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Modifications of the Ornstein–Zernike relation and the LMBW equations in the canonical ensemble via Hilbert-space methods

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Abstract

The application of the density functional formalism to the canonical ensemble is of practical interest in cases where there is a marked difference between, say, the canonical and the grand canonical ensemble (cavities or pores). An important role is played by the necessary modification of the famous Ornstein–Zernike relation between the pair correlation and the direct correlation function, as the former is no longer invertible in the strict sense in (finite) canonical ensembles. Here we approach the problem from a different direction which may complement the density functional approach. In particular, we develop rigorous canonical ensemble versions of the LMBW equations, relating density gradient and exterior potential in the presence of explicit (singular) containing potentials. This is accomplished with the help of an integral operator and Hilbert space methods, yielding among other things representations of the direct correlation function on certain subspaces. The results are particularly noteworthy and transparent if the segregating potential is a linear (gravitational) one. In this case the modifications in the LMBW equations can be expressed as pure, seemingly non-local integrations over the container boundaries.

1. Introduction

Recently there has been renewed interest in the application of the density functional method to the canonical ensemble (CE). One of the more practical reasons is the investigation of fluids in cavities or pores that are so small that the results depend on the choice of the ensemble (see, e.g., [1] or, for a short review, [2]). One of the methods that has turned out to be quite useful for the description of finite systems consists of the so-called density functional theory.

However, in its customary form this method requires the use of a grand canonical ensemble (GCE), i.e. an open system. Consequently this restriction has led to the (re)consideration of the question of how far the methods of density functional theory can be transferred to the case of closed systems that have to be described in the framework of a CE (cf [3] and the more recent papers [4–7]).

It is the constraint of a fixed number of particles which causes certain technical problems. The reason is discussed in the following. We note that these problems have already been observed in the past several times but, as remarked by Ramshaw [3], have occasionally been lost sight of or glossed over.

The density functional method is based on the observation that for a *finite* system the external potential, $v(r)$, and the one-particle density, $\rho(r)$, are standing in a one-to-one relation in a gas or fluid (see [8]). We note however that there may arise problems as to this property if one passes to the thermodynamic limit and one is in a regime where the system develops long-range correlations as, e.g., in the situation of phase transitions or spontaneous symmetry breaking.

In finite systems, however, this result leads, via the functional variation of $\rho(r)$ with respect to $v(r')$ and vice versa, to an important relation between the two-particle correlation function, $H(r, r')$ and its inverse, $C(r, r')$, the *direct correlation function*. This relation is frequently called the *Ornstein–Zernike relation*.

It has already been observed by Mermin [8], that this uniqueness relation cannot hold in the CE (in a finite volume), as the density remains the same under a constant shift of the external potential. The direct consequence of this fact is that

$$\int_V H(r, r') dr' = 0 \quad (1)$$

in the CE in a finite volume, V . Put differently, if we regard H, C as the kernels of the corresponding integral operators, \mathbf{H}, \mathbf{C} on some function spaces, the constant functions are *zero eigenfunctions* of \mathbf{H} . This implies that it cannot be straightforwardly inverted and hence the direct correlation function, C , is (or rather seems to be) ill-defined (see appendix). This is, in a nutshell, the *problem of the Ornstein–Zernike relation* in the CE.

The above phenomenon has been observed in the literature several times, but, nevertheless, it seems that it is by no means widely known (this has also been remarked upon in, e.g., [3]). We think it is the underlying psychological reason why people usually prefer to use the GCE without really being aware of the above result (on the surface it is the fact that in functional derivations one has to keep the particle number constant).

There have been several attempts in the past to remedy this problem (see the papers [3, 5–7] already cited above). As far as we can see, all of them seem to employ the functional variation method and arrive at more or less different recipes.

We entered this field from a slightly different direction. Our main interest centred around the long-standing and controversial issue of the behaviour of the, say, liquid–gas interface when treated from practically first principles, that is, within the regime of microscopic statistical mechanics. An important role in this context is played by the famous LMBW equations and their corresponding hierarchies [9, 10] (see the next sections). The underlying common assumption in both fields is the above mentioned one-to-one dependence between exterior field and one-particle density.

In [11] we discussed in quite some detail what can happen if there exist long-range correlations in the system or in the interface between coexisting phases (as, e.g., for vanishing gravitational field in the liquid–gas interface). We note that one cannot avoid these problems by making the calculations in finite systems and passing to the thermodynamic limit afterwards. In that case one has to control the uniformity of convergence of various expressions in this

limit which is typically lost. For more discussion in this direction see also [12] or [13] and further references therein.

The present paper is organized as follows: in section 2 the first LMBW equation (the one involving the density–density correlation H) is dealt with in the framework of the CE. In particular, the exceptional significance of boundary terms brought about by the necessary confining part of the exterior potential is exhibited. Moreover, for the special case where the non-confining (segregating) part of the potential is chosen to be linear, it is shown that only boundary integrations survive on the rhs of the LMBW equation, which corroborates the important role of long-ranged correlations and the delicacy of interchanging limits.

In section 3 we derive a suitable generalization of the Ornstein–Zernike relation for the CE case. In contrast to previous methods discussed in the literature, we refrain from explicit recourse to density functional theory. Extensive use is made instead of Hilbert space methods, the main point being the restriction of the non-invertible integral operator \mathbf{H} to a subspace where it is again invertible. The correction terms for the Ornstein–Zernike relation appearing in our approach are then compared with those in the previous proposals [3, 5–7].

Our results allow in particular for an immediate derivation of a (generalized) version of the second LMBW equation (the one involving the direct correlation function C) for the CE. This is done in section 4 and it turns out that boundary terms also have great significance for the case of the second LMBW equation. In fact, whenever the non-confining part of the exterior potential is chosen to be linear, the integrations involved can be shown to completely reduce to boundary integrations again.

The paper is then concluded with a summary. Furthermore, an appendix is devoted to the fixing of some elementary notions and notations.

2. The first LMBW equation in the canonical ensemble

In the following we will study systems in a finite closed container, V , the walls being explicitly incorporated via appropriate *containing potentials*. We now briefly describe how the containing potential is fed into the respective expressions. We split the total external potential into a *segregating (bulk) potential* and a *containing potential*.

$$v(r) = v_s(r) + v_c(r). \quad (2)$$

One of the technical advantages of this method is that one can perform the calculations as if one were in an infinite system since v_c brings all quantities down to zero outside of V (see below). Furthermore, we can perform a rigorous *scaling limit* of $v_c(r)$ near the walls, thus getting an exact expression for systems being contained by *ideal hard walls*.

We start with a realistic wall potential, v_c , which is assumed to be only dependent on the coordinate normal to the wall and which is concentrated in a thin layer adjacent to the system boundary, ∂V , with v_c diverging smoothly to $+\infty$ at the boundary and being $+\infty$ outside V . For reasons of simplicity we illustrate the procedure with the help of a wall sitting at $x = 0$, the system being contained in the half-space $x \leq 0$.

Assumption 2.1. $v_c(x)$ is assumed to be smooth for $x \leq 0$, $v_c(x)$ being identically zero for $x \leq -a_0 < 0$ and $v_c(x) = +\infty$ for $x \geq 0$.

An infinitely hard wall is represented by the scaling limit, $\lambda \rightarrow \infty$, of $v_c^\lambda(x) = v_c(\lambda x)$. It is instructive to control various quantities when one of the coordinates passes through the wall. Under these circumstances the expressions are dominated by the term $\exp(-\beta v_c(r))$, with $v_c(r) \rightarrow \infty$ at the wall. That is, we have for finite systems (where all the expressions can be rigorously controlled),

$$H(r, r') = f(r, r') \exp(-\beta v_c(r')) \quad (3)$$

with $f(r, r')$ continuous across the system boundary as long as r is sitting in the bulk. The same applies to $\rho(r)$ for r passing through the wall. We have

$$\rho(r) = f(r) \exp(-\beta v_c(r)) \quad (4)$$

with $f(r)$ again being continuous across the wall.

In contrast to most of the approaches to the topic described in the introduction, we want to choose the route via a rigorous derivation of the LMBW equations, which describe the relation between $\nabla\rho(r)$ and $\nabla v(r)$ by means of the correlation functions $H(r, r')$ and $C(r, r')$.

The LMBW hierarchies were described in [9, 10] with the help of *density functional* methods. It is not made entirely explicit what happens with boundary terms if one uses containing potentials and/or performs the *thermodynamic limit*, $N, V \rightarrow \infty$, in the presence of possible *long-range correlations*. Concerning this particular important point, we had an interesting discussion with Lovett some time ago (see [14]; also [15]). He told us that [15] was in part influenced by our earlier work in [11] (see in particular section 5.3 of [15] to get a feeling of the epistemological problems underlying the need to perform a thermodynamic limit).

In the following we show how to cope appropriately with the possible singular terms which may emerge in this limit. The important point is that, in order to enclose a finite system in a container (unless one uses, e.g., periodic boundary conditions, which are a little bit artificial, as long as one does not perform a thermodynamic limit in the end), one should not gloss over the necessary bounding terms, which, as we showed rigorously, may have an effect even in this limit.

In [11] we started from the so-called Kubo–Martin–Schwinger (KMS) property of equilibrium systems which holds in finite as well as in infinite systems. We showed that both the BBGKY hierarchy and the first LMBW hierarchy emerge rigorously as the two opposite ends of one and the same scaling procedure, as long as certain *cluster properties* are fulfilled. If these cluster properties are violated, extra boundary terms may survive with possible severe consequences for concepts like the *Trizenberg–Zwanzig* formula for the surface tension.

As a particular result of [11] it turns out that for finite systems held together by an explicit containing potential of the sort described above, the first LMBW equation rigorously holds in the CE case (provided the containing potential is correctly dealt with). That is, we have for the first member of the hierarchy:

$$\nabla\rho(r) = -\beta \int H(r, r') \nabla v(r') \, dr' \quad (5)$$

with $v = v_s + v_c$. What interests us here is the term on the rhs including the containing potential v_c . It reads:

$$-\beta \int H(r, r') \nabla v_c(r') \, dr'. \quad (6)$$

We can simulate ideal hard walls by the method described above. Using again as an illustration a wall, sitting at $x = 0$ and being supported in $(-a_0, 0)$ with $v_c = \infty$ for $x \geq 0$, we can rigorously perform the scaling process with $v_c^\lambda(x) := v_c(\lambda x)$ and get (for the wall described above):

$$-\beta \int H(r, r') \partial_x v_c^\lambda(r') \, dr' = -\beta \int f(r, r') \exp(-\beta v_c^\lambda(x)) \partial_x v_c^\lambda(x) \, dx \, dr'^{(d-1)} \quad (7)$$

(d denoting the space dimension).

Making a variable transformation, $x' := \lambda x$, we get

$$\int f(r, r'; x'/\lambda) \partial_{x'} \exp(-\beta v_c(x')) \, dx' \, dr'^{(d-1)} \quad (8)$$

where the meaning of the abbreviations should be clear. In the limit $\lambda \rightarrow \infty$ we hence get for the x' -integration (with $v_c(-a_0) = 0$, $v_c(0) = +\infty$):

$$\int f(r, r'; x = 0) \left(\int_{-a_0}^0 \partial_x \exp(-\beta v_c(x)) dx \right) dr'^{(d-1)} = - \int f(r, r'; x = 0) dr'^{(d-1)}. \quad (9)$$

Note that for a realistic (i.e. unscaled) containing potential, $H(r, r') \rightarrow 0$ strongly for $r' \rightarrow \partial V$ from the interior of V . In the case of an ideal hard wall (scaling limit) we have in general

$$H(r, r') \rightarrow H_+(r, r') \neq 0 \quad (10)$$

for $r' \rightarrow \partial V$ with the plus sign denoting the limit taken from the interior of V . For r' lying outside of V , $H(r, r')$ is of course zero in both cases with H_+ usually having a jump-discontinuity.

Conclusion 2.2. *In the case of an ideal hard wall the LMBW equation reads*

$$\nabla \rho(r) = -\beta \int_V H(r, r') \nabla v_s(r') dr' - \int_{\partial V} H_+(r, r') d\bar{o}' \quad (11)$$

with $d\bar{o}'$ the outwardly oriented (vector-valued) surface element. Note that $H_+(r, r')$ now depends only on the segregation potential v_s .

Remark. We ignore the situation near possible points of the containing surface, ∂V , where the surface normal may change discontinuously. These points do not contribute in the scaling limit as they are of measure zero and can be avoided anyway by making the surface smooth.

Frequently the external gravitational potential is represented by a linear term, $v_s(r) := mgz$, namely

$$\nabla v_s(r) = mge_z \quad (12)$$

(e_z being the unit vector in z -direction). While for infinite systems one has to take into account the unboundedness from below of such a linear term, everything is well defined for a finite volume.

Our above version of the first LMBW equation in the CE has the following, as we think, interesting consequence.

Observation 2.3. *As a result of the exact vanishing of $\int_V H(r, r') dr'$ and the assumed linearity of v_s , we have*

$$\nabla \rho(r) = -\beta \int H(r, r') \nabla v_c(r') dr' \quad (13)$$

or

$$\nabla \rho(r) = - \int_{\partial V} H_+(r, r') d\bar{o}'. \quad (14)$$

Conclusion 2.4. *As the containing potential is assumed to have its support restricted to a thin layer adjacent to the walls of the container, H or H_+ must include macroscopic (long-range) density correlations between the infinitesimal neighbourhood of the container walls and the interior of the vessel as long as $\nabla \rho(r) \neq 0$.*

In [16] this phenomenon was attributed to finite size effects in the CE. A function like $\rho^{(2)}(r, r')$ with r' near or at the wall can be related to the *conditional probability* for finding a particle at position r in the bulk, say, under the assumption that another particle is sitting at a fixed position, r' , near the wall. For free systems or short range correlations this quantity is expected to be (approximately) related to the two-particle distribution function for a $(N - 1)$ -particle system within V .

The consequence for the two-particle correlation function, $H(r, r')$, is that for large separation (r in the bulk, r' near the wall), i.e. $|r - r'| \rightarrow \infty$ in a necessarily vague (or, rather, pragmatic) sense in a large but finite system, it does not go exactly to zero in a CE but a finite size effect term of the order $O(N^{-1})$ survives.

These observations therefore furnish us with an exceedingly transparent example for which we can scrutinize some of the problems posed by Lovett and Buff in section 5.3 of [15]. In particular, it can now be clearly seen that there are indeed cases for which the structure at remote boundaries determines the local state of a system. The main point to be stated here is that this feature can nevertheless be brought into accord with the option to perform a thermodynamic limit. This is due to the extreme non-uniformity of the latter. For every single finite system with $N = \text{constant}$ the density gradient is expressed exclusively in terms of boundary integrations without explicit recourse to the segregating part of the potential due to the vanishing of $\int H(r, r') dr'$. On the other hand, after having performed the thermodynamic limit, the information previously encoded in the boundary terms seems to have become unaccessible. However, it is by no means lost! It has merely been shifted to the segregating potential term which ceases to vanish in the $N = \infty$ case as the constant functions are no longer zero eigenfunctions of \mathbf{H} there.

We have already emphasized in [11] the important point that the interchange of limits in the derivation of the LMBW equation may be a delicate matter, as the various limits might behave in a highly non-uniform way. Here we have seen that in the CE such non-uniform behaviour is even indispensable in order to have meaningful thermodynamic limit states!

Remark. As was already mentioned, a linear segregating potential is unbounded from below, and it is therefore necessary to retain parts of the boundary walls in order to keep the system stable as $N, V \rightarrow \infty$. This does however not invalidate the above considerations.

For the ideal gas these effects can be easily calculated. Without an external potential $v_s(r)$ we have

$$\rho^{(2)}(r, r') - \rho(r)\rho(r') = V^{-2}(N^2 - N) - V^{-2}N^2 = -(N/V)V^{-1} \sim N^{-1}. \quad (15)$$

With $v_s(r)$ non-zero (and $r \neq r'$) we get:

$$H(r, r') = \rho^{(2)}(r, r') - \rho(r)\rho(r') = -N \exp(-\beta(v(r) + v(r'))) \left(\int \exp(-\beta v(r)) dr \right)^{-2}. \quad (16)$$

The details of the scaling with the size of the system can be inferred from the following set up. We take, e.g., a rectangular parallelepiped with area of the base equal to A , height equal to h and with the base located at $z = 0$, the exterior potential being only z -dependent. We arrive at:

$$H(r, r') = -NA^{-2} \left(\int \exp(-\beta v(z)) dz \right)^{-2} \exp(-\beta(v(r) + v(r'))) \quad (17)$$

and in the particular case $v(z) = mgz$ this is equal to

$$-NA^{-2}(\beta mg)^2(1 - e^{-\beta(mgh)})^{-2} \exp(-\beta(mgz + mgz')). \quad (18)$$

Inserting the corresponding terms in the expression for $H(r, r')$, $r \neq r'$, in the GCE we get on the other hand for the ideal gas:

$$\rho^{(2)}(r, r') - \rho(r)\rho(r') = 0. \quad (19)$$

If we take the limit $h \rightarrow \infty$ with N/A kept fixed, we end up with the *barometric formula*:

$$H(z, 0) = (N/A)A^{-1}(\beta mg)^2 \exp(-\beta mgz). \quad (20)$$

That is, H scales as A^{-1} . The LMBW equation leads to

$$d/dz(\rho(z)) = (N/A)(\beta mg)^2 \exp(-\beta mgz). \quad (21)$$

or

$$\rho(z) = (N/A)(\beta mg) \exp(-\beta mgz). \quad (22)$$

Conclusion 2.5. *The local law between density and exterior potential is in the LMBW equation hidden in the non-local integration over the container walls. It can, however, be shown that in the case of the ideal gas this reduces basically to an application of Gauss's divergence theorem.*

Remark. Even in the case of a zero external field and ideal hard walls the individual contributions of the walls on $\nabla\rho(r)$ in the bulk are non-vanishing and of mean-field type. In a finite volume and the ideal gas, however, they exactly compensate for each other such that we have in fact $\nabla\rho(r) = 0$, as is the case by calculating $\rho(r)$ directly. Once again we see from this that care has to be taken when performing the thermodynamic limit as the contributions do not decay and are independent of the distance of the respective walls!

3. The direct correlation function in the canonical ensemble

The ordinary Ornstein–Zernike relation

$$\int C(r, r'')H(r'', r') dr'' = \delta(r - r') \quad (23)$$

can be rewritten in integral operator notation as

$$\mathbf{C}\mathbf{H} = \mathbf{1} \quad (24)$$

where the integral operators \mathbf{C} and \mathbf{H} are defined as follows:

$$(\mathbf{C}f)(r) = \int C(r, r')f(r') dr'; \quad (\mathbf{H}f)(r) = \int H(r, r')f(r') dr'. \quad (25)$$

That is, \mathbf{C} is nothing but the (left) operator inverse of \mathbf{H} in some properly chosen linear space.

Some remarks are perhaps in order here concerning the reason for introducing Hilbert spaces in the following. In contrast to, say, quantum theory, there is no inner theoretical reason to employ the Hilbert space formalism. The operator \mathbf{H} lives on a certain space of functions. As the corresponding integral kernel $H(r, r')$ strongly decreases like $\exp(-\beta v_c(r'))$ when r' approaches the container walls, even singular functions like $\nabla v(r')$ are in the domain of definition of \mathbf{H} (see below). On the other hand, typically $C(r, r')$ diverges with the same degree when r' approaches the container walls. Hence it is only defined on a smaller space of functions than, e.g., $L^2(V)$. We conclude that \mathbf{H} naturally lives on a function space larger than $L^2(V)$, while \mathbf{C} lives on a smaller subspace of $L^2(V)$. In any case, \mathbf{C} is defined in the range of \mathbf{H} which is dense in $L^2(V)$ whenever \mathbf{H} does not possess (proper) eigenfunctions with eigenvalue zero. However, the validity of this latter property can only be expected if one works within the GCE.

If one works in the CE instead and again chooses $\mathfrak{H} = L^2(V)$ as the Hilbert space, it is immediately obvious that \mathbf{H} cannot be inverted there, since, as was already pointed out in the introduction (see also the appendix), as a direct consequence of

$$\int H(r, r') dr' = 0 \quad (26)$$

it possesses the constant functions as proper eigenfunctions with eigenvalue zero.

However, due to the fact that we introduced a Hilbert space of functions as the domain of definition for \mathbf{H} we now have the important technical notions of orthogonality and symmetric operators at our disposal, and we hence automatically know that eigenspaces are orthogonal and left invariant by the corresponding symmetric operator. In particular, these properties straightforwardly lead to the finding that a restricted form of invertibility for \mathbf{H} is still present. To demonstrate this, let us carry through the just mentioned standard decomposition of the Hilbert space \mathfrak{H} into a direct sum of the eigenspace \mathfrak{H}_0 belonging to the eigenvalue zero and its orthogonal complement \mathfrak{H}_0^\perp :

$$\mathfrak{H} = \mathfrak{H}_0 \oplus \mathfrak{H}_0^\perp. \quad (27)$$

As $H(r, r') = H(r', r)$, the integral operator \mathbf{H} is symmetric in \mathfrak{H} . Therefore it leaves invariant the subspace \mathfrak{H}_0^\perp and is invertible there.

Under the premise that $\rho[v]$ and $\rho[\hat{v}]$ differ whenever the external potentials v and \hat{v} differ by more than a constant [8], it seems natural to assume that only the constant functions are annihilated by \mathbf{H} , i.e. that \mathfrak{H}_0 is one-dimensional. In this case \mathfrak{H}_0^\perp is given by

$$\mathfrak{H}_0^\perp = \left\{ f \mid \int f(r) dr = 0 \right\}. \quad (28)$$

(The Hilbert spaces considered in this section consist, of course, of equivalence classes of functions rather than the functions themselves. For simplicity reasons we suppress this fact here.)

A problem which we already addressed is that the Hilbert space $\mathfrak{H} = L^2(V)$ does not exhaust the full set of physically relevant functions on which one wants to define the operator \mathbf{H} (cf, e.g., the LMBW equations). That is, in order to also incorporate these singular functions into the Hilbert space formalism, which is desirable on physical grounds, we have to modify the above ordinary Lebesgue measure.

The mentioned divergencies can, e.g., be compensated for by the vanishing of the density $\rho(r)$ which roughly behaves as $\exp(-\beta v_c(r))$ in the vicinity of the container boundary. That is, one possibility consists of replacing the Hilbert space $L^2(V)$ with the Hilbert space $L^2(V, \rho(r) dr)$ in which the measure is now chosen as $\rho(r) dr$ instead of dr . While not being in $L^2(V)$, the containing potentials and their derivatives are now naturally contained in $L^2(V, \rho(r) dr)$.

One should, however, emphasize that this choice is evidently *not* unique. Other options like, e.g., the replacement of $\rho(r)$ with the corresponding ideal gas density

$$\rho_{\text{id}}(r) = \frac{N \exp(-\beta v(r))}{\int \exp(-\beta v(r)) dr} \quad (29)$$

or with the quantity $N(\partial\rho(r)/\partial N)_v$ (provided the latter expression is well-defined and positive) is possible. As we shall see below, this latter choice would, in particular, lead to results which are in some sense comparable with the treatment in [5, 6].

In order to keep matters as general as possible, we therefore introduce the Hilbert space

$$\tilde{\mathfrak{H}} = L^2(V, \tilde{\rho}(r) dr) \quad (30)$$

where the measure $\tilde{\rho}(r) dr$ fulfils the normalization condition

$$\int \tilde{\rho}(r) dr = N. \quad (31)$$

Moreover, we require $\tilde{\rho}(r)$ to be capable of compensating for the singular behaviour of ∇v at the container boundaries. Thus, each of the above-mentioned quantities ρ , ρ_{id} , $N(\partial\rho/\partial N)_v$ turns out to be a possible candidate for $\tilde{\rho}$.

As a consequence, while $H(r, r')$ is unique by its definition as a canonical expectation value of a certain microscopic observable and does not depend on the choice of the Hilbert space measure, the situation turns out to be quite different for $C(r, r')$. We think this observation is one of the virtues of our more functional-analytically oriented approach.

An additional interesting feature of the Hilbert space $\tilde{\mathfrak{H}}$ shows up if one deals with systems that still consist of a finite number of particles N but for which the volume is infinite. Such systems still make sense, e.g., in those cases where the confinement of particles comes about by the use of polynomial wells, i.e. potentials $v(r)$ which diverge $\sim |r|^n$ as $|r| \rightarrow \infty$.

The constant functions are no longer elements of $\tilde{\mathfrak{H}}$ in such a $V = \infty$ case, but the integral operator \mathbf{H} can still be applied to them and they are still annihilated. Therefore, the eigenvalue zero would be an improper eigenvalue lying outside the discrete part of the spectrum.

In contrast to this, the constant functions are still contained in $\tilde{\mathfrak{H}}$:

$$\|1\|^2 = \int \tilde{\rho}(r) \, dr = N < \infty. \tag{32}$$

Therefore, zero is still an ordinary (proper) eigenvalue of \mathbf{H} here.

The price one has to pay for this adaptation of the Hilbert space consists of the fact that the integral operator \mathbf{H} is no longer symmetric, since

$$\langle f, \mathbf{H}g \rangle = \int f(r)(\mathbf{H}g)(r)\tilde{\rho}(r) \, dr = \int f(r)H(r, r')g(r')\tilde{\rho}(r) \, dr' \, dr \tag{33}$$

is different from

$$\langle \mathbf{H}f, g \rangle = \int (\mathbf{H}f)(r')g(r')\tilde{\rho}(r') \, dr' = \int f(r)H(r, r')g(r')\tilde{\rho}(r') \, dr' \, dr. \tag{34}$$

Among other things, this leads to the unpleasant feature that the subspace $\tilde{\mathfrak{H}}_0^\perp$ in the self-explanatory decomposition

$$\tilde{\mathfrak{H}} = \tilde{\mathfrak{H}}_0 \oplus \tilde{\mathfrak{H}}_0^\perp \tag{35}$$

is not left invariant by \mathbf{H} , which means that a straightforward inversion is no longer possible there.

However, one immediately notices that the modified integral kernel

$$H'(r, r') = \frac{H(r, r')}{\tilde{\rho}(r)} \tag{36}$$

leads to a symmetric integral operator \mathbf{H}' , since

$$\begin{aligned} \langle f, \mathbf{H}'g \rangle &= \int f(r)(\mathbf{H}'g)(r)\tilde{\rho}(r) \, dr = \int f(r)H(r, r')g(r') \, dr' \, dr \\ &= \int f(r)H(r', r)g(r') \, dr' \, dr = \int (\mathbf{H}'f)(r')g(r')\tilde{\rho}(r') \, dr' = \langle \mathbf{H}'f, g \rangle. \end{aligned} \tag{37}$$

Moreover, the eigenfunctions of \mathbf{H} and \mathbf{H}' with eigenvalue zero coincide. Thus, as \mathbf{H}' is symmetric, it leaves $\tilde{\mathfrak{H}}_0^\perp$ invariant. Restriction to this subspace therefore makes an inversion of \mathbf{H}' possible.

As the elements of $\tilde{\mathfrak{H}}_0$ are annihilated by \mathbf{H}' , one therefore gets the following modification of the Ornstein–Zernike relation for the CE case:

$$\mathbf{C}'\mathbf{H}' = \mathbf{P}^\perp \tag{38}$$

with \mathbf{P}^\perp denoting the projection operator onto the subspace $\tilde{\mathfrak{H}}_0^\perp$.

Since

$$(\mathbf{C}'\mathbf{H}', f)(r) = \int C'(r, r')H'(r', r'')f(r'') \, dr' \, dr'' = \int C'(r, r')\frac{H(r', r'')}{\tilde{\rho}(r')}f(r'') \, dr' \, dr'', \tag{39}$$

it is immediately clear that the direct correlation function $C(r, r')$ and its corresponding integral operator \mathbf{C} have to be introduced via

$$C(r, r') = \frac{C'(r, r')}{\tilde{\rho}(r')}. \quad (40)$$

Thus, the modified Ornstein–Zernike relation for the CE can also be rewritten as

$$\mathbf{C}\mathbf{H} = \mathbf{P}^\perp. \quad (41)$$

Remark 3.1. While an inverse of \mathbf{H}' does not exist outside $\tilde{\mathfrak{H}}_0^\perp$, a symmetric extension of the operator \mathbf{C}' can be defined on at least a dense subset of the full Hilbert space $\tilde{\mathfrak{H}}$, namely the linear combinations of elements from the range of \mathbf{H}' (which is at least dense in $\tilde{\mathfrak{H}}_0^\perp$) and $\tilde{\mathfrak{H}}_0$. In particular, $\tilde{\mathfrak{H}}_0$ is always left invariant by such an—of course non-unique—extension of \mathbf{C}' .

If one again assumes that $\tilde{\mathfrak{H}}_0$ is one-dimensional, i.e. that \mathbf{H} and \mathbf{H}' only annihilate the constant functions, this implies

$$\int C'(r, r') dr' = \text{constant} \quad (42)$$

and hence we have the useful identity

$$\int C(r, r') \tilde{\rho}(r') dr' = \text{constant}. \quad (43)$$

Furthermore, $\tilde{\mathfrak{H}}_0^\perp$ is then given by

$$\tilde{\mathfrak{H}}_0^\perp = \left\{ f \mid \langle 1, f \rangle = \int f(r) \tilde{\rho}(r) dr = 0 \right\} \quad (44)$$

and \mathbf{P}^\perp is defined as follows:

$$(\mathbf{P}^\perp f)(r) = f(r) - \frac{\langle 1, f \rangle}{\|1\|^2} = f(r) - \frac{1}{N} \int f(r) \tilde{\rho}(r) dr. \quad (45)$$

The modification of the Ornstein–Zernike relation for the CE can therefore be expressed as

$$\int C(r, r'') H(r'', r''') f(r''') dr'' dr''' = f(r) - \frac{1}{N} \int f(r) \tilde{\rho}(r) dr. \quad (46)$$

If one replaces $f(r)$ with the delta function $\delta(r - r')$ concentrated at an arbitrary but fixed point r' , the following final form emerges.

Conclusion 3.2. A modified Ornstein–Zernike relation in the CE can be written down as follows:

$$\int C(r, r'') H(r'', r') dr'' = \delta(r - r') - \frac{\tilde{\rho}(r')}{N}. \quad (47)$$

Roughly speaking, our version of a modified Ornstein–Zernike relation differs from the one given in [5, 6] by the appearance of the term $\tilde{\rho}(r')/N$ instead of $(\partial\rho(r')/\partial N)_v$.

To be more specific, let us compare our relations (43), (47), i.e.

$$\int C(r, r'') H(r'', r') dr'' + \frac{\tilde{\rho}(r')}{N} = \delta(r - r'), \quad (48)$$

$$\int C(r, r') \frac{\tilde{\rho}(r')}{N} dr' = \text{constant} \quad (49)$$

with the generalized Ornstein–Zernike relations that have been given as equations (52) and (53) in [6]:

$$\int C(r, r'') H(r'', r') dr'' + \left(\frac{\partial \rho(r')}{\partial N} \right)_v = \delta(r - r'), \quad (50)$$

$$\int C(r, r') \left(\frac{\partial \rho(r')}{\partial N} \right)_v dr' = \beta \left(\frac{\partial \mu}{\partial N} \right)_v. \quad (51)$$

The difference of these latter relations to ours above is twofold. On the one hand it consists in the already mentioned replacement of $\tilde{\rho}(r')/N$ with $(\partial \rho(r')/\partial N)_v$. This difference reflects the freedom of choice for the measure of the Hilbert space $\tilde{\mathfrak{H}}$ in our approach and would become non-existent with the particular definition $\tilde{\rho}(r) dr = N(\partial \rho(r)/\partial N)_v dr$ (provided the expression on the rhs is a well-defined positive measure at all). On the other hand it turns out that the constant on the rhs of (51) is no longer arbitrary but has a definite value (corresponding to a definite extension of the operator \mathbf{C}'). Both differences can therefore be characterized as an implication of some freedom of choice in our approach which is not present in that of [5] and [6].

A brief remark is in order here concerning the results in [3, 7] and their relation to that of [5, 6]. We think that in both approaches the guiding idea is to mollify the CE in order to make it more akin to the GCE case. This can be achieved in, on the surface, slightly different but nevertheless closely related ways. The strategy pursued in [5, 6] is to embed the CE with fixed particle number N into an enlarged parameter space, thus making a variation with respect to N possible (see, however, the related short discussion in our summary at the end of the paper). Another possibility is to make the system resemble an open system by truncating the weakly decaying tails (coming from the constancy of N) in the correlation functions as in [3] or [7]. Both strategies lead to closely interconnected results (cf section 3.4 of [6]) and correspond, as we have seen, to a particular choice in our own approach.

However, notwithstanding the fact that equations (50), (51) are the natural outcome of the inversion formalism of the extended variable approach in [5] and [6], it should be stressed that there is no obligation to also make the corresponding choices for the measure and the constant in our approach. Quite to the contrary, there is a certain amount of freedom which allows us to adopt some considerably simpler expressions. Furthermore, in the following we shall frequently deal with expressions where the operator \mathbf{C}' is solely applied to elements from the range of \mathbf{H}' . In these cases we need not even worry about definite extensions of \mathbf{C}' . It is therefore obvious that—contrary to $H(r, r')$ —the direct correlation function $C(r, r')$ is by no means a uniquely defined quantity in our approach. This has the advantage that it is to some extent possible to simplify matters by using ‘tailor-made’ definitions for C .

To further clarify the contents of the present chapter, it might be useful to deal with the ideal gas as a relatively simple but thereby also fully tractable example. The expressions $\rho(r) dr$, $\rho_{\text{id}}(r) dr$, and $N(\partial \rho(r)/\partial N)_v dr$ all coincide in this case and represent an obvious choice for our measure $\tilde{\rho} dr$. In the CE we have

$$H_{\text{id}}(r, r') = \rho_{\text{id}}(r) \delta(r - r') - \frac{1}{N} \rho_{\text{id}}(r) \rho_{\text{id}}(r'). \quad (52)$$

With $\tilde{\rho} = \rho_{\text{id}}$ we are therefore led to

$$H'_{\text{id}}(r, r') = \frac{H_{\text{id}}(r, r')}{\rho_{\text{id}}(r)} = \delta(r - r') - \frac{\rho_{\text{id}}(r')}{N} \quad (53)$$

which means that $\tilde{\mathfrak{H}}_0$ is indeed one-dimensional and that \mathbf{H}'_{id} is simply given as

$$\mathbf{H}'_{\text{id}} = \mathbf{P}^\perp. \quad (54)$$

After restriction to the subspace $\tilde{\mathfrak{H}}_0^\perp$, we thus get $\mathbf{H}'_{\text{id}} = \mathbf{1}$ and its inverse is trivially given as $\mathbf{C}'_{\text{id}} = \mathbf{1}$ there. This immediately leads to

$$C'_{\text{id}}(r, r') = \delta(r - r'). \quad (55)$$

For the time being, this expression is only valid on $\tilde{\mathfrak{H}}_0^\perp$. However, its validity can immediately be extended to the full Hilbert space $\tilde{\mathfrak{H}}$ (see remark 3.1). Thus, in this case the direct correlation function reads

$$C_{\text{id}}(r, r') = \frac{C'_{\text{id}}(r, r')}{\rho_{\text{id}}(r')} = \frac{\delta(r - r')}{\rho_{\text{id}}(r)}. \quad (56)$$

Hence we end up with exactly the same expression as for the GCE. Of course one has again to keep in mind here that the above extension of \mathbf{C}'_{id} from $\tilde{\mathfrak{H}}_0^\perp$ to $\tilde{\mathfrak{H}}$ is by no means a unique one. So it should not come as a surprise that, e.g., the direct correlation function $C_{\text{id}}(r, r')$ arrived at in equation (73) of [6] differs from our expression by a constant.

As a further result we notice that the range of \mathbf{H}'_{id} consists of the full subspace $\tilde{\mathfrak{H}}_0^\perp$. This in turn allows for a definition of \mathbf{C}'_{id} on the full Hilbert space $\tilde{\mathfrak{H}}$. Thus, the reservation ‘on at least a dense subset’ made in remark 3.1 is unnecessary here.

It is therefore interesting to deal with the question as to how far this desirable property is also transferable to the non-ideal case. It will turn out in the following that a positive answer can be given for a rather large class of systems if we make the special choice $\tilde{\rho}(r) = \rho(r)$. For a thorough discussion of the mathematics involved the reader may consult, e.g., [17].

For $\tilde{\rho}(r) = \rho(r)$ we have (see appendix):

$$H'(r, r') = \frac{H(r, r')}{\rho(r)} = \delta(r - r') + h(r, r')\rho(r'). \quad (57)$$

This corresponds to the natural decomposition

$$\mathbf{H}' = \mathbf{1} + \mathbf{h}' \quad (58)$$

with

$$(\mathbf{h}'f)(r) = \int h(r, r')f(r')\rho(r') dr'. \quad (59)$$

We now require \mathbf{h}' to be a Hilbert–Schmidt operator on $\tilde{\mathfrak{H}}$, i.e.

$$\int |h(r, r')|^2 \rho(r)\rho(r') dr dr' < \infty. \quad (60)$$

Under this proviso the Hilbert–Schmidt theorem tells us that \mathbf{h}' is a completely continuous symmetric operator possessing a purely discrete spectrum with zero as its only possible limit (accumulation) point. Thus, the symmetric operator $\mathbf{H}' = \mathbf{1} + \mathbf{h}'$ also has a purely discrete spectrum, but now with 1 as its only possible limit point. As an immediate consequence, the inverse of \mathbf{H}' is defined on the full subspace $\tilde{\mathfrak{H}}_0^\perp$ because the critical eigenvalue of \mathbf{H}' is the eigenvalue zero which, according to our preceding discussion, can at most be finitely degenerated. The above result is also a particular example for the so-called ‘Fredholm alternative’ which states that whenever \mathbf{k} is a completely continuous operator on a Hilbert space, then either $(\mathbf{1} + \mathbf{k})^{-1}$ is defined everywhere or $\mathbf{1} + \mathbf{k}$ possesses an eigenvector with eigenvalue zero.

It should finally be remarked that the simple form of the above natural decomposition (58) of \mathbf{H}' highly depends on the particular choice of $\rho(r) dr$ as our Hilbert space measure. For any other choice of the measure a non-trivial multiplication operator would show up instead of the

1, thus making an analogous reasoning as above more complicated. In particular, equation (57) had to be replaced with

$$H'(r, r') = \frac{H(r, r')}{\tilde{\rho}(r)} = \sqrt{\frac{\rho(r)}{\tilde{\rho}(r)}} \left(\delta(r - r') + \sqrt{\frac{\rho(r)\rho(r')}{\tilde{\rho}(r)\tilde{\rho}(r')}} h(r, r') \tilde{\rho}(r') \right) \sqrt{\frac{\rho(r')}{\tilde{\rho}(r')}} \quad (61)$$

and it turns out that the further discussion would crucially depend on the properties of the multiplication operator $\sqrt{\rho/\tilde{\rho}}$ in the general case.

Thus, again we see that matters can be kept simple due to the freedom of making the most suitable choice for the Hilbert space measure.

4. The second LMBW equation in the canonical ensemble

Now we are ready to examine what expression replaces the second LMBW equation (the one including the direct correlation function) when the CE is used instead of the GCE.

As was already pointed out in section 2, the first LMBW equation

$$(\mathbf{H}\nabla v)(r) = \int H(r, r') \nabla v(r') \, dr' = -\frac{1}{\beta} \nabla \rho(r) \quad (62)$$

is still valid when the CE is used. Due to the containing part of the potential, the derivatives of $v(r)$ are strongly divergent in the vicinity of the container boundary. The replacement of \mathfrak{H} with $\tilde{\mathfrak{H}}$ therefore finds its justification here. Again putting $\tilde{\mathfrak{H}} = L^2(V, \tilde{\rho}(r) \, dr)$, we get

$$(\mathbf{H}'\nabla v)(r) = -\frac{1}{\beta} \frac{\nabla \rho(r)}{\tilde{\rho}(r)}. \quad (63)$$

The operator \mathbf{H}' transforms elements of $\tilde{\mathfrak{H}}$ into elements of $\tilde{\mathfrak{H}}_0^\perp$, and this is reflected in the fact that

$$\left\langle 1, \frac{\nabla \rho}{\tilde{\rho}} \right\rangle = \int \nabla \rho(r) \, dr = 0 \quad (64)$$

due to the vanishing of $\rho(r)$ at the container boundary.

The operator \mathbf{C}' can safely be applied to both sides of the above LMBW equation and this leads to

$$(\mathbf{C}'\mathbf{H}'\nabla v)(r) = -\frac{1}{\beta} \left(\mathbf{C}' \frac{\nabla \rho}{\tilde{\rho}} \right)(r) = -\frac{1}{\beta} (\mathbf{C}\nabla \rho)(r). \quad (65)$$

Employing the modified Ornstein–Zernike relation $\mathbf{C}'\mathbf{H}' = \mathbf{P}^\perp$, we are thus immediately led to

$$(\mathbf{C}\nabla \rho)(r) = -\beta (\mathbf{P}^\perp \nabla v)(r) \quad (66)$$

or, if $\tilde{\mathfrak{H}}_0$ is again assumed to be one-dimensional, to the following

Conclusion 4.1. *The second LMBW equation in the CE can be written as*

$$\int C(r, r') \nabla \rho(r') \, dr' = -\beta \left(\nabla v(r) - \frac{1}{N} \int \tilde{\rho}(r) \nabla v(r) \, dr \right). \quad (67)$$

Therefore—in contrast to the unaltered first LMBW equation—this second one may differ from its grand canonical counterpart. The difference, however, ceases to exist for those choices of the measure where $\mathbf{P}^\perp \nabla v = \nabla v$, i.e. where the components of ∇v are already elements of $\tilde{\mathfrak{H}}_0^\perp$.

An example for this latter property is provided by the choice $\tilde{\rho}(r) = \rho_{\text{id}}(r)$ as equation (29) immediately implies

$$\int \rho_{\text{id}}(r) \nabla v(r) \, dr = -\frac{1}{\beta} \int \nabla \rho_{\text{id}}(r) \, dr = 0 \quad (68)$$

due to the vanishing of ρ_{id} at the container boundary.

There is, however, an even more remarkable example:

Observation 4.2. *Within the CE we have*

$$\int \rho(r) \nabla v(r) \, dr = 0. \quad (69)$$

Hence, for the choice $\tilde{\rho}(r) = \rho(r)$ the components of $\nabla v(r)$ already lie in the orthogonal subspace $\tilde{\mathfrak{H}}_0^\perp$. Since ∇v contains both the segregating and the containing potential, we also have

$$\int \rho(r) \nabla v_s(r) \, dr = - \int \rho(r) \nabla v_c(r) \, dr. \quad (70)$$

Proof. The explicit inclusion of the containing potential greatly facilitates the calculations as we can perform all manipulations in the full \mathbb{R}^n (with the Boltzmann weight being zero for all configurations with the position of at least one particle lying outside the volume V). We assume that the interaction potential $U(r_1, \dots, r_N)$ between the N particles is translation invariant. By v_a we denote the exterior potential translated by an arbitrary vector $a \in \mathbb{R}^n$:

$$v_a(r) = v(r + a). \quad (71)$$

Under these assumptions a simple variable transform shows that the canonical partition function $Q_N[v]$ remains invariant under translations of v :

$$Q_N[v] = Q_N[v_a]. \quad (72)$$

The same holds for the logarithm and hence for the free energy. Differentiation with respect to a at $a = 0$ immediately yields the desired result. \square

The above result can also be shown in a slightly different way by employing the following equation which—again for the case of a translation invariant interaction potential—states that the time derivative of the momentum density must have zero expectation value in thermal equilibrium (cf, e.g., section 2 of [18]):

$$\text{Div } \pi(r) + \rho(r) \nabla v(r) = 0. \quad (73)$$

Due to the appearance of the divergence of the pressure tensor $\pi(r)$ in this equation, $\int \rho(r) \nabla v(r) \, dr$ can be re-expressed as a surface integral. Shifting the surface of integration beyond the container boundaries one again sees that this integral is in fact zero.

The physical ramifications of this result are interesting. They show that the condition of equilibrium entails an *a priori* compensation of the global force exerted by the segregating potential on the system and the forces of constraint, provided by the container walls and acting on the nearby elements of the fluid or gas. This can most easily be seen in the case of the ideal gas (see our above calculations).

Moreover, it is immediately seen that in those cases where well-behaved differentiation of $\int \rho(r) \nabla v(r) \, dr$ with respect to N is possible, we also have

$$\int \left(\frac{\partial \rho(r)}{\partial N} \right)_v \nabla v(r) \, dr = 0. \quad (74)$$

Thus, whenever $\tilde{\rho}(r) = N(\partial \rho(r) / \partial N)_v$ is a possible choice, we have a further case for which $\mathbf{P}^\perp \nabla v = \nabla v$.

In concluding this section we just give one little example for the implications which are brought about by the above results. Let the external potential as usual be divided into a segregating and a containing part. In particular, we choose the segregating part to be a linear (gravitational) potential:

$$v(r) = v_s(r) + v_c(r) = mgr + v_c(r). \tag{75}$$

(Here and in the following g denotes a constant vector which can, e.g., be used to define the z -direction.)

Then, due to

$$\nabla v_s(r) - \frac{1}{N} \int \tilde{\rho}(r) \nabla v_s(r) dr = mg - \frac{mg}{N} \int \tilde{\rho}(r) dr = mg - mg = 0, \tag{76}$$

the segregating part of $v(r)$ drops out from the rhs of the second LMBW equation and we are left with

$$(\mathbf{C}\nabla\rho)(r) = -\beta \left(\nabla v_c(r) - \frac{1}{N} \int \tilde{\rho}(r) \nabla v_c(r) dr \right). \tag{77}$$

(Strictly speaking, the segregating potential remains, of course, present to some extent in those cases where we choose a $\tilde{\rho}$ that implicitly or explicitly depends on it.)

The containing potential $v_c(r)$ can be chosen such that it identically vanishes for r outside an arbitrarily small vicinity of the container boundary ∂V . If r is sufficiently distant from this boundary, it therefore lies outside the support of v_c and the last equation reduces to

$$(\mathbf{C}\nabla\rho)(r) = \frac{\beta}{N} \int \tilde{\rho}(r) \nabla v_c(r) dr. \tag{78}$$

As in the GCE, where $(\mathbf{C}\nabla\rho)(r) = -\beta mg$ for r sufficiently distant from the boundary, $(\mathbf{C}\nabla\rho)(r)$ is still constant in the canonical case, but the value of this constant can be quite different in general. With special choices such as, e.g.,

$$\tilde{\rho}(r) = \frac{N \exp(-\beta v_c(r))}{\int \exp(-\beta v_c(r)) dr} \tag{79}$$

it can even be made to vanish!

Moreover, as we have already seen,

$$\frac{1}{N} \int \tilde{\rho}_0(r) \nabla v(r) dr = mg + \frac{1}{N} \int \tilde{\rho}_0(r) \nabla v_c(r) dr = 0 \tag{80}$$

whenever $\tilde{\rho}_0$ denotes any of the expressions $\rho, \rho_{id}, N(\partial\rho/\partial N)_v$. This allows us to express the difference with the GCE case somewhat more explicitly:

$$(\mathbf{C}\nabla\rho)(r) = -\beta mg + \frac{\beta}{N} \int (\tilde{\rho}(r) - \tilde{\rho}_0(r)) \nabla v_c(r) dr. \tag{81}$$

This leads to the interesting fact that the whole information about the value of $(\mathbf{C}\nabla\rho)(r)$ in the CE as well as about its possible difference with the corresponding GCE value $-\beta mg$ is contained in the values of certain functions on the support of ∇v_c , i.e. in an extremely small vicinity of the container boundary.

This last statement can even be made somewhat more explicit by the observation that one of course can also make the transition from smooth containing potentials to ideal hard walls here. Proceeding in an analogous way as in section 2, we are left with

$$(\mathbf{C}\nabla\rho)(r) = \frac{1}{N} \int_{\partial V} \tilde{\rho}_+(r) d\bar{o} = -\beta mg + \frac{1}{N} \int_{\partial V} (\tilde{\rho}_+(r) - \tilde{\rho}_{0+}(r)) d\bar{o} \tag{82}$$

where the index ‘+’ once more denotes the limit taken from the interior of V .

5. Summary

In the preceding sections we developed a method to establish a kind of Ornstein–Zernike relation in the CE which is complementary to the more common density functional approach. In the CE the main problem is that the two-particle correlation function, when viewed as an integral operator \mathbf{H} , inevitably has a zero eigenvalue and thus cannot be straightforwardly inverted. Its inverse \mathbf{C} , representing the direct correlation function, therefore seems to be ill-defined.

Several suggestions have been made in the past to deal with or to circumvent this problem. In contrast to most of the treatments, we emphasize an explicit operator theoretical point of view. We show that \mathbf{H} can be inverted on some appropriate subspace of a certain function space being endowed with an adapted scalar product and being orthogonal to the constant functions which represent the eigenfunctions with eigenvalue zero. We introduce several intermediary function spaces by means of which it becomes particularly transparent that (and moreover in what precise sense) \mathbf{C} is non-unique on the full function space, the non-uniqueness stemming both from the chosen particular intermediary function space and the genuine non-uniqueness of the operator extension from a subspace to the full function space.

We note that these intermediary spaces are practically unavoidable if one wants to apply \mathbf{H} and \mathbf{C} to their natural space of functions which comprise also singular functions like, e.g., $\nabla v_c(r)$, v_c denoting the containing potential confining the system to a finite container. These latter functions occur in the LMBW equations which represent a natural context for such relations and which we therefore treated as a straightforward application. To put it in a nutshell, while H is genuinely unique due to its explicit expression in statistical mechanics, this is not so for C . Different intermediary spaces and different extensions lead to slightly different expressions for the direct correlation function which, however, are all fulfilling a restricted Ornstein–Zernike relation for the CE.

A connection of our approach with the ones developed earlier in the realm of density functional theory can be made in those cases where the quantity $(\partial\rho(r)/\partial N)_v$ is well-defined and positive such that $N(\partial\rho(r)/\partial N)_v dr$ is a possible choice for the measure of our Hilbert space.

In this context it should perhaps be pointed out that the uniqueness or even well-definedness of quantities involving partial derivatives with respect to N is by no means self-evident. While the formal differentiation with respect to N can be given a qualitative meaning in the realm of phenomenological thermodynamics (i.e. in some kind of thermodynamic limit where one can make use of the equivalence of ensembles), we think the situation is much less clear whenever one wants to generate such expressions without transcending the realm of the CE. This is even more so if one aims at the description of systems where the particle number is so small that the difference of ensembles becomes perceptible. The main problem occurring here is that the particle number N shows up in the dimension of the phase space volume and thus in the phase space measure as basically a discrete number. It is therefore not entirely evident how one should technically define unique continuous derivatives with respect to N without dismissing the confinement to the CE case. This problem was also observed by Ray [19] who even claims that there is no useful way to carry out such differentiations in general.

One of the virtues of our approach therefore consists in the possibility to circumvent the above problem by choosing simpler measures such as $\rho(r) dr$ or $\rho_{id}(r) dr$ for our Hilbert space. Furthermore, differentiation with respect to N also plays a decisive role for the constant on the rhs of equation (51). However, the non-uniqueness of the direct correlation function in our approach also enables us to alter this constant. It is therefore again possible to avoid differentiation with respect to N here.

As a further advantageous feature of the mentioned non-uniquenesses we finally note that the corresponding freedom of choice quite often allows for certain simplifications of procedures.

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Appendix

For the convenience of the reader and in order to fix the notation we provide a short list of general relations. The *pair correlation functions*, $H(r, r')$, $h(r, r')$, are defined as

$$H(r, r') := \rho^{(2)}(r, r') + \rho(r)\delta(r - r') - \rho(r)\rho(r'), \quad (83)$$

$$h(r, r') := \frac{\rho^{(2)}(r, r') - \rho(r)\rho(r')}{\rho(r)\rho(r')} =: g(r, r') - 1 \quad (84)$$

with the ordinary molecular distribution functions $\rho(r)$, $\rho^{(2)}(r, r')$ (see e.g. [20]). The physical meaning of $H(r, r')$ can be inferred from the relation

$$H(r, r') = \langle \delta n(r)\delta n(r') \rangle \quad (85)$$

with $\langle \dots \rangle$ denoting the ensemble expectation value and $\delta n(r)$ being the true microscopic observable

$$\delta n(r) := n(r) - \langle n(r) \rangle = n(r) - \rho(r), \quad n(r) := \sum_i \delta(r - r_i). \quad (86)$$

This identity exhibits the fluctuation content of $H(r, r')$.

The *Ornstein–Zernike relation* which in its general form can only hold in the GCE (see below) defines the *direct correlation function* and reads

$$\int C(r, r')H(r', r'') \, dr' = \delta(r - r'') \quad (87)$$

or with

$$C(r, r') := \delta(r - r')/\rho(r) - c(r, r') \quad (88)$$

we have

$$h(r, r'') - c(r, r'') = \int h(r, r')\rho(r')c(r', r'') \, dr' = \int c(r, r')\rho(r')h(r', r'') \, dr'. \quad (89)$$

Working in the CE in a finite volume V and inserting the expressions for $\rho^{(2)}$ and ρ , we get the remarkable identity

$$\int_V H(r, r') \, dr' = (N - 1)\rho(r) + \rho(r) - N\rho(r) = 0. \quad (90)$$

In other words, the integral operator \mathbf{H} with kernel $H(r, r')$ annihilates the constant functions and therefore cannot be inverted. The Ornstein–Zernike relation in its usual form (87) is thus unavailable in the CE case.

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