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An Alternative Construction of the Percus–Yevick Equation Based on the Equilibrium BBGKY Hierarchy

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The existing derivations of the Percus–Yevick equation are not readily extendable into the nonequilibrium domain. In particular, the elegant Percus functional construction relies on a test particle theorem which lacks an exact nonequilibrium generalization. We propose here a new construction which utilizes some elementary ideas of functional expansions together with the equilibrium BBGKY hierarchy of equations. Also, we feel this new construction provides fresh insight into the physical basis of the equilibrium Percus–Yevick equation.

KEY WORDS: Structure of liquids; kinetic and transport theory of fluids; Percus–Yevick equation.

1. INTRODUCTION

The equilibrium Percus–Yevick (PY) equation for the two-particle distribution function is perhaps the best existing description of a fluid consisting of particles interacting via a hard-core potential energy.(4) Comparison with the computer Monte Carlo studies(4,26,18) indicates the Percus–Yevick equation is a good description for all particle densities except very near the solid phase. The success of the equilibrium Percus–Yevick equation strongly suggests the nonequilibrium analog should be constructed.[2] Previously we reported on our construction of a nonequilibrium analog of the Percus–Yevick equation(21) based on the method which we describe and apply here to the original equilibrium problem.

Examination of the existing constructions of the equilibrium Percus–Yevick equation(15,16) indicates none are suitable, without modification, for

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[2] The equilibrium PY equation has the further interesting property of exact solvability for the hard-core model even though the equation is nonlinear.(12,19,23,24)

generalization to the nonequilibrium domain. Specifically, the Percus functional construction(16) of the Percus–Yevick equation is not immediately generalizable, since functional methods are not sufficiently well developed for problems in classical statistical mechanics. A great deal of progress has recently been made on this problem(11) and it is reasonable to expect functional methods will advance to the point where classical statistical mechanical problems can be confronted with confidence. A second, more formidable difficulty resides in the fact that the test particle theorem[3] has no exact analog in the nonequilibrium domain.(16) The test particle theorem will have to be replaced by some more general, inclusive principle before progress can be made.

The difficulties of the usual functional methods are circumvented here by the introduction of a method which does not rely on the test particle theorem.(21) The method which we give here utilizes some elementary ideas of functional expansions(22) together with the equilibrium BBGKY[4] hierarchy of equations.(1,2,6,9,27) The method described here and the Percus functional method(16) are different in formulation but they nonetheless share a common point of view. Insight into a system in both methods is obtained by observing how physical changes in the system produce corresponding changes in the functional describing the system. However, the particular kind of system change contemplated is quite different in the two methods.

The Percus functional method utilizes a system change resulting from the insertion (or removal) of a particle that was not originally part of the system. Since the number of particles is not fixed, one is forced to formulate the statistical problem in the grand canonical ensemble.(8,16) One proceeds to study how a functional property of the system changes due to the presence of the additional particle. Experience has shown the choice of the appropriate functional for study apparently depends upon the nature of the interparticle interaction. Mathematically, one expands a chosen functional in a Taylor series of some function and generally only the first term of the expansion is kept. Both the functional and the function of the expansion are chosen in a somewhat ad hoc manner. Physical arguments sometimes help in this choice, but usually it is the accuracy of the resulting integral equation that in the end justifies the choice. A simple example of this procedure is the Coulomb gas system, where the appropriate functional is the single-particle distribution for a system in an external field, while the function of the expansion is the external field itself. Application of the test particle theorem relating the single-particle distribution of the system in an external field to the two-particle distribution of a uniform system without external field leads to the well-known Debye–Hückel integral equation,(5,16) which describes reasonably well

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[3] The test particle theorem is embodied in Eqs. (6.1) and (6.4), pp. II-70, 71 of Ref. 16.

[4] Bogoliubov, Born, Green, Kirkwood, and Yvon.(1,2,9,27)

the weakly coupled plasma.(3) The Coulomb gas problem is an interesting example since another choice for the functional leads to the convolution-hypernetted chain (CHNC) equation, which describes the plasma somewhat better. Neither the CHNC functional nor the Debye–Hückel functional can be shown to be a priori better for describing a plasma in a certain domain.

The functional-hierarchy method described here also contemplates a system change; however, in this case one examines how the change in position of a particle affects the properties of the system. In this method, the number of particles remains fixed, so that the grand canonical ensemble is not necessary. In addition, we invoke some simple ideas of functional power series, but the functional Taylor series is not used per se, since we will not introduce the functional derivative. Instead, the coefficients of the functional expansion are determined by utilizing the equilibrium BBGKY hierarchy of equations in a manner described later. Again, as in the Percus functional method, the choice for the functional is quite arbitrary. We will, however, give a somewhat new physical motivation for the particular functional chosen for consideration in the construction of the Percus–Yevick equation.

The system change for the functional-hierarchy method based on the change in position of a particle is related to the system change produced by an external field as utilized in the functional test particle method. Specifically, the test particle theorem indicates the external field can be due to a particle not considered part of the system. The change in the external field can be produced in two related ways: the strength of the coupling of the test particle with the other particles can be varied, or alternatively, the position of the test particle can be changed. There is thus an underlying physical connection between the functional-test particle method and the functional-hierarchy method.

2. THE EQUILIBRIUM HIERARCHY; CLUSTER FUNCTIONS

We will utilize the usual statistical distribution functions[5] $F(\mathbf{r}_1)$, $F(\mathbf{r}_1, \mathbf{r}_2)$, $F(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, etc. as defined by Fisher.(6) Specifically, we will use the

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[5] The distribution functions are defined and discussed in Section 1 of Chapter 2 of Ref. 6. Fisher also discusses the utility of the two-particle distribution function in the remainder of Chapter 2. In the definitions (1a)–(1c), Ω is the volume of the N-particle system and Q is the configuration integral given by

$$Q = \int \exp[-\beta V(\mathbf{r}_1, \ldots, \mathbf{r}_N)]\, d\mathbf{r}_1 \cdots d\mathbf{r}_N$$

Also, $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature. The interparticle potential energy will be assumed to have the two-body additive form

$$V(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \tfrac{1}{2} \sum_{\alpha=1}^{N} \sum_{\substack{\beta=1 \\ (\alpha \neq \beta)}}^{N} V(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)$$

Notice that since the N particles are identical, we have $F(\mathbf{r}_1, \mathbf{r}_2) = F(\mathbf{r}_2, \mathbf{r}_1)$, $F(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = F(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3)$, etc.

definitions

$$F(\mathbf{r}_1) = \Omega \int Q^{-1} \exp[-\beta V(\mathbf{r}_1, \ldots, \mathbf{r}_N)]\, d\mathbf{r}_2 \cdots d\mathbf{r}_N \tag{1a}$$

$$F(\mathbf{r}_1, \mathbf{r}_2) = \Omega^2 \int Q^{-1} \exp[-\beta V(\mathbf{r}_1, \ldots, \mathbf{r}_N)]\, d\mathbf{r}_3 \cdots d\mathbf{r}_N \tag{1b}$$

$$F(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \Omega^3 \int Q^{-1} \exp[-\beta V(\mathbf{r}_1, \ldots, \mathbf{r}_N)]\, d\mathbf{r}_4 \cdots d\mathbf{r}_N \tag{1c}$$

The equilibrium BBGKY hierarchy is obtained by differentiating each of the distribution functions with respect to $\mathbf{r}_1$ and performing a simple rearrangement.[6] We shall utilize only the first two equations of the hierarchy:

$$(\partial/\partial\mathbf{r}_1)F(\mathbf{r}_1) = \rho \int d\mathbf{r}_2\, (\partial/\partial\mathbf{r}_1)\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\}F(\mathbf{r}_1, \mathbf{r}_2) \tag{2a}$$

$$\begin{aligned}\{(\partial/\partial\mathbf{r}_1) &+ (\partial/\partial\mathbf{r}_1)[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}F(\mathbf{r}_1, \mathbf{r}_2) \\ &= \rho \int d\mathbf{r}_3\, (\partial/\partial\mathbf{r}_1)\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_3|)\}F(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\end{aligned} \tag{2b}$$

The hierarchy of equations may be utilized for the calculation of the distribution functions in various ways, depending upon the system under consideration. For example, Bogoliubov(1) assumed the distribution functions of low-density gas systems are analytic in the density and he then showed this assumption leads to the usual Mayer expansion.(1,3) The Coulomb gas system requires a different treatment of the BBGKY hierarchy, since the coefficients of the Mayer expansion diverge.(3) The classical remedy(1,3,20) is the introduction of the cluster functions $C(\mathbf{r}_1)$, $C(\mathbf{r}_1, \mathbf{r}_2)$, $C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, etc. defined via

$$C(\mathbf{r}_1) = F(\mathbf{r}_1) \tag{3a}$$

$$C(\mathbf{r}_1, \mathbf{r}_2) = F(\mathbf{r}_1, \mathbf{r}_2) - F(\mathbf{r}_1)F(\mathbf{r}_2) \tag{3b}$$

$$\begin{aligned}C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = {} & F(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - F(\mathbf{r}_1)F(\mathbf{r}_2, \mathbf{r}_3) - F(\mathbf{r}_2)F(\mathbf{r}_1, \mathbf{r}_3) \\ & - F(\mathbf{r}_3)F(\mathbf{r}_1, \mathbf{r}_2) + 2F(\mathbf{r}_1)F(\mathbf{r}_2)F(\mathbf{r}_3)\end{aligned} \tag{3c}$$

$$\vdots$$

It is easy to invert Eqs. (3a)–(3c) and express the distribution functions in terms of the cluster functions. One obtains[7]

$$F(\mathbf{r}_1) = C(\mathbf{r}_1) \tag{4a}$$

$$F(\mathbf{r}_1, \mathbf{r}_2) = C(\mathbf{r}_1, \mathbf{r}_2) + C(\mathbf{r}_1)C(\mathbf{r}_2) \tag{4b}$$

$$\begin{aligned}F(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = {} & C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + C(\mathbf{r}_1)C(\mathbf{r}_2, \mathbf{r}_3) + C(\mathbf{r}_2)C(\mathbf{r}_1, \mathbf{r}_3) \\ & + C(\mathbf{r}_3)C(\mathbf{r}_1, \mathbf{r}_2) + C(\mathbf{r}_1)C(\mathbf{r}_2)C(\mathbf{r}_3)\end{aligned} \tag{4c}$$

$$\vdots$$

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[6] The BBGKY hierarchy of equations is derived in Section 1 of Chapter 4 of Ref. 6. The thermodynamic limit [$(N, \Omega) \to \infty$ such that $(N/\Omega) \to \rho$, the density] has been taken in Eqs. (2a) and (2b).

[7] It is easy to show (see Fisher(6)) that $F(\mathbf{r}_1) = 1$ for spatially homogeneous systems without external fields and also $F(\mathbf{r}_1, \mathbf{r}_2) = F(|\mathbf{r}_1 - \mathbf{r}_2|)$.

Utilization of Eqs. (4a)–(4c) to eliminate the distribution functions in the BBGKY hierarchy (2a)–(2b) yields a hierarchy of equations of the form

$$(\partial/\partial\mathbf{r}_1)C(\mathbf{r}_1) = \rho\int d\mathbf{r}_2\,(\partial/\partial\mathbf{r}_1)\{-\beta V(|\mathbf{r}_1-\mathbf{r}_2|)\}C(\mathbf{r}_1,\mathbf{r}_2) = 0 \qquad \text{(5a)}$$

$$\begin{aligned}&\{(\partial/\partial\mathbf{r}_1) + (\partial/\partial\mathbf{r}_1)[\beta V(|\mathbf{r}_1-\mathbf{r}_2|)]\}C(\mathbf{r}_1,\mathbf{r}_2)\\ &\quad + (\partial/\partial\mathbf{r}_1)\{\beta V(|\mathbf{r}_1-\mathbf{r}_2|)\}\\ &\quad = \rho\int d\mathbf{r}_3\,(\partial/\partial\mathbf{r}_1)\{-\beta V(|\mathbf{r}_1-\mathbf{r}_3|)\}[C(\mathbf{r}_2,\mathbf{r}_3) + C(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)] \qquad \text{(5b)}\end{aligned}$$

The cluster functions have the desirable property of vanishing whenever any particle of the cluster is removed a large distance from the remaining particles of the cluster. Our interest in this paper is on the hard-core system, but we shall nonetheless have a use for the cluster functions. Clearly, the density expansion of the distribution function approach is useful for low-density hard-core systems. Unfortunately, for hard-core, moderate- and high-density systems the density expansion approach is not appropriate and a substitute must be found. The cluster functions will be utilized as a useful substitute for the density expansion method in a manner we will describe in the next section.

3. THE FUNCTIONAL EXPANSION IN THE INTERACTION OF THE TWO-PARTICLE CLUSTER FUNCTION

We previously mentioned that one classical method of treating the BBGKY hierarchy of Eqs. (2a)–(2b) is to assume each of the distributions functions (1a)–(1c) has an expansion in powers of the density. The equations of the hierarchy may be solved iteratively and one thus obtains the usual Mayer expansion. The same procedure can be applied to the hierarchy (5a)–(5b) written in terms of the correlation functions. Specifically one obtains the second cluster function in the form

$$\begin{aligned}C(|\mathbf{r}_1-\mathbf{r}_2|) &= f(|\mathbf{r}_1-\mathbf{r}_2|) + \rho\{\exp[-\beta V(|\mathbf{r}_1-\mathbf{r}_2|)]\}\\ &\quad\times\left[\int d\mathbf{r}_3 f(|\mathbf{r}_1-\mathbf{r}_3|)f(|\mathbf{r}_3-\mathbf{r}_2|) + O(\rho^2)\right] \qquad \text{(6)}\end{aligned}$$

where $f(|\mathbf{r}_1-\mathbf{r}_2|) = \exp(-\beta V(|\mathbf{r}_1-\mathbf{r}_2|) - 1$ is the Mayer f-function. This result is usually expressed in terms of the distribution function (see Refs. 1, 3, and 13, for example), but later we will utilize expansion (6) to motivate our construction of the equilibrium Percus–Yevick equation. We also previously noted that expansion (6) cannot be applied to the Coulomb gas problem, since, among other things, the integrals forming the coefficients of the expansion diverge. The cluster functions were originally introduced at this point to deal with this problem.(3,20) One assumes the cluster functions have expansions in the plasma parameter γ defined by $\gamma = e^2/k_BT\lambda_D$, where the Debye length λ_D is defined by $\lambda_D \equiv (k_B T/4\pi\rho e^2)^{1/2}$, where e is the charge on an electron and ρ is the particle density. The assumption that the cluster functions are analytic in γ allows one to again solve the BBGKY hierarchy of equations by an iterative procedure. One subsequently obtains to first order in γ the Debye–Hückel expression for the two-particle cluster function $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ of a plasma

$$C(|\mathbf{r}_1 - \mathbf{r}_2|) = -\frac{\gamma\lambda_D \exp(-|\mathbf{r}_1 - \mathbf{r}_2|/\lambda_D)}{|\mathbf{r}_1 - \mathbf{r}_2|} + O(\gamma^2) \tag{7}$$

with the higher order terms in γ also computable.[6]

The construction of the Percus–Yevick equation we present here does not involve parameter expansions. Instead, we shall assume the existence of more general functional expansions. To illustrate the procedure, we will begin by obtaining the Debye–Hückel result, Eq. (7), via the functional-hierarchy method. Let us assume the cluster functions have functional expansions in the interaction $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ of the form

$$\begin{aligned} C(\mathbf{r}_1, \mathbf{r}_2) = {} & A_0(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3\, V(|\mathbf{r}_1 - \mathbf{r}_3|)A_1(\mathbf{r}_3, \mathbf{r}_2) \\ & + \int d\mathbf{r}_3\, d\mathbf{r}_4\, V(|\mathbf{r}_1 - \mathbf{r}_3|)V(|\mathbf{r}_1 - \mathbf{r}_4|) \\ & \times A_2(\mathbf{r}_4, \mathbf{r}_3, \mathbf{r}_2) + O(V^3) \end{aligned} \tag{8a}$$

$$\begin{aligned} C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = {} & B_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \int d\mathbf{r}_4\, V(|\mathbf{r}_1 - \mathbf{r}_4|)B_1(\mathbf{r}_4, \mathbf{r}_3, \mathbf{r}_2) \\ & + \int d\mathbf{r}_4\, d\mathbf{r}_5\, V(|\mathbf{r}_1 - \mathbf{r}_4|)V(|\mathbf{r}_1 - \mathbf{r}_5|) \\ & \times B_2(\mathbf{r}_5, \mathbf{r}_4, \mathbf{r}_3, \mathbf{r}_2) + O(V^3) \end{aligned} \tag{8b}$$

The form of the expansions (8a)–(8b) is justified by noting that if one chooses $\mathbf{r}_1 = 0$ (in a sense placing particle 1 at the origin), then Eq. (8a) takes the general form for the functional expansion given by Volterra.[22] A similar observation can be made concerning Eq. (8b) and also all the other higher order cluster functional expansions. We, however, do not wish to fix particle 1 at the origin, since we will soon determine the coefficients of the functional expansion (8a) by utilizing the equilibrium BBGKY hierarchy of equations which were obtained by varying the position of particle 1 through the process of differentiation. Also, one should note that the variable $\mathbf{r}_1$ must reside in each factor of the interaction $V(|\mathbf{r}_1 - \mathbf{r}_k|)$ since if $\mathbf{r}_1$ is removed far from the remaining particles of the system, then one expects the cluster function to vanish. The coefficients of the functional expansion are chosen independent of $\mathbf{r}_1$ for simplicity. The leading terms of expansions (8a) and (8b), that is,

A_0, B_0, etc., must vanish, since if particle 1 is removed from the cluster, then the interaction $V(|\mathbf{r}_1 - \mathbf{r}_k|)$ vanishes and the cluster functions must also vanish.

The higher order coefficients A_1, B_1, etc. are obtained by substitution of the functional expansions (8a) and (8b) into the hierarchy equations (5a)–(5b). Specifically, one obtains

$$\begin{aligned}(\partial/\partial\mathbf{r}_1)\int d\mathbf{r}_3\, V(|\mathbf{r}_1 - \mathbf{r}_3|)A_1(\mathbf{r}_3, \mathbf{r}_2) + (\partial/\partial\mathbf{r}_1)\{\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\} \\ = \rho\int d\mathbf{r}_3\, (\partial/\partial\mathbf{r}_1)\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_3|)\} \\ \times \left[\int d\mathbf{r}_4\, V(|\mathbf{r}_2 - \mathbf{r}_4|)A_1(\mathbf{r}_4, \mathbf{r}_3)\right] \qquad (9)\end{aligned}$$

where we kept only the first-order terms in the interaction $V(|\mathbf{r}_k - \mathbf{r}_1|)$. If we now utilize the expansions (8a) and (8b) we can write Eq. (9) in the form

$$\begin{aligned}(\partial/\partial\mathbf{r}_1)C(\mathbf{r}_1, \mathbf{r}_2) + (\partial/\partial\mathbf{r}_1)\{\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\} \\ = \rho\int d\mathbf{r}_3\, (\partial/\partial\mathbf{r}_1)\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_3|)\}C(\mathbf{r}_3, \mathbf{r}_2) \qquad (10)\end{aligned}$$

and integration yields immediately

$$C(\mathbf{r}_1, \mathbf{r}_2) + \{\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\} = \rho\int d\mathbf{r}_3\, \{-\beta V(|\mathbf{r}_1 - \mathbf{r}_3|)\}C(\mathbf{r}_3, \mathbf{r}_2) \qquad (11)$$

the usual Debye–Hückel integral equation, which leads to the result given in Eq. (7). We utilized Eq. (8a) to write Eq. (10) in terms of the cluster function since it is easier to solve the resulting equation (11) for the cluster function $C(\mathbf{r}_1, \mathbf{r}_2)$ than it is to solve the corresponding equation for A_1. We could have proceeded to solve for the coefficient A_1, but this would not be useful for our purpose. Notice that the two-particle cluster function resulting from Eq. (11) is accurate to first order in the interaction. We have shown that utilization of the cluster functional expansions (8a) and (8b) allows us to make contact with the Debye–Hückel theory

One computational point deserves further comment. When the functional expansions (8a) and (8b) are substituted into the BBGKY hierarchy the order of a term in the interaction is not simply determined by the number of times the interaction V appears. Rather, the order of a term is determined by the number of times the interaction appears with the particle coordinate $\mathbf{r}_1$. For example, a term containing the combination $V(|\mathbf{r}_1 - \mathbf{r}_3|)V(|\mathbf{r}_2 - \mathbf{r}_4|)$ is a first-order term since $\mathbf{r}_1$ appears only once in the interaction. The similar term containing the combination $V(|\mathbf{r}_1 - \mathbf{r}_2|)V(|\mathbf{r}_1 - \mathbf{r}_3|)$ is of second order since

$\mathbf{r}_1$ appears twice. The reasons for these rules[8] should be physically apparent, given our discussion of the form chosen for the functional expansions (8a) and (8b). We should also mention that $C(\mathbf{r}_2, \mathbf{r}_3)$ of Eq. (5b) has an expansion in $V(|\mathbf{r}_1 - \mathbf{r}_\alpha|)$, but the contributions of this expansion are of second order in $V(|\mathbf{r}_1 - \mathbf{r}_\alpha|)$ in Eq. (9) and are therefore neglected.

The approach we have outlined leading to the Debye–Hückel integral equation is useful for the Coulomb gas problem. Unfortunately, such a functional expansion is not useful for the hard-core system even at low density since the kernel of the integral equation (11) is not well behaved. If we are to have a theory of dense, hard-core systems, then the naive functional expansion will have to be replaced by a more powerful approach.

4. AN IMPROVED FUNCTIONAL EXPANSION AND THE KIRKWOOD–SALSBURG (GENERA) EQUATION

The poor convergence properties of the functional expansions (8a) and (8b) of the cluster function in powers of the interaction leads us to consider other alternative functionals. As a motivation, we consider a strategy found useful in improving the convergence of the expansion of a function $f(x)$ if $f(x)$ can be written as a product of two functions $h(x)$ and $k(x)$. We also assume $h(x)$ is a tabulated, well-known function of x and therefore does not require expansion. Frequently there are cases where the expansion of $f(x) = h(x)k(x)$ converges slowly while the expansion of $k(x)$ converges rapidly. It is more sensible in this case to extract the known function $h(x)$ and first compute the expansion of $k(x)$. One then obtains $f(x)$ by multiplication of $k(x)$ by $h(x)$. As an example, consider the function $f(x) = (1 + x)\exp(-x)$, which has an expansion in x which alternates and converges slowly. If, alternatively, we treat $\exp(-x)$ as a known, tabulated function, then we may first expand $k(x) = (1 + x)$ in powers of x and then obtain $f(x)$ utilizing $f(x) = k(x)h(x)$, where $h(x) = \exp(-x)$. This example is of course trivial since the expansion of $k(x)$ terminates and is simply $1 + x$.

A strategy similar to that described above may be applied to the N-particle problem, where the consequences are not so trivial. We return to the virial expansion (6), which we rewrite in the form

$$\begin{aligned}\{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}[C(|\mathbf{r}_1 - \mathbf{r}_2|) - f(|\mathbf{r}_1 - \mathbf{r}_2|)]& \\ = \rho \int d\mathbf{r}_3 f(|\mathbf{r}_1 - \mathbf{r}_3|) f(|\mathbf{r}_3 - \mathbf{r}_2|) + O(\rho^2)& \qquad (12)\end{aligned}$$

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[8] One might argue that we should not have expanded $C(\mathbf{r}_2, \mathbf{r}_3)$ appearing in Eq. (9) since the cluster does not contain particle 1. We agree, but nonetheless we chose to expand $C(\mathbf{r}_2, \mathbf{r}_3)$ to illustrate the counting procedure just described, since the situation is more complicated in the nonequilibrium case where we treat particles 1 and 2 on an equal footing. In any case, the final result, Eq. (11), is unaffected by our expanding or not expanding $C(\mathbf{r}_2, \mathbf{r}_3)$.

When the density of the system is sufficiently low, the terms on the left-hand side of Eq. (12) give a first approximation for the cluster function $C(|\mathbf{r}_1 - \mathbf{r}_2|)$. Furthermore, all the terms involving the direct interaction between particles one and two have been written on the left-hand side of Eq. (12); the terms on the right-hand side of Eq. (12) are those terms involving indirect interactions between particles one and two mediated by the remaining particles of the system.

These considerations encourage us to propose $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ as an alternative functional for the N-particle system, where $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ is defined by

$$\eta(|\mathbf{r}_1 - \mathbf{r}_2|) \equiv \{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}[C(|\mathbf{r}_1 - \mathbf{r}_2|) - f(|\mathbf{r}_1 - \mathbf{r}_2|)] \tag{13}$$

The hope is that a functional expansion of $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ in powers of the interaction might have better convergence properties than the functional expansion (8a) of the cluster function $C(|\mathbf{r}_1 - \mathbf{r}_2|)$.

One contemplates a functional expansion of $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ in the $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ similar to expansion (8):

$$\begin{aligned}\eta(\mathbf{r}_1, \mathbf{r}_2) = \eta_0(\mathbf{r}_1, \mathbf{r}_2) &+ \int d\mathbf{r}_3\, V(|\mathbf{r}_1 - \mathbf{r}_3|)\eta_1(\mathbf{r}_3, \mathbf{r}_2) \\ &+ \int d\mathbf{r}_3\, d\mathbf{r}_4\, V(|\mathbf{r}_1 - \mathbf{r}_3|)V(|\mathbf{r}_1 - \mathbf{r}_4|) \\ &\times \eta_2(\mathbf{r}_4, \mathbf{r}_3, \mathbf{r}_2) + O(V^3)\end{aligned} \tag{14}$$

We proceed to determine the coefficients of the expansion (14) in a manner similar to that employed previously when we determined the coefficients of the expansions (8a) and (8b) via the BBGKY hierarchy. One immediately observes that the first coefficient $\eta_0(|\mathbf{r}_1 - \mathbf{r}_2|)$ must be zero. This result follows from the fact that $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ itself vanishes as $\mathbf{r}_1$ is taken to infinity. The remaining coefficients of the expansion (14) are determined by first differentiating Eq. (13) with respect to $\mathbf{r}_1$ and obtaining

$$\begin{aligned}(\partial/\partial\mathbf{r}_1)\eta(|\mathbf{r}_1 - \mathbf{r}_2|) = {} & \{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}(\partial/\partial\mathbf{r}_1)C(|\mathbf{r}_1 - \mathbf{r}_2|) \\ &+ \{1 + \eta(|\mathbf{r}_1 - \mathbf{r}_2|)\}(\partial/\partial\mathbf{r}_1)\{\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\}\end{aligned} \tag{15}$$

Then, utilizing the second equation of the BBGKY hierarchy (5b) together with definition (13), one obtains

$$\begin{aligned}&(\partial/\partial\mathbf{r}_1)\eta(|\mathbf{r}_1 - \mathbf{r}_2|) \\ &\quad = \rho\{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\} \int d\mathbf{r}_3\, (\partial/\partial\mathbf{r}_1)\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_3|)\} \\ &\quad \times [C(\mathbf{r}_2, \mathbf{r}_3) + C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)]\end{aligned} \tag{16}$$

Substitution of expansions (14) and (8) into Eq. (16) and neglecting second and higher order terms in the interaction as before leads to

$$\begin{aligned}\partial/\partial \mathbf{r}_1 \int d\mathbf{r}_3\, V(|\mathbf{r}_1 - \mathbf{r}_3|)\eta_1(\mathbf{r}_3, \mathbf{r}_2) \\ = \rho \int d\mathbf{r}_3\, (\partial/\partial \mathbf{r}_1)\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_3|)\} \int d\mathbf{r}_4\, V(|\mathbf{r}_2 - \mathbf{r}_4|) A_1(\mathbf{r}_4, \mathbf{r}_3)\end{aligned} \tag{17}$$

In obtaining Eq. (17) we utilized the same counting procedure as used before in obtaining Eq. (9). Integrating Eq. (17) with respect to $\mathbf{r}_1$ and utilizing expansions (8) and (14) yields to lowest order in the interaction

$$\begin{aligned}\{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}[C(|\mathbf{r}_1 - \mathbf{r}_2|) - f(|\mathbf{r}_1 - \mathbf{r}_2|)] \\ = \rho \int d\mathbf{r}_3\, \{-\beta V(|\mathbf{r}_1 - \mathbf{r}_3|)\} C(|\mathbf{r}_3 - \mathbf{r}_2|)\end{aligned} \tag{18}$$

which is an equation of the Kirkwood–Salsburg (KS) genera. In obtaining the above result, we also utilized the definition (13). The connection with the KS equation$^{(8,10)}$ is more apparent if one writes the cluster function $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ in terms of the distribution function $F(|\mathbf{r}_1 - \mathbf{r}_2|)$ via definition (3). The original KS equation has the same form as Eq. (18) except that the KS equation treats all the particles as strongly coupled and hence the Mayer function $f(|\mathbf{r}_1 - \mathbf{r}_2|)$ appears in the integral instead of the "bare" interaction. We could also have performed such a "strong" coupled expansion here, but this would deflect us from our purpose of obtaining the Percus–Yevick equation.

5. IMPROVEMENT OF THE CONVERGENCE OF THE SECOND FUNCTIONAL EXPANSION VIA UTILIZATION OF BURMANN'S THEOREM

5.1. Inversion of the Cluster Functional Expansion in the Interaction

Previously, we considered two functional expansions; expansion (8) for the cluster functional $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ and expansion (14) for the function $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$. The functionals $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ and $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ are obviously closely related. Since the two functionals are so closely related, their "difference" is in some sense small and one might expect the expansion of $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ in powers of $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ to converge rapidly [or at least more rapidly than either expansions (8) or (14)].

The situation just described parallels a similar problem in function theory. There one considers two functions which have expansions in the same parameter. The convergence of one of the expansions can sometimes be improved by utilizing Burmann's theorem.[9] One simply inverts one of the expansions so that one has the parameter expanded in terms of the function. Then one uses this expansion to eliminate the parameter in the second function expansion, hopefully obtaining a more rapidly converging expansion.

We will use the functional analog of Burmann's theorem to improve the convergence of the functional expansions (8) and (14). We assume that the inverse functional expansion of $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ in powers of the cluster functional $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ has the form

$$\begin{aligned}\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\} &= D_0(|\mathbf{r}_1 - \mathbf{r}_2|) + \int d\mathbf{r}_3\, D_1(|\mathbf{r}_2 - \mathbf{r}_3|) C(|\mathbf{r}_3 - \mathbf{r}_1|) \\ &\quad + \int d\mathbf{r}_3\, d\mathbf{r}_4\, D_2(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) C(|\mathbf{r}_3 - \mathbf{r}_1|) C(|\mathbf{r}_4 - \mathbf{r}_1|) + O(C^3) \qquad (19)\end{aligned}$$

This form of the inverse functional expansion is made plausible if again one takes $\mathbf{r}_1 = 0$, placing particle one at the origin. Then Eq. (19) takes the standard form for a functional expansion as described by Volterra.⁽²²⁾ Apparently the first coefficient $D_0(|\mathbf{r}_1 - \mathbf{r}_2|)$ vanishes since the cluster functional $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ vanishes when the interaction becomes zero. In principle, one determines the remaining coefficients D_1, D_2, etc. by substituting expansion (19) into expansion (8a). One thus determines the D_1, D_2, etc. in terms of the A_1, A_2, etc., which are presumed known.

The procedure just described is not particularly useful for the purposes we have in mind, that is, the construction of the Percus–Yevick equation. We obtain a more useful result by substitution of expansion (19) to eliminate the interaction $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ in Eq. (11), thus obtaining a condition on $D_1(|\mathbf{r}_1 - \mathbf{r}_2|)$. Note that the cluster function $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ of Eq. (11) is valid only to first order in the interaction. We have not determined A_1 explicitly since this is unnecessary for our purposes.

It is conventional to write the singular part of D_1 separately from the nonsingular part. Thus we define the direct correlation function D via

$$D_1(|\mathbf{r}_2 - \mathbf{r}_1|) = \delta(\mathbf{r}_2 - \mathbf{r}_1) - \rho D(|\mathbf{r}_2 - \mathbf{r}_1|) \qquad (20)$$

Substitution of Eq. (20) into (19) and dropping the second order terms of C yields

$$\begin{aligned}\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\} &= C(|\mathbf{r}_1 - \mathbf{r}_2|) - \rho \int d\mathbf{r}_3\, D(|\mathbf{r}_2 - \mathbf{r}_3|) C(|\mathbf{r}_3 - \mathbf{r}_1|) \qquad (21)\end{aligned}$$

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[9] See, for example, Whittaker and Watson,⁽²⁵⁾ pp. 128–132, for a discussion of Burmann's theorem.

Next we utilize (21) to eliminate the interaction $V(|\mathbf{r}_2 - \mathbf{r}_1|)$ in Eq. (11) for the purpose of obtaining a condition on the direct correlation function $D(|\mathbf{r}_2 - \mathbf{r}_1|)$:

$$\begin{aligned} \rho \int d\mathbf{r}_3\, D(|\mathbf{r}_2 - \mathbf{r}_3|)C(|\mathbf{r}_3 - \mathbf{r}_1|) &\\ = \rho \int d\mathbf{r}_3\, C(|\mathbf{r}_1 - \mathbf{r}_3|)C(|\mathbf{r}_3 - \mathbf{r}_2|) &\\ - \rho^2 \int d\mathbf{r}_3 \left[\int d\mathbf{r}_4\, D(|\mathbf{r}_3 - \mathbf{r}_4|)C(|\mathbf{r}_4 - \mathbf{r}_1|)\right] C(|\mathbf{r}_3 - \mathbf{r}_2|) & \qquad (22) \end{aligned}$$

In Eq. (22) we have dropped all the second-order terms in the cluster function C. It might appear that we have kept second-order terms in (22) containing the cluster function combination $C(|\mathbf{r}_4 - \mathbf{r}_1|)C(|\mathbf{r}_3 - \mathbf{r}_2|)$. Note that there is only one cluster function which contains particle one. Hence, by our method of counting discussed previously, we must consider this a first-order term. Rearranging Eq. (22) slightly, one obtains a condition on $D(|\mathbf{r}_1 - \mathbf{r}_2|)$ which is known as the Ornstein–Zernike relation[10]

$$C(|\mathbf{r}_2 - \mathbf{r}_4|) = D(|\mathbf{r}_2 - \mathbf{r}_4|) + \rho \int d\mathbf{r}_3\, D(|\mathbf{r}_4 - \mathbf{r}_3|)C(|\mathbf{r}_3 - \mathbf{r}_2|) \qquad (23)$$

5.2. Obtaining the Percus–Yevick Equation

Substituting the inverse functional expansion (21) into the second functional expansion (18), one obtains the functional expansion of $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ to lowest order in the cluster function $C(|\mathbf{r}_1 - \mathbf{r}_2|)$:

$$\begin{aligned} \{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}[C(|\mathbf{r}_1 - \mathbf{r}_2|) - f(|\mathbf{r}_1 - \mathbf{r}_2|)] &\\ = \rho \int d\mathbf{r}_3\, [C(|\mathbf{r}_1 - \mathbf{r}_3|) &\\ - \rho \int d\mathbf{r}_4\, D(|\mathbf{r}_3 - \mathbf{r}_4|)C(|\mathbf{r}_4 - \mathbf{r}_1|)]C(|\mathbf{r}_3 - \mathbf{r}_2|) & \qquad (24) \end{aligned}$$

One might think we have achieved our goal of expressing $\eta(|\mathbf{r}_1 - \mathbf{r}_2|)$ as a functional of $C(|\mathbf{r}_1 - \mathbf{r}_2|)$ and indeed we have; however, it is possible to go further. Equation (24) is one relationship between the direct correlation function D and the cluster function C, but the Ornstein–Zernike relation (23) represents a second relation between the same two functions. It is possible to eliminate the direct correlation function and obtain an integral equation for the cluster function alone in terms of the interaction.

[10] See Ornstein and Zernike$^{(14)}$ and also Percus,$^{(16)}$ p. II-59, Eq. (5.6).

Utilization of the Ornstein–Zernike relation (23) in Eq. (24) yields

$$\{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}[C(|\mathbf{r}_1 - \mathbf{r}_2|) - f(|\mathbf{r}_1 - \mathbf{r}_2|)] = \rho \int d\mathbf{r}_4\, D(|\mathbf{r}_2 - \mathbf{r}_4|)C(|\mathbf{r}_4 - \mathbf{r}_1|) \tag{25}$$

Utilization of the Ornstein–Zernike relation (23) once again in Eq. (25) yields an explicit relation for the direct correlation function in terms of the cluster function

$$D(|\mathbf{r}_1 - \mathbf{r}_2|) = \{1 - \exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}[C(|\mathbf{r}_1 - \mathbf{r}_2|) + 1] \tag{26}$$

Utilization of Eq. (26) to eliminate the direct correlation function in (25) yields finally

$$\begin{aligned}\{\exp[\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)]\}[C(|\mathbf{r}_1 - \mathbf{r}_2|) + 1] &= 1 + \rho \int d\mathbf{r}_3 \{1 - \exp[\beta V(|\mathbf{r}_2 - \mathbf{r}_3|)]\} \\ &\quad \times [C(|\mathbf{r}_2 - \mathbf{r}_3|) + 1]C(|\mathbf{r}_3 - \mathbf{r}_1|)\end{aligned} \tag{27}$$

which is the Percus–Yevick equation written in terms of the cluster function. In obtaining Eq. (27), we utilized the definition for the Meyer f-function in terms of the interaction energy. The usual form of the Percus–Yevick equation[11] is obtained by utilizing Eq. (3b) to eliminate the cluster function in favor of the distribution function.

We thus have obtained the Percus–Yevick equation without utilizing the test particle theorem. Some ideas of functional expansions were introduced, but these were functional expansions for systems without external field. Superficially, the Percus functional construction is much shorter than our construction; however, this is deceptive since one should also include the test particle theorem in the Percus construction. The construction of the Percus–Yevick equation we have just presented is less elegant than the Percus construction. The strongest argument for our method of construction is its applicability to the nonequilibrium domain. As previously mentioned, application of the Percus functional method to this domain is problematic.

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[11] See Percus,(16) p. II-76, Eq. (6.13).

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