Thermodynamically consistent truncations of distribution function hierarchies

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In this paper we initiate a study of the closure problem in the statistical mechanical theory of fluids, with particular emphasis on the problem of identifying thermodynamically consistent truncations of distribution function hierarchies. Our approach is: (i) to choose an appropriately restricted set of variables for the reduced distribution functions $\rho^{(n)}$ and to generate corresponding hierarchies; (ii) to retain, for a $k$th order truncation, all those equations involving only the $\rho^{(n)}$ with $n< k$; and (iii) to choose the truncation for which all these equations can be satisfied simultaneously. In this paper we focus on the problem of identifying self-consistent, third-order truncations for translationally invariant systems. We show that the analytical approach taken provides guidance in the construction of such closures and we comment on the factors involved in implementing numerically a specific choice of closure identified in our study.

I. INTRODUCTION

In classical equilibrium statistical mechanics, the reduced distribution functions $\rho^{(n)}(r_1\cdots r_n)$ play a central role since the average of any physical quantity can be computed from them. There are many hierarchical relationships among these distribution functions. They are found by differentiating any $\rho^{(n)}$ with respect to some parameter and expressing the resulting average in terms of higher order distribution functions. Some standard examples result from differentiating $\rho^{(n)}$ with respect to: (i) the temperature—giving a hierarchy relating $\partial \rho^{(n)}/\partial T$ to $\rho^{(n+1)}$ and $\rho^{(n+2)}$; (ii) the fugacity—relating $\partial \rho^{(n)}/\partial \mu$ to $\rho^{(n+1)}$; (iii) any position coordinate $r_i$—relating $\nabla \rho^{(n)}$ to $\rho^{(n+1)}$ (the BBGKY hierarchy); (iv) the strength of the potential energy coupling a particular particle to the others—giving the Kirkwood coupling parameter hierarchy. More general hierarchical relations can be generated by differentiating $\rho^{(n)}$ with respect to any parameter upon which the system's potential energy depends. The number of such sets of relations depends on the class of intermolecular potentials under consideration and could be very large if the potentials contain many parameters. Each hierarchy is itself an infinite set of relationships between the $\rho^{(n)}$. It is characteristic of the hierarchies formed by differentiation that, if the system potential energy contains only one- and two-particle potentials, the derivative of $\rho^{(n)}$ is given in terms of, at most, $\rho^{(n)}$, $\rho^{(n+1)}$, and $\rho^{(n+2)}$.

A number of approximate theories of the reduced distribution functions are based on these hierarchies. They are formed by assuming that some finite order distribution function $\rho^{(k)}$ can be functionally related to only lower order distribution functions, i.e., that $\rho^{(k)} = F(\rho^{(k-1)}, \rho^{(k-2)}, \ldots, \rho^{(0)})$ for some assumed functional $F$. This assumption can often be used to truncate a chosen infinite hierarchy to a finite set of integrodifferential equations determining $\rho^{(n)}$ for $n<k$. The functions $\rho^{(n)}$, $n> k$, are indeterminate and the hierarchical equations for $n>k$ are neglected. We shall call such approximations $k$th order truncations. Different approximate $\rho^{(n)}$ result from choosing various decoupling functionals $F$ and various hierarchies.

As examples of such theories, we mention: (i) attempts to describe the fluid-solid transition by Kirkwood and others from second order truncation of the BBGKY hierarchy; (ii) use of the Kirkwood superposition approximation to effect a third order truncation of either the BBGKY hierarchy or the coupling parameters hierarchy to describe the translationally invariant states of fluids; (iii) recent work of Rice and co-workers using a third order truncation of the BBGKY hierarchy based on a modified superposition principle suggested by formal summations of virial expansions; (iv) a generalized superposition principle yielding a fourth order truncation of the BBGKY hierarchy. There are numerous other examples and, in addition, structurally similar theories often arise in the Green's function approach to the quantum mechanical many body problem.

It has been noted many times in the literature that these theories suffer from various inconsistencies. For example, in any of the above theories which determine $\rho^{(2)}$, there are three ways of computing the pressure. From the virial expression, by integrating the compressibility sum rule, and by integrating the internal energy equation. Each of these methods is based on a member of a different hierarchy. The correct distribution functions of course satisfy all the hierarchies and would give the same pressure by all three methods. In the approximate theories, the distribution functions are computed from a particular hierarchy and generally do not satisfy the others, and hence such theories produce three different pressure equations of state. An even more drastic inconsistency occurs in the usual fourth order truncations of the BBGKY hierarchy where it is known that the solutions.
depend on arbitrary choices of paths of integration and are therefore also not unique. A general view of these inconsistency problems is this: The various hierarchies give expressions for the derivatives of the distribution functions with respect to all of the variables upon which they depend. A given \( k \) th order truncation will reduce these infinite hierarchies to a finite set of equations involving \( k - 1 \) distribution functions and their derivatives. Solving these equations is equivalent to integrating the directional derivatives of the distribution function, from some point (low density, large \( r \), etc.) where they are known, along some path in the space of independent variables, to some general final point. In order that the theory produce unique values for the \( \rho^{(n)} \), this integration must be path independent; that is, the hierarchical expressions for the first derivatives must produce the same mixed second derivatives. The truncations in use do not have this property and hence, for example, constructing the pressure by integrations along different paths produces different equations of state.

One could escape this dilemma by specifying, for a given truncation, some particular path of integration. This is usually done by assuming that the truncation is valid for certain of the hierarchies but not for others. Arguments of this kind are sometimes made by them who are usually not very compelling and there seems to be no general principle by which one could associate a particular path of integration with a particular truncation. A second approach might be to view this lack of uniqueness as a quality test of the truncation assumption. That is, if a given truncation produces results which show large variation with choice of path, it is a "bad" approximation. One should simply be done with it and search for truncations which give less path dependent variation and are therefore more consistent.

In this paper we take a third point of view. We want to impose the consistency requirements as conditions on the truncation in the general form of a self-consistent theory. Our approach is to: (i) choose an "appropriately" restricted set of variables for the \( \rho^{(n)} \) and to generate the corresponding hierarchies; (ii) retain, for a \( k \) th order truncation, all those equations involving only the \( \rho^{(n)} \) with \( n < k \); (iii) choose the truncation so that all of these equations can be simultaneously satisfied. In this paper we apply this approach to the problem of self-consistent, third-order truncations for translationally invariant systems. The choices we make are hardy unique at any stage of the development; nevertheless, this approach does provide considerable guidance in the construction of such theories.

In Sec. II we discuss the choice of hierarchies and in Sec. III the truncations. In Sec. IV we consider the prospects for the numerical solution of such systems of equations.

II. THE CHOICE OF HIERARCHICAL EQUATIONS

We restrict ourselves to systems of identical particles with translationally and rotationally invariant two-body forces, i.e., systems for which the potential energy has the form

\[
U_N(r_1, \ldots, r_N) = \sum_{i=2}^{N} \phi(|r_i - r_j|)
\]  

(2.1)

We work, initially, in the grand canonical ensemble so that at a later stage in our development the thermodynamic limit may be taken conveniently. The distribution functions are defined by

\[
\rho^{(n)}(r_1, \ldots, r_N) = \frac{1}{Z} \sum_{\lambda} \frac{1}{|l - n|!} \int \cdots \int e^{-\beta U_i} d\tau_{n+1} \cdots d\tau_i ,
\]

(2.2)

where \( \beta = 1/kT \) is the inverse temperature, \( V \) is the volume,

\[
z = \left( \frac{2\pi \hbar^2 \gamma}{mkT} \right)^{-3/2} e^{\mu/kT} ,
\]

(2.3)

(where \( \mu \) is the usual chemical potential) and

\[
Z = \sum_{\lambda} \frac{1}{|l - n|!} \int \cdots \int e^{-\beta U_i} d\tau_{n+1} \cdots d\tau_i .
\]

(2.4)

For translationally invariant systems

\[
\rho^{(1)}(r_i) = \langle N \rangle / V = \rho
\]

(the particle density) and \( \rho^{(0)} = \rho / kT \), where \( \rho \) is the pressure. For the moment we keep \( V \) finite, but all the \( \rho^{(n)} \) are expected to have well-behaved, \( V \to \infty \) limits for single phase states.

In addition to the explicitly indicated dependence on the coordinates \( r_i \), the \( \rho^{(n)} \) depend on the variables \( V, z, \) and \( \beta \) and any parameters \( \{ \lambda \} \) which might appear in the pair potentials \( \phi(|r_i, r_j|, \{ \lambda \}) \). For example, the Lennard-Jones potential depends on two parameters (range and strength) whereas the hard sphere-square well potential is defined by three parameters.\(^6\) There is an infinite hierarchy corresponding to each of these variables, formed by differentiating each of the \( \rho^{(n)} \) with respect to that variable. For which of these hierarchies should we require the truncation assumption to be consistent? It is clear that we want to consider those corresponding to \( V, \beta, z \) and the coordinates \( r \) since, in general, we would hope that our theory would not require us to fix the values of any of these variables. If we want our theory to treat all potentials within a given family then we should consider hierarchies corresponding to those parameters defining the family of potentials of interest. Here it is clear that some "reasonable" choice must be made since, in principle, the potentials could contain infinitely many parameters. Since we are interested in systems of identical particles, we shall require at least that the family of potential energies we consider be symmetric in all the particle variables. This requirement eliminates those hierarchies, such as the Kirkwood coupling parameter hierarchy, which are generated by differentiating the \( \rho^{(n)} \) with respect to parameters which distinguish particular particles. The rationale is simply that processes that vary the properties of a single particle are unrealistic and requiring the theory to be consistent with such processes is of low priority.

We give below the hierarchies corresponding to the above choice of variables. Since we are interested in third-order truncations we list, for each hierarchy, only those equations which do not involve any \( \rho_n \) for \( n > 3 \).

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We consider first the volume derivatives of the $\rho_s$. The usual method is to rescale the coordinates in Eqs. (2.2) and (2.4) by $r = V^{1/3}$ so the integrations are over the unit cube, differentiate with respect to the now explicit $V$ dependence in the integrands, and then transform back to the original variables $r$. This gives for the volume derivatives of $\rho (0)$ and $\rho (1)$:

$$\frac{\partial \rho (0)}{\partial V} = -\rho (0) V + \frac{1}{V^2} \int \rho (1) \, d(1)$$

$$\frac{\beta}{6 V^2} \int \left[ (r_1 - r_2) \cdot \nabla \phi (1,2) \rho (2) \, d(2) \right] \, d(2)$$

and

$$\frac{\partial \rho (1)}{\partial V} = \frac{1}{V} \int \rho (2) \, d(2)$$

$$\frac{\beta}{3 V} \int (r_2 - r_1) \cdot \nabla \phi (1,2) \rho (2) \, d(2)$$

$$\frac{\beta}{6 V} \int \left[ (r_2 - r_1) \cdot \nabla \phi (2,3) \rho (3) \, d(2,3) \right] \, d(2)$$

$$\times d(2) \, d(3) - \rho (1) (1) \frac{\partial}{\partial V} (V \rho (0)),$$

where we have indicated the particle coordinates in these expressions by their indices. The volume derivatives of the higher $\rho (n)$ involve $\rho (n)$ or higher terms. In the thermodynamic limit $V \to \infty$, we expect the distribution functions to behave as

$$\rho (n) (V) \approx \rho (n) + V - n \rho \frac{\partial}{\partial V} \rho (0),$$

where the limit function $\rho (n)$ and the correction term $\rho \frac{\partial}{\partial V} \rho (0)$ are well behaved for single phase states and $\alpha$ is some positive constant. We also expect the limit $\rho (n)$ to be translationally invariant. Using these properties we multiply Eq. (2.5) by $V$ and let $V \to \infty$ to obtain

$$\rho (0) = \rho (1) - \frac{\beta}{6} \int (r_1 - r_2) \cdot \nabla \phi (1,2)$$

$$\times \rho (2) \, d(2),$$

i.e., the usual virial expression for the pressure $[\rho (0) = p / k T, \rho (1) = \rho]$. The $V \to \infty$ limit of Eq. (2.6) is more delicate. We show in Appendix A that as $V \to \infty$, Eqs. (2.5) and (2.6) imply

$$\rho (2) (1,2) = \rho (1) (1) \rho (1) (2) \, d(2)$$

$$+ \frac{\beta}{3} \int (r_1 - r_2) \cdot \nabla \phi (1,2) \rho (2) \, d(2)$$

$$= \frac{\beta}{6} \int (r_2 - r_1) \cdot \nabla \phi (2,3)$$

$$\times \left[ \rho (3) (1,2,3) - \rho (1) \rho (2) (2,3) \right] \, d(2) \, d(3).$$

This relation, which seems largely unknown, is found in Ref. (9), Eq. (38).

We consider next the $z$ (fugacity) derivatives of the $\rho (n)$. The calculations are straightforward and the results are well known. They are, in the limit $V \to \infty$, and up to order $\rho (3)$:

$$z \frac{\partial \rho (0)}{\partial z} = \rho (0)$$

$$z \frac{\partial \rho (1)}{\partial z} = \rho (1) + \int \rho (2) (1,2) - \rho (1) \rho (1) \, d(2),$$

$$z \frac{\partial \rho (2)}{\partial z} = 2 \rho (2) (1,2) + \int \rho (3) (1,2,3)$$

$$- \rho (1) \rho (2) (1,2) \, d(2).$$

Equation (2.9) gives density as a $z$ derivative of the grand potential and Eq. (2.10) is the usual compressibility sum rule. Equation (2.11) is also known although it is usually written in the form of a density derivative.

The temperature hierarchy has two equations relating distribution functions of order three or less. They are, in the $V \to \infty$ limit,

$$\frac{\partial \rho (0)}{\partial \beta} = -\frac{1}{\beta} \int \phi (1,2) \rho (2) (1,2) \, d(2)$$

$$\frac{\partial \rho (1)}{\partial \beta} = -\int \phi (1,2) \rho (2) (1,2) \, d(2)$$

$$\phi (2,3) [\rho (3) (1,2,3)$$

$$- \rho (1) \rho (2) (2,3) \, d(2) \, d(3).$$

The BBGKY hierarchy follows from differentiating with respect to the coordinate $r_i$. For a translationally invariant system of identical particles, there is only one (vector) equation at third order:

$$\nabla_i \rho (2) (1,2) = -\beta \rho (2) (1,2) \nabla_i \phi (1,2)$$

$$- \beta \nabla_i \phi (1,3) \rho (3) (1,2,3) \, d(3).$$

Finally, if we consider a family of pair potentials $\phi (r, [\lambda])$ which depend on a set of parameters $[\lambda] = [\lambda_1, \lambda_2, ..., \lambda_n]$, there will be a truncated hierarchy corresponding to each $\lambda_i$. They are, up to third order, of the form

$$\frac{\partial \rho (0)}{\partial \lambda_i} = -\frac{\beta}{2} \int \frac{\partial \phi (1,2, [\lambda])}{\partial \lambda_i} \rho (2) (1,2) \, d(2),$$

$$\frac{\partial \rho (1)}{\partial \lambda_i} = -\beta \rho (1,2, [\lambda]) \frac{\partial \phi (1,2, [\lambda])}{\partial \lambda_i} \rho (2) (1,2) \, d(2)$$

$$- \beta \frac{\partial \phi (2,3, [\lambda])}{\partial \lambda_i} \rho (3) (1,2,3)$$

$$- \rho (1) \rho (2) (2,3) \, d(2) \, d(3).$$

for each parameter $\lambda_i$.

The strongest consistency requirement on a third order theory would be to require a functional relation between $\rho (3)$, $\rho (2)$, $\rho (1)$, and $\rho (0)$ capable of satisfying all of the equations, (2.7)–(2.16). To construct such a relation, one must know how many unknown functions (functional degrees of freedom, so to speak) should appear in the functional, and for this reason it is essential to understand how many of the equations (2.7)–(2.16) are functionally independent. For example, if we restrict ourselves to a two-parameter family of pair potentials of the form

$$\phi (r, [\lambda]) = \lambda_1 u (r / \lambda_1),$$

then Eqs. (2.15) and (2.16) are implied by other equations in
the set. It’s easy to see that derivatives with respect to $\lambda_1$ are equivalent to temperature derivatives so Eqs. (2.15) and (2.16), for $\lambda_1$, are the same as Eqs. (2.12) and (2.13). Similarly, we show in Appendix D that derivatives with respect to the range parameter, say $\lambda_2$, can be expressed in terms of volume, coordinate, and $z$ derivatives and therefore are redundant with these hierarchies. These results follow from ordinary dimensional analysis and are just a statement of the law of corresponding states for potentials of this type. We emphasize that for a consistent theory covering more complex families of potentials, one would have independent equations of the type Eqs. (2.15) and (2.16).

There are three other relationships in the set Eqs. (2.7)–(2.14) which are independent of any assumptions concerning the truncation functional. They are best seen by considering the four equations which explicitly involve $\rho^{\alpha\beta}$: Eqs. (2.8), (2.11), (2.13), and (2.14). By multiplying Eqs. (2.11) and (2.14) by appropriate factors and integrating over a coordinate, it is possible to eliminate the $\rho^{\alpha\beta}$ dependent terms between pairs of equations. This can be done in three independent ways and gives rise to three independent linear relationships among the set, Eqs. (2.7)–(2.14); these relationships can be used to reduce the set of equations by three equations in a variety of ways. Specifically, we show in Appendix C that the five equations, Eqs. (2.7), (2.9), (2.11), (2.12), and (2.14), are sufficient to derive the remaining ones. We rewrite these equations in terms of the more usual variables, $p = \rho^{\alpha\beta} / \beta$, $\rho = \rho^{\alpha\beta}$ and the dimensionless distribution functions $g^{\alpha\beta}$, where $\rho^{\alpha\beta} = \rho^{\alpha\beta} g^{\alpha\beta}$. Thus,

$$
\rho = \rho / \beta - \frac{1}{\beta} \rho^2 \int (r_1 - r_2) \nabla \phi (1,2) g^{(2)}(1,2) d(2),
$$

(2.18)

$$
\beta \frac{\partial \rho}{\partial z} = \rho,
$$

(2.19)

$$
\rho \frac{\partial}{\partial z} g^{(2)}(1,2) = 2 \rho^2 g^{(2)}(1,2)
$$

(2.20)

$$
\rho \left[ g^{(3)}(1,2,3) - g^{(2)}(1,2) \right] d(3)
$$

(2.21)

$$
\beta \rho \left[ \nabla \phi (1,3) g^{(2)}(1,2,3) d(3) \right]
$$

(2.22)

The other equations [Eqs. (2.8), (2.10), and (2.13)] will, of course, be true and can be used in theoretical manipulations but they can be derived from the sufficient set, Eqs. (2.18)–(2.22). In the above equations, the independent variables are $\rho$, $\beta$, and $\rho$, appropriate to the grand ensemble. For actual calculations, it is usually more convenient to use either $\rho$ or $\rho$, rather than $\rho$, as the independent variable. We can use Eqs. (2.19) and (2.21) to convert $\rho$ derivatives (at constant $\beta$) into $\rho$ derivatives (at constant $\beta$), and to convert $\beta$ derivatives (at constant $\rho$) into $\beta$ derivatives (at constant $\rho$) in the remaining equations by the usual partial derivative manipulations. Equations (2.10) and (2.13) can be used in a similar way if we prefer to use $\rho$ as an independent variable. So long as the sufficient set Eqs. (2.18)–(2.22) is satisfied, none of the above changes of variables can lead to any inconsistencies or change the physical content of the theory. For our discussions of thermodynamic consistency, the set Eqs. (2.18)–(2.22) is convenient.

All of the equations we have considered have appeared in various places in the literature and did not originate with us. Our development so far has been just to show the sense in which Eqs. (2.7)–(2.16) are a “complete” set of hierarchical equations (to order three) and to show that Eqs. (2.18)–(2.22) are a sufficient set to ensure the thermodynamic consistency of all the quantities predicted by the theory.

### III. Identification of a Consistent Truncation

In addition to Eqs. (2.18)–(2.22), there are three other structural properties of distribution functions with which the theory must be compatible. The distributions $g^{\alpha\beta}$ must be invariant under the interchange of any pair of coordinates. In single phase states, the $g^{\alpha\beta}$ also must have the correct long-range behavior, i.e.,

$$
g^{\alpha\beta}(r_1,\ldots,r_n) \rightarrow g^{\alpha\beta}(r_1,\ldots,r_{n-1}) \text{ as } r_n \rightarrow \infty.
$$

(3.1)

For potentials which are infinite at short range (corresponding to strong short range repulsive forces) the distribution functions must vanish at short range, i.e.,

$$
g^{\alpha\beta}(r_1,\ldots,r_n) \rightarrow 0 \text{ if any } |r_i - r_j| < 0.
$$

(3.2)

It is clear, for example, that in the usual superposition approximation

$$
g^{(3)}(1,2,3) = g^{(2)}(1,2) g^{(2)}(1,3) g^{(2)}(2,3),
$$

(3.3)

g^{(3)}(r,z,\beta)

will have the above three properties if $g^{(2)}$ has them.

Before considering the consistency requirements, it is useful to review the known inconsistencies of the superposition truncation. If the relation (3.3) is used in Eq. (2.22), a first order integrodifferential equation for $g^{(2)}$ results which can be solved for all $r$, $\rho$, and $\beta$, with the boundary condition $g^{(2)}(r) = 1$ as $r \rightarrow \infty$. However, if Eq. (3.3) is used in Eq. (2.20) [with Eqs. (2.18) and (2.19)], the resulting equation for $g^{(2)}$ can be integrated with the boundary condition $g^{(2)}(r \rightarrow \infty) = 0$. The two resulting $g^{(2)}$ are not the same. Either of these $g^{(2)}$ can be used in Eqs. (2.18), (2.19), or (2.21) [with appropriate boundary conditions and use of Eqs. (2.10) and (2.13)] to generate three relations between $p$, $\rho$, and $\beta$. These relations are again not the same. These inconsistencies are known empirically through numerical studies or analytically by solving the equations with power series expansions in the density. (These calculations are, again, usually done with $\rho$ as the independent variable rather than $z$.) Some reflection on the structure of Eqs. (2.18)–(2.22) suggests that there are enough equations to determine two functions of $\rho$, $\beta$, and three functions of $\rho$, $\beta$. The difficulty with superposition from this point of view is that it involves only one unknown function of $\rho$, $\beta$. Clearly, we need more degrees of freedom in formulating a truncation assumption.

To proceed, let us assume that $g^{(2)}(r,z,\beta)$ can be written as a product of a short-range factor $\rho(r,z,\beta)$ and another range factor $\rho(r,z,\beta)$; thus we write

$$
\rho^{(2)}(r,z,\beta) = \rho(r,z,\beta) \rho(r,z,\beta).
$$

(3.4)

This factorization is partly defined by the zero fugacity
boundary condition
\[ \phi(r, 0, \beta) = e^{-\Delta \Phi(r)} \quad \xi(r, 0, \beta) = \frac{1}{1 + \beta r} \]

we may write
\[ \phi(r, 0, \beta) = \frac{1}{1 + \beta r} \]

The spatial boundary conditions are
\[ \phi(\infty, z, \beta) = 1 \]

Conceptually, this separation corresponds to a part \( \phi \), rapidly varying at short range, dominated by the direct interaction of two molecules and which satisfies the short range condition
\[ \lim_{|r| \to \infty} \phi(r, z, \beta) = 0 \]

and a somewhat smoother part \( \xi \), nearly constant at a short range, which represents the correlations mediated by other particles. We now generalize superposition by writing \( g^{(3)} \) as a local function of \( \phi \) and \( \xi \) of no more than cubic order in each. Consider the expression
\[ g^{(3)}(1, 2, 3) = \phi(1, 2) \phi(1, 3) \phi(2, 3) \]

Moreover, \( a, b, c, d \) are independent of coordinates but may depend on \( \Delta \beta \). This expression is symmetric in particle indices. The product of three \( \phi \) factors causes \( g^{(3)} \) to vanish whenever two coordinates approach each other, and it is easy to check that the second structural condition (3.1) will be satisfied if
\[ a + 2b + c = 0, \quad b + 2c + d = 1 \]

So, only two of the coefficients, say \( a \) and \( b \), are independent. The superposition approximation corresponds to the choice
\[ a = b = c = 0, \quad d = 1 \]

The structural difference in the way \( \phi \) and \( \xi \) appear in Eq. (3.8) is because \( \beta \) need not vanish at small \( r \). Now, Eqs. (3.4) and (3.8) provide a generalization of superposition which appears to be capable of satisfying simultaneously Eqs. (2.18)-(2.22). When Eqs. (3.4) and (3.8) are substituted into Eqs. (2.18)-(2.22), we have five equations for the functions \( \phi(r, z, \beta) \), \( \xi(r, z, \beta) \), \( \rho(z, \beta) \), \( \rho(z, \beta) \), \( \alpha(z, \beta) \), and \( b(z, \beta) \). It seems we have too many functions of \( z, \beta \) and need somehow to eliminate \( a \) or \( b \). A natural choice might be to keep only up to quadratic terms in \( \beta \) in Eq. (3.8), i.e., to set \( d = 0 \) so that \( b = -\beta(2a + 1) \). However such a choice is made, it must involve considerations other than thermodynamic consistency. With such a choice, however, and with appropriate boundary conditions, it appears that Eqs. (2.18)-(2.22) would determine the unknown functions.

For coupled nonlinear equations of this complexity, it is difficult even to give proofs of existence or uniqueness of solutions and, in practice, one must rely on numerical techniques of solution. It may turn out, upon numerical investigation, that the forms (3.4) and (3.8) are, for one reason or another, ill chosen. (There are surely many other forms compatible with the arguments we have introduced.) It is our view, however, that any choice of truncation will have an ad hoc flavor that can be mitigated only by structural requirements of some sort or by requirements of simplicity. As reasons for considering Eqs. (3.4) and (3.8), we reiterate that this truncation: (i) is a generalization of a relation (superposition) which is known to be fairly accurate for several particle configurations; (ii) appears to be capable of satisfying a rather natural and complete set of thermodynamic relationships and; (iii) leads to a set of equations whose numerical solution appears possible with known techniques and existing computers. We turn to a preliminary discussion of this last point in the following section.

IV. FIXED POINT METHODS OF SOLUTION

If Eqs. (3.4) and (3.8) are substituted into Eqs. (2.18)-(2.22), a coupled set of nonlinear integrodifferential equations result for the five functions \( \phi, \xi, \rho, \alpha, \) and \( \beta \) whose exact structure we will not need for the following general discussion. Such equations can always be put in a so-called "fixed point" form
\[ f_\alpha(x) = F_\alpha([f_\beta(x)]) \]

where the \( F_\alpha \) are functionals of all the unknown functions \( f_\beta \) of some set of variables \( x \). This task can, in fact, be done in an infinite variety of ways. If the functionals \( F_\alpha \) are of any simplicity (and they certainly are in our case), one normally tries to solve these equations numerically by a first-order iterative process as follows. Suppose we have an \( n \)th order approximation \( f_\beta^n(x) \) for the unknown functions. Then to each fixed point form Eq. (4.1) there corresponds a procedure for generating the \( n + 1 \)th-order approximation, i.e.,
\[ f_\alpha^{n+1}(x) = F_\alpha([f_\beta^n(x)]) \]

For different fixed point forms Eq. (4.1) of the same set of equations, one generates different iterative schemes Eq. (4.2) some of which may diverge. However, in certain circumstances, one can show that a properly chosen fixed point form will lead to an iterative scheme such that \( f_\alpha^n(x) \) converges, as \( n \to \infty \), to a solution of Eq. (4.1). (For a discussion of these conditions, which depend on the eigenvalues of the functional derivatives of the \( F_\alpha \), see Ref. 11.) In practice, however, these equations are so complex that it is difficult to predict a priori if a given iterative scheme will converge. Accordingly, in practice one simply chooses a particular iterative form, guided by past experience with similar equations, realizes it numerically by evaluating Eq. (4.2), and then tests empirically the convergence. 11 Convergent iterative schemes for the superposition closure have been used and our equations, while more complex, are structurally similar. For states in which the correlations are short ranged (of a few molecular diameters) the spatial variable \( r \) can be...
kept fairly small in the numerical calculations and the computational problems (of computer space and time) should be manageable. Near the critical point of the fluid, however, where the correlations are long ranged and where our past experience\textsuperscript{11} suggests that the convergence of first-order iterative schemes becomes very slow, the difficulties associated with numerically solving these equations cascade. Here, though, one can take advantage of the anticipated long-range structure of the correlation functions, and devise analytical methods, such as the moment expansion method introduced in Ref. 12 and developed further in Refs. 13 and 16 to augment the numerical studies.\textsuperscript{11,14,15}

V. CONCLUDING REMARKS

The theory we have presented here is certainly not uniquely specified by the requirements of thermodynamic consistency. The set of parameters for which consistency is required is arbitrary and can be chosen only on physical grounds. The order at which one truncates the resulting hierarchies is, in principle, arbitrary though in practice higher-order truncations are numerically difficult. Having made these choices, the resulting equations plus the structural requirements on the distribution functions suggest certain forms of truncation but, again, do not determine a unique truncation. Our method does, however, produce a $k$th order theory in which any average, which can be computed from the distribution function of order $k$ or less, has a unique value.

The problem of thermodynamic consistency of the Percus–Yevick and of the hypernetted-chain equations has been discussed in the literature.\textsuperscript{17–19} It is well known that, for either of these equations for the pair distribution function, the pressures computed from the virial, compressibility, and energy equations are different. Lado,\textsuperscript{17} and also Verlet,\textsuperscript{18} have proposed modifications of these equations which would at least produce agreement between the virial and compressibility pressures. Weyland\textsuperscript{19} has discussed the consistency problem for similar theories. Lado, Fokos, and Ashcroft\textsuperscript{20} have a modification of the hypernetted chain equation in which the pressure and energy equations of state are consistent. A thermodynamically consistent generalization of the mean spherical approximation has been proposed by Héye, Lebowitz, and Stell.\textsuperscript{21} From our point of view, these theories are of second order since the method for computing $\rho^{(2)}$ does not involve $\rho^{(3)}$. [Nor do these theories provide any way of computing $\rho^{(3)}$.] Accordingly, for these theories, we would keep equations involving only $\rho^{(n)}$ for $n < 2$, that is, Eqs. (2.7), (2.9), (2.10), and (2.21). It is easy to check that requiring these equations to be satisfied is equivalent to the requirement that the virial, compressibility, and energy methods yield the same pressure.

There are also hierarchical relations between the distribution functions which do not result from differentiation and which we have not considered. Examples are the Kirkwood–Salsburg integral equations,\textsuperscript{1,22} and also a hierarchy of equations derived by Green\textsuperscript{23} in his proposed renormalization group for fluids. The Kirkwood–Salsburg hierarchy has the structural property that each equation involves distribution functions of all order. To truncate these to a finite set requires assumptions on all the higher-order distribution functions and therefore the thermodynamic consistency problem cannot naturally be restricted to averages computed from only a finite number of distribution functions, i.e., the truncation assumptions will not naturally produce a finite thermodynamic consistency problem. The equations of Green\textsuperscript{23} cannot be formulated consistently within a class of potentials containing only one and two body potentials but require the consideration of potentials directly coupling sets of any number of particles. The problems of truncating such equations and the associated consistency requirements are much more complex and the physical meaning much less clear than in the structurally simpler hierarchies which we have considered in this paper.

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APPENDIX A: VOLUME DERIVATIVES AND THE INFINITE VOLUME LIMIT

Suppose the particles are confined in a cube of volume $V = L^3$. In Eq. (2.3) for $\Xi$ and Eq. (2.2) for $\rho^{(1)}$ we rescale the integration variables by $t = r/L$, differentiate with respect to $L$, and then return to the original variables $r$. We obtain (using $3V \delta V / \delta V = L \delta / \delta L$)

\begin{equation}
3V \frac{\partial}{\partial V} \ln \Xi = 3 \int \rho^{(1)}(1) d(1) \left( \frac{2}{\beta} \left[ \frac{3}{2} \int \rho^{(1)}(1,2) d(2) \right] \rho^{(1)}(1,2) d(1) d(2) \right)
\end{equation}

and

\begin{equation}
3V \frac{\partial}{\partial V} \rho^{(1)} = 3 \rho^{(1)}(1) d(1) \left( \frac{3}{\beta} \int \rho^{(1)}(1,2) d(2) \right) \left( \frac{2}{\beta} \left[ \frac{3}{2} \int \rho^{(1)}(1,2) d(2) \right] \rho^{(1)}(1,2) d(1) d(2) \right)
\end{equation}

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where the volume $V$ is finite. If we substitute Eq. (A1) into (A2) and combine terms, we have

$$3V \frac{\partial}{\partial V} \rho^2 \nu = 3 \int_{V} \left( \rho^2 \nu^{(1,2)} - \rho^2 \nu^{(1)} \rho^2 \nu^{(2)} \right) d(2) + \nu \int_{V} r_2 \nabla \phi^{(1,2)} d(2)$$

$$- \frac{1}{2} \beta \int_{V} \left( r_2 - r_3 \right) \nabla \phi^{(2,3)} \left[ \rho^{2} \nu^{(2,3)} - \rho^{2} \nu^{(1,2,3)} \right] d(2) d(3),$$

where the subscript $V$ explicitly indicates the finite volume. Now, in the grand canonical ensemble, there are no $1/1$ correction terms to the first and third integrands at large distances; hence the $V \to \infty$ limits can be taken inside the integrals on the right. Furthermore,

$$V \frac{\partial}{\partial V} \rho^2 \nu \to 0 \text{ as } V \to \infty$$

We can also replace

$$\int_{V} r_2 \nabla \phi^{(1,2)} d(2)$$

by

$$\int_{V} (r_2 - r_1) \nabla \phi^{(1,2)} d(2)$$

since, for systems with rotationally invariant potentials, the integral of the term involving $r_1$ vanishes. Hence, Eq. (A3) yields, as $V \to \infty$, Eq. (2.8).

**APPENDIX B: AN INTEGRATION IDENTITY**

Suppose a function of three coordinate vectors $h \left( r_1, r_2, r_3 \right)$ satisfies:

(i) translation invariance:

$$h \left( r_1 + a, r_2 + a, r_3 + a \right) = h \left( r_1, r_2, r_3 \right);$$

(ii) particle interchange symmetry in the first two variables:

$$h \left( r_1, r_2, r_3 \right) = h \left( r_2, r_1, r_3 \right);$$

(iii) reflection symmetry:

$$h \left( -r_1, -r_2, -r_3 \right) = h \left( r_1, r_2, r_3 \right).$$

Suppose further that $h$ vanishes rapidly enough with $r_3$ that the infinite volume integral

$$\int_{V} h \left( r_1, r_2, r_3 \right) dr_3$$

exists. Then,

$$\int_{V} h \left( r_1, r_2, r_3 \right) dr_3 = \frac{1}{2} \left( r_1 + r_2 \right) \int_{V} h \left( r_1, r_2, r_3 \right) dr_3.$$  \hspace{1cm} (B1)

**Proof**

Change the integration variable to $t = r_3 - r_1 - r_2$ and successively use (i), (ii), and (iii). Thus,

$$\int_{V} h \left( r_1, r_2, r_3 \right) dr_3 = \int \left( r_1 + r_2 + t \right) h \left( r_1, r_2, t + r_1 + r_2 \right) dt$$

$$= \int \left( r_1 + r_2 + t \right) h \left( -r_2, -r_1, t \right) dt$$

$$= \int \left( r_1 + r_2 + t \right) h \left( -r_1, r_2, t \right) dt$$

$$= \int \left( r_1 + r_2 + t \right) h \left( r_1, r_2, t \right) dt$$

$$= \int \left( r_1 + r_2 - t \right) h \left( r_1, r_2, t \right) dt$$

Changing integration variables by setting $t = r_3$ gives the desired result.
APPENDIX C: RELATIONS AMONG Eqs. (2.7)–(2.14)

We derive here three independent relations among Eqs. (2.7)–(2.14).

We derive first a relation between Eqs. (2.9), (2.11), (2.12), and (2.13). We multiply Eq. (2.11) by $\phi(1,2)$ and integrate over particle 2. Then

$$
\int \frac{d}{dz} \rho^{(3)}(1,2) \phi(1,2) \, d(2) + \int \phi(1,2) [\rho^{(0)}(1,2,3) + \rho^{(1)}(1,2,3)] \, d(3) \, d(2)
$$

The second integral on the right-hand side of Eq. (C1) becomes, upon exchange of the order of integration

$$
\int \phi(1,2) [\rho^{(0)}(1,2,3) - \beta \rho^{(2)}(1,2,1)] \, d(2) \, d(1)
$$

The result of the $d(2)$ integration is, by translation invariance, a function of the difference $r_1 - r_2$, and therefore the $d(3)$ integration can be replaced by a $d(1)$ integration giving

$$
\int \phi(1,2) [\rho^{(0)}(1,2,3) - \rho^{(1)}(1,2,3)] \, d(2) \, d(1)
$$

Since this integral is independent of $r_1$, we can, by translational invariance, exchange the labels 1 and 3 and write Eq. (C1) as

$$
\int \frac{d}{dz} [\rho^{(2)}(1,2) \phi(1,2) \, d(2) + \phi(3,2) [\rho^{(0)}(1,2,3) + \rho^{(2)}(1,2,3)] \, d(2) \, d(3)]
$$

where we have used Eq. (2.12) in the term on the left-hand side. If we exchange the $z$ and $\beta$ derivatives in this term and use Eq. (2.9), then Eq. (C2) becomes Eq. (2.13). We have derived Eq. (2.13) from the other three equations because we have chosen to omit Eq. (2.13) from the sufficient set, Eqs. (2.18)–(2.22). More generally, it is clear that Eq. (2.11) with any two of the other three equations will imply the remaining one so that we could choose, for example, to eliminate Eq. (2.9) or (2.12) rather than Eq. (2.13).

As a preliminary to deriving the other two relations, we consider the relationship of the following three integrals:

$$
I = \int \int [r_1 - r_2] \nabla \phi(1,2) \rho^{(0)}(1,2,3) \, d(3) \, d(2),
$$

$$
J = \int \int [(r_1 - r_2) \nabla] \phi(1,2) \rho^{(0)}(1,2,3) - \rho^{(1)}(1,2,3) \, d(3) \, d(2),
$$

$$
K = \int \int [(r_1 - r_2) \nabla] \phi(1,2) \rho^{(0)}(1,2,3) - \rho^{(1)}(1,2,3) \, d(2) \, d(3)
$$

We shall show that

$$
J = 2I = K. \quad (C3)
$$

Consider first $I$ and $J$. We can subtract a term $\rho^{(1)}(1,2,3)$ from $\rho^{(0)}$ in $I$, since its integral will vanish, and then exchange labels on integration variables to obtain

$$
\int \int [(r_1 - r_2) \nabla] \phi(1,2) [\rho^{(0)}(1,2,3) - \rho^{(1)}(1,2,3)] \, d(2) \, d(3)
$$

If we interchange the order of integration and use the identity of Appendix B to replace the $r_1$ factor by a $\frac{1}{2} (r_1 + r_2)$ factor, we find

$$
\int \int [(r_1 - r_2) \nabla] \phi(1,2) [\rho^{(0)}(1,2,3) + \rho^{(1)}(1,2,3)] \, d(3) \, d(2)
$$

To compare $J$ and $K$ note that if, in the expression for $J$, we do the $d(2)$ integration first, the result is, by translational invariance, a function of the difference $r_1 - r_2$. Hence, we can integrate over $r_1$ rather than $r_1$ and $J$ can be written

$$
J = \int \int [(r_1 - r_2) \nabla] \phi(1,2) [\rho^{(0)}(1,2,3) + \rho^{(1)}(1,2,3)] \, d(2) \, d(1)
$$

However, if we relabel the variables of integration, viz. $r_1 \rightarrow r_2$ and $r_2 \rightarrow r_1$, the resulting expression is just $K$. So, $J = K$.

We now derive Eq. (2.8) from Eq. (2.14). In Eq. (2.14) we replace $\nabla_1$ by $- \nabla_2$ and $\rho^{(2)}$ by $\rho^{(2)} - \rho^{(1)}$. On the left-hand side of this equation, take the inner product with $(r_2 - r_1)$ and integrate over $r_2$ to obtain
\[
\int \left( r_2 - r_1 \right) \nabla_2 \left[ \rho^{(2)}(1,2) - \rho^{(1)}(1,2) \right] d(2) = -\beta \int \left( \left( r_2 - r_1 \right) \nabla_1 \phi(1,2) \right) \rho^{(2)}(1,2) d(2)
\]
\[
-\beta \int \int \left( \left( r_2 - r_1 \right) \nabla_1 \phi(1,3) \right) \rho^{(3)}(1,2,3) d(2) d(3)
\]

(C4)

The second integral on the right-hand side of Eq. (C4) is \( \beta J \) and therefore can be replaced by \( \frac{1}{\beta} \beta K \). The integral on the left-hand side can be integrated by parts so that overall:

\[
3 \int \left[ \rho^{(2)}(1,2) - \rho^{(1)}(1,2) \right] d(2) = -\beta \int \left( \left( r_2 - r_1 \right) \nabla_1 \phi(1,2) \right) \rho^{(2)}(1,2) d(2)
\]
\[
+ \beta \int \int \left( \left( r_2 - r_1 \right) \nabla_2 \phi(2,3) \right) \left[ \rho^{(1)}(1,2,3) + \rho^{(3)}(1,2,3) \right] d(2) d(3)
\]

which is Eq. (2.8).

Finally, we show that Eq. (2.10) follows from Eqs. (2.7), (2.9), (2.11), and (2.14). If Eq. (2.11) is multiplied by \( (r_1 - r_2) \nabla \phi(1,2) \)

and integrated over \( d(2) \), we find:

\[
z \frac{\partial}{\partial z} \int \left( \left( r_1 - r_2 \right) \nabla \phi(1,2) \right) \rho^{(2)}(1,2) d(2) = 2 \int \left( \left( r_1 - r_2 \right) \nabla \phi(1,2) \right) \rho^{(2)}(1,2) d(2) + J.
\]

Using Eqs. (2.7) and (2.9) in the term on the left-hand side, we obtain:

\[
6z \frac{\partial}{\partial z} \rho^{(1)} - 6z \rho^{(1)} = 2\beta \int \left( \left( r_1 - r_2 \right) \nabla \phi(1,2) \right) \rho^{(2)}(1,2) d(2) + \beta J.
\]

Now, we have shown that Eq. (2.8) follows from Eq. (2.14) and can be written as

\[
\int \left[ \rho^{(2)}(1,2) - \rho^{(1)}(1,2) \right] d(2) + \frac{1}{\beta} \beta K = \frac{1}{\beta} \beta K.
\]

When \( J \) and \( K \) are eliminated between the last two equations (using \( J = K \), Eq. (2.10) results.

We have thus shown in this Appendix that Eqs. (2.8), (2.10), and (2.13) will be satisfied if the sufficient set Eqs. (2.18)-

(2.22) are satisfied.

APPENDIX D: DIMENSIONAL PROPERTIES OF THE \( \rho^{(n)} \)

Suppose \( \lambda \) is a range parameter in the intermolecular potential

\[
\phi(\frac{r}{\lambda}) = u(r/\lambda).
\]

From the definition of \( \mathcal{E} \) and of \( \rho^{(n)} \), it is easy to see that if we rescale all lengths by a factor \( \alpha \) we have

\[
\mathcal{E}(\alpha^{-3}z\lambda, \alpha^3 V) = \mathcal{E}(z\lambda, \lambda_V)
\]

which implies

\[
\alpha^3 \rho^{(n)}(\alpha^{-3}z\lambda, \alpha^3 V) = \rho^{(n)}(z\lambda, \lambda_V).
\]

For \( n > 1 \) we have

\[
\alpha^3 \rho^{(n)}(\alpha r_1, \ldots, \alpha r_n, \alpha^{-3}z\lambda, \alpha^3 V) = \rho^{(n)}(r_1, \ldots, r_n, z\lambda, \lambda_V).
\]

Differentiating Eqs. (D3) and (D4) with respect to \( \alpha \) and setting \( \alpha = 1 \) yields

\[
3 \rho^{(0)} - 3z \frac{\partial \rho^{(0)}}{\partial z} + \lambda \frac{\partial \rho^{(0)}}{\partial \lambda} + 3V \frac{\partial \rho^{(0)}}{\partial V} = 0
\]

and for \( n > 1 \),

\[
3n \rho^{(n)} + \sum_{i=1}^{n} r_i \nabla_i \rho^{(n)} - 3z \frac{\partial \rho^{(n)}}{\partial z} + \lambda \frac{\partial \rho^{(n)}}{\partial \lambda} + 3V \frac{\partial \rho^{(n)}}{\partial V} = 0
\]

Equations (D5) and (D6) show that derivatives with respect to the range parameter \( \lambda \) can be expressed in terms of previously considered derivatives. Therefore, \( \lambda \) differentiation of the \( \rho^{(n)} \) does not produce an independent hierarchy of equations.


