Journal of Statistical Physics, Vol. 24, No. 2, 1981

A Nonequilibrium Analog of the Percus–Yevick Equation

R. L. Varley[1]

Received February 21, 1979; revised August 13, 1979

A new theoretical description of nonequilibrium phenomena has been obtained that is analogous to the very successful Percus–Yevick equation of equilibrium fluids. The success of the equilibrium Percus–Yevick theory in describing hard-core systems suggests the nonequilibrium analog will also be quite good. Previously, we reported a new construction of the equilibrium Percus–Yevick equation which is applicable in the nonequilibrium domain and utilizes the BBGKY hierarchy in addition to some elementary ideas of functional expansions. The nonequilibrium Percus–Yevick theory contains an appealing physical picture wherein two fluid particles interact via an effective interaction Liouville operator which is the "true" interaction Liouville operator weighted by the (renormalized) second correlation function. The Percus–Yevick analog equation includes the usual "simple ring" and "repeated ring" dynamical processes in addition to more unusual "ring within ring" processes. The equilibrium Percus–Yevick theory indicates these "ring within ring" processes should be quantitatively important especially for dense gases and liquids.

KEY WORDS: Kinetic theory; transport theory; Percus–Yevick equation.

1. INTRODUCTION

Previously, we gave a brief report of a new theoretical description of nonequilibrium phenomena analogous to the very successful Percus–Yevick equilibrium theory of liquids.(53) Here we describe in some detail how the nonequilibrium analog equation was constructed, and also we show the relation of this new equation to other recent work. This new equation is of considerable interest since the equilibrium Percus–Yevick

---

This research was supported in part by a grant from the Faculty Research Award Program of the City University of New York.

[1] Hunter College, City University of New York, New York, N.Y.

equation(44) 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.(50) The success of the equilibrium Percus–Yevick theory motivated the nonequilibrium analog which we have constructed. A future paper will be devoted to various tests of the nonequilibrium analog of the Percus–Yevick equation provided by recent computer studies.(1,58) Before presenting our construction we find it useful to give, in broad outline, some history of nonequilibrium phenomena to place this new equation in context.

Much of our present theoretical understanding of nonequilibrium phenomena is embodied in the Boltzmann kinetic equation.(5,9,10) The Boltzmann equation is accepted as a good description of nonequilibrium phenomena in low-density gases for its ability to predict both laser light scattering spectra and autocorrelation functions obtained via computer molecular dynamics studies.(1,9,10) It was natural to seek an extension of the Boltzmann equation into the dense gas and liquid domain; however, adaptations of Boltzmann's intuitive construction to gases of moderate density were largely unfruitful, except for the one successful extension of Enskog.(19,10)

Further development did not occur in the nonequilibrium theory of dense fluids until the Boltzmann–Enskog equation was obtained in a more deductive manner from the Liouville equation through the work of Bogoliubov,(3) Born and Green, (6) and Kirkwood(31) in the 1940s. Workers in the field expected nonequilibrium functions such as transport coefficients to have virial expansions in density much as an equilibrium property like pressure has a virial expansion.(20) Dorfman and Cohen,(16) Frieman and Goldman,(23) and Weinstock(55) carefully investigated the virial expansion of the one-particle, nonequilibrium distribution function. They found the surprising result that the Choh–Uhlenbeck term, that is, the term following the Boltzmann–Enskog term in the density expansion, diverges for long times.

The divergence difficulty was isolated to certain terms of the perturbation expansion known as "ring terms" because of their topology. The ring terms correspond to long-range dynamically correlated processes. Kawasaki and Oppenheim(30) suggested the most divergent terms in each power of the density be selected and summed separately. This selective summation of the ring terms to all orders in density (of the naive density expansion) produced a logarithmic term in the density expansions of transport coefficients, and thus a first-order replacement of the virial expansion was found.

The upheaval in kinetic theory produced by the discovery of the divergences in the density expansions was amplified by the discovery in the computer molecular dynamics studies of Alder *et al.*(1) that the velocity autocorrelation did not decay exponentially for long times as expected classically on the basis of the Boltzmann equation. It was noticed by Dorfman and Cohen(17) that the ring terms would also yield this nonexponential $t^{-3/2}$ behavior of the velocity autocorrelation function for long times in addition to producing the logarithmic terms in the density expansion of the transport coefficients. Pomeau(48) gave an explanation of the long-time tail of the velocity autocorrelation function utilizing a cluster truncation of a (pseudo) Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy where the interaction Liouville operator is replaced by the T-scattering operator. Pomeau also introduced the eigenfunction, perturbation method for the study of the ring collision operator and found that theories based on the ring collision operator still contain divergences in two dimensions beyond those divergences previously uncovered. This work of Pomeau(48) and the related work of Ernst and Dorfman(21) contain certain "repeated ring terms" in addition to the simple "ring" terms discussed previously.

Gradually, the importance of the static Enskog correction to the Boltzmann equation was appreciated anew. It was acknowledged that such Enskog-like corrections would have to be included in addition to the ring dynamic events in order to obtain a kinetic theory of dense gases and liquids. Particularly notable work in this regard is the work of Mazenko,(40) Lebowitz and Resibois,(34) Gross,(27) Dorfman and Cohen,(18) and De Schepper and Cohen.(14) It also developed that the Enskog correction was related to the short-time (high-frequency) behavior of the correlation functions.

The work described here is a further step toward an adequate theory of nonequilibrium phenomena in dense fluids. Analogies between the equilibrium and nonequilibrium problems have historically been a chief source of inspiration in the nonequilibrium domain even though the analogies sometimes fail.(11,16) The similarity in the equilibrium and nonequilibrium problems led us to investigate some of the more recent work in the equilibrium theory of fluids with the hope of exploiting it. It was natural therefore to consider the Percus–Yevick theory(44,45) which provides an integral equation for the two-particle distribution function in terms of the interparticle potential. Here we describe a construction of a generalization of this successful equilibrium theory to the nonequilibrium domain.

The historical summary just given is by no means complete. Ernst *et al.*(20) have reviewed the work in kinetic theory up to the discovery of the divergences, while Pomeau and Resibois(47) have reviewed the more recent work. Papers of Boltzmann(5) and his contemporaries and the controversies of Loschmidt(38) and Zermelo(60) are given in the historical account by

Brush.(8) The next section, Section 2, is a short description of the correlation function formulation of the BBGKY hierarchy and nonequilibrium problems.(27,33,40) We make no attempt to recall all the required derivations and instead rely heavily on the work of Mazenko.(40) The linearized cluster expansions are also introduced(21) and a memory function for the cluster function is defined.(42,61) Section 3 makes contact with the low-density Boltzmann theory(10) and the Lenard–Balescu–Guernsey (LBG)(2,29,35) theory of the electron gas. The usual treatment of the LBG theory is via a parameter(54) expansion. Here we utilize a more sophisticated functional expansion and the ideas presented in this section form the basis of the eventual construction of the Percus–Yevick nonequilibrium analog equation. In Section 4 we attempt to improve the convergence of the functional expansion introduced in Section 3 at least for the case of hard-core potentials. A nonequilibrium analog of the Kirkwood–Salsburg equation(32) is found as a result of this calculation. The equilibrium theory of fluids leads us to expect that an even better theory can be found for nonequilibrium hard-core systems, so we proceed in Section 5 to construct the nonequilibrium analog of the Percus–Yevick equation.(44) We invoke the functional analog of Burmann's theorem(56) to invert the functional expansion of Section 3. The nonequilibrium analog of the Ornstein–Zernike(43) relation is found as a condition of the coefficient on the inverse expansion. The inverse functional expansion is then utilized to improve the convergence of the second functional expansion discussed in Section 4 and the result to lowest order is the nonequilibrium Percus–Yevick analog. The final section, Section 6, involves a comparison of the nonequilibrium Percus–Yevick theory with some other recent theories of nonequilibrium phenomena. We also present a physical picture of the dynamical processes included in the nonequilibrium Percus–Yevick analog theory.

2. NONEQUILIBRIUM BBGKY HIERARCHY; CORRELATION FUNCTIONS; CLUSTER FUNCTIONS; THE MEMORY FUNCTION

The nonequilibrium Percus–Yevick equation is constructed in terms of the correlation functions $C^U(1;\bar{1}\,|\,t)$, $C^U(12;\bar{1}\,|\,t)$, $C^U(123;\bar{1}\,|\,t)$, etc., defined by

$$C^U(1;\bar{1}\,|\,t) = \langle \delta f(1\,|\,t)\delta f(\bar{1})\rangle \tag{1a}$$

$$C^U(12;\bar{1}\,|\,t) = \langle \delta g(12\,|\,t)\delta f(\bar{1})\rangle \tag{1b}$$

$$C^U(123;\bar{1}\,|\,t) = \langle \delta g(123\,|\,t)\delta f(\bar{1})\rangle, \qquad \text{etc.} \tag{1c}$$

using the expressions given in Eqs. (5) and (6). The brackets $\langle \cdots \rangle$ denote an average over a canonical ensemble

$$\langle \cdots \rangle \equiv \int \frac{e^{-\beta H[U]}}{Z[U]} \cdots d\Gamma \tag{2}$$

of an N-particle system in an external field $U(\mathbf{r}_\alpha)$ described by a Hamiltonian $H[U]$ of the form

$$H[U] \equiv \sum_{\alpha=1}^{N} \frac{p_\alpha^2}{2m} + \frac{1}{2} \sum_{\substack{\alpha=1 \\ \{\alpha\neq\beta\}}}^{N} \sum_{\beta=1}^{N} V(|\mathbf{r}_\alpha - \mathbf{r}_\beta|) + \sum_{\alpha=1}^{N} U(\mathbf{r}_\alpha) \tag{3}$$

and the partition function $Z[U]$ is given by

$$Z[U] \equiv \int e^{-\beta H[U]} \, d\Gamma \tag{4}$$

These definitions of the correlation functions are similar to those introduced by Mazenko$^{(40)}$ when the external field is set to zero, as will be done here at the end of our construction of the Percus–Yevick nonequilibrium analog equation. Here we assume the N particles are identical, each having mass m and interacting by means of a potential energy $V(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)$ which depends upon the distance between the particles. The αth particle has momentum $\mathbf{p}_\alpha$ and position $\mathbf{r}_\alpha$ and the integration of the ensemble average Eq. (2) is over all of N-particle phase space $d\Gamma = d\mathbf{r}_1 d\mathbf{p}_2 \cdots d\mathbf{r}_N d\mathbf{p}_N$. The temperature of the canonical ensemble is characterized by the usual parameter $\beta = 1/k_B T$, where k_B is the Boltzmann constant.

The correlation functions (1) are easily shown to be equivalent to the usual reduced distribution functions obtained by integration of the N-particle nonequilibrium distribution for the case of small deviations from the equilibrium state.$^{(3,22,34,40)}$ While this restricts the kinds of problems that may be studied, the correlation functions have the advantage of specified initial conditions, so there is no ambiguity in the statement of the nonequilibrium problem. Furthermore, many quantities of physical interest can be obtained quite easily from the first correlation function $C^U \cdot (1; \bar{1} \mid t)$.$^{(22,40)}$ The correlation functions defined in Eq. (1) have a generic form in the sense that none of the N particles is selected for special treatment. This is accomplished by the introduction of "singular phase functions" $f(1)$, $g(12)$, $g(123)$, etc., where

$$f(1) \equiv \sum_{\alpha=1}^{N} \delta(1 - q_\alpha) \tag{5a}$$

$$g(12) \equiv \sum_{\substack{\alpha=1 \\ \{\alpha\neq\beta\}}}^{N} \sum_{\beta=1}^{N} \delta(1 - q_\alpha)\delta(2 - q_\beta) \tag{5b}$$

$$g(123) \equiv \sum_{\alpha=1}^{N} \sum_{\substack{\beta=1 \\ \{\alpha\neq\beta\neq\gamma\}}}^{N} \sum_{\gamma=1}^{N} \delta(1 - q_\alpha)\delta(2 - q_\beta)\delta(3 - q_\gamma) \tag{5c}$$

etc. In definitions (5), the phase variables of the αth particle are denoted by $q_\alpha \equiv (\mathbf{p}_\alpha, \mathbf{r}_\alpha)$. The phase variables represent the actual positions and momenta of particles of the system and they are involved in the canonical averages. The external variables $1 \equiv (\boldsymbol{\pi}_1, \mathbf{x}_1)$, etc. are in this sense simply parameters upon which the correlation functions depend. It proves convenient to introduce augmented singular phase space functions $\delta f(1)$, $\delta g(12)$, $\delta g(123)$, etc. defined by

$$\delta f(1) \equiv f(1) - \langle f(1) \rangle \tag{6a}$$

$$\delta g(12) \equiv g(12) - \langle g(12) \rangle \tag{6b}$$

$$\delta g(123) \equiv g(123) - \langle g(123) \rangle \tag{6c}$$

etc. The augmented functions allow us to focus on the deviations from equilibrium, which are the central interest of this paper.

Since there is a close connection between the usual nonequilibrium reduced distribution functions and the correlation functions of definitions (1), it is not surprising that the correlation functions satisfy a BBGKY hierarchy of equations.[2] The first two equations of the BBGKY hierarchy in the correlation function notation appear as

$$\left\{ \frac{\partial}{\partial t} + i\left[L_f(1) + L_U(1) \right] \right\} C^U(1; \bar{1} \,|\, t) + i \int d2\, L_I(12) C^U(12; \bar{1} \,|\, t) = 0 \tag{7a}$$

$$\begin{aligned} &\left\{ \frac{\partial}{\partial t} + i\left[L_f(12) + L_I(12) + L_U(12) \right] \right\} C^U(12; \bar{1} \,|\, t) \\ &\quad + i \int d3 \left[L_I(13) + L_I(23) \right] C^U(123; \bar{1} \,|\, t) = 0 \end{aligned} \tag{7b}$$

In the above equations, the free one- and two-particle Liouville operators $L_f(1)$ and $L_f(12)$, respectively, are given by

$$L_f(1) = -i \frac{\boldsymbol{\pi}_1}{m} \cdot \frac{\partial}{\partial \mathbf{x}_1} \quad \text{and} \quad L_f(12) = -i \left(\frac{\boldsymbol{\pi}_1}{m} \cdot \frac{\partial}{\partial \mathbf{x}_1} + \frac{\boldsymbol{\pi}_2}{m} \cdot \frac{\partial}{\partial \mathbf{x}_2} \right) \tag{8}$$

The interaction Liouville operator $L_I(12)$ for the interparticle interaction is given by

$$L_I(12) = i \frac{\partial V(\mathbf{x}_1 - \mathbf{x}_2)}{\partial \mathbf{x}_1} \cdot \left(\frac{\partial}{\partial \boldsymbol{\pi}_1} - \frac{\partial}{\partial \boldsymbol{\pi}_2} \right) \tag{9}$$

while the interaction Liouville operators $L_U(1)$, $L_U(12)$ for the external field

---

[2] We follow the usual procedure of the kinetic theory literature of referring to the set of equations developed by Bogoliubov,(3) Born and Green,(6,26) Kirkwood,(31) and Yvon(59) as the "BBGKY hierarchy of equations."

$U(\mathbf{x}_1)$ are given by

$$L_U(1) = i\frac{\partial U(\mathbf{x}_1)}{\partial \mathbf{x}_1} \cdot \frac{\partial}{\partial \boldsymbol{\pi}_1} \quad \text{and} \quad L_U(12) = L_U(1) + L_U(2) \tag{10}$$

One of the earliest applications of the BBGKY hierarchy was to transport phenomena in low-density gases.(3) The Boltzmann equation(3,40) is obtained by assuming the correlation functions are analytic in the density and by utilizing some mathematical device to introduce irreversibility, replacing the Boltzmann "molecular chaos" assumption.(5) Perhaps the most elegant and simple of these devices is the memory function method,(42) which will be introduced later and will be employed in our construction of the nonequilibrium Percus–Yevick analog equation.

The procedure just described is unsuitable for the Coulomb gas problem since the coefficients of the density expansion of the correlation functions diverge owing to the long-range nature of the Coulomb force. The situation is ameliorated by considering expansions of the correlation functions in terms of a "Coulomb coupling parameter" which replaces the density as the expansion parameter. The actual calculations are complicated, but some relief is provided by the introduction of the cluster functions, which effectively "weaken the correlations between particles." Specifically the cluster functions vanish whenever a member of the "cluster of particles" is removed physically in distance and time away from the other members. Here we are not particularly interested in the Coulomb gas problem; however, we will have a use for the cluster functions because the property just described makes the functional expansions of the cluster functions relatively simple in comparison with the corresponding functional expansions of the correlation functions.

The cluster functions $\chi^U(1;\bar{1}\,|\,t)$, $\chi^U(12;\bar{1}\,|\,t)$, $\chi^U(123;\bar{1}\,|\,t)$, etc. can be defined in terms of the correlation functions in a variety of ways. One should keep in mind that the correlation functions are related to the nonequilibrium distribution functions only for fluctuations close to equilibrium and therefore it is appropriate to utilize the linearized cluster functions following the work of Ernst and Dorfman(21,53) and others:

$$C^U(1;\bar{1}\,|\,t) = \chi^U(1;\bar{1}\,|\,t) \tag{11a}$$

$$C^U(12;\bar{1}\,|\,t) = \chi^U(12;\bar{1}\,|\,t) + \{1 + P_{12}\}\langle f(1)\rangle \chi^U(2;\bar{1}\,|\,t) \tag{11b}$$

$$\begin{aligned} C^U(123;\bar{1}\,|\,t) = {} & \chi^U(123;\bar{1}\,|\,t) + \{1 + P_{12} + P_{13}\}\langle f(1)\rangle \chi^U(23;\bar{1}\,|\,t) \\ & + \{1 + P_{13} + P_{23}\}\langle g(12)\rangle \chi^U(3;\bar{1}\,|\,t) \end{aligned} \tag{11c}$$

etc. These equations are quite easily inverted and we obtain

$$\chi^U(1;\bar{1}\,|\,t) = C^U(1;\bar{1}\,|\,t) \tag{12a}$$

$$\chi^U(12;\bar{1}\,|\,t) = C^U(12;\bar{1}\,|\,t) - \{1 + P_{12}\}\langle f(1)\rangle C^U(2;\bar{1}\,|\,t) \tag{12b}$$

$$\begin{aligned}\chi^U(123;\bar{1}\,|\,t) = C^U(123;\bar{1}\,|\,t) &- \{1 + P_{12} + P_{13}\}\langle f(1)\rangle C^U(23;\bar{1}\,|\,t)\\ &- \{1 + P_{13} + P_{23}\}\langle g(12)\rangle C^U(3;\bar{1}\,|\,t)\end{aligned} \tag{12c}$$

etc. The equilibrium quantities $\langle f(1)\rangle$, $\langle g(12)\rangle$, $\langle g(123)\rangle$, etc. appearing in Eqs. (11) and (12) are ensemble averages defined by Eq. (2) of the singular phase space function defined by Eq. (5). They are simply related to the usual spatial equilibrium distributions $g(\mathbf{x}_1)$, $g(\mathbf{x}_1, \mathbf{x}_2)$, etc. via

$$ng(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1) = \langle f(1)\rangle \tag{13a}$$

$$n^2 g(\mathbf{x}_1, \mathbf{x}_2)\phi(\boldsymbol{\pi}_1)\phi(\boldsymbol{\pi}_2) = \langle g(12)\rangle \tag{13b}$$

$$n^3 g(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)\phi(\boldsymbol{\pi}_1)\phi(\boldsymbol{\pi}_2)\phi(\boldsymbol{\pi}_3) = \langle g(123)\rangle \tag{13c}$$

Here we utilize n for the equilibrium particle density and the Boltzmann distribution is given by $\phi(\boldsymbol{\pi}) = (\beta/2\pi m)^{3/2}\exp(-\beta\pi^2/2m)$. When the external field $U(\mathbf{r}_1)$ is switched off, the single-particle distribution becomes unity $g(\mathbf{x}) \to 1$ and the two-particle distribution becomes a function only of the distance between the two particles $g(\mathbf{x}_1, \mathbf{x}_2) \to g(|\mathbf{x}_1 - \mathbf{x}_2|)$. The permutation symbol P_{12} interchanges the indices of the particles 1 and 2 in the function following the permutation symbol.

One can easily show utilizing Eqs. (12) that the cluster functions χ^U have the "cluster property," but perhaps a few words of explanation would be appropriate. The barred index to the right of the semicolon is not involved in the cluster property, so the $\chi^U(12;\bar{1}\,|\,t)$ of Eq. (12b) is considered first. When particle 1 is spatially separated from particle 2 at time t then one obtains from definition (1b) $C^U(12;\bar{1}\,|\,t) \simeq \{1 + P_{12}\}\langle f(1)\rangle C^U(2;\bar{1}\,|\,t)$ and the right-hand side of Eq. (12b) vanishes. One therefore sees that $\chi^U(12;\bar{1}\,|\,t)$ is zero whenever particle 1 is "far from" particle 2 and thus $\chi^U(12;\bar{1}\,|\,t)$ has the cluster property.

Mazenko,(40) Lebowitz and Resibois,(34) and Gross(28) have chosen to introduce more complicated cluster functions which are useful if one wishes to discuss the short-time contributions to the kinetic equations which are important for the high-frequency and high-density behavior of the correlation functions. Here we are interested in presenting a pedagogically simple treatment, and, furthermore, these linearized cluster functions are adequate for the discussion of interesting phenomena such as the long-time "tail" of the velocity autocorrelation function.(1)

Expressions (11) can be utilized to eliminate the correlation functions in the BBGKY hierarchy equations (7). One thus obtains the BBGKY hierarchy of equations expressed in terms of the cluster functions. The first equation of this hierarchy is

$$\begin{aligned}&\left[z - L_f(1) - L_U(1)\right]\hat{\chi}^U(1;\bar{1}\,|\,z)\\ &\qquad - \int d^2 L_I(12)\{1 + P_{12}\} ng(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\hat{\chi}^U(2;\bar{1}\,|\,z)\\ &\quad = \chi^U(1;\bar{1}\,|\,t = 0) + \int d2\, L_I(12)\hat{\chi}^U(12;\bar{1}\,|\,z)\end{aligned} \tag{14}$$

The time variable in Eq. (14) has been Laplace-transformed utilizing the definition(40,46)

$$\hat{f}(z) = -i\int_0^{\infty} dt\, e^{izt} f(t) \qquad \text{with} \quad \operatorname{Im} z > 0 \tag{15}$$

where $\hat{f}(z)$ is the Laplace transform of the function $f(t)$. The Laplace transform is introduced since, among other things, the memory function formalism which is introduced shortly is most conveniently utilized in the Laplace transform domain of time.

Previously we mentioned that the primitive secular divergence will be removed by introducing the memory function(42,57,61) formalism. Specifically, the memory function $\hat{R}(1;\bar{1}\,|\,z)$ is defined via[3]

$$\begin{aligned}&\left[z - L_f(1) - L_U(1)\right]\hat{\chi}^U(1;\bar{1}\,|\,z)\\ &\qquad - \int d2\, L_I(12)\{1 + P_{12}\} ng(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\hat{\chi}^U(2;\bar{1}\,|\,z)\\ &\quad = \chi^U(1;\bar{1}\,|\,t = 0) + \int d2\, \hat{R}(1;2\,|\,z)\hat{\chi}^U(2;\bar{1}\,|\,z)\end{aligned} \tag{16}$$

If one introduces an inverse to the one-particle cluster function $\hat{\chi}^U(1;\bar{1}\,|\,z)$ via

$$\int d\bar{1}\, \hat{\chi}^U(1;\bar{1}\,|\,z)\hat{\chi}^U(\bar{1};2\,|\,z)^{-1} = \delta(1-2) \tag{17}$$

then one obtains an explicit expression for the memory function by comparing Eqs. (14) and (16) and utilizing the inverse one-particle cluster function defined by (17). One obtains

$$\hat{R}(1;\bar{2}\,|\,z) = \int d2\, L_I(12) \int d\bar{1}\, \hat{\chi}^U(12;\bar{1}\,|\,z)\hat{\chi}^U(\bar{1};\bar{2}\,|\,z)^{-1} \tag{18}$$

Introducing the following definitions for the "renormalized" two-particle cluster function $\hat{R}(1,2;\bar{1}\,|\,z)$, the "renormalized" three-particle cluster func-

---

[3] The memory function for the cluster function introduced here differs from that defined in Ref. 53.

tion $\hat{R}(1,2,3;\bar{1}\,|\,z)$, etc.

$$\hat{R}(12;\bar{1}\,|\,z) \equiv \int d\bar{2}\,\hat{\chi}^{U}(12;\bar{2}\,|\,z)\,\hat{\chi}^{U}(\bar{2};\bar{1}\,|\,z)^{-1} \tag{19}$$

$$\hat{R}(123;\bar{1}\,|\,z) \equiv \int d\bar{2}\,\hat{\chi}^{U}(123;\bar{2}\,|\,z)\,\hat{\chi}^{U}(\bar{2};\bar{1}\,|\,z)^{-1} \tag{20}$$

one obtains the first two equations of the BBGKY hierarchy in the following form.

2.1. First Equation of Hierarchy

$$\begin{aligned}
&\left[z - L_f(1) - L_U(1)\right]\hat{\chi}^{U}(1;\bar{1}\,|\,z) \\
&\quad - \int d2\, L_I(12)\{1 + P_{12}\}\, n g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\hat{\chi}^{U}(2;\bar{1}\,|\,z) \\
&\quad = \chi^{U}(1;\bar{1}\,|\,t=0) + \int d2 \int d\bar{2}\, L_I(12)\hat{R}^{U}(12;\bar{2}\,|\,z)\hat{\chi}^{U}(\bar{2};\bar{1}\,|\,z)
\end{aligned} \tag{21a}$$

2.2. Second Equation of Hierarchy[4]

$$\begin{aligned}
&\left[z - L(12)\right]\hat{R}^{U}(12;\bar{2}\,|\,z) - L_I(12)\{1 + P_{12}\}\, n g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\,\delta(2 - \bar{2}) \\
&\quad = \int d\bar{1}\,\chi^{U}(12;\bar{1}\,|\,t=0)\hat{\chi}^{U}(\bar{1};\bar{2}\,|\,z)^{-1} \\
&\qquad + \int d3\,\{1 + P_{12}\}\, L_I(13)\Big[\{1 + P_{13}\}\, n g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\hat{R}^{U}(23;\bar{2}\,|\,z) \\
&\qquad + \hat{R}^{U}(123;\bar{2}\,|\,z)\Big] \\
&\qquad + \int d3\,\{1 + P_{12}\}\, L_I(13)\Big[\{1 + P_{13}\}\, n^2\{g(\mathbf{x}_1\mathbf{x}_2) \\
&\qquad - g(\mathbf{x}_1)g(\mathbf{x}_2)\}\phi(\boldsymbol{\pi}_1)\phi(\boldsymbol{\pi}_2)\,\delta(3 - \bar{2})\Big]
\end{aligned} \tag{21b}$$

where the memory function $\hat{R}(1;\bar{2}\,|\,z)$ and the "renormalized" two-particle cluster function $\hat{R}(12;\bar{1}\,|\,z)$ are related by (18) if one utilizes definition (19)

$$\hat{R}^{U}(1;\bar{2}\,|\,z) = \int d2\, L_I(12)\hat{R}^{U}(12;\bar{2}\,|\,z) \tag{22}$$

Our use of the BBGKY hierarchy equations (21) is limited to the domain of asymptotic long times. Experience indicates(21) that we may

---

[4] In Eq. (21b) we utilized the definition $L(12) = L_f(12) + L_I(12) + L_U(12)$.

safely neglect $\chi^{U}(12;\bar{1}\,|\,t=0)$ for the calculation of the long-time behavior of $\hat{\chi}^{U}(1;\bar{1}\,|\,z)$. We neglect this "initial condition" term in the sections that follow. This contribution is important if we are to have a theory that is valid for liquid densities. Here we are primarily interested in the dynamical processes since we wish to make our construction of the nonequilibrium Percus–Yevick analog pedagogically as simple as possible. In a future paper we will describe how this important contribution is included in the nonequilibrium analog of the Percus–Yevick theory.

3. THE FUNCTIONAL EXPANSION OF THE RENORMALIZED SECOND CLUSTER FUNCTIONAL IN POWERS OF THE INTERACTION LIOUVILLE OPERATOR TO LOWEST ORDER

Previously, we mentioned that one classical method(3,13) of treating the BBGKY hierarchy of equations is to assume each of the distribution functions has an expansion in powers of the density. This approach works well in the equilibrium case, but fails in the nonequilibrium domain in the limit of long times even if one utilizes a method such as the memory function to remove the primitive secular divergences.(16,23,55) Nonetheless, for finite times the density expansion can provide some insight into the more important dynamical processes. The density expansion approach can, of course, be applied as well to correlation functions and also to the cluster functions. If one assumes the "renormalized" second cluster function $\hat{R}^{U}(12;\bar{1}\,|\,z)$ has a density expansion of the form[5]

$$\hat{R}^{U}(12;\bar{1}\,|\,z) = nG_2(12\,|\,z)\Big[\hat{R}_1(12;\bar{1}\,|\,z) + n\hat{R}_2(12;\bar{1}\,|\,z) + \cdots\Big] \tag{23}$$

then one immediately obtains from the second BBGKY equation (21b)

$$\hat{R}_1(12;\bar{1}\,|\,z) = L_I(12)\{1 + P_{12}\}\,g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\delta(2-\bar{1}) \tag{24}$$

where we have also utilized an expansion similar to (23) for $\hat{R}^{U}(123;\bar{1}\,|\,z)$. Substitution of (24) in the first equation of the BBGKY hierarchy, Eq. (21a), leads quickly to the usual form of the linearized Boltzmann equation.(4,34,53)

We mentioned earlier the particular usefulness of the cluster functions in connection with the Coulomb gas problem. The standard procedure is to expand the cluster functions (or here, the "renormalized" cluster functions) in powers of the plasma parameter in a manner similar to expansion (23). The lowest-order theory is the usual Lenard,(35) Balescu,(2) Guernsey(29) kinetic equation. Here we follow a somewhat different procedure to set the

---

[5] The two-particle Green's function $G_2(12\,|\,z) \equiv \{z - L(12)\}^{-1}$ is utilized in Eq. (23).

stage for the eventual construction of the nonequilibrium Percus–Yevick equation in Section 5.

The construction of the nonequilibrium Percus–Yevick equation(53) does not involve parameter expansions. Instead we shall assume the existence of more general functional expansions.(54) We will illustrate the procedure by obtaining the LBG result which is the nonequilibrium analog of the Debye–Hückel(7,12) equilibrium theory. Let us assume the "renormalized" clusters have functional expansions of the form

$$\hat{R}^U(12;\bar{1}\,|\,z) = A_0(12;\bar{1}\,|\,z) + \int d3\,\{1 + P_{12}\}\,L_I(13)A_1(32;\bar{1}\,|\,z) + \int d3 \int d4\,\{1 + P_{12}\}\,L_I(13)L_I(14)A_2(432;\bar{1}\,|\,z) + \cdots \tag{25a}$$

$$\hat{R}^U(123;\bar{1}\,|\,z) = B_0(123;\bar{1}\,|\,z) + \int d4\,\{1 + P_{12}\}\,L_I(14)B_1(432;\bar{1}\,|\,z) + \int d4 \int d5\,\{1 + P_{12}\}\,L_I(14)L_I(15)B_2(5432;\bar{1}\,|\,z) + \cdots \tag{25b}$$

The form of the functional expansions (25) is the nonequilibrium generalization of the corresponding equilibrium functional expansions. The zeroth-order terms $A_0(12;\bar{1}\,|\,z)$, $B_0(123;\bar{1}\,|\,z)$, etc. vanish for reasons that are similar to those used in the corresponding equilibrium case.

Substitution of the functional expansions (25) into the equation (21b) of the BBGKY hierarchy for the "renormalized" cluster functions yields[6]

$$\begin{aligned}\hat{R}^U(12;\bar{1}\,|\,z) = {} & G_f(12\,|\,z)L_I(12)\{1 + P_{12}\}\,ng(\mathbf{x}_1)\phi(\pi_1)\,\delta(2 - \bar{1}) \\ & + G_f(12\,|\,z)\int d3\,\{1 + P_{12}\}\,L_I(13)\{1 + P_{13}\}\,ng(\mathbf{x}_1)\phi(\pi_1) \\ & \times \hat{R}^U(23;\bar{1}\,|\,z)\end{aligned} \tag{26}$$

In obtaining Eq. (26) we first kept the lowest-order terms in the interaction Liouville operator after substitution of expansions (25) in the hierarchy equations (21). We then utilized the expansions (25) to reintroduce the "renormalized" cluster functions, since the resulting equation (26) for the "renormalized" cluster function $\hat{R}^U(12;\bar{1}\,|\,z)$ is easier to solve than the equation for the functional expansion coefficient $A_1(32;\bar{1}\,|\,z)$.

Equation (26) is solved utilizing methods of singular integral equations

---

[6] The terms $\int d3\,\{L_I(13) + L_I(23))\}\,n\phi(\pi_3)\hat{R}(12;\bar{1}\,|\,z)$ vanish in Eq. (26) if the external field is set to zero, since then $g(x_1) = 1$. The external field was introduced to retain these quantitatively important terms. See p. 174 of Ref. 53 for further discussion. We also utilized the definition of the free-particle Green's function given by $G_f(12) = \{z - L_f(12)\}^{-1}$.

for the "renormalized" second cluster function $\hat{R}(12;\bar{1}\,|\,z)$. When one substitutes this form of $\hat{R}(12;\bar{1}\,|\,z)$ into the first equation of the BBGKY hierarchy (21b) one obtains the well-known LBG theory.[7]

The approach we have described is useful for the long-range Coulomb interaction; however, for gases having hard-core interactions there are difficulties. One suspects an expansion in the interaction Liouville operator might be appropriate for those regions of phase space where the Coulomb potential is weak. The singular nature of the hard-core interaction presents difficulties, since for some regions there is no interaction at all but at short distances the interaction is very strong. Some revision of the functional expansion procedure is thus required.

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

The poor convergence properties of the functional expansions (25) of the "renormalized" cluster function $\hat{R}^U(12;\bar{1}\,|\,z)$ in powers of the interaction Liouville operator $L_I(12)$ leads us to consider other alternative functionals. We respond to the situation by seeking an alternative to the functional $\hat{R}^U(12;\bar{1}\,|\,z)$ utilizing an argument similar to one introduced in our previous work on an alternative construction of the equilibrium Percus–Yevick equation.$^{(53)}$ The strategy in the equilibrium case was to examine the virial expansion of the cluster function for insight into the possible form of an improved functional. We follow that procedure here and rewrite the virial expansion of the "renormalized" second cluster function (23) in the form

$$G_2(12\,|\,z)^{-1}\Big[\hat{R}^U(12;\bar{1}\,|\,z) - nG_2(12\,|\,z)L_I(12)\{1+P_{12}\}g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\,\delta(2-\bar{1})\Big]$$

$$= n^2\hat{R}_2(12;\bar{1}\,|\,z) + n^3\hat{R}_3(12;\bar{1}\,|\,z) + \cdots \qquad (27)$$

where we utilized the Boltzmann result (24) in the lowest-order term. The Choh–Uhlenbeck term $\hat{R}_2(12;\bar{1}\,|\,z)$ and all higher-order terms in (27) involve the indirect interaction of particles one and two mediated by the remaining particles of the system.

---

[7] Gell-Mann and Brueckner$^{(25)}$ and others have treated the corresponding quantum mechanical problem. Macke$^{(39)}$ appears to have left out the terms just mentioned since they do not occur in the equilibrium problem.

These considerations encourage us to propose $\hat{\eta}(12;\bar{1}\,|\,z)$ as an alternative functional for the N-particle system, where $\hat{\eta}(12;\bar{1}\,|\,z)$ is defined by

$$\hat{\eta}(12;\bar{1}\,|\,z) = G_2(12\,|\,z)^{-1}\Big[\hat{R}^{U}(12;\bar{1}\,|\,z) - nG_2(12\,|\,z)L_I(12) \times \{1 + P_{12}\}\, g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\,\delta(2-\bar{1})\Big] \tag{28}$$

The hope is that a functional expansion of $\hat{\eta}(12;\bar{1}\,|\,z)$ in powers of the interaction Liouville operator $L_I(12)$ might have better convergence properties than the functional expansion (25).

If one contemplates a functional expansion of $\hat{\eta}(12;\bar{1}\,|\,z)$ in powers of $L_I(12)$ similar to (25)

$$\hat{\eta}(12;\bar{1}\,|\,z) = \hat{\eta}_0(12;\bar{1}\,|\,z) + \int d3\,\{1 + P_{12}\}L_I(13)\hat{\eta}_1(32;\bar{1}\,|\,z) + \int d3\int d4\,\{1 + P_{12}\}L_I(13)L_I(14)\hat{\eta}_2(432;\bar{1}\,|\,z) + \cdots \tag{29}$$

one obtains to first order in the interaction Liouville operator an equation which is a nonequilibrium analog of the Kirkwood–Salsburg equilibrium$^{(32)}$ equation:

$$G_2(12\,|\,z)^{-1}\Big[\hat{R}^{U}(12;\bar{1}\,|\,z) - nG_2(12\,|\,z)L_I(12)\{1+P_{12}\}\, g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\,\delta(2-\bar{1})\Big] = \int d3\,\{1 + P_{12}\}L_I(13)\{1 + P_{13}\}ng(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\hat{R}^{U}(23;\bar{1}\,|\,z) \tag{30}$$

Equation (30) was obtained by first constructing a hierarchy equation by operating on $\hat{\eta}(12;\bar{1}\,|\,z)$ with $\{z - L_2(12)\}$. One obtains a hierarchy equation involving the second and third "renormalized" cluster functions defined by Eqs. (19) and (20). We then utilized the functional expansions (29) and (25) in this hierarchy equation and dropped second- and higher-order terms in the interaction Liouville operator. Finally, we utilized definition (28) to write the result (30) in terms of $\hat{R}^{U}(12;\bar{1}\,|\,z)$, an equation which is accurate to first order in $L_I(12)$.

The equilibrium Kirkwood–Salsburg equation$^{(32)}$ is an improvement over the Debye–Hückel equation$^{(12)}$ at least for systems with hard-core interactions. One might expect a similar situation to hold in the nonequilibrium domain, but we will not stop here since the equilibrium theory leads us to expect a still better equation, which will be obtained in the next section.

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

5.1. Inversion of the "Renormalized" Cluster Functional Expansion in the Interaction

Previously, we considered two functional expansions: expansion (25a) for the "renormalized" second cluster function $\hat{R}^U(12;\bar{1}\,|\,z)$ and expansion (29) for the functional $\hat{\eta}(12;\bar{1}\,|\,z)$. The functionals $\hat{R}^U(12;\bar{1}\,|\,z)$ and $\hat{\eta}(12;\bar{1}\,|\,z)$ are obviously closely related, and one might expect the expansion of $\hat{\eta}(12;\bar{1}\,|\,z)$ in powers of $\hat{R}^U(12;\bar{1}\,|\,z)$ to converge rapidly [or at least more rapidly than either expansion (25a) or expansion (29)]. These observations are similar to those made in the equilibrium case.$^{(53)}$

We utilize the functional analog of Burmann's theorem$^{(56)}$ to improve the convergence of expansions (25a) and (29). We first assume an inverse functional expansion of the form

$$\begin{aligned} &G_f(12\,|\,z)L_I(12)\{1+P_{12}\}ng(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\,\delta(2-\bar{1}) \\ &\quad = D_0(12\,|\,z) + \int d3\,\{1+P_{12}\}D_1(23\,|\,z)\hat{R}^U(13;\bar{1}\,|\,z) + \cdots \end{aligned} \tag{31}$$

This expansion is the nonequilibrium generalization of the inverse functional expansion of the potential $V(|\mathbf{r}_1-\mathbf{r}_2|)$ in powers of the cluster function $C(|\mathbf{r}_1-\mathbf{r}_2|)$. The lowest-order term $D_0(12\,|\,z)$ vanishes because of the cluster property of the $\hat{R}^U(12;\bar{1}\,|\,z)$.

The coefficients of the inverse functional expansion $D_1(12\,|\,z)$, etc. are found by substitution of (31) into the expansion (25a). This procedure is not particularly useful here. Instead we substitute the expansion (31) in Eq. (26) to obtain a condition of $D_1(12\,|\,z)$. This is permissible since Eqs. (26) and (25a) are equivalent, to lowest order in the interaction Liouville operator $L_I(12)$. We follow the procedure used in the equilibrium case and introduce the direct correlation functional $D(23\,|\,z)$ defined by $\{1+P_{12}\}D_1(23\,|\,z) = \delta(2-3) - \{1+P_{12}\}D(23\,|\,z)$. One then substitutes (31) into (26) and one obtains, after a simple manipulation, a condition on the direct correlation function $D(12\,|\,z)$ which is the nonequilibrium analog of the Ornstein–Zernike relation

$$\begin{aligned} &\{1+P_{12}\}D(24\,|\,z) \\ &\quad = G_f(12\,|\,z)\{1+P_{12}\}G_f(14\,|\,z)^{-1}\int d\bar{1}\,\hat{R}^U(24;\bar{1}\,|\,z) \\ &\quad\quad - G_f(12\,|\,z)\{1+P_{12}\} \\ &\quad\quad \times \int d3\,G_f(13\,|\,z)^{-1}\{1+P_{13}\}D(34\,|\,z)\int d\bar{1}\,\hat{R}^U(23;\bar{1}\,|\,z) \end{aligned} \tag{32}$$

We kept terms to first order in $\hat{R}^U(12;\bar{1}\,|\,z)$ in obtaining (32).

5.2. Obtaining the Percus–Yevick Equation

Substitution of the inverse functional expansion (31) in the second functional expansion (30) yields the functional expansion of $\hat{\eta}(12;\bar{1}\,|\,z)$ in powers of the "renormalized" second cluster function $\hat{R}^U(12;\bar{1}\,|\,z)$:

$$
\begin{aligned}
&G_2(12\,|\,z)^{-1}\Big[\hat{R}^U(12;\bar{1}\,|\,z)\\
&\qquad -nG_2(12\,|\,z)L_I(12)\{1+P_{12}\}\,g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\,\delta(2-\bar{1})\Big]\\
&\quad=\int d3\,\{1+P_{12}\}\,G_f(13\,|\,z)^{-1}\int d\bar{2}\,\hat{R}^U(13;\bar{2}\,|\,z)\\
&\qquad-\int d3\,\{1+P_{12}\}\,G_f(13\,|\,z)^{-1}\int d\bar{4}\,\{1+P_{13}\}\,D(34\,|\,z)\\
&\qquad\times\int d\bar{2}\,\hat{R}^U(14;\bar{2}\,|\,z)\hat{R}^U(23;\bar{1}\,|\,z)
\end{aligned}
\tag{33}
$$

Equation (30) is the equivalent to expansion (29) at least to lowest order. Equation (30), which is expressed in terms of $\hat{R}^U(12;\bar{1}\,|\,z)$, is less complicated than (29) written in terms of the expansion coefficients $\hat{\eta}_1(12;\bar{1}\,|\,z)$, $A_1(12;\bar{1}\,|\,z)$, etc. If one subsequently utilizes the nonequilibrium analog of the Ornstein–Zernike relation (32), one obtains an expression for the direct correlation functional, which in turn can be utilized to eliminate $D(12\,|\,z)$ in expansion (33). This procedure yields

$$
\begin{aligned}
&G_2(12\,|\,z)^{-1}\Big[\hat{R}^U(12;\bar{1}\,|\,z)\\
&\qquad -nG_2(12\,|\,z)L_I(12)\{1+P_{17}\}\,g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\,\delta(2-\bar{1})\Big]\\
&\quad=\int d3\,\{1+P_{12}\}\Big[L_I(13)\int d\bar{2}\,\hat{R}^U(13;\bar{2}\,|\,z)\\
&\qquad+nL_I(13)\{1+P_{13}\}\,g(\mathbf{x}_1)\phi(\boldsymbol{\pi}_1)\Big]\hat{R}^U(23;\bar{1}\,|\,z)
\end{aligned}
\tag{34}
$$

which is nonequilibrium analog of the Percus–Yevick equation written in terms of the "renormalized" cluster functional $\hat{R}^U(12;\bar{1}\,|\,z)$. In Section 6, we write the nonequilibrium Percus–Yevick analog equation in terms of the "renormalized" correlation functions so that the form of the equation is closer to the expression usually given for the equilibrium Percus–Yevick equation.

6. COMPARISON WITH OTHER THEORIES

Previously, when we reported our nonequilibrium analog of the Percus–Yevick equation we wrote the equation in terms of the "renormalized" correlation functions $\hat{\Gamma}(12;\bar{1}\,|\,z)$. The "renormalized" correlation functions occur naturally if one returns to the BBGKY hierarchy equation (7a)

$$\{z - L_f(1)\}\hat{C}(1;\bar{1}\,|\,z) = C(1;\bar{1}\,|\,t=0) + \int d2\, L_I(12)\hat{C}(12;\bar{1}\,|\,z) \tag{35}$$

where we have Laplace-transformed the time variable with definition (15). We introduce a memory function $\hat{\Gamma}(1;\bar{1}\,|\,z)$ via the equation

$$\{z - L_f(1)\}\hat{C}(1;\bar{1}\,|\,z) = C(1;\bar{1}\,|\,t=0) + \int d2\, \hat{\Gamma}(1;2\,|\,z)\hat{C}(2;\bar{1}\,|\,z) \tag{36}$$

which is obviously similar to Eq. (16), which defines the memory function $\hat{R}(1;\bar{1}\,|\,z)$ for the cluster functions. If one follows a procedure similar to the one utilized following Eq. (16), one obtains an explicit equation for the memory function $\hat{\Gamma}(1;\bar{1}\,|\,z)$ in terms of the "renormalized" second correlation function $\hat{\Gamma}(12;\bar{1}\,|\,z)$

$$\hat{\Gamma}(1;\bar{2}\,|\,z) = \int d2\, L_I(12)\hat{\Gamma}(12;\bar{2}\,|\,z) \tag{37}$$

The "renormalized" second correlation function $\hat{\Gamma}(12;\bar{1}\,|\,z)$ is defined by

$$\hat{\Gamma}(12;\bar{2}\,|\,z) = \int d\bar{1}\, \hat{C}(12;\bar{1}\,|\,z)\hat{C}(\bar{1};\bar{2}\,|\,z)^{-1} \tag{38}$$

A useful relationship between the "renormalized" second correlation function $\hat{\Gamma}(12;\bar{2}\,|\,z)$ and the "renormalized" second cluster function $\hat{R}(12;\bar{2}\,|\,z)$ is easily obtained by substitution of Eq. (11a) into Eqs. (37) and (38), yielding[8]

$$\hat{\Gamma}(12;\bar{2}\,|\,z) = \hat{R}(12;\bar{2}\,|\,z) + \{1 + P_{12}\}n\phi(\pi_1)\,\delta(2-\bar{2}) \tag{39}$$

Utilization of (39) in Eq. (34) yields the nonequilibrium Percus–Yevick analog equation in the form

$$\begin{aligned}
&\left[G_2(12\,|\,z)^{-1}\hat{\Gamma}(12;\bar{1}\,|\,z) - nG_f(12\,|\,z)^{-1}\{1 + P_{12}\}\phi(\pi_1)\,\delta(2-\bar{1})\right]\\
&\quad = \int d3\,\{1 + P_{12}\}L_I(13)\int d\bar{2}\,\hat{\Gamma}(13;\bar{2}\,|\,z)\\
&\qquad \times\left[\hat{\Gamma}(23;\bar{1}\,|\,z) - n\{1 + P_{23}\}\phi(\pi_2)\,\delta(3-\bar{1})\right]
\end{aligned} \tag{40}$$

where we also utilized the identity $G_2(12\,|\,z)^{-1} = G_f(12\,|\,z)^{-1} - L_I(12)$, which follows immediately from the definitions of the Green's functions.

---

[8] Here and elsewhere in this section we have chosen the external field U to vanish since it is no longer necessary. When the external field vanishes, the equilibrium distribution $g(\mathbf{x}_1)$ becomes unity. Nonlinear cluster functions could have been introduced instead of definitions (12) instead of the artifice of the external field, but this would cause other difficulties. (See Section 3.)

Equation (40) is the nonequilibrium analog of the Percus–Yevick equation(44,45)

$$\begin{aligned}&\{\exp[\beta V(|\mathbf{r}_1-\mathbf{r}_2|)]\}\,g(\mathbf{r}_1\mathbf{r}_2)-1\\&\quad=\int d\mathbf{r}_3\,n\{1-\exp[\beta V(|\mathbf{r}_1-\mathbf{r}_3|)]\}\,g(\mathbf{r}_1\mathbf{r}_3)[g(\mathbf{r}_3\mathbf{r}_2)-1]\end{aligned}\tag{41}$$

The nonequilibrium theory consists of both Eq. (40) and Eq. (36), which is little more than the first equation of the BBGKY hierarchy written in the memory function formalism. The set of equations is utilized by first solving Eq. (40) for the "renormalized" second correlation function $\hat{\Gamma}(12;\bar{1}\,|\,z)$, from which one constructs the memory function $\hat{\Gamma}(1;\bar{2}\,|\,z)$ via Eq. (37). One then solves Eq. (36) for the first correlation function $\hat{C}(1;\bar{1}\,|\,z)$ with a known approximate memory function $\hat{\Gamma}(1;\bar{1}\,|\,z)$.

The virial expansion provides a convenient framework for comparison of the various nonequilibrium (and equilibrium) theories.(11,13) Although the virial expansion is not appropriate in the long-time limit for the nonequilibrium case, since the coefficients diverge, one can nonetheless make the comparison between two theories at a finite time, where there is no problem. The virial expansion is also a nice device, since the terms can be represented pictorially as some real dynamical processes. Nonequilibrium theories can thus be classified in terms of the types of nonequilibrium processes they include.

If one assumes that the "renormalized" second correlation function $\hat{\Gamma}(12;\bar{1}\,|\,z)$ has a virial (density) expansion of the form

$$\hat{\Gamma}(12;\bar{1}\,|\,z)=n\left[\hat{\Gamma}_1(12;\bar{1}\,|\,z)+n\hat{\Gamma}_2(12;\bar{1}\,|\,z)+n^2\hat{\Gamma}_3(12;\bar{1}\,|\,z)+\cdots\right]\tag{42}$$

one obtains from the nonequilibrium analog of the Percus–Yevick equation (40) approximations for the $\hat{\Gamma}_\alpha(12;\bar{1}\,|\,z)$. If one assumes that the memory function $\hat{\Gamma}(1;\bar{1}\,|\,z)$ has an expansion similar to (42), one obtains via (37) the following:

$$\hat{\Gamma}_1(1;\bar{1}\,|\,z)=\int d2\,T(12)\{1+P_{12}\}\phi(\pi_1)\,\delta(2-\bar{1})\tag{43a}$$

$$\begin{aligned}\hat{\Gamma}_2(1;\bar{1}\,|\,z)=&\int d2\int d3\,T(12)G_f(12)\{1+P_{12}\}\,T(13)\\&\times\{1+P_{13}\}\phi(\pi_1)G_f(23)T(23)\{1+P_{23}\}\phi(\pi_2)\,\delta(3-\bar{1})\end{aligned}\tag{43b}$$

The above are "ring" dynamical events found in the theories of Dorfman and Cohen,(17) Ernst and Dorfman,(21) Kawasaki and Oppenheim,(30) and others. The third-order term $\hat{\Gamma}_3(1;\bar{1}\,|\,z)$ is written as the sum of three terms

$$\hat{\Gamma}_3(1;\bar{1}\,|\,z)=\hat{\Gamma}_3^{\mathrm{R}}(1;\bar{1}\,|\,z)+\hat{\Gamma}_3^{\mathrm{RR}}(1;\bar{1}\,|\,z)+\hat{\Gamma}_3^{\mathrm{PY}}(1;\bar{1}\,|\,z)\tag{44}$$

The first contribution of (44) is the "ring" contribution $\hat{\Gamma}_3^{\mathrm{R}}(1;\bar{1}\,|\,z)$ given by

$$\begin{aligned}\hat{\Gamma}_3^{\mathrm{R}}(1;\bar{1}\,|\,z) = \int d2 \int d3 \int d4\, & T(12) G_f(12)\{1+P_{12}\} T(13) \\ & \times \{1+P_{13}\}\phi(\pi_1) G_f(23)\{1+P_{23}\} T(24) \\ & \times \{1+P_{24}\}\phi(\pi_2) G_f(34) T(34)\{1+P_{34}\}\phi(\pi_3)\,\delta(4-\bar{1}) \qquad (45\mathrm{a})\end{aligned}$$

and is also found in the Ernst and Dorfman$^{(21)}$ and Kawasaki and Oppenheim$^{(30)}$ theories. Figure 1 is a representation of a typical "ring" dynamical process contained in the third-order term $\hat{\Gamma}_3^{\mathrm{R}}(1;\bar{1}\,|\,z)$. The next contribution to Eq. (44) is the "repeated ring" contribution $\hat{\Gamma}_3^{\mathrm{RR}}(1;\bar{1}\,|\,z)$ defined by

$$\begin{aligned}\hat{\Gamma}_3^{\mathrm{RR}}(1;\bar{1}\,|\,z) = \int d2 \int d3 \int d4\, & T(12) G_f(12)\{1+P_{12}\} T(13) \\ & \times \{1+P_{13}\}\phi(\pi_1) G_f(23) T(23) G_f(23) \\ & \times \{1+P_{23}\} T(24)\{1+P_{24}\}\phi(\pi_2) G_f(34) \\ & \times T(34)\{1+P_{34}\}\phi(\pi_3)\,\delta(4-\bar{1}) \qquad (45\mathrm{b})\end{aligned}$$

A typical "repeated ring" process contained in (45b) is represented in Fig. 2. The Ernst and Dorfman theory$^{(21)}$ contains the simple "ring" and "repeated ring" contributions to all orders in density. The final contribution to (44) is the Percus–Yevick part of the third-order term $\hat{\Gamma}_3^{\mathrm{PY}}(1;\bar{1}\,|\,z)$ and it is given by

$$\begin{aligned}\hat{\Gamma}_3^{\mathrm{PY}}(1;\bar{1}\,|\,z) = \int d2 \int d3 \int d4\, & T(12) G_f(12)\{1+P_{12}\} T(13) \\ & \times G_f(13)\{1+P_{13}\} T(14)\{1+P_{14}\}\phi(\pi_1) \\ & \times G_f(34) T(34)\{1+P_{34}\}\phi(\pi_3) G_f(23) \\ & \times T(23)\{1+P_{23}\}\phi(\pi_2)\,\delta(3-\bar{1}) \qquad (45\mathrm{c})\end{aligned}$$

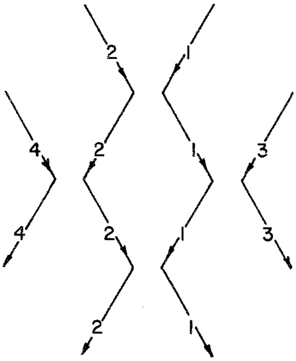

Fig. 1. Typical "ring" dynamical event contained in $\hat{\Gamma}_3^{\mathrm{R}}(1;\bar{1}\,|\,z)$ of Eq. (45a).

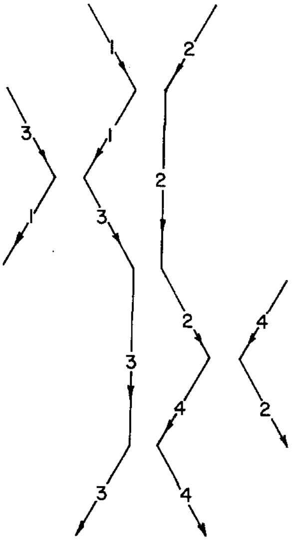

Fig. 2. Typical "repeated ring" dynamical event contained in $\hat{\Gamma}_3^{RR}(1; \bar{1} \mid z)$ of Eq. (45b).

Figure 3 is a representation of a typical "Percus–Yevick" dynamical process of the third order in density. This sort of "ring within ring" process has been examined by de Schepper and Ernst$^{(15)}$ in two dimensions. They found that by selecting and summing these diagrams to all orders in density, one obtains a velocity autocorrelation function which behaves asymptotically in time as $[t(\ln t)^{1/2}]^{-1}$. The velocity autocorrelation function calculated$^{(17)}$ on the basis of selecting and summing the "simple ring" and "repeated ring" terms to all orders in the density has an asymptotic behavior in time of $t^{-d/2}$, where d is the dimensionality of the system, either 2 or 3. The computer molecular dynamics simulations$^{(1,58)}$ yield results which are consistent with both of these predictions to within the "experimental" accuracy. When faster and larger computers become available the simulations will no doubt be done to greater accuracy and for longer times than the current 100 collision times, so that the "true" asymptotic behavior of the velocity autocorrelation can be determined. The Percus–Yevick nonequilibrium analog equation (40) contains both "ring" and "ring within ring" terms in a "closed form" expression, so it should be possible to determine the velocity autocorrelation for all times. We have solved the nonequilibrium analog of the Percus–Yevick equation (40) utilizing an "eigenfunction, perturbation" method and have found an asymptotic behavior of the velocity autocorrelation in the form $t^{-3/2}$ in three dimensions. This will be presented in a future publication, since it is somewhat involved. A kinetic model solution of the Percus–Yevick nonequilibrium analog should give a prediction of how and when the asymp-

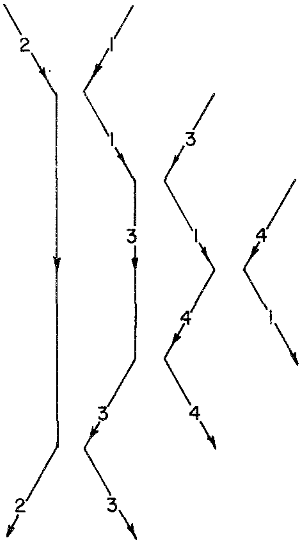

Fig. 3. Typical "ring within ring" dynamical event contained in $\hat{\Gamma}_3^{\mathrm{PY}}(1;\bar{1}\,|\,z)$ of Eq. (45c), the Percus–Yevick contribution of third order in density.

totic behavior for the velocity autocorrelation is obtained in two dimensions as well as for three dimensions.$^{(24,37)}$

Examination of the form of the nonequilibrium Percus–Yevick analog equation (40) provides us with another physical interpretation of the Percus–Yevick approximation in a dynamical (nonequilibrium) context. Notice that one can obtain Eq. (40) from the BBGKY hierarchy equation (21b) by (1) neglecting the third "renormalized" cluster function $\hat{R}^U(123;\bar{1}\,|\,z)$ and by (2) replacing the interaction Liouville operator $L_I(13)$ appearing under the integral by an effective interaction Liouville operator $L_I^{\mathrm{eff}}(12)$ given by

$$\begin{aligned} L_I^{\mathrm{eff}}(13) &= L_I(13)\int d\bar{2}\,\hat{\Gamma}(13;\bar{2}\,|\,z) \\ &= \left\{G_f(13\,|\,z)^{-1} - G_2(13\,|\,z)^{-1}\right\}\int d\bar{2}\,\hat{\Gamma}(13;\bar{2}\,|\,z) \qquad (46) \end{aligned}$$

which is the interaction Liouville operator "weighted" by the "renormalized" second correlation function. Thus the nonequilibrium Percus–Yevick approximation consists of the intuitive picture of two excitations of the fluid interacting via an effective interaction Liouville operator given by (46). The form of $L_I^{\mathrm{eff}}(13)$ is evidentally the result of the collective motion of the remaining particles of the fluid not included in the excitations. This effective interaction Liouville operator is the nonequilibrium generalization of the effective interaction potential energy $V^{\mathrm{eff}}(12)$ of the equilibrium domain. The equilibrium Percus–Yevick approximation for the effective interaction potential energy is essentially the true interaction energy weighted by the two-particle equilibrium distribution function:

$$\begin{aligned} V^{\text{eff}}(|\mathbf{x}_1 - \mathbf{x}_2|) &= \{1 - \exp[\beta V(|\mathbf{x}_1 - \mathbf{x}_2|)]\} g(|\mathbf{x}_1 - \mathbf{x}_2|) \\ &\simeq [-\beta V(|\mathbf{x}_1 - \mathbf{x}_2|)] g(|\mathbf{x}_1 - \mathbf{x}_2|) \end{aligned} \tag{47}$$

where $V^{\text{eff}}(|\mathbf{x}_1 - \mathbf{x}_2|)$ in the first expression is the Percus–Yevick approximation for the direct correlation function. The second approximate expression is valid only for systems of weak interparticle interactions and we have mentioned it here only to help in making a intuitive connection between the equilibrium and nonequilibrium theories.

The Percus–Yevick theory has thus been generalized to the nonequilibrium domain in a form which is relatively simple and therefore useful. The nonequilibrium theory has the several interesting and appealing features described above. We will present the asymptotic calculation of the velocity autocorrelation function in a separate publication. Work is now in process toward including the initial contributions in the second hierarchy equation so that the nonequilibrium Percus–Yevick theory can be applied to fluids of higher density.

REFERENCES

1. B. J. Alder and T. E. Wainwright, *Phys. Rev. Lett.* **18**:988 (1967); *Phys. Rev. A* **1**:18 (1970); B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* **53**:3813 (1970).
2. R. Balescu, *Phys. Fluids* **3**:52 (1960).
3. N. N. Bogoliubov, *Problems of a Dynamical Theory in Statistical Physics* (1946), reprinted in *Studies in Statistical Mechanics*, Vol. 1, J. deBoar and G. E. Uhlenbeck, eds. (Wiley-Interscience, New York, 1962).
4. C. D. Boley, *Phys. Rev. A* **5**:986 (1972); C. D. Boley and R. C. Desai, *Phys. Rev. A* **7**:1700, 2192 (1973).
5. L. Boltzmann, *Sitzungsber Akad. Wiss.* (*Vienna*) **66**:275 (1872); translated in *Kinetic Theory*, Vol. 2, S. G. Brush, ed. (Pergamon, New York, 1966).
6. M. Born and H. Green, *Proc. R. Soc. London Ser. A* **188**:10 (1946); **189**:103 (1947); **191**:168 (1947).
7. R. Brout and P. Carruthers, *Lectures on the Many-Electron Problem* (Wiley-Interscience, New York, 1963), p. 314.
8. S. G. Brush, *Kinetic Theory*, Vols. 1–3 (Pergamon, New York, 1965, 1966, 1972).
9. C. Cercignani, *Mathematical Methods in Kinetic Theory* (Plenum, New York, 1969).
10. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1970).
11. E. G. D. Cohen, *Physica* **28**:1025, 1045, 1060 (1962).
12. P. Debye and E. Hückel, *Phys. Z.* **24**:185 (1923).
13. J. deBoer, *Rep. Prog. Phys.* **12**:305 (1949).
14. I. M. De Schepper and E. G. D. Cohen, *Phys. Lett.* **55A**:385 (1976).
15. I. M. De Schepper and M. H. Ernst, *Physica* **87A**:35 (1977).
16. J. R. Dorfman and E. G. D. Cohen, *Phys. Lett.* **16**:124 (1965); *J. Math. Phys.* **8**:282 (1967).

17. J. R. Dorfman and E. G. D. Cohen, *Phys. Rev. Lett.* **25**:1257 (1970); *Phys. Rev. A* **6**:776 (1972).
18. J. R. Dorfman and E. G. D. Cohen, *Phys. Rev. A* **12**:292 (1975).
19. D. Enskog, *Kungliga Svenska Vetenskapsakademiens Handlingar* (1922); translation in *Kinetic Theory*, Vol. 3, S. G. Brush, ed. (Pergamon, New York, 1972).
20. M. H. Ernst, L. K. Haines, and J. R. Dorfman, *Rev. Mod. Phys.* **41**:296 (1969).
21. M. H. Ernst and J. R. Dorfman, *Physica* **61**:157 (1972).
22. D. Forster and P. C. Martin, *Phys. Rev. A* **2**:1575 (1970); D. Forster, *Phys. Rev. A* **9**:943 (1974).
23. E. A. Frieman and R. Goldman, *Bull. Am. Phys. Soc.* **10**:531 (1965); *J. Math. Phys.* **7**:2153 (1966); **8**:1410 (1967).
24. P. M. Furtado, G. F. Mazenko, and S. Yip, *Phys. Rev. A* **14**:869 (1976).
25. M. Gell-Mann and K. A. Brueckner, *Phys. Rev.* **106**:364 (1957).
26. H. Green, *Molecular Theory of Fluids* (Amsterdam, 1952; Dover, New York, 1969).
27. E. P. Gross, *J. Nucl. Energy, Part C* **2**:73 (1961).
28. E. P. Gross, *Ann. Phys. (NY)* **69**:42 (1972).
29. R. L. Guernsey, The Kinetic Theory of Ionized Gases, Ph.D. thesis, University of Michigan (1960); *Phys. Fluids* **5**:322 (1962); **7**:1600 (1964).
30. K. Kawasaki and I. Oppenheim, *Phys. Rev.* **139**:A1763 (1965).
31. J. Kirkwood, *J. Chem. Phys.* **14**:180 (1946); **15**:72 (1947).
32. J. Kirkwood and Z. Salsburg, *Discuss. Faraday Soc.* **15**:28 (1953).
33. Y. L. Klimontovich, *The Statistical Theory of Non-Equilibrium Processes in a Plasma* (Pergamon, New York, 1967); *Sov. Phys.-JETP* **6**:753 (1958).
34. J. L. Lebowitz, J. K. Percus, and J. Sykes, *Phys. Rev.* **188**:487 (1969).
35. A. Lenard, *Ann. Phys. (NY)* **10**:390 (1960).
36. R. L. Liboff, *Introduction to the Theory of Kinetic Equations* (Wiley, New York, 1969).
37. D. Lieberworth, Velocity Correlations in Moderately Dense Gases, Ph.D. thesis, Rockefeller University, New York (1976); *Phys. Lett.* **58A**:209 (1976).
38. J. Loschmidt, *Wien. Bern.* **73**:139 (1876).
39. W. Macke, *Z. Naturforsch.* **5A**:192 (1950).
40. G. F. Mazenko, *Phys. Rev. A* **7**:209, 222 (1973); **9**:360 (1974).
41. P. C. Martin, E. D. Siggia, and H. A. Rose, *Phys. Rev. A* **8**:423 (1973).
42. H. Mori, *Prog. Theor. Phys.* **33**:423 (1963).
43. L. S. Ornstein and F. Zernike, *Proc. Akad. Sci. (Amsterdam)* **17**:793 (1914); reprinted in *Classical Fluids*, H. L. Frisch and J. L. Lebowitz, eds. (Benjamin, New York, 1964).
44. J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**:1 (1958).
45. J. K. Percus, The Pair Distribution Function in Classical Statistical Mechanics, in *The Equilibrium Theory of Classical Fluids*, H. L. Frisch and J. L. Lebowitz, eds. (Benjamin, New York, 1964).
46. L. A. Pipes and L. R. Harvill, *Applied Mathematics for Engineers and Physicists* (McGraw-Hill, New York, 1970).
47. Y. Pomeau and P. Resibois, *Phys. Lett. (Phys. Rep.)* **19C**:63 (1975).
48. Y. Pomeau, *Phys. Rev. A* **3**:1174 (1971).
49. P. Resibois and J. L. Lebowitz, *J. Stat. Phys.* **12**:483 (1975).
50. H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, eds., *Physics of Simple Liquids* (North-Holland, Amsterdam, 1968).
51. H. D. Ursell, *Proc. Cambridge Philosophical Soc.* **23**:685 (1927).
52. L. van Hove, *Phys. Rev.* **95**:249 (1954).
53. R. L. Varley, *Phys. Lett.* **66A**:41 (1978); Toward a Nonequilibrium Theory of Liquids: A Nonequilibrium Analogue of the Percus–Yevick Equation, Ph.D. thesis, Brandeis University, Waltham, Massacusetts (1976).

54. V. Volterra, *The Theory of Functionals* (Dover, New York, 1959).
55. J. Weinstock, *Phys. Rev.* **140A**:460 (1965).
56. E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, London, 1965).
57. E. Wigner and V. F. Weisskopf, *Z. Phys.* **63**:54 (1930).
58. W. W. Wood, in *Fundamental Problems in Statistical Mechanics III*, E. G. D. Cohen, ed. (North-Holland, Amsterdam, 1977).
59. J. Yvon, *La Theorie Statistique des Fluids et l'Equation d'Etat*, (Hermann, Paris, 1935).
60. E. Zermelo, *Ann. Phys.* (*Leipzig*) **57**:485 (1896); **59**:793 (1896); translated in *Kinetic Theory*, Vol. 2, S. G. Brush, ed. (Pergamon, New York, 1966).
61. R. Zwanzig, *Phys. Rev.* **124**:983 (1961).