

## The extended variable space approach to density functional theory in the canonical ensemble

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 11907

(<http://iopscience.iop.org/0953-8984/14/46/302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

### Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 17:26

Please note that [terms and conditions apply](#).

# The extended variable space approach to density functional theory in the canonical ensemble

J A White<sup>1</sup> and A González

Departamento de Física Aplicada, Universidad de Salamanca, 37008 Salamanca, Spain

E-mail: white@usal.es and ags@usal.es

Received 7 June 2002, in final form 2 July 2002

Published 8 November 2002

Online at [stacks.iop.org/JPhysCM/14/11907](http://stacks.iop.org/JPhysCM/14/11907)

## Abstract

Density functional theory (DFT) of classical fluids in the canonical ensemble (CE) is studied by means of Legendre transform techniques in an extended variable space. The constraint that arises from having a fixed number of particles  $N$  is incorporated into the theory by considering  $N$  and its conjugate, the CE chemical potential  $\mu$ , as additional variables in the DFT analysis of the problem. The method allows for obtaining an Ornstein–Zernike (OZ) equation in the CE. A comparison is made with other approaches to the problem. In particular,  $\mu$  is identified with the Lagrange multiplier related to the fixed- $N$  constraint and a further Legendre transform leads to an equivalent OZ equation equal to that of the grand canonical ensemble (GCE) in terms of functional derivatives stripped off from their asymptotic behaviour. The CE analogous to the GCE direct correlation function is introduced as an excess (over ideal) quantity in terms of which we obtain a CE compressibility equation.

## 1. Introduction

Density functional theory (DFT) of classical fluids is based on the fact that the free energy can be expressed as a functional of the inhomogeneous equilibrium density, and this functional yields all the relevant information of the fluid [1–5].

The DFT approach is equivalent to the more traditional statistical mechanics description of the fluid in terms of the partition function expressed as a functional of the external potential. It is well known that the change from one representation to the other can be presented as a functional Legendre transform in which the external potential and the inhomogeneous density are conjugate variables [3, 6, 7]. That this transformation can be made is ensured by the Hohenberg–Kohn theorems for DFT [1, 2, 5] or equivalently by the convexity properties of the involved functionals [7]. In the grand canonical ensemble (GCE) this Legendre transform leads in a natural way to the formulation of the Ornstein–Zernike (OZ) equation for the

<sup>1</sup> Author to whom any correspondence should be addressed.

inhomogeneous fluid as a matrix inversion relation. That is, the product of the Hessian matrix of the direct transform by its inverse (the Hessian of the inverse transform) is equal to the identity matrix [3]. Of course, one of these matrices is related to the total correlation function and the other to the direct correlation function of the fluid so that the familiar OZ relation in these terms is easily recovered [3].

In the canonical ensemble (CE), however, a direct extension of these ideas is not possible because of the normalization condition for the total correlation function, which implies that the related Hessian matrix is singular and therefore not invertible [8, 9]. In this paper, we shall see how this difficulty can be solved by resorting to an extended variable space in which the chemical potential and the number of particles are used as additional variables in a Legendre transform approach to DFT in the CE. Furthermore, we shall see how a straightforward connection to previous approaches to the problem [8, 9] can be made by means of Legendre transform techniques. These techniques have been exploited by Nalewajski *et al* [10] in the field of DFT of electronic systems.

This paper is structured as follows. In section 2 we briefly present the main steps for the Legendre transform approach to DFT in the GCE and how it leads naturally to the OZ equation. Section 3 is devoted to the CE. In section 3.1 we show how the direct extension of the GCE procedure cannot lead to a CE–OZ relation due to the singular behaviour of the Hessian matrix. This singular behaviour is ascribed to the fixed- $N$  constraint that arises from the normalization of the equilibrium density. In spite of this fact, a Euler–Lagrange equation for the density is obtained by means of the Lagrange multiplier technique. In section 3.2 we consider an extended variable space in which one can reformulate the DFT in the CE, obtaining the same Euler–Lagrange equation as in section 3.1 but with a non-singular Hessian matrix. In section 3.3 we obtain an OZ equation in terms of the Hessian matrix for the extended variable space. By means of an additional Lagrange transform, in section 3.4 we obtain an equivalent OZ equation, which turns out to coincide with the results obtained by Ramshaw [8] and by Hernando and Blum [9], by considering the asymptotic behaviour of the fluid correlations [11]. In section 4 we apply the results of the paper to some simple cases. We first consider the ideal gas for which we obtain a free-energy functional in the CE and check the consistency of the different OZ relations previously obtained. We next define the direct correlation function in the CE as an excess (over ideal) second functional derivative of the CE functional. Finally, the application of the theory to the uniform fluid leads to an OZ equation in the CE which only differs from the GCE–OZ equation by a  $1/N$  term. We also obtain a compressibility equation in the CE analogous to its GCE counterpart. We conclude with a brief summary of the main results of the paper. A preliminary account of this work has been presented elsewhere [12].

## 2. DFT and Legendre transforms in the grand canonical ensemble

We consider a classical fluid in the GCE (fixed temperature  $T$  and chemical potential  $\mu_{gc}$ ) in the presence of an external potential  $V_{ext}(\mathbf{r})$ . For this system the grand partition function  $\Xi$  is a functional of  $v_{gc}(\mathbf{r}) \equiv \mu_{gc} - V_{ext}(\mathbf{r})$  and can be written as

$$\Xi[v_{gc}] = \sum_{N=0}^{\infty} \frac{\Lambda^{-3N}}{N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp[-\beta U_{int}(\mathbf{r}_1, \dots, \mathbf{r}_N)] \prod_{i=1}^N \exp[\beta v_{gc}(\mathbf{r}_i)] \quad (1)$$

where  $\Lambda$  is the de Broglie thermal wavelength,  $\mathbf{r}_i$  is the position of particle  $i$ ,  $\beta = 1/k_B T$ , and  $U_{int}$  is the interparticle potential. In terms of  $\Xi$  the grand potential  $\Omega_{gc}$  can be expressed as

$$-\beta \Omega_{gc}[v_{gc}] = \ln \Xi[v_{gc}], \quad (2)$$

and, as is well known, its functional derivative yields the inhomogeneous equilibrium density

$$\rho_{gc}(\mathbf{r}) = -\frac{\delta\Omega_{gc}[v_{gc}]}{\delta v_{gc}(\mathbf{r})}. \quad (3)$$

If one wishes to consider a functional of the variable  $\rho_{gc}$  instead of  $v_{gc}$  without any loss of information, the usual procedure is to perform a Legendre transform of  $\Omega_{gc}$ . The new functional is given by

$$\mathcal{F}_{gc}[\rho_{gc}] = \Omega_{gc}[v_{gc}[\rho_{gc}]] + \int \rho_{gc}(\mathbf{r})v_{gc}(\mathbf{r}, [\rho_{gc}]) d\mathbf{r}, \quad (4)$$

where we have made explicit that  $v_{gc}$  is the (generalized) potential that determines  $\rho_{gc}$  via equation (3). It is clear that  $\mathcal{F}_{gc}$  is the well-known intrinsic Helmholtz free energy in the GCE. The usual variational principle of DFT is now introduced by means of the following functional which depends both on  $\hat{\rho}$  and on  $v_{gc}$

$$\Omega_{v_{gc}}[\hat{\rho}] = \mathcal{F}_{gc}[\hat{\rho}] - \int \hat{\rho}(\mathbf{r})v_{gc}(\mathbf{r}) d\mathbf{r}. \quad (5)$$

Minimizing  $\Omega_{v_{gc}}[\hat{\rho}]$  with respect to  $\hat{\rho}$  at constant  $v_{gc}$  we obtain the usual Euler–Lagrange equation

$$\left. \frac{\delta\mathcal{F}_{gc}[\hat{\rho}]}{\delta\hat{\rho}(\mathbf{r})} \right|_{\hat{\rho}=\rho_{gc}} - v_{gc}(\mathbf{r}) = 0, \quad (6)$$

where the minimum is attained for the equilibrium density  $\rho_{gc}$  and  $\Omega_{v_{gc}}[\hat{\rho}]|_{\hat{\rho}=\rho_{gc}} = \Omega_{gc}$ , that is,  $\Omega_{v_{gc}}$  reduces to the grand potential. In the preceding derivation we have obtained the intrinsic free energy from a Legendre transform of the grand potential. It is instructive to see that the inverse route can also be taken. This is the involution property of the Legendre transform. We rewrite equation (6) as

$$v_{gc}(\mathbf{r}) = \frac{\delta\mathcal{F}_{gc}[\rho_{gc}]}{\delta\rho_{gc}(\mathbf{r})} \quad (7)$$

where  $\rho_{gc}$  is the equilibrium density. The Legendre transform of  $\mathcal{F}_{gc}$  is a functional ( $\Omega_{gc}$ ) that depends on  $v_{gc}$  and is obtained from

$$\Omega_{gc}[v_{gc}] = \mathcal{F}_{gc}[\rho_{gc}[v_{gc}]] - \int \rho_{gc}(\mathbf{r}, [v_{gc}])v_{gc}(\mathbf{r}) d\mathbf{r}. \quad (8)$$

Now we have made explicit that  $\rho_{gc}$  is the density that determines  $v_{gc}$  via equation (7). We next consider the following functional of  $\rho_{gc}$  and  $\hat{v}$

$$\mathcal{F}_{\rho_{gc}}[\hat{v}] = \Omega_{gc}[\hat{v}] + \int \rho_{gc}(\mathbf{r})\hat{v}(\mathbf{r}) d\mathbf{r}. \quad (9)$$

For this functional we have the variational principle

$$\left. \frac{\delta\mathcal{F}_{\rho_{gc}}[\hat{v}]}{\delta\hat{v}(\mathbf{r})} \right|_{\hat{v}=v_{gc}} = \left. \frac{\delta\Omega_{gc}[\hat{v}]}{\delta\hat{v}(\mathbf{r})} \right|_{\hat{v}=v_{gc}} + \rho_{gc}(\mathbf{r}) = 0. \quad (10)$$

The second equality in equation (10) reduces to equation (3) and, when  $\hat{v} = v_{gc}$ ,  $\mathcal{F}_{\rho_{gc}}[\hat{v}]$  becomes the free energy  $\mathcal{F}_{gc}$ . This variational principle has been rigorously derived by Caillol using the convexity properties of the involved functionals [7]. These convexity properties imply that the Hessian matrices

$$\frac{\delta\rho_{gc}(\mathbf{r}_1)}{\delta v_{gc}(\mathbf{r}_2)} = -\frac{\delta^2\Omega_{gc}[v_{gc}]}{\delta v_{gc}(\mathbf{r}_1)\delta v_{gc}(\mathbf{r}_2)} \quad (11)$$

and

$$\frac{\delta v_{gc}(\mathbf{r}_1)}{\delta \rho_{gc}(\mathbf{r}_2)} = \frac{\delta^2 \mathcal{F}_{gc}[\rho_{gc}]}{\delta \rho_{gc}(\mathbf{r}_1) \delta \rho_{gc}(\mathbf{r}_2)} \quad (12)$$

which define the change of variables  $\rho_{gc} \leftrightarrow v_{gc}$  are not singular and inverse to each other, i.e.

$$\int \frac{\delta v_{gc}(\mathbf{r}_1)}{\delta \rho_{gc}(\mathbf{r}_3)} \frac{\delta \rho_{gc}(\mathbf{r}_3)}{\delta v_{gc}(\mathbf{r}_2)} d\mathbf{r}_3 = \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (13)$$

where  $\delta(x)$  is the usual delta function. This equation is the OZ relation for an inhomogeneous fluid written in compact notation [3].

### 3. DFT in the canonical ensemble

#### 3.1. The failure of the single-variable formalism

In the CE the partition function  $Q_N$  is a function of the (fixed) number of particles  $N$  and a functional of the external potential  $V_{ext}(\mathbf{r})$ . It can be written as

$$Q_N[V_{ext}] = \frac{\Lambda^{-3N}}{N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp[-\beta U_{int}(\mathbf{r}_1, \dots, \mathbf{r}_N)] \prod_{i=1}^N \exp[\beta V_{ext}(\mathbf{r}_i)]. \quad (14)$$

In terms of  $Q_N$ , the CE free energy  $F_N$  can be expressed as

$$-\beta F_N[V_{ext}] = \ln Q_N[V_{ext}], \quad (15)$$

and its functional derivative w.r.t.  $V_{ext}$  is the CE equilibrium density

$$\rho(\mathbf{r}) = \frac{\delta F_N[V_{ext}]}{\delta V_{ext}(\mathbf{r})}. \quad (16)$$

A Legendre transform from  $F_N[V_{ext}]$  to a new functional that depends of  $N$  and  $\rho$  must be done with caution because equation (16) does not define a good change of variables since the corresponding Hessian matrix

$$\frac{\delta^2 F_N[V_{ext}]}{\delta V_{ext}(\mathbf{r}_1) \delta V_{ext}(\mathbf{r}_2)} = \frac{\delta \rho(\mathbf{r}_1)}{\delta V_{ext}(\mathbf{r}_2)} \quad (17)$$

is singular. This is due to the normalization constraint

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad (18)$$

which implies

$$\int \frac{\delta \rho(\mathbf{r}_1)}{\delta V_{ext}(\mathbf{r}_2)} d\mathbf{r}_1 = \frac{\delta N}{\delta V_{ext}(\mathbf{r}_2)} = 0. \quad (19)$$

Consequently, an OZ equation equivalent to equation (13) cannot be obtained using the present approach [12].

As an aside, we note that equation (19) is equivalent to the usual normalization relations for the different two-body correlation functions of the fluid in the CE. These functions are related to the above functional derivative via (see, for example, [13])

$$\begin{aligned} -\beta^{-1} \frac{\delta \rho(\mathbf{r}_1)}{\delta V_{ext}(\mathbf{r}_2)} &= G(\mathbf{r}_1, \mathbf{r}_2) = \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2) \\ &= \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2) + \rho(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2) \end{aligned} \quad (20)$$

where  $G$  is the density–density correlation function,  $\rho^{(2)}$  is the two-body density, and  $h$  is the total correlation function. From equations (19) and (20) we obtain the well-known results (in the CE)

$$\int G(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = 0, \quad (21)$$

$$\int \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = (N - 1)\rho(\mathbf{r}_2) \quad (22)$$

and

$$\int \rho(\mathbf{r}_1)h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = -1 \quad (23)$$

where we have used equation (18).

In spite of the singular behaviour of the Hessian matrix we proceed with the proposed Legendre transform. The new functional is obtained from

$$\bar{F}(N, [\rho]) = F_N[V_{ext}] - \int \rho(\mathbf{r})V_{ext}(\mathbf{r}) d\mathbf{r}, \quad (24)$$

where the variable  $V_{ext}$  must be eliminated using equations (15) and (16). Let us assume that this elimination can be done. In this case, due to the constraint (19), one has that the functional  $\bar{F}$  only depends on the density, i.e.

$$\bar{F}(N, [\rho]) = \bar{F}\left(\int \rho(\mathbf{r}) d\mathbf{r}, [\rho]\right) \equiv \mathcal{F}[\rho]. \quad (25)$$

In order to introduce a variational principle in the same way as we did in the GCE we consider the functional

$$F_{V_{ext}}[\hat{\rho}] = \mathcal{F}[\hat{\rho}] + \int \hat{\rho}(\mathbf{r})V_{ext}(\mathbf{r}) d\mathbf{r}, \quad (26)$$

which depends both on  $V_{ext}$  and on  $\hat{\rho}$ . The minimization must be done taking into account the fixed- $N$  constraint (equation (18)) and thus one must resort to the Lagrange multiplier technique. We obtain

$$\left. \frac{\delta \mathcal{F}[\hat{\rho}]}{\delta \hat{\rho}(\mathbf{r})} \right|_{\hat{\rho}=\rho} + V_{ext}(\mathbf{r}) = \mu. \quad (27)$$

This is the usual Euler–Lagrange equation in the CE (see [4]) where  $\mathcal{F}$  is the intrinsic CE free-energy functional. The Lagrange multiplier  $\mu$  is determined using equation (18) and can be identified with the chemical potential. We see that the singular behaviour of the Hessian matrix can be bypassed by means of the Lagrange multiplier technique but only in part; we have a Euler–Lagrange equation for the CE equilibrium density but we lack an OZ relation which in the GCE arises in a natural way. In the following subsection, we reformulate the problem using an extended variable space in which the Lagrange multiplier is the conjugate variable of  $N$  and the corresponding Hessian is not a singular matrix so that an OZ relation can be formulated.

### 3.2. The extended variable space formalism in the canonical ensemble

Taking into account that the CE free energy defined in equation (15) is a function of  $N$  and a functional of  $V_{ext}$  we consider the Legendre transform from the set  $\{N, V_{ext}\}$  to the new set  $\{\mu, \rho\}$ , where the equations for the change of variables are the following well-known

expressions for the equilibrium density and the chemical potential (of course,  $\rho$  and  $\mu$  differ from those of the GCE) in terms of derivatives of  $F_N$

$$\rho(\mathbf{r}) = \left( \frac{\delta F_N[V_{ext}]}{\delta V_{ext}(\mathbf{r})} \right)_N \quad (28)$$

and

$$\mu = \left( \frac{\partial F_N[V_{ext}]}{\partial N} \right)_{V_{ext}}. \quad (29)$$

The Legendre transform is given by

$$U(\mu, [\rho]) = F(\mu, [\rho]) - \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}, \mu, [\rho]) d\mathbf{r} - \mu \int \rho(\mathbf{r}) d\mathbf{r}, \quad (30)$$

where we have used  $N = \int \rho(\mathbf{r}) d\mathbf{r}$  (equation (18)) and we define  $F(\mu, [\rho]) \equiv F_{\int \rho(\mathbf{r}) d\mathbf{r}}[V_{ext}(\mu, [\rho])]$ . We next consider the following functional that depends on both  $\{\hat{\mu}, \hat{\rho}\}$  and  $\{N, V_{ext}\}$ :

$$F_{N, V_{ext}}(\hat{\mu}, [\hat{\rho}]) = U(\hat{\mu}, [\hat{\rho}]) + \int \hat{\rho}(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \hat{\mu} N, \quad (31)$$

for which one has the variational principle

$$\left( \frac{\delta U(\hat{\mu}, [\hat{\rho}])}{\delta \hat{\rho}(\mathbf{r})} \right)_{\hat{\mu}} \Big|_{\hat{\mu}=\mu, \hat{\rho}=\rho} + V_{ext}(\mathbf{r}) = 0 \quad (32)$$

and

$$\left( \frac{\partial U(\hat{\mu}, [\hat{\rho}])}{\partial \hat{\mu}} \right)_{\hat{\rho}} \Big|_{\hat{\mu}=\mu, \hat{\rho}=\rho} + N = 0. \quad (33)$$

Here  $\mu$  and  $\rho$  are the equilibrium chemical potential and density and, for these equilibrium values,  $F_{N, V_{ext}}(\hat{\mu}, [\hat{\rho}])$  reduces to the Helmholtz free energy, i.e. one has

$$F_{N, V_{ext}}(\hat{\mu} = \mu, [\hat{\rho} = \rho]) = F_N[V_{ext}]. \quad (34)$$

Substituting equation (30) into (33) and taking into account equation (18) one finds that the functional

$$\mathcal{F} \equiv U + \mu \int \rho(\mathbf{r}) d\mathbf{r} = F(\mu, [\rho]) - \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}, \mu, [\rho]) d\mathbf{r} \quad (35)$$

does not depend on  $\mu$  and coincides with the functional introduced in equation (25). Since  $\mathcal{F} = \mathcal{F}[\rho]$ , from equation (32) we obtain

$$\frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r})} + V_{ext}(\mathbf{r}) = \mu \quad (36)$$

which is the same CE Euler–Lagrange equation for the equilibrium density obtained previously (equation (27)) using the Lagrange multiplier technique, where  $\mu$  is the Lagrange multiplier associated to the constraint (18) and  $\mathcal{F}$  is the intrinsic free-energy functional in the CE.

### 3.3. Ornstein–Zernike relations

The Legendre transform considered in section 3.2 assumes that the change of variables  $\{N, V_{ext}\} \leftrightarrow \{\mu, \rho\}$  is well defined. It is clear that  $\{N, V_{ext}\}$  determine all properties of the system and thus (via equations (28) and (29)) the new variables  $\{\mu, \rho\}$ . The question is whether the opposite is true, i.e. can  $\{\mu, \rho\}$  determine  $\{N, V_{ext}\}$ ? The answer is yes, and is provided by the Hohenberg–Kohn theorems for DFT [5] which state that  $V_{ext}$  is determined,

within an additive constant ( $\mu$ ), by  $\rho$ . Of course,  $\rho$  determines  $N$  by quadrature. Since the transform  $\{N, V_{ext}\} \leftrightarrow \{\mu, \rho\}$  is well defined one finds that the corresponding Hessian matrices are not singular and each inverse of the other, i.e.

$$\frac{\partial(N, V_{ext})}{\partial(\mu, \rho)} \frac{\partial(\mu, \rho)}{\partial(N, V_{ext})} = \text{Id} \quad (37)$$

where Id is the identity matrix in the extended variable space. More explicitly

$$\int \left( \frac{\delta \rho(\mathbf{r}_3)}{\delta V_{ext}(\mathbf{r}_1)} \right)_N \left( \frac{\delta V_{ext}(\mathbf{r}_2)}{\delta \rho(\mathbf{r}_3)} \right)_\mu d\mathbf{r}_3 + \left( \frac{\delta \mu}{\delta V_{ext}(\mathbf{r}_1)} \right)_N \left( \frac{\partial V_{ext}(\mathbf{r}_2)}{\partial \mu} \right)_\rho = \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (38)$$

$$\int \left( \frac{\delta \rho(\mathbf{r}_3)}{\delta V_{ext}(\mathbf{r}_1)} \right)_N \left( \frac{\delta N}{\delta \rho(\mathbf{r}_3)} \right)_\mu d\mathbf{r}_3 + \left( \frac{\delta \mu}{\delta V_{ext}(\mathbf{r}_1)} \right)_N \left( \frac{\partial N}{\partial \mu} \right)_\rho = 0 \quad (39)$$

$$\int \left( \frac{\partial \rho(\mathbf{r}_3)}{\partial N} \right)_{V_{ext}} \left( \frac{\delta V_{ext}(\mathbf{r}_2)}{\delta \rho(\mathbf{r}_3)} \right)_\mu d\mathbf{r}_3 + \left( \frac{\partial \mu}{\partial N} \right)_{V_{ext}} \left( \frac{\partial V_{ext}(\mathbf{r}_2)}{\partial \mu} \right)_\rho = 0 \quad (40)$$

$$\int \left( \frac{\partial \rho(\mathbf{r}_3)}{\partial N} \right)_{V_{ext}} \left( \frac{\delta N}{\delta \rho(\mathbf{r}_3)} \right)_\mu d\mathbf{r}_3 + \left( \frac{\partial \mu}{\partial N} \right)_{V_{ext}} \left( \frac{\partial N}{\partial \mu} \right)_\rho = 1. \quad (41)$$

These equations can be simplified by means of equations (18) and (36). On the one hand, equation (18) implies

$$\left( \frac{\delta N}{\delta \rho(\mathbf{r}_3)} \right)_\mu = 1 \quad (42)$$

and

$$\left( \frac{\partial N}{\partial \mu} \right)_\rho = 0, \quad (43)$$

which substituted into equations (39) and (41) lead, respectively, to

$$\int \left( \frac{\delta \rho(\mathbf{r}_2)}{\delta V_{ext}(\mathbf{r}_1)} \right)_N d\mathbf{r}_2 = 0 \quad (44)$$

and

$$\int \left( \frac{\partial \rho(\mathbf{r}_3)}{\partial N} \right)_{V_{ext}} d\mathbf{r}_3 = 1. \quad (45)$$

We note that equations (44) and (45) can also be obtained by direct derivation of equation (18). We also note that equation (44) is equation (19) written in the extended variable space formalism. On the other hand, equation (36) implies

$$\left( \frac{\partial V_{ext}(\mathbf{r}_2)}{\partial \mu} \right)_\rho = 1 \quad (46)$$

and

$$\left( \frac{\delta V_{ext}(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)} \right)_\mu = -\frac{\delta^2 \mathcal{F}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}. \quad (47)$$

The symmetry of the latter equation can be seen as a direct consequence of the following Maxwell relations that arise from the Legendre transform

$$\left( \frac{\delta \rho(\mathbf{r}_1)}{\delta V_{ext}(\mathbf{r}_2)} \right)_N = \left( \frac{\delta \rho(\mathbf{r}_2)}{\delta V_{ext}(\mathbf{r}_1)} \right)_N = -\beta G(\mathbf{r}_1, \mathbf{r}_2) \quad (48)$$



$$\left(\frac{\partial \rho(\mathbf{r}_1)}{\partial N}\right)_{V_{ext}} = \left(\frac{\delta \mu}{\delta V_{ext}(\mathbf{r}_1)}\right)_N \quad (49)$$

$$\left(\frac{\delta V_{ext}(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)}\right)_\mu = \left(\frac{\delta V_{ext}(\mathbf{r}_2)}{\delta \rho(\mathbf{r}_1)}\right)_\mu = -\frac{\delta^2 \mathcal{F}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \equiv -\beta^{-1} L(\mathbf{r}_1, \mathbf{r}_2) \quad (50)$$

$$\left(\frac{\partial V_{ext}(\mathbf{r}_1)}{\partial \mu}\right)_\rho = \left(\frac{\delta N}{\delta \rho(\mathbf{r}_1)}\right)_\mu, \quad (51)$$

where we have defined the ‘inverse’ kernel  $L$  and identified the density–density correlation function  $G$ . Next, substituting equation (46) into equations (38) and (40), and using the preceding Maxwell relations, we obtain

$$\int G(\mathbf{r}_1, \mathbf{r}_3) L(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 + \left(\frac{\partial \rho(\mathbf{r}_1)}{\partial N}\right)_{V_{ext}} = \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (52)$$

$$\int \left(\frac{\partial \rho(\mathbf{r}_3)}{\partial N}\right)_{V_{ext}} L(\mathbf{r}_1, \mathbf{r}_3) d\mathbf{r}_3 = \beta \left(\frac{\partial \mu}{\partial N}\right)_{V_{ext}} \quad (53)$$

which are the OZ relations in the CE.

### 3.4. Yet another Ornstein–Zernike relation

Let us consider the ‘inverse’ route to the single-variable approach of section 3.1. Taking into account the Euler–Lagrange equation (27) we consider that, instead of  $V_{ext}$ , the conjugate variable of  $\rho$  is the generalized external potential

$$v(\mathbf{r}) \equiv \mu - V_{ext}(\mathbf{r}) = \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r})} \quad (54)$$

which is, of course, different from the GCE  $v_{gc}$ . Then, we are now in a situation analogous to that of section 2: equation (54) together with the CE intrinsic free-energy functional  $\mathcal{F}$  allows one to consider a Legendre transform that leads to a CE functional  $\Omega[\rho]$  defined like its GCE counterpart (8). Again, one has a variational principle like that of equation (10) and analogous to the OZ relation (13) but now formulated in the CE:

$$\int \frac{\delta v(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_3)} \frac{\delta \rho(\mathbf{r}_3)}{\delta v(\mathbf{r}_2)} d\mathbf{r}_3 = \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (55)$$

Of course, the above procedure is only possible if the transform  $\rho \leftrightarrow v$  is a good change of variables and equation (55) is well defined in the CE. This can be demonstrated by noticing that this equation has been previously obtained by Ramshaw [8] and by Hernando and Blum [9] following a completely different approach based on the asymptotic behaviour of the two-body correlation functions in the CE fluid [11]. Furthermore, as we show below, equation (55) is equivalent to the OZ relations obtained in section 3.3. In order to compare with the functions  $G(\mathbf{r}_1, \mathbf{r}_2)$  and  $L(\mathbf{r}_1, \mathbf{r}_2)$  defined in equations (48) and (50), respectively, let us denote

$$\hat{G}(\mathbf{r}_1, \mathbf{r}_2) = \beta^{-1} \frac{\delta \rho(\mathbf{r}_1)}{\delta v(\mathbf{r}_2)} \quad (56)$$

and

$$\hat{L}(\mathbf{r}_1, \mathbf{r}_2) = \beta \frac{\delta v(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)}, \quad (57)$$

so that equation (55) can be re-expressed as

$$\int \hat{G}(\mathbf{r}_1, \mathbf{r}_3) \hat{L}(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 = \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (58)$$

In what follows, we show that this equation is indeed equivalent to the OZ relations (52) and (53). We first obtain appropriate expressions for  $\hat{G}$  and  $\hat{L}$  in terms of  $G$  and  $L$ , respectively, and then we show the equivalence. Taking into account that the CE density  $\rho$  is the same for all Legendre representations, we consider  $\rho = \rho(\mathbf{r}, N, [V_{ext}])$  and, using the chain rule for derivation, we obtain

$$\begin{aligned}\beta\hat{G}(\mathbf{r}_1, \mathbf{r}_2) &= \int \left( \frac{\delta\rho(\mathbf{r}_1)}{\delta V_{ext}(\mathbf{r}_3)} \right)_N \frac{\delta(\mu - v(\mathbf{r}_3))}{\delta v(\mathbf{r}_2)} d\mathbf{r}_3 + \left( \frac{\partial\rho(\mathbf{r}_1)}{\partial N} \right)_{V_{ext}} \frac{\delta N}{\delta v(\mathbf{r}_2)} \\ &= \beta G(\mathbf{r}_1, \mathbf{r}_2) + \left( \frac{\partial\rho(\mathbf{r}_1)}{\partial N} \right)_{V_{ext}} \frac{\delta N}{\delta v(\mathbf{r}_2)}\end{aligned}\quad (59)$$

where we have used equations (44) and (48). Next, considering that  $\hat{G}(\mathbf{r}_1, \mathbf{r}_2) = \hat{G}(\mathbf{r}_2, \mathbf{r}_1)$ ,  $G(\mathbf{r}_1, \mathbf{r}_2) = G(\mathbf{r}_2, \mathbf{r}_1)$ , and taking into account equations (44) and (45), we obtain

$$\frac{\delta N}{\delta v(\mathbf{r}_2)} = \int \beta\hat{G}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = C \left( \frac{\partial\rho(\mathbf{r}_2)}{\partial N} \right)_{V_{ext}} \quad (60)$$

where a further integration leads to

$$C = \int \frac{\delta N}{\delta v(\mathbf{r}_1)} d\mathbf{r}_1 = \int \int \beta\hat{G}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (61)$$

So, we obtain the result of Ramshaw [8]

$$\beta\hat{G}(\mathbf{r}_1, \mathbf{r}_2) = \beta G(\mathbf{r}_1, \mathbf{r}_2) + C \left( \frac{\partial\rho(\mathbf{r}_1)}{\partial N} \right)_{V_{ext}} \left( \frac{\partial\rho(\mathbf{r}_2)}{\partial N} \right)_{V_{ext}} \quad (62)$$

with  $C$  given by equation (61). Furthermore, from the definitions of  $L$  and  $\hat{L}$  one has

$$\hat{L}(\mathbf{r}_1, \mathbf{r}_2) = \beta \frac{\delta^2 \mathcal{F}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} \equiv L(\mathbf{r}_1, \mathbf{r}_2). \quad (63)$$

Using equations (62) and (63), from equation (52) we obtain

$$\begin{aligned}&\int \hat{G}(\mathbf{r}_1, \mathbf{r}_3) \hat{L}(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 - \delta(\mathbf{r}_1 - \mathbf{r}_2) \\ &= - \left( \frac{\partial\rho(\mathbf{r}_1)}{\partial N} \right)_{V_{ext}} \left[ 1 - \frac{C}{\beta} \int \hat{L}(\mathbf{r}_1, \mathbf{r}_3) \left( \frac{\partial\rho(\mathbf{r}_3)}{\partial N} \right)_{V_{ext}} d\mathbf{r}_3 \right]\end{aligned}\quad (64)$$

which becomes the OZ relation (58) because, using equations (57) and (60) and the chain rule for derivation, one has

$$\frac{C}{\beta} \int \hat{L}(\mathbf{r}_1, \mathbf{r}_3) \left( \frac{\partial\rho(\mathbf{r}_3)}{\partial N} \right)_{V_{ext}} d\mathbf{r}_3 = \int \frac{\delta v(\mathbf{r}_3)}{\delta\rho(\mathbf{r}_1)} \frac{\delta N}{\delta v(\mathbf{r}_3)} d\mathbf{r}_3 = \frac{\delta N}{\delta\rho(\mathbf{r}_1)} = 1. \quad (65)$$

From equations (65) and (53) one obtains

$$\beta \left( \frac{\partial\mu}{\partial N} \right)_{V_{ext}} = C^{-1}, \quad (66)$$

in agreement with the results of Ramshaw [8] and Lebowitz and Percus [11].

Finally, we note that it is not difficult to show that the results of Ramshaw [8] lead to the results obtained in section 3.3, i.e. equation (58) together with equations (62), (63) and (66) yield the OZ relations (52) and (53).

## 4. Applications

### 4.1. The ideal gas

The Helmholtz free energy of the classical ideal gas is given by

$$-\beta F_N[V_{ext}] = N \log \left( \Lambda^{-3} \int \exp[-\beta V_{ext}(\mathbf{r})] d\mathbf{r} \right) - \log N!. \quad (67)$$

From equation (28) we obtain

$$\rho(\mathbf{r}, N, [V_{ext}]) = N \frac{\exp[-\beta V_{ext}(\mathbf{r})]}{\int \exp[-\beta V_{ext}(\mathbf{r})] d\mathbf{r}} \quad (68)$$

and from equation (29)

$$-\beta \mu(N, [V_{ext}]) = \log \left( \Lambda^{-3} \int \exp[-\beta V_{ext}(\mathbf{r})] d\mathbf{r} \right) - (\log N!)', \quad (69)$$

where the prime (') denotes derivation w.r.t.  $N$ . These results can be inverted. From equations (68) and (69) we obtain

$$-\beta V_{ext}(\mathbf{r}, \mu, [\rho]) = -\beta \mu + \log(\Lambda^3 \rho(\mathbf{r})) + (\log N!)' - \log N, \quad (70)$$

where  $N = N[\rho] = \int \rho(\mathbf{r}) d\mathbf{r}$  is trivially obtained from integration of equation (68). Inserting these expressions into equation (35) yields the intrinsic free-energy functional of the ideal gas in the CE [12]

$$\beta \mathcal{F}_{id}[\rho] = - \int \rho(\mathbf{r}) (\log(\Lambda^3 \rho(\mathbf{r})) - 1) d\mathbf{r} + \phi \left( \int \rho(\mathbf{r}) d\mathbf{r} \right) \quad (71)$$

with  $\phi(x) = \log x! - x \log x + x$ . This functional differs from the well-known result in the GCE by the term  $\phi(\int \rho(\mathbf{r}) d\mathbf{r})$ , i.e. by  $\phi(N)$ . For large  $N$ ,  $\phi(N) \approx (\log N)/2$ , in agreement with the saddle point approximation of [14].

From equation (35) one has  $U_{id}(\mu, [\rho]) = \beta \mathcal{F}_{id}[\rho] - \mu \int \rho(\mathbf{r}) d\mathbf{r}$ . Substituting this expression in equations (31)–(34), which define the variational principle in the extended variable space, we recover the results (67)–(69) for the Helmholtz free energy, the density and the chemical potential, respectively. Of course, equation (71) together with the Euler–Lagrange equation (27) and the constraint (18) yield the same results.

In what follows, we test the OZ equations (52) and (53) for the ideal gas. The density–density correlation function is readily obtained from equations (68) and (48). We obtain the result

$$G_{id}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \frac{1}{N} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2), \quad (72)$$

where, from equation (20) we obtain the well-known result for the total correlation function  $h_{id} = -1/N$ . The ‘inverse’ kernel is obtained from equations (70) and (50):

$$L_{id}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)} \delta(\mathbf{r}_1 - \mathbf{r}_2) - \frac{1}{N} + (\log N!)'. \quad (73)$$

Inserting these results into equation (52) we obtain for the ideal gas

$$\left( \frac{\partial \rho(\mathbf{r}_1)}{\partial N} \right)_{V_{ext}} = \frac{\rho(\mathbf{r}_1)}{N} \quad (74)$$

and, substituting equations (73) and (74) into equation (53) we obtain

$$\beta \left( \frac{\partial \mu_{id}}{\partial N} \right)_{V_{ext}} = (\log N!)''. \quad (75)$$

Equations (74) and (75) coincide, respectively, with the results that one would directly obtain from derivation of equations (68) and (69), which shows the consistency of the OZ relations (52) and (53).

On the other hand, if we consider the modified density–density correlation function (62), we obtain

$$\hat{G}_{id}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2) + \left( \frac{1}{N^2(\log N!)''} - \frac{1}{N} \right) \rho(\mathbf{r}_1)\rho(\mathbf{r}_2). \quad (76)$$

Following Ramshaw [8] and Hernando and Blum [9], one can introduce a modified total correlation function  $\hat{h}$  via  $\hat{G}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\hat{h}(\mathbf{r}_1, \mathbf{r}_2) + \rho(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2)$ . In the present case, this function reduces to  $\hat{h}_{id} = (N^2(\log N!)'')^{-1} - N^{-1}$ . Since, for large  $N$ ,  $(\log N!)'' \sim N^{-1} + O(N^{-2})$ , we obtain that  $\hat{h}_{id}$  is equal to  $h_{id}$  stripped off from its leading asymptotic behaviour, in agreement with previous results [9]. Finally, taking into account that  $\hat{L} = L$ , one can check that equations (76) and (73) fulfil the OZ relation (58).

#### 4.2. The direct correlation function in the CE

In analogy with the GCE we introduce the CE direct correlation function  $c^{(2)}$  as

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\delta^2(\mathcal{F}[\rho] - \mathcal{F}_{id}[\rho])}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} \quad (77)$$

with  $\mathcal{F}_{id}$  given by equation (71). Using equations (77) and (50) the ‘inverse’ kernel (50) can be rewritten as

$$L(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)}\delta(\mathbf{r}_1 - \mathbf{r}_2) - \frac{1}{N} + (\log N!)'' - c^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \quad (78)$$

From this expression and (20) one can rewrite the OZ relations (52) and (53) in terms of the total and the direct correlation functions. We obtain

$$h(\mathbf{r}_1, \mathbf{r}_2) = c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \int \rho(\mathbf{r}_3)c^{(2)}(\mathbf{r}_1, \mathbf{r}_3)h(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 - \frac{1}{\rho(\mathbf{r}_2)} \left( \frac{\partial\rho(\mathbf{r}_2)}{\partial N} \right)_{V_{ext}} \quad (79)$$

and

$$\beta \left( \frac{\partial\mu}{\partial N} \right)_{V_{ext}} = \beta \left( \frac{\partial\mu_{id}}{\partial N} \right)_{V_{ext}} + \frac{1}{\rho(\mathbf{r}_1)} \left( \frac{\partial\rho(\mathbf{r}_1)}{\partial N} \right)_{V_{ext}} - \frac{1}{N} - \int \left( \frac{\partial\rho(\mathbf{r}_2)}{\partial N} \right)_{V_{ext}} c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2, \quad (80)$$

where we have used equation (75). Multiplying equation (80) by  $\rho(\mathbf{r}_1)$ , integrating over  $\mathbf{r}_1$  and using equation (45), we obtain

$$\beta \left( \frac{\partial\mu}{\partial N} \right)_{V_{ext}} = \beta \left( \frac{\partial\mu_{id}}{\partial N} \right)_{V_{ext}} - \frac{1}{N} \int \int \rho(\mathbf{r}_1) \left( \frac{\partial\rho(\mathbf{r}_2)}{\partial N} \right)_{V_{ext}} c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (81)$$

We note that this important relation can be considered as the CE version of the GCE compressibility equation. We also note that the related equation in terms of the total correlation function is simply the normalization relation (23).

Finally, from equations (80) and (81), we obtain the following relation that links the derivative of the density w.r.t.  $N$  to the direct correlation function:

$$\left( \frac{\partial\rho(\mathbf{r}_2)}{\partial N} \right)_{V_{ext}} = \frac{\rho(\mathbf{r}_2)}{N} \left( 1 + \int \int \rho(\mathbf{r}_1) \left( \frac{\partial\rho(\mathbf{r}_3)}{\partial N} \right)_{V_{ext}} (c^{(2)}(\mathbf{r}_2, \mathbf{r}_3) - c^{(2)}(\mathbf{r}_1, \mathbf{r}_3)) d\mathbf{r}_1 d\mathbf{r}_3 \right). \quad (82)$$

### 4.3. The uniform fluid

The equations derived in the previous subsection are notably simplified in the uniform limit. In this limit, one has  $\partial\rho/\partial N = \rho/N$  because  $\rho = N/V$ , where  $V$  is the volume of the system. Therefore, equation (79) becomes

$$h(r_{12}) = c^{(2)}(r_{12}) + \rho \int c^{(2)}(r_{13})h(r_{32}) \, dr_3 - \frac{1}{N} \quad (83)$$

where  $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ . We have taken into account that the uniform fluid is both translationally and rotationally invariant. This equation only differs by the term  $1/N$  from its GCE analogue. From equation (81) one obtains the compressibility equation

$$(\rho k_B T \chi)^{-1} = (\rho k_B T \chi_{id})^{-1} - \rho \int c^{(2)}(r) \, dr \quad (84)$$

where  $r = |\mathbf{r}|$ . Following Lebowitz and Percus [11] we have considered the identity  $(\rho \chi)^{-1} = N(\partial\mu/\partial N)_{V_{ext}}$ , where  $\chi$  is the isothermal compressibility of the system.

## 5. Summary

In this paper we have shown how the use of Legendre transform techniques can be of great help in the DFT analysis of fluids in the CE.

The direct generalization to the CE of the GCE approach leads to a Hessian matrix that is singular due to the fixed- $N$  constraint. This singular behaviour does not allow for deriving an OZ relation as in the GCE. In spite of this, by resorting to the Lagrange multiplier technique, one can still obtain a Euler–Lagrange equation for the equilibrium density. The Lagrange multiplier associated to the fixed- $N$  constraint turns out to be the chemical potential  $\mu$ .

The failure of the direct approach to give an OZ relation in the CE is bypassed by considering an extended variable space in which  $N$  and  $\mu$  are considered as conjugate variables that, in addition to the density and the external potential, play an important role in the variational treatment of the problem. In this approach, the related Hessian matrix is no longer singular and an OZ equation is obtained by equating the product of the Hessian matrix by its inverse to the identity matrix. The OZ relations can be further simplified by taking into account the fixed- $N$  constraint and the Maxwell relations that arise naturally in the theory. We obtain a set of two equations linking the density–density correlation function  $G$ , the ‘inverse’ kernel  $L$  and the derivatives  $(\partial\rho(\mathbf{r})/\partial N)_{V_{ext}}$  and  $(\partial\mu/\partial N)_{V_{ext}}$ .

The CE Euler–Lagrange equation suggests an additional Legendre transform with a non-singular Hessian matrix and thus another equivalent OZ relation can be formulated. This new relation is the same as that previously obtained by Ramshaw [8] and by Hernando and Blum [9] by considering the asymptotic behaviour of the two-body correlation function. While the modified inverse kernel  $\hat{L}$  involved in the new OZ equation coincides with the former one  $L$ , the modified density–density correlation function  $\hat{G}$  is equal to the former one  $G$  stripped off from its asymptotic behaviour.

The application of the extended variable space formalism to the ideal gas allows us to obtain the CE intrinsic free-energy functional  $\mathcal{F}_{id}$ . The CE direct correlation function  $c^{(2)}$  is then defined as the second functional derivative w.r.t. the density of the excess over the ideal free-energy functional. The OZ relation is rewritten in terms of  $c^{(2)}$  and the total correlation function  $h$ . Finally, for the uniform fluid in the CE, one can obtain a compressibility equation and an OZ equation that only differs from its GCE counterpart by the term  $1/N$ .

## Acknowledgments

We are grateful for financial support from the Comisión Interministerial de Ciencia y Tecnología of Spain under grant PB 98-0261 and from Junta de CyLyFSE under grant SA097/01.

## References

- [1] Evans R 1979 *Adv. Phys.* **28** 143
- [2] Parr R G and Yang W 1989 *Density-Functional Theory of Atoms and Molecules* (Oxford: Oxford University Press)
- [3] Evans R 1992 *Fundamentals of Inhomogeneous Fluids* ed D Henderson (New York: Dekker) p 85
- [4] Ashcroft N W 1995 *Density Functional Theory* ed E K U Gross and R M Dreizler (New York: Plenum) p 581
- [5] Kohn W 1995 *Density Functional Theory* ed E K U Gross and R M Dreizler (New York: Plenum) p 3
- [6] Argaman N and Makov G 2000 *Am. J. Phys.* **68** 69
- [7] Caillol 2001 *Preprint cond-mat/0104390*
- [8] Ramshaw J D 1980 *Mol. Phys.* **41** 219
- [9] Hernando J A and Blum L 2001 *J. Phys.: Condens. Matter* **13** L577  
Hernando J A 2001 *Preprint cond-mat/0106569*
- [10] Nalewajski R F and Parr R G 1982 *J. Chem. Phys.* **77** 399  
Nalewajski R F and Capitani J F 1982 *J. Chem. Phys.* **77** 2514  
Baekelandt B G, Cedillo A and Parr R G 1995 *J. Chem. Phys.* **103** 8548
- [11] Lebowitz J L and Percus J K 1961 *Phys. Rev.* **122** 1675
- [12] White J A and Velasco S 2001 *Europhys. Lett.* **54** 475
- [13] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)
- [14] White J A, González A, Román F L and Velasco S 2000 *Phys. Rev. Lett.* **84** 1220