. It is easy to prove, using the Gibbs–Bogoliubov inequality [1], that the minimum is reached when

the equilibrium profile $\tilde{n}^{(1)}$ is used. This completes the proof of the extension of the HKSM theorem to the CE. As the N-modified direct correlation function hierarchy $\{\tilde{c}^{(s)}\}$ can be started by

$$\tilde{c}^{(1)}(\boldsymbol{x}) = \beta \frac{\delta \tilde{F}^{exc}\left[\tilde{n}^{(1)}\right]}{\delta \tilde{n}^{(1)}(\boldsymbol{x})}$$

we have proved that all of our N-modified functions can be generated by functional differentiation recipes having the formal structure as of equations (2), (4) and (5).

Summarizing, we have shown that a new *hierarchical* set of N-modified distribution and correlation functions can be built using the same rules and formal structure of the conventional canonical functions with the proviso that the modified external fields must be used in order to strip them off of their asymptotic behaviour. Using these functions we have also proved that the HKSM theorem of the GCE can be extended to the CE. In a forthcoming paper a detailed derivation that includes mixtures will be published.

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