Variational methods for the solution of the Ornstein-Zernicke equation in inhomogeneous systems

R. Paul[1] and S. J. Paddison[2]

[1]*Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4*
[2]*Computational Nanoscience Group, Motorola Inc., Los Alamos Research Park, Los Alamos, New Mexico 87544*
(Received 20 August 2002; published 22 January 2003)

We show that the Ornstein-Zernicke equation and other equations of similar form obey a variational principle that can be used to derive approximate solutions. This method requires the use of an initial trial solution where the variational solution possesses a stationary "point" with respect to the trial solution when the latter is equal to the exact solution. We show that with even a very simple form of the trial solution the results are quite reasonable. Furthermore, we have demonstrated that by combining the variational method with an iterative expansion of the Ornstein-Zernicke equation it is possible to develop a self-consistent method of writing the direct correlation function.

I. INTRODUCTION

During the past three decades the study of condensed matter has emerged as one of the areas of most intense activity [1]; it is, indeed, impossible to present even a superficial summary of the developments. In this introductory section we mention only a very small "slice" of the relevant literature. From an experimental perspective, the structure factors for a vast number of systems have been made accessible through the advances in x-ray and neutron scattering technologies. The Fourier transforms of the structure factor are related to the pair correlation function $h(1,2)$, where the two numerals 1 and 2 are the abbreviations for the complete set of coordinates required for the specification of two arbitrary molecules. This function is readily derived from basic statistical mechanics and therefore constitutes the gateway for the interpretation of the experimental data.

Three methods of study have emerged as possible approaches that may be adopted for the investigation of these systems.

(1) The classical partition function may be expressed as sums of irreducible cluster integrals and the pair correlation function computed from this expansion [2–5]. If the system can be expressed in terms of the grand canonical partition function then several powerful theorems can be used and the calculation is rendered very elegant. If, however, the systems consist of a finite number of (molecular) species then the validity of these theorems is rather doubtful.

(2) If the canonical partition function can be written for the system then by application of the methods of functional differentiation it can easily be shown that the pair correlation function must satisfy an integral equation known as the Ornstein-Zernicke equation [6,7]. The Ornstein-Zernicke equation has been the subject of extensive studies. Starting with the work of Wertheim [8], who solved the equation for a hard-sphere fluid, Blum and co-workers have developed methods that are applicable to fluids with fairly complex structures [9–12].

(3) A complete computer based analysis employing the full power of simulation techniques may be employed.

In this paper we will investigate the second approach and develop the tools that are needed to solve the Ornstein-Zernicke equation. As indicated above, this important equation has been extensively studied but a considerable body of the literature is directed toward homogeneous systems with translational invariance. Our interest in the subject arose from the need to understand the thermodynamic properties of nanopores that are found in polymeric membranes used in the construction of fuel cells [13–16]. It is evident that for such systems the criterion of translational invariance fails to hold. There are, of course a large variety of other phenomena where translational invariance is not valid: surface wetting and electrode processes are but two such examples.

II. BRIEF REVIEW OF THE ORNSTEIN-ZERNICKE EQUATION

It is not the purpose of this section to once again present the derivation of a well-known equation for which excellent accounts can be found in the literature, but rather to introduce the notation and the framework within which the solution is sought. The basic quantities to be utilized in this paper may be introduced as follows.

(i) We consider systems with N molecules for which the Hamiltonian H_T can be written as

$$H_T(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N, 1, 2, \ldots, N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + H(1, 2, \ldots, N),$$

$$H(1, 2, \ldots, N) \equiv \sum_{i=1}^{N} \phi(i) + \sum_{i<j}^{N} \psi(i,j).$$

Here, the first term in H_T is the total kinetic energy, where it is assumed that molecule i possesses momentum $\mathbf{p}_i$ and mass m. The quantity H is the total interaction energy, which we assume to consist of one-body $\phi(i)$ and two-body $\psi(i,j)$ potential energy terms only.

(ii) With the above Hamiltonian the full canonical partition function immediately becomes

$$Q_N = \frac{1}{N! \Lambda^{3N}} q_N \equiv \frac{Q_N^{\mathrm{id}}}{V} q_N,$$

where

$$\Lambda = \left(\frac{2\pi\beta\hbar^2}{m} \right)^{1/2},$$

$$q_N = \int \prod_{i=1}^{N} di \, z^*(i) \exp\left(-\beta \sum_{i<j}^{N} \psi(i,j) \right),$$

$$z^*(i) = e^{-\beta\phi(i)}, \quad \beta = 1/kT. \tag{1}$$

In the above equations V is the volume of the system, $\hbar$ is Planck's constant, k is the Boltzmann constant, and T is the absolute temperature. As is well known from elementary statistical mechanics, Q_N^{id} is the partition function of an ideal gas and does not depend upon the potential energy of the system. The factor q_N contains all the information that arises as a result of the nonideality of the system and contains the basic ingredients that are needed for the computation of the pair correlation function; it is this quantity that will be of primary concern in the present work and it will be henceforth referred to as the *configuration integral*.

(iii) The full N-body distribution function is given by

$$n_N(1,2,\ldots,N) = \frac{1}{q_N} \exp[-\beta H(1,2,\ldots,N)].$$

An arbitrary m-body distribution function with $m < N$ can be obtained from n_N by integration over the $N-m$ variables:

$$n_m(1,2,\ldots,m) = \frac{N!}{(N-m)!} \int \prod_{i=m+1}^{N} di \, n_N(1,2,\ldots,N).$$

(iv) The dimensionless m-body g_m distribution function is defined by

$$g_m(1,2,\ldots,m) = \frac{n_m(1,2,\ldots,m)}{\prod_{i=1}^{m} n_1(i)}.$$

The two-body function g_2 is often written without the subscript 2 as simply g.

(v) The experimentally important pair correlation function alluded to above is defined by

$$h(1,2) = g(1,2) - 1.$$

(vi) The m-body distribution functions are obtained by functional differentiation of the configuration integral:

$$n_m(1,2,\ldots,m) = \frac{1}{q_N} \prod_{i=1}^{m} z^*(i) \frac{\delta^m}{\prod_{i=1}^{m} \delta z^*(i)} q_N. \tag{2}$$

(vii) From Eq. (2) it follows that

$$z^*(2) \frac{\delta n_1(1)}{\delta z^*(2)} \equiv \frac{\delta n_1(1)}{\delta \ln z^*(2)}$$

$$= n_1(1)\delta(1,2) + n_1(1)n_1(2)h(1,2); \tag{3}$$

here, $\delta(1,2)$ is the Dirac delta function.

(viii) The direct correlation function $c(1,2)$ is defined by

$$c(1,2) \equiv \frac{\delta \ln[n_1(1)/z^*(1)]}{\delta n_1(2)} = \frac{1}{n_1(1)} \delta(1,2) - \frac{\delta \ln z^*(1)}{\delta n_1(2)}. \tag{4}$$

(ix) Equation (4) provides the inverse of Eq. (3) and the two may be combined to yield the Ornstein-Zernicke equation

$$h(1,2) = c(1,2) + \int d\bar{1} \, c(1,\bar{1}) n_1(\bar{1}) h(\bar{1},2). \tag{5}$$

Since the Ornstein-Zernicke equation is an integral equation it can be solved by using an iterative technique and the first few terms are as follows:

$$h(1,2) = c(1,2) + \int d\bar{1} \, c(1,\bar{1}) n_1(\bar{1}) c(\bar{1},2)$$

$$+ \int d\bar{1} \, d\bar{2} \, c(1,\bar{1}) n_1(\bar{1}) c(\bar{1},\bar{2}) n_1(\bar{2}) c(\bar{2},2) + \cdots$$

$$\equiv h^{(0)}(1,2) + h^{(1)}(1,2) + \cdots. \tag{6}$$

Unfortunately, while such an expansion does converge, the rate of convergence tends to be slow and the complexity of each successive term increases in a dramatic fashion. Therefore iterative series do not provide a practical method of solution. It is easy to see that Eq. (5) may also be rewritten in the following form, since the same iterative expansion series is produced from it:

$$h(1,2) = c(1,2) + \int d\bar{1} \, h(1,\bar{1}) n_1(\bar{1}) c(\bar{1},2). \tag{7}$$

Thus, both methods of writing the Ornstein-Zernicke equation are completely equivalent and both will be used in this work.

It is the Ornstein-Zernicke equation that is an important source for the pair correlation function; however, the following facts must be considered in using this equation.

(i) Before the pair correlation function can be computed from the Ornstein-Zernicke equation the direct correlation function c must be available since it is still an unknown quantity. There are several prescriptions, commonly referred to as *closure relations*, that have been developed for the computation of c. While it is not the purpose of this paper to present a discussion of the closure relations, the principles presented here do have an impact on some of these relations.

(ii) The Ornstein-Zernicke equation is an integral equation that must be solved before the pair correlation function can be extracted from it. If we consider a system that possesses the property of translational invariance then such a solution is possible; however, for inhomogeneous systems such as those found in nanopores and in a variety of other important situations the criterion of translational invariance does not hold and either a numerical or an approximate solution must be sought. In most cases, even when the condition of translational invariance holds, the application of numerical methods for solving integral equations has to be used. These numerical methods require an initial guess function $c^{(I)}$ or $h^{(I)}$,

which is then substituted in the Ornstein-Zernicke equation and an improved version $c^{(II)}$ or $h^{(II)}$ computed, the process being repeated until convergence is achieved. Hansen and McDonald [1] point to the slow rate of convergence even if a reasonable guess has initially been made; a situation that deteriorates with increasing complexity of the fluid. It follows therefore that there is a need to develop optimization methods that can be used either to produce approximate solutions of an analytic nature or to assist in the convergence process. This paper is devoted to the development of one such method.

The Ornstein-Zernicke equation possesses an overall form that resembles the form of another integral equation, which arises in quantum field theory, namely, the Dyson equation. Rosenberg and Tolchin [17] showed that it is possible to derive a variational theorem for the Dyson equation and in this paper we present a variational theorem for the Ornstein-Zernicke equation. Furthermore, we show that the variational method can be used to select a self-consistent form for the direct correlation function.

III. VARIATIONAL THEOREM OBEYED BY THE ORNSTEIN-ZERNICKE EQUATION

In order to develop a formalism that is expressible within the language of functional algebra it is expedient to begin with a very obvious statement: the search for a solution of the Ornstein-Zernicke equation is completely equivalent to solving the functional equation

$$\mathfrak{I}[h(1,2)]=0, \qquad (8)$$

where

$$\mathfrak{I}[h(1,2)]\equiv h(1,2)-c(1,2)-\int d\bar{1}\, h(1,\bar{1})n_1(\bar{1})c(\bar{1},2). \qquad (9)$$

The Taylor expansion of $\mathfrak{I}[h]$ about a trial solution h_t and the retention of the linear term only results in the production of the simplest approximate solution of this functional equation:

$$\mathfrak{I}[h(1,2)]\approx\mathfrak{I}[h_t(1,2)]+\int d\bar{1}\, d\bar{2}\, \Omega(1,2;\bar{1},\bar{2})[h(\bar{1},\bar{2})$$
$$-h_t(\bar{1},\bar{2})]+O[(h-h_t)^2]$$
$$=0, \qquad (10)$$

where we have introduced a function Ω dependent upon four variables:

$$\Omega(i,j;k,n)\equiv\left[\frac{\delta\mathfrak{I}[h(i,j)]}{\delta h(k,n)}\right]_{h=h_t}. \qquad (11)$$

The solution referred to above may be extracted from Eq. (10) by introducing the inverse function Ω^{-1} defined in the following manner:

$$\int d\bar{i}\, d\bar{j}\, \Omega^{-1}(i,k;\bar{i},\bar{j})\Omega(\bar{i},\bar{j};l,j)$$
$$=\int d\bar{i}\, d\bar{j}\, \Omega(i,k;\bar{i},\bar{j})\Omega^{-1}(\bar{i},\bar{j};l,j)=\delta(i,l)\,\delta(j,k). \qquad (12)$$

Inserting Ω^{-1} in Eq. (10), we obtain an approximate solution h_v:

$$h_v(1,2)=h_t(1,2)-\int d\bar{1}\, d\bar{2}\, \Omega^{-1}(1,2;\bar{1},\bar{2})\mathfrak{I}[h_t(\bar{1},\bar{2})]. \qquad (13)$$

Equation (10) results from an approximation in which all second and higher order errors have been neglected; it follows, therefore, that h_v must contain errors of second and higher orders only. From the perspective of the present work the most important feature of Eq. (13) can be understood if it is realized that h_t differs from the exact pair correlation function through a first order error $(h-h_t)$, and similarly Eq. (10) shows that $\mathfrak{I}[h_t]$ incorporates a first order error while h_v contains second order errors. It therefore follows that Eq. (13) may be viewed as a transformation that removes first order errors, which is a feature that will be exploited with advantage. It should be evident that this stage in the calculation is analogous to the well-known Newtonian method for calculating the roots of nonlinear algebraic equations and, if continued in the spirit of that method, the next stage would involve employing h_v as the trial function in a second iteration. The process of iterations would finally lead to a self-consistent solution. It is not our purpose, however, to develop such a scheme.

The function h_v obeys a variational theorem that can be readily proved by taking the functional derivative of Eq. (13) with respect to the trial function h_t and then setting $h_t=h$ in the resulting equation:

$$\left[\frac{\delta h_v(1,2)}{\delta h_t(3,4)}\right]_{h_t=h}=\left[\frac{\delta h_t(1,2)}{\delta h_t(3,4)}\right]_{h_t=h}-\int d\bar{1}\, d\bar{2}\, \Omega^{-1}(1,2;\bar{1},\bar{2})$$
$$\times\left[\frac{\delta\mathfrak{I}[h_t(\bar{1},\bar{2})]}{\delta h_t(3,4)}\right]_{h_t=h}$$
$$=\delta(1,3)\,\delta(2,4)$$
$$-\int d\bar{1}\, d\bar{2}\, \Omega^{-1}(1,2;\bar{1},\bar{2})\Omega(\bar{1},\bar{2};3,4)$$
$$=0. \qquad (14)$$

In deriving Eq. (14), use has been made of Eqs. (11) and (12) and it proves the variational property of the function h_v. In other words, when we consider the set X of all possible trial functions, the function h_v possesses a "stationary point" when the trial function becomes equal to the exact correlation function h. This feature justifies the use of the subscript v in h_v. From a practical standpoint it is possible to obtain the "best" solution to the Ornstein-Zernicke by using a trial

function h_t with a certain number of parameters and then determining these parameters by setting the derivative of h_v with respect to these parameters equal to zero. The mathematical machinery required to further develop the variational method will be presented later in this paper.

From a fundamental perspective [18] it is imperative that the precise properties of the space X be carefully discussed. We present this analysis in the following manner.

(1) Any element $u \in X$ must, clearly, be the function of two space variables r and r' for which numerical symbols such as 1 and 2 have been hitherto used. For the purposes of studying the structural and metrical properties of X it is convenient to adopt the non-numerical symbolism. It is important to bear in mind the fact that each of these variables is an abbreviation for the complete set of coordinates required for the specification of any arbitrary molecule.

(2) Given any pair of elements $u \in X$ and $v \in X$ we require that the linear combination $w = au + bv \in X$ with a and b being arbitrary members of the real field. This condition is, indeed, essential for the practical implementation of our method since we will make use of linear combinations of functions with the coefficients of combination as variational parameters. This property ensures that X is a linear manifold in the space of all functions.

(3) As a consequence of (1) and (2) it follows that given $u \in X$, $v \in X$, and $w \in X$ the following must hold:

$$v + t(w - v) \in X, \quad 0 \le t \le 1.$$

Thus, X constitutes a *convex* set.

(4) As in any functional space it is possible to introduce a variety of different norms, but in the present case the following is the most convenient definition:

$$\|u\| = \max_{r,r'} |u(r,r')|.$$

(5) The norm introduces a *natural metric*:

$$d(u,v) = \|u - v\|.$$

(6) Within this metric we assume that X contains the limits of all sequences chosen from it and thus constitutes a normed linear space in its natural metric and qualifies as a *Banach* space.

(7) At this stage a very important difference between the variational theorems used in the solution of differential equations (for example, the Schrödinger equation of quantum mechanics) and the present one must be clearly emphasized. In the former (differential equations) the variational functional (the energy in the case of the Schrödinger equation) is generated from the functions in the set X and is not a member of this set. In the present case we see from Eqs. (8)–(13) that h_v is itself an approximate solution of the Ornstein-Zernicke equation; thus $h_v \in X$ and therefore, as a functional, shares the property of convexity with X.

It will be convenient for later purposes to rewrite Eq. (13). To start, we write the inverse function Ω^{-1} as follows:

$$\Omega^{-1}(i,j;k,l) = \delta(i,k)\,\delta(j,l) - x(i,j;k,l). \quad (15)$$

Here, $x(i,j;k,l)$ is a new and still unknown function. Secondly, the functional $\Im[h_t]$ can be written from Eq. (9) as

$$\Im[h_t(1,2)] = h_t(1,2) - h_u(1,2),$$

the function h_u being defined as follows:

$$h_u(1,2) \equiv c(1,2) + \int d\bar{1}\, h_t(1,\bar{1}) n_1(\bar{1}) c(\bar{1},2).$$

The meaning of h_u is obvious since it corresponds to the result of the first order iteration that ensues from the substitution of h_t in the right hand side of Eq. (7). Equation (13) now becomes

$$h_v(1,2) = h_u(1,2) + \int d\bar{1}\, d\bar{2}\, x(1,2;\bar{1},\bar{2})$$

$$\times [h_t(\bar{1},\bar{2}) - h_u(\bar{1},\bar{2})]. \quad (16)$$

Once again it is important to reemphasize the *error transforming properties* of Eq. (16) from the fact that both h_u and h_t contain first order errors while h_v contains second order errors. In general it is possible to first compute h_u from a given h_t and then calculate the unknown function $x(i,j;k,l)$ by requiring Eq. (14) to hold. We return to this matter later in the paper.

Although Eq. (16) has been derived in the context of the Ornstein-Zernicke equation it is in fact a general property that can be derived for any integral equation with the same overall form as the Ornstein-Zernicke equation. The general derivation is worth summarizing in the following basic steps.

(i) Consider an arbitrary linear integral equation

$$\psi(A,B) = \varphi(A,B) + \int d\bar{A}\, d\bar{B}\, K(A,B;\bar{A},\bar{B}) \psi(\bar{A},\bar{B});$$

$$(17)$$

here A and B are any general and arbitrary set of variables with ψ the unknown function the form of which is sought; φ and K are known functions.

(ii) A trial solution ψ_t is inserted in the right hand side of Eq. (17) and an improved solution ψ_u calculated:

$$\psi_u(A,B) = \varphi(A,B) + \int d\bar{A}\, d\bar{B}\, K(A,B;\bar{A},\bar{B}) \psi_t(\bar{A},\bar{B}).$$

It is evident that ψ_u must be characterized by first order errors ($\psi - \psi_t$).

(iii) A variational solution, characterized by errors of second and higher orders, of a form similar to Eq. (16) is easily derived by proceeding through the same sequence of steps:

$$\psi_v(A,B) = \psi_u(A,B) + \int d\bar{A}\, d\bar{B}\, k(A,B;\bar{A},\bar{B})$$

$$\times [\psi_u(\bar{A},\bar{B}) - \psi_t(\bar{A},\bar{B})]. \quad (18)$$

k plays the role of the function x in Eq. (16).

(iv) Because ψ_v is a variational solution it must satisfy the standard variational equation

$$\left[\frac{\delta \psi_v(A,B)}{\delta \psi_t(C,D)}\right]_{\psi_t=\psi}=0. \tag{19}$$

(v) Equation (19) immediately leads to an integral equation for the function k:

$$k(A,B;C,D)=p(A,B;C,D)$$
$$+\int d\bar{A}\, d\bar{B}\, k(A,B;\bar{A},\bar{B})p(\bar{A},\bar{B};C,D), \tag{20}$$

where

$$p(A,B;C,D)\equiv\left[\frac{\delta \psi_u(A,B)}{\delta \psi_1(C,D)}\right]_{\psi_t=\psi}.$$

(vi) Equation (20) has the same overall form as the Ornstein-Zernicke equation but this time involves four variables in each function. It is evident that a hierarchy of integral equations involving, in each stage, an increment of two variables can be derived from the underlying variational properties.

In the case of the Ornstein-Zernicke equation a particularly important simplifying feature is present by virtue of the fact that the function K is linearly related to φ. This property allows the function Ω^{-1} to be computed. Taking a functional derivative of Eq. (9) in the following manner the explicit form of Ω is easily calculated:

$$\left[\frac{\delta \Im[h(1,2)]}{\delta h(3,4)}\right]_{h=h_t}=\Omega(1,2;3,4)=\frac{\delta h(1,2)}{\delta h(3,4)}$$
$$-\int d\bar{1}\frac{\delta h(1,\bar{1})}{\delta h(3,4)}n_1(\bar{1})c(\bar{1},2)$$
$$=\delta(1,3)\delta(2,4)-\delta(1,3)n_1(4)c(2,4). \tag{21}$$

Combining Eqs. (21) and (15) we have

$$\int d\bar{1}\, d\bar{2}\, \Omega^{-1}(1,2;\bar{1},\bar{2})\Omega(\bar{1},\bar{2};3,4)$$
$$=\int d\bar{1}\, d\bar{2}[\delta(1,\bar{1})\delta(2,\bar{2})-x(1,2;\bar{1},\bar{2})][\delta(\bar{1},3)\delta(\bar{2},4)$$
$$-\delta(\bar{1},3)n_1(4)c(\bar{2},4)]=\delta(1,3)\delta(2,4)$$
$$-\delta(1,3)n_1(4)c(2,4)-x(1,2;3,4)$$
$$+\int d\bar{2}\, x(1,2;3,\bar{2})n_1(4)c(\bar{2},4).$$

The last three terms in this result will vanish [which must be the case if Eqs. (15) and (21) are to be the inverse of each other] if we select

$$x(1,2;3,4)=-\delta(1,3)n_1(4)h(2,4),$$

$$x(1,2;3,\bar{2})=-\delta(1,3)n_1(\bar{2})h(2,\bar{2}),$$

and employ the Ornstein-Zernicke equation with suitable variable changes. Thus we see that the desired Ω^{-1} is, in general, given by

$$\Omega^{-1}(i,j;k,l)=\delta(i,k)\delta(j,l)+\delta(i,k)n_1(l)h(l,j).$$

Unfortunately, the inverse still contains the unknown pair correlation function h and we replace it by a second trial function h_τ:

$$\Omega^{-1}(i,j;k,l)=\delta(i,k)\delta(j,l)+\delta(i,k)n_1(l)h_\tau(l,j). \tag{22}$$

Substituting Eq. (22) in Eq. (13) we obtain an approximation for the pair correlation function h_v:

$$h_v(1,2)=c(1,2)+\int d\bar{1}\, h_t(1,\bar{1})n_1(\bar{1})c(\bar{1},2)$$
$$-\int d\bar{1}\, h_t(1,\bar{1})n_1(\bar{1})h_\tau(\bar{1},2)$$
$$+\int d\bar{1}\, c(1,\bar{1})n_1(\bar{1})h_\tau(\bar{1},2)$$
$$+\int d\bar{1}\, d\bar{2}\, h_t(1,\bar{2})n_1(\bar{2})c(\bar{2},\bar{1})n_1(\bar{1})h_\tau(\bar{1},2). \tag{23}$$

The insertion of a second trial function h_τ results in the introduction of the first order error $(h-h_\tau)$ in h_v. Despite this fact h_v still retains its variational property, which we now demonstrate. Taking the functional derivative of Eq. (23) with respect to the trial functions h_t (3,4) and h_τ (3,4) and replacing any residual functions h_t and/or h_τ by the exact solution h, we get

$$\left[\frac{\delta h_v(1,2)}{\delta h_t(3,4)}\right]_{\substack{h_t=h\\h_\tau=h}}=-\delta(1,3)n_1(4)\left[h(4,2)-c(4,2)\right.$$
$$\left.-\int d\bar{1}\, c(4,\bar{1})n_1(\bar{1})h(\bar{1},2)\right]$$
$$=0, \tag{24}$$

$$\left[\frac{\delta h_v(1,2)}{\delta h_\tau(3,4)}\right]_{\substack{h_t=h\\h_\tau=h}}=-\delta(2,4)n_1(3)\left[h(1,3)-c(1,3)\right.$$
$$\left.-\int d\bar{1}\, c(1,\bar{1})n_1(\bar{1})h(\bar{1},3)\right]$$
$$=0. \tag{25}$$

The right hand sides of both these equations vanish because the exact correlation function h must, by hypothesis, obey the Ornstein-Zernicke equation.

From a practical standpoint we may now select the trial functions h_t and h_τ to contain arbitrary sets of parameters:

$$h_t(i,j) = h_t(i,j;a_1,a_2,\ldots,a_M),$$

$$h_\tau(i,j) = h_\tau(i,j;b_1,b_2,\ldots,b_M).$$

When these are substituted in Eq. (23) we obtain

$$h_v = h_v(i,j;a_1,a_2,\ldots,a_M,b_1,b_2,\ldots,b_M). \qquad (26)$$

The parameters can be computed by invoking the variational property of h_v:

$$\left(\frac{\partial h_v}{\partial a_j}\right) = 0 \quad j=1,2,\ldots,M,$$

$$\left(\frac{\partial h_v}{\partial b_j}\right) = 0 \quad j=1,2,\ldots,M. \qquad (27)$$

Once the set of $2M$ simultaneous *algebraic* equations (27) have been solved for the parameters a_j and b_j and the results substituted in h_v, the "best" variational approximation to the solution of the Ornstein-Zernicke is obtained.

The methodology developed above does not provide us with a suitable prescription for the choice of the trial functions h_t and h_τ; and these are left to the judgment of the investigator. In general it is best to use functions that incorporate as much physical and chemical information about the system as possible. It is hoped that the method will find extensive applications to systems where the simplifications from translational invariance are not available. In such instances the trial functions could be taken by parametrizing the pair correlation function of a closely allied system with translational invariance and then using the variational method for calculating the parameters. Another guiding principle in making choices of the trial functions would be the simplicity of these functions so that the necessary mathematical operations such as integrations and the solution of algebraic equations can be easily carried out.

IV. NUMERICAL ASSESSMENT OF THE POTENTIAL APPLICABILITY OF THE VARIATIONAL METHOD

The advantage of any variational method lies in the freedom that it provides in choosing a trial solution to the problem. In making this choice it is expedient to select a function that will allow the relevant mathematical operations such as integrations to be easily carried out. This advantage must, however, be balanced against the quality of the desired result. It therefore becomes imperative that any choice must be tested against available and reliable results. Unfortunately, in applying the techniques to problems that lack translational invariance we are treading on relatively uncharted territories and are obliged to return to simple systems for which well-defined results are available. Once again we use the hard-sphere fluid model since it provides us with analytical results. It is important to emphasize the central aim of this section: It is not our purpose to merely show the form of the formulas that are produced from the hard-sphere model, since they abound in the literature, *but rather to show that with even an absurdly simple form of trial solutions the*

variational method we have presented above produces reasonable answers.

As has already been stated, any application of the Ornstein-Zernicke equation necessitates a definition of the direct correlation function. For the hard-sphere fluids previous work [1,19,20] has shown that the so-called Percus-Yevick approximation for the direct correlation function provides reliable results at least for homogeneous systems. According to the Percus-Yevick approximation

$$c^{(\mathrm{PY})}(i,j) = \{1 - e^{-\beta\psi(i,j)}\}\{h(i,j)+1\}.$$

Here, the particle-particle interaction potential $\psi(i,j)$ is infinite if the spheres overlap and zero otherwise. When substituted in the Ornstein-Zernicke equation, keeping in mind the fact that for a homogeneous fluid the one-body distribution function $n_1(i)$ must become equal to the fluid density n, an integral equation in only a single unknown quantity ensues. Wertheim [8] obtained an analytic solution for the direct correlation function from the resulting integral equation, of the form

$$c^{(\mathrm{PY})}(|\mathbf{r}-\mathbf{r}'|) = -H(\sigma-|\mathbf{r}-\mathbf{r}'|)\frac{1}{\sigma^3}(\lambda_0 + \lambda_1|\mathbf{r}-\mathbf{r}'|$$
$$+ \lambda_2|\mathbf{r}-\mathbf{r}'|^3),$$

$$\lambda_0 = \frac{\sigma^3}{\Delta}\left(1+\frac{1}{3}n\pi\sigma^3\right)^2, \quad \lambda_1 = -\frac{n\pi\sigma^5}{\Delta}\left(1+\frac{1}{12}n\pi\sigma^3\right)^2,$$

$$\lambda_2 = \frac{n\pi}{12}\lambda_0, m\Delta = \left(1-\frac{1}{6}n\pi\sigma^3\right)^4.$$

σ is the radius of the excluded volume within which the centers of two molecules cannot penetrate and $H(x)$ is the Heaviside step function, defined in the conventional manner:

$$H(x) = \begin{cases} 0 & \text{for } x<0, \\ 1 & \text{for } x\geq 0. \end{cases}$$

It is imperative to bear in mind the fact that the direct correlation function derived by Wertheim is still only a solution of the Percus-Yevick approximation to the Ornstein-Zernicke equation and therefore the superscript (PY) plays a cardinal role in emphasizing its approximate nature. Further improvements on the solution may be obtained, even for a homogeneous system, by inserting $c^{(\mathrm{PY})}(|\mathbf{r}-\mathbf{r}'|)$ in the Ornstein-Zernicke equation:

$$h(\mathbf{r}_1,\mathbf{r}_2) = c^{(\mathrm{PY})}(|\mathbf{r}_1-\mathbf{r}_2|) + n\int d\mathbf{r}_3 c^{(\mathrm{PY})}(|\mathbf{r}_1-\mathbf{r}_3|)h(\mathbf{r}_3,\mathbf{r}_2).$$
$$(28)$$

The desired improvements, which we now carry out, will result by solving Eq. (28).

Given the properties of the hard-sphere potential $\psi(i,j)$ it must follow that when $|\mathbf{r}_i-\mathbf{r}_j|\leq\sigma$ then $h(|\mathbf{r}_i-\mathbf{r}_j|)=-1$. Moreover, it is for precisely these values of the spatial argument that $h(|\mathbf{r}_i-\mathbf{r}_j|)$ possesses its largest absolute values and, therefore, we have a benchmark solution available with
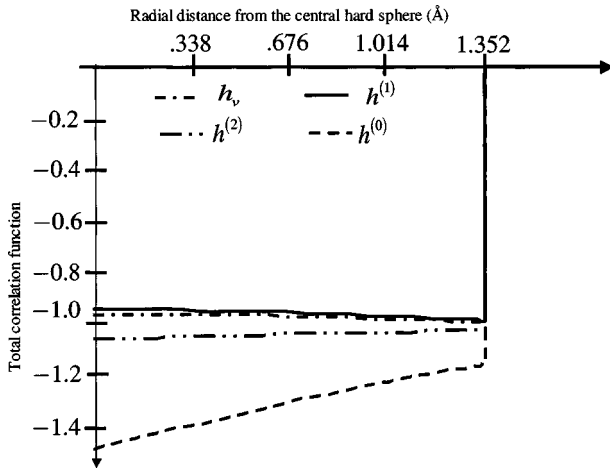
FIG. 1. Total correlation function for water with hard sphere radius of 1.35 Å.

which every approximate solution of the Ornstein-Zernicke equation, for a fluid composed of hard spheres, must be compared. The comparison (with -1) can, of course, only be made in the spatial domain $|\mathbf{r}_i - \mathbf{r}_j| \leqslant \sigma$. There is absolutely no reason why the calculation should be limited to this small domain except one of expediency; we wish to present a rapid demonstration of the efficacy of the variational method in a region where the pair correlation function acquires its maximum values. The extension to larger intermolecular distances and, indeed, to more realistic problems will be presented in future work.

In order to make useful comparisons we select, for the present, the following four approximate solutions of Eq. (28). (1) The zero order solution $h^{(0)}(|\mathbf{r}_i - \mathbf{r}_j|)$ in the iterative expansion in Eq. (6). Clearly in this approximation we are equating the correlation function with the direct correlation function itself. (2) The first order solution $h^{(1)}(|\mathbf{r}_i - \mathbf{r}_j|)$ in the iterative expansion in Eq. (6). (3) The second order solution $h^{(2)}(|\mathbf{r}_i - \mathbf{r}_j|)$ in the iterative expansion in Eq. (6). (4) The variational solution $h_v(|\mathbf{r}_i - \mathbf{r}_j|)$ obtained in Eq. (23). We select the trial functions h_t and h_τ to be of the same form and with a very simple structure:

$$h_t(|\mathbf{r}_i - \mathbf{r}_j|) = h_\tau(|\mathbf{r}_i - \mathbf{r}_j|) = aH(\sigma - |\mathbf{r}_i - \mathbf{r}_j|). \quad (29)$$

Here, a is the variational parameter that must be determined in order to evaluate the variational correlation function h_v.

Although Eq. (28) is strictly valid only for homogeneous systems, one of our goals is to investigate the thermodynamic properties of nanopores in various industrially important polymer electrolytes. We will use the densities that are appropriate to the water content of Nafion membranes. In Fig. 1 the results of the calculations for water with a hard sphere radius of $\sigma = 1.35$ Å are displayed.

The purpose of the calculations that we have presented in this section is to examine the usefulness of the variational approach for the solution of the Ornstein-Zernicke equation. We have also compared the results with that of the iterative approach. The main conclusions may be summarized in the following manner.

(1) The zero order approximation $h^{(0)}$ is certainly a very poor approximation since it tends toward negative values that are less than -1 and therefore of an unphysical nature. Clearly this is not surprising since, in essence, $h^{(0)}$ is the same as the direct correlation function between two particles and therefore ignores the role of all the other particles in the system.

(2) The second order iterate $h^{(2)}$ performs worse than the first order iterate $h^{(1)}$, since as in the case of $h^{(0)}$ it leads to nonphysical values that are less than -1. This is a reflection of the slow convergence of the iterative series and one would have to include higher terms in order to rectify the errors induced by $h^{(2)}$. It is important to point out that even at the second order iteration the results are extremely complicated.

(3) Given the simple form of the trial functions [Eq. (29)] the resulting algebraic expression for the pair correlation function is much more compact than that produced by $h^{(2)}$. It would, indeed be possible to present this formula explicitly; however, no further insight would be obtained thereby and we have therefore not done so. Despite the relatively compact nature of the resulting equation the variational method performs well and does not tend toward unphysical values.

(4) It is important to keep in mind the fact that the accuracy of the results of the variational calculation is limited by the ansatz used for writing an explicit form for the direct correlation function. This problem was alluded to in an earlier paper by Barker and Henderson [21] and reiterated in a more recent paper by Yuste and Santos [22].

V. SELF-CONSISTENT CHOICE OF THE DIRECT CORRELATION FUNCTION

Equation (23) shows that even though a variational solution of the Ornstein-Zernicke equation can be obtained it remains of very little value unless an expression for the direct correlation function c is available. This aspect has been already alluded to above in the context of the closure relations and a numerical example that employs one of the well-known closure relations was employed in the previous section. In general, there are two broad classes of closure relations that are commonly used.

(i) A closed analytic expression for c is chosen, based upon some physical or chemical considerations. This choice will be referred to as an ansatz. In this category of approximations is the mean spherical [23] approximation where the direct correlation function is taken to be simply $-\beta\psi(i,j)$. Recently, Blum and Herrera [24] postulated that a Yukawa type potential can approximate the direct correlation function. Other analytic expressions based on the local density approximation (LDA), where the direct correlation function is replaced by a Dirac δ function, and the weighted LDA have been used [20]. In all these cases the chosen function can be directly inserted in Eq. (23) and the variational expression for the pair correlation function obtained through Eq. (27).

(ii) The direct correlation function is written as a functional of the pair correlation function:

$$c(i,j) = c[h(i,j)]. \quad (30)$$

Two well-known examples of such a relationship are the Percus-Yevick equation

$$c^{(PY)}(i,j) = \{1 - e^{-\beta\psi(i,j)}\}\{h(i,j)+1\} \qquad (31)$$

and the hypernetted chain equation

$$c^{(HNC)}(i,j) = -\beta\psi(i,j) + h(i,j) - \ln\{h(i,j)+1\}.$$

In this paper we present a third approach, which uses the Ornstein-Zernicke equation itself along with a variational method to derive a self-consistent form for the direct correlation function. The Ornstein-Zernicke equation is first rewritten in a form such that the direct correlation function becomes the unknown quantity:

$$c(1,2) = h(1,2) - \int d\bar{1}\, h(1,\bar{1})n_1(\bar{1})c(\bar{1},2). \qquad (32)$$

The iterative expansion of this integral equation follows immediately and is given by

$$c(1,2) = h(1,2) - \int d\bar{1}\, h(1,\bar{1})n_1(\bar{1})h(\bar{1},2)$$
$$+ \int d\bar{1}\, d\bar{2}\, h(1,\bar{1})n_1(\bar{1})h(\bar{1},\bar{2})n_1(\bar{2})h(\bar{2},2) + \cdots. \qquad (33)$$

When Eq. (33) is truncated at different levels a sequence of approximations for the direct correlation function results and each one may be considered to be a functional of the form of Eq. (30). These approximations are, of course, very poor in quality and are improved by the use of the variational method presented below.

We begin by taking a trial function c_t for the direct correlation function (this could be any function that is selected by the ansatz in the first approach discussed above), substituting it in the Ornstein-Zernicke equation, and solving the resultant integral equation to obtain an approximate pair correlation function, which will be designated by the symbol h_s:

$$h_s(1,2) = c_t(1,2) + \int d\bar{1}\, c_t(1,\bar{1})n(\bar{1})h_s(\bar{1},2). \qquad (34)$$

Since Eq. (34) is an integral equation, in the absence of translational invariance it is solved variationally by the application of Eq. (23). Once the pair correlation function h_s has been computed it is substituted in the truncated form of Eq. (33) and the new correlation function thus derived is given the symbol c_u:

$$c_u(i,j) = c_u[h_s(i,j)]. \qquad (35)$$

In the next stage, in order to ensure that the direct correlation function does not contain errors that are lower than second order, Eq. (16) is applied, which yields the desired variational direct correlation function:

$$c_v(1,2) = c_u(1,2) + \int d\bar{1}\, d\bar{2}\, y(1,2;\bar{1},\bar{2})[c_u(\bar{1},\bar{2}) - c_t(\bar{1},\bar{2})]. \qquad (36)$$

The function $y(i,j;k,l)$ plays the role of $x(i,j;k,l)$ in Eq. (16). Since c_v is a variationally derived function it must satisfy

$$\left[\frac{\delta c_v(1,2)}{\delta c_t(3,4)}\right]_{c_t=c} = 0. \qquad (37)$$

Consequently, differentiating Eq. (36) with respect to the initial trial function c_t and setting the result equal to zero an integral equation for $y(i,j;k,l)$ is obtained:

$$y(1,2;3,4) = \alpha(1,2;3,4) + \int d\bar{1}\, d\bar{2}\, y(1,2;\bar{1},\bar{2})\alpha(\bar{1},\bar{2};3,4), \qquad (38)$$

where

$$\alpha(i,j;k,l) \equiv \frac{\delta c_u(i,j)}{\delta c_t(k,l)}. \qquad (39)$$

The overall form of this integral equation is very similar to that of the Ornstein-Zernicke equation; therefore the general discussion that was presented in the context of the general integral Eq. (17) is directly applicable. The consequence of the similarity is that a solution given by either Eq. (16) or Eq. (23) can be obtained immediately:

$$y_v(1,2;3,4) = \alpha(1,2;3,4) + \int d\bar{1}\, d\bar{2}\, y_t(1,2;\bar{1},\bar{2})\alpha(\bar{1},\bar{2};3,4)$$
$$- \int d\bar{1}\, d\bar{2}\, y_t(1,2;\bar{1},\bar{2})y_\tau(\bar{1},\bar{2};3,4)$$
$$+ \int d\bar{1}\, d\bar{2}\, \alpha(1,2;\bar{1},\bar{2})y_\tau(\bar{1},\bar{2};3,4)$$
$$+ \int d\bar{1}\, d\bar{2}\, d\bar{3}\, d\bar{4}\, y_t(1,2;\bar{3},\bar{4})\alpha(\bar{3},\bar{4};\bar{1},\bar{2})$$
$$\times y_\tau(\bar{1},\bar{2};3,4), \qquad (40)$$

where y_t and y_τ are two trial functions.

α is most readily calculated by using Eq. (35) and the chain rule:

$$\alpha(1,2;3,4) = \frac{\delta c_u(1,2)}{\delta c_t(3,4)} = \frac{\delta c_u[h_s(1,2)]}{\delta c_t(3,4)}$$
$$= \int d\bar{1}\, d\bar{2}\, \frac{\delta c_u(1,2)}{\delta h_s(\bar{1},\bar{2})}\frac{\delta h_s(\bar{1},\bar{2})}{\delta c_t(3,4)}, \qquad (41)$$

where the function h_s is given by Eq. (35). Using a diagrammatic representation of the iterative expansion of Eq. (34), the functional differentiation $\delta h_s/\delta c_t$ involved in this equation can be carried out. The procedure necessary is conveniently summarized in the following steps.
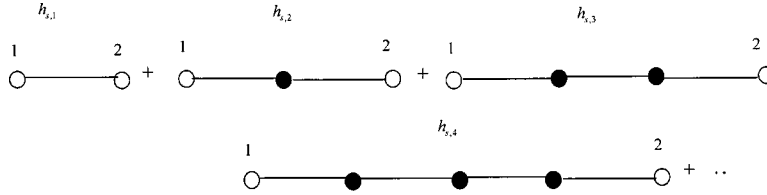
FIG. 2. Diagrammatic expansion of the approximate pair correlation function.

(1) The iterative expansion leads in a standard way to the expression

$$h_s(1,2) = c_t(1,2) + \int d\bar{1}\, c_t(1,\bar{1}) n_1(\bar{1}) c_t(\bar{1},2)$$

$$+ \int d\bar{1}\, d\bar{2}\, c_t(1,\bar{1}) n_1(\bar{1}) c_t(\bar{1},\bar{2}) n_1(\bar{2}) c_t(\bar{2},2)$$

$$+ \cdots .$$

(2) The above expansion contains two root points 1 and 2, which are not integrated over and are designated as white circles. The field points, which are integrated over, carry the one-body distribution function n_1, and are represented by black circles. The trial function c_t are represented as bonds as displayed in Fig. 2.

(3) The Dirac delta function $\delta(i,j)$, appearing as a result of the functional differentiation, is represented by two white circles labeled i and j that are directly joined to each other.

(4) Thus, as an example, the functional derivative of the fourth order term $(h_{s,4})$ in the iterative expansion may be represented according to Fig. 3.

(5) When the functional differentiation of each term in the diagrammatic representation of the iterative expansion is carried out and the results resummed the following outcome is easily seen.

(a) The sum of all terms of the type of diagram (a) yields

$$\delta(1,3) n_1(4) h_s(4,2).$$

The factor of n_1 arises from the conversion of a black to a white circle and, as has already been indicated, the former contain an implicit factor of n_1.

(b) The sum of all terms of type (b) and type (c) is equal to the sum of all diagrams produced by the product

$$n_1(3) h_s(1,3) n_1(4) h_s(4,2).$$

(c) The sum of all terms of type (d) results in

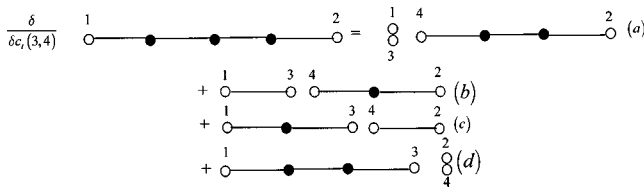$$\delta(4,2) n_1(3) h_s(1,3).$$

FIG. 3. Diagrammatic functional differentiation of the fourth order term.

(d) To the set of terms considered above must also be added the result of the functional differentiation of $h_{s,1}$, which is a unique term in that it does not include any field points. The form of the resultant expression is easily seen to be

$$\delta(1,3)\delta(4,2).$$

Collecting all the terms, the above functional differentiation can be put in a general form:

$$\frac{\delta h_s(i,k)}{\delta c_t(l,j)} = n_1(l) h_s(i,l) n_1(j) h_s(k,j) + \delta(i,l) n_1(j) h_s(k,j)$$

$$+ \delta(k,j) n_1(l) h_s(i,l) + \delta(i,l)\delta(k,j) \quad (42)$$

The functional derivative $\delta c_u / \delta h_s$ can be obtained from Eq. (35).

Finally, Eqs. (35) and (42) provide all the functions that are needed for the computation of α and thus of the direct correlation function c_v.

In order to ensure that the steps presented in this section are completely clear we present an example of the calculation. The objective of this example is to clarify the mathematical steps involved rather than to study a real system for which the computational details would obscure the essence of the derivation. The computation is summarized in the following steps.

(i) From Eq. (33) only the first term is considered and so Eq. (30) takes the form

$$c[h] \approx h. \quad (43)$$

(ii) The trial function c_t is taken to be a simplified version of Eq. (4) in which the second term is replaced by an unknown parameter b to be determined variationally:

$$c_t(1,2) = \frac{1}{n_1(1)} \delta(1,2) + b. \quad (44)$$

If, in Eq. (44), we set $b=0$ then the direct correlation function becomes the local density approximation, which has already found numerous applications [20].

(iii) c_t thus defined is substituted in Eq. (34) and the pair correlation function h_s computed variationally by the application of Eqs. (23) and (27). The two trial functions h_t and h_τ are again taken to be of very simple forms, $h_t = a$ and $h_\tau = a$, with the parameter a variationally determined:

$$h_s(1,2) = \frac{\delta(1,2)}{n_1(1)} + K(b),$$

$$K(b) \equiv a + b + 2a^2 q_1 + abq_1 + a^2 bq_1^2 + ab(a+q), \quad (45)$$

$$a = -\frac{1+2bq_1}{2(b+2q_1+bq_1^2)}.$$

q_1 is the one-body configuration integral whose value may be computed from Eq. (1) with $N=1$.

(iv) Since the direct correlation function has been selected to have the form given by Eq. (43) it follows that the function c_u defined by Eq. (35) must be equal to h_s defined by Eq. (45):

$$c_u(1,2) = h_s(1,2).$$

From Eq. (45) it follows that

$$c_u(1,2) - c_t(1,2) = K(b) - b. \tag{46}$$

(v) The derivative of c_u with respect to h_s is now given by

$$\frac{\delta c_u(1,2)}{\delta h_s(\bar{1},\bar{2})} = \delta(1,\bar{1})\,\delta(2,\bar{2}).$$

Using Eq. (42) we get

$$\frac{\delta h_s(\bar{1},\bar{2})}{\delta c_t(3,4)} = \delta(\bar{1},3)\,\delta(\bar{2},4) + \delta(\bar{2},4)n_1(3)\left[K(b) + \frac{\delta(\bar{1},3)}{n_1(\bar{1})}\right]$$

$$+ \delta(\bar{1},3)n_1(4)\left[K(b) + \frac{\delta(\bar{2},4)}{n_1(\bar{2})}\right] + n_1(3)$$

$$\times \left[K(b) + \frac{\delta(\bar{1},3)}{n_1(\bar{1})}\right]n_1(4)\left[K(b) + \frac{\delta(\bar{2},4)}{n_1(\bar{2})}\right].$$

Substituting these two derivatives in Eq. (41) followed by the required integration yields

$$\alpha(1,2;3,4) = \delta(1,3)\,\delta(2,4) + \delta(2,4)n_1(3)\left[K(b) + \frac{\delta(1,3)}{n_1(1)}\right]$$

$$+ \delta(1,3)n_1(4)\left[K(b) + \frac{\delta(2,4)}{n_1(2)}\right] + n_1(3)$$

$$\times \left[K(b) + \frac{\delta(1,3)}{n_1(1)}\right]n_1(4)\left[K(b) + \frac{\delta(2,4)}{n_1(2)}\right].$$

$$\tag{47}$$

(vi) The expression for α thus calculated is substituted in Eq. (40) after suitable choices for the trial functions y_t and y_τ have been made to obtain the solution y_v. Since the aim of this example is to illustrate the computation rather than produce accurate results it is sufficient, for the present purposes, to set

$$y(1,2;3,4) \approx \alpha(1,2;3,4). \tag{48}$$

(vii) Substituting Eqs. (46), (47), and (48) in Eq. (36), we obtain the direct correlation function

$$c_v(1,2) = \frac{\delta(1,2)}{n_1(1)} + \phi(b),$$

$$\phi(b) = K(b) + [K(b) - b][2 + K(b)q_1]^2. \tag{49}$$

(viii) The parameter b is finally found by differentiating Eq. (49) with respect to b, setting the answer equal to zero, and solving for b. Therefore b is a solution of the equation

$$\frac{d\phi(b)}{db} = 0.$$

In general, the solution of the resulting algebraic equation must be obtained by numerical methods.

Finally, it is important to make some remarks comparing the variational method presented in this paper with other variational methods that abound in statistical mechanics. Perhaps one of the most important variational theorems is the one obeyed by the grand potential in connection with the equilibrium density. Evans [6] presents an excellent account of this theorem in connection with the liquid-vapor phase interface. After showing that the grand potential is a functional of the one-body density, the theorem demonstrates that the former possesses a minimum with respect to the latter at equilibrium. The variational theorem that we present is of a mathematical nature that would appear whenever an integral equation of a form similar to the Ornstein-Zernicke equation is considered.

VI. CONCLUSIONS

In this paper we have presented a very general theorem that is obeyed by the Ornstein-Zernicke equation and by any integral equation that possesses the same overall form. The main utility of this result lies in the fact that it provides us with the tools for obtaining approximate solutions and therefore constitutes an alternative to the more expensive numerical methods. As is common with all variational techniques the quality of the result obtained depends critically upon the initial guesses that are made in connection with the trial solutions. However, the flexibility provided in the choice of the trial function does provide the investigator the added benefit of using functions that can be easily manipulated in mathematical terms. Integral equations possessing forms that are similar to the Ornstein-Zernicke equation are very common and can be found in a variety of different situations. From the discussion we have presented in this paper these equations too will obey the variational principle derived above. For example, recently, Cortis, Rossky, and Friesner [25] showed that it is possible to derive molecular origin-site forms of the Ornstein-Zernicke equation and it would be of interest to solve these equations using the present method.

The applications of the methodology presented to real systems, in particular to the thermodynamics of nanopores, will be presented in forthcoming work.

[1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

[2] T. Morita and K. Hiroike, Prog. Theor. Phys. **25**, 537 (1961).

[3] G. Stell, *The Equilibrium Theory of Classical Fluids* (Benjamin, New York, 1964).

[4] J. M. Bomont and J. L. Bretonnet, J. Chem. Phys. **114**, 4141 (2001).

[5] B. J. Berne, *Statistical Mechanics* (Plenum, New York, 1977), Part A.

[6] R. Evans, Adv. Phys. **28**, 143 (1979).

[7] P. Tarazona and R. Evans, Mol. Phys. **47**, 1033 (1982).

[8] M. Wertheim, Phys. Rev. Lett. **10**, 321 (1963).

[9] L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1972).

[10] L. Blum, F. Vericat, and J. N. Herrera-Pacheo, J. Stat. Phys. **66**, 249 (1992).

[11] L. Degreve and L. Blum, Physica A **224**, 550 (1996).

[12] L. Blum and M. Ubriaco, Mol. Phys. **98**, 829 (2000).

[13] S. J. Paddison, R. Paul, and T. A. Zawodzinski, Jr., J. Electrochem. Soc. **147**, 617 (2000).

[14] S. J. Paddison, R. Paul, and T. A. Zawodzinski, Jr., J. Chem. Phys. **115**, 7753 (2001).

[15] S. J. Paddison, R. Paul, and K.-D. Kreuer, Phys. Chem. Chem. Phys. **4**, 1151 (2002).

[16] S. J. Paddison and R. Paul, Phys. Chem. Chem. Phys. **4**, 1158 (2002).

[17] L. Rosenberg and S. Tolchin, Phys. Rev. A **8**, 1702 (1973).

[18] M. M. Vainberg, *Variational Methods for the Study of Nonlinear Operators* (Holden-Day, San Francisco, 1964).

[19] B. Götzelman, A. Haase, and S. Dietrich, Phys. Rev. E **53**, 3456 (1996).

[20] B. Götzelman and S. Dietrich, Fluid Phase Equilib. **150-151**, 565 (1998).

[21] A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).

[22] S. B. Yuste and A. Santos, Phys. Rev. A **43**, 5418 (1990).

[23] J. L. Lebowitz and J. K. Percus, Phys. Rev. **144**, 251 (1966).

[24] L. Blum and J. N. Herrera, Mol. Phys. **95**, 425 (1998).

[25] C. M. Cortis, P. J. Rossky, and R. A. Friesner, J. Chem. Phys. **107**, 6400 (1997).