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Renormalized Theory of the Time-Dependent Pair Distribution Function. I. General Formulation

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A classical renormalized theory of a time-dependent pair-distribution function (TDPDF), previously introduced by Oppenheim and Bloom, is presented. An equation of motion for the TDPDF is derived in which the memory function of the system appears. This is then split into a part which contains only static correlation functions and a part which describes the dynamics. The mean field approximation is discussed in some detail and contact is made with the theory of Oppenheim and Bloom.

KEY WORDS: Renormalized kinetic theory; correlation functions; time-dependent pair-distribution function.

1. INTRODUCTION AND SUMMARY

In the course of developing their theory of nuclear magnetic relaxation (NMR) in gases and liquids some fifteen years ago, Oppenheim and Bloom$^{(1)}$ found it convenient to introduce the concept of a time-dependent pair-distribution function (TDPDF). For a classical gas, which is the case of present interest, it is defined as the following correlation function:

$$g(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1'\mathbf{r}_2'; t) = \left\langle \sum_{\alpha\neq\beta} \delta[\mathbf{r}_1 - \mathbf{r}_\alpha(0)]\, \delta[\mathbf{r}_2 - \mathbf{r}_\beta(0)]\, \delta[\mathbf{r}_1' - \mathbf{r}_\alpha(t)]\, \delta[\mathbf{r}_2' - \mathbf{r}_\beta(t)] \right\rangle \qquad (1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of two particles of the system and the

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angular brackets symbolize an average over an equilibrium ensemble. Physically, the TDPDF can be interpreted as the probability that the coordinates of the two particles are $\mathbf{r}_1'$ and $\mathbf{r}_2'$ at time t given that their values were $\mathbf{r}_1$ and $\mathbf{r}_2$ at a previous time, e.g., $t = 0$.

In their paper,(1) Oppenheim and Bloom gave an approximate evaluation of (1). Briefly stated, their method is based on an expansion of the dynamics of the system to a constant-acceleration approximation (CAA) coupled with the requirement that the symmetry properties of $g(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1'\mathbf{r}_2'; t)$ be satisfied. The net result of this approximation is the factorization of the TDPDF into a term involving the static pair-distribution function and a term that describes the dynamics of the system as if the particles were free. This fact was also clearly pointed out more recently by Hynes and Deutch,(2) who showed that the CAA is a particular case of the generalized linear trajectory approximation.

In the following years, the theory of Oppenheim and Bloom has been used rather extensively, particularly in the study of NMR problems. A review of this field, with references to earlier work, has been given by Bloom and Oppenheim.(3) The results of such studies showed that the evaluation of the correlation function (1) within the CAA appeared to be accurate enough for the purpose of calculating the nuclear spin relaxation time T_1. However, the usefulness of the TDPDF is not limited to NMR only; it is also the natural quantity in terms of which typical two-particle phenomena—such as collision-induced absorption—are expressed. For this reason Miller *et al.*(4) recently used the CAA in their analysis of collision-induced absorption spectra in a dilute gas and compared the result with both experiment and model calculations. The conclusion they draw from such a comparison is that, insofar as the calculation of line shapes is concerned, the CAA is a poor approximation (particularly at low frequencies) when a realistic potential is used. While this is unfortunate, in view of the considerable simplification introduced by the CAA in the evaluation of the correlation function (1), it is not an unexpected result. In fact, as pointed out by Oppenheim and Bloom in their original article,(1) the CAA is expected to be a good approximation only when the intermolecular potential is slowly varying and head-on collisions are negligible. At the same time, the wide range of phenomena to which a knowledge of the TDPDF is relevant makes it seem desirable to subject this particular correlation function to further study.

It is the purpose of this paper to propose a different theory for a time-dependent correlation function, which is a slight generalization of the TDPDF defined in (1), but which reduces to it in the appropriate limit. More precisely, the following time-dependent correlation function is considered:

$$C(12, 1'2'; t) \equiv \left\langle \sum_{\alpha \neq \beta} \delta[1 - \alpha(0)]\, \delta[2 - \beta(0)]\, \delta[1' - \alpha(t)]\, \delta[2' - \beta(t)] \right\rangle \tag{2}$$

where $1 \equiv (\mathbf{r}_1, \mathbf{p}_1)$ is a "field" point, $\alpha(t) \equiv (\mathbf{r}_1(t), \mathbf{p}_1(t))$ are the phase-space coordinates of particle 1, and similarly for the remaining labels. It is therefore obvious that (2) is just the extension of the TDPDF to phase space; for simplicity this extension shall be given the same name.

The main difference between the present theory and the Oppenheim–Bloom theory is that in the present evaluation of $C(12, 1'2'; t)$ no approximations will be made at the level of the equations of motion of the particles. Rather, an exact equation of motion for the correlation function itself shall be derived, and then approximations to this equation are studied. In so doing, it will be seen that the present theory is renormalized in the sense that the bare interaction no longer appears.

Section 2 introduces the requisite definitions and presents a calculation of certain thermodynamic averages which are relevant to later developments. These averages are static correlation functions whose evaluation is straightforward once the equilibrium ensemble has been specified. In principle, both the canonical and the grand canonical ensembles are suitable for this task. However, because of mathematical difficulties concerning the invertibility of certain static correlation functions in the canonical ensemble,(5) the expressions are couched mainly in terms of the grand canonical ensemble.

In Section 3 an equation of motion for the correlation function (2) is derived. As much of the recent work on modern kinetic theory has shown, successively higher order phase-space correlation functions obey a hierarchy of equations which are analogous to the BBGKY hierarchy(6) of classical kinetic theory. Several methods have been devised to derive closed equations of motion for various correlation functions of interest. There are features common to the various methods, but it would be out of place to comment on them here. Suffice it to say that in this section the method used by Mazenko in his theory of self-diffusion(8) and of the density autocorrelation function(7) will be closely followed. The end result is that the equation of motion for the TDPDF is expressed in terms of the memory function, which in turn can be written as a sum of a static part $\Sigma^{(s)}$ and a collisional part $\Sigma^{(c)}$ [see Eq. (32)]. The latter contains the dynamics of the system and has a rather complicated structure; the former, on the other hand, contains only static correlation functions, which can be evaluated explicitly. As is well known, one of the advantages of introducing the memory function is that it is expected to be a better behaved quantity than the correlation function itself, thus affording a more systematic and secure way of making approximations.

Recognizing the complicated structure of the collisional part of the memory function, an approximation is employed in which $\Sigma^{(c)}$ is neglected while $\Sigma^{(s)}$ is kept intact. The resulting approximate equation for the TDPDF is analyzed in some detail in Section 4. As it turns out, this equation no longer contains the bare potential explicitly, but rather the mean force potential appears, and in this sense the present theory is renormalized. Thus, in this approximation, the pair of correlated particles appear to be free-streaming in the presence of a mean field set up by the remaining particles of the system. This is therefore a description of the behavior of the TDPDF which is, conceptually, at the same level as the Vlasov–Zwanzig equation for the singlet distribution function.(9–10)

In the course of discussing the implications of the approximate equation, contact is also made with the Oppenheim–Bloom theory of the TDPDF. Specifically it is shown that to lowest order in the density expansion the present theory reduces to the *starting point* of the Oppenheim–Bloom method for evaluating the TDPDF. In particular, the free-particle case is trivially seen to give the same (exact) result. Of course, as should be clear from what has already been said, the present method of evaluating the correlation function is radically different from the previous theory and much more general in scope.

Finally, in the last section, a few remarks are made on a plan for attacking the problem of solving the approximate equation in general, by taking advantage of the form of the eigenfunctions of the two-body Liouville operator.(11)

2. DEFINITIONS AND STATIC CORRELATION FUNCTIONS

Consider a system consisting of N classical monatomic particles, with the Hamiltonian

$$H = \sum_{\alpha=1}^{N} \frac{\mathbf{p}_\alpha^{\,2}}{2m} + \frac{1}{2} \sum_{\alpha \neq \beta = 1}^{N} v(\mathbf{r}_\alpha - \mathbf{r}_\beta) \tag{3}$$

where $\mathbf{r}_\alpha$ and $\mathbf{p}_\alpha$ are the phase-space coordinates of the αth particle and $v(\mathbf{r}_\alpha - \mathbf{r}_\beta)$ is the usual pairwise additive central potential. The system is assumed to be in (absolute) equilibrium in a volume V at a temperature $T = (k_B\beta)^{-1}$, where k_B is the Boltzmann constant.

In the present theory of the TDPDF the fundamental field is the phase-space density associated with two tagged particles, say particles 1 and 2, and defined as

$$\Gamma(12) = [N(N-1)]^{1/2}\, \delta(1-1')\, \delta(2-2') \tag{4}$$

where the unprimed labels refer to points in phase space (external variables) and the primed ones to the coordinates of the particles (internal variables).(8) In addition to the fundamental field (4), it will also be necessary to consider the field

$$\Gamma(123) = \Gamma(12) \sum_{\alpha=1}^{N} \delta(3-\alpha') \tag{5}$$

which correlates particles 1 and 2 with a third one. In a similar fashion higher order fields can also be taken into account.

Indicating the equilibrium averages by angular brackets, and with the understanding that $N = \langle N \rangle$ when working in the grand canonical ensemble, the averages of the fields (4) and (5) are

$$\langle \Gamma(12) \rangle = [N(N-1)]^{-1/2} n^2 g(\mathbf{r}_1 - \mathbf{r}_2)\phi(p_1)\phi(p_2) \tag{6}$$

and

$$\langle \Gamma(123) \rangle = [N(N-1)]^{-1/2} n^3 g(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\phi(p_1)\phi(p_2)\phi(p_3) \tag{7}$$

where n is the number density, $\phi(p_i)$ is the absolute Maxwellian

$$\phi(p_i) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left(-\frac{\beta}{2m} p_i^2\right) \tag{8}$$

and the pair and triplet distribution functions are introduced as

$$n^2 g(\mathbf{r}_1 - \mathbf{r}_2) = \left\langle \sum_{\alpha \neq \beta = 1}^{N} \delta(\mathbf{r}_1 - \mathbf{r}_\alpha)(\mathbf{r}_2 - \mathbf{r}_\beta) \right\rangle \tag{9a}$$

and

$$n^3 g(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3) = \left\langle \sum_{\alpha \neq \beta \neq \gamma = 1}^{N} \delta(\mathbf{r}_1 - \mathbf{r}_\alpha)\, \delta(\mathbf{r}_2 - \mathbf{r}_\beta)\, \delta(\mathbf{r}_3 - \mathbf{r}_\gamma) \right\rangle \tag{9b}$$

As is clear from (6) and (7), the equilibrium averages of these fields vanish in the thermodynamic limit, $N \to \infty$, $V \to \infty$, with $n = N/V = \text{const}$. Because of this, such average values can be neglected when considering the correlations between the fields defined above. Thus, working now explicitly in the grand canonical ensemble, the four-point correlation function $C(12, 1'2')$ is given as

$$\begin{aligned} C(12, 1'2') &= \langle \Gamma(1'2')\Gamma(12) \rangle \\ &= \Xi^{-1} \sum_{N=2}^{\infty} \frac{\zeta^N}{h^{3N} N!} \int d\bar{1} \cdots d\bar{N} \{\exp[-\beta H(\bar{1}, \dots, \bar{N})]\} \\ &\quad \times N(N-1)\, \delta(1' - \bar{1})\, \delta(2' - \bar{2})\, \delta(1 - \bar{1})\, \delta(2 - \bar{2}) \end{aligned} \tag{10}$$

where $\Xi(\beta, \zeta, V)$ is the grand canonical partition function, $\zeta = e^{\beta\mu}$ is the fugacity, and $H(1, \dots, N)$ is the Hamiltonian (3). Carrying out the average indicated in (10), we obtain

$$C(12, 1'2') = n^2 g(\mathbf{r}_1 - \mathbf{r}_2)\phi(p_1)\phi(p_2)\, \delta(1 - 1')\, \delta(2 - 2') \tag{11}$$

Higher order static correlation functions can be evaluated in a similar manner. Thus, for example, $C(123, 1'2')$ is given as

$$\begin{aligned} C(123, 1'2') &= \langle \Gamma(1'2')\Gamma(123) \rangle \\ &= n^3 g(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\phi(p_1)\phi(p_2)\phi(p_3)\, \delta(1 - 1')\, \delta(2 - 2') \end{aligned} \tag{12}$$

There is another quantity which will be required in the sequel; this is the inverse of the four-point correlation function (11), i.e., a function C^{-1} such that

$$\begin{aligned}\delta(1-1')\,\delta(2-2') &= \int d3\,d4\,C^{-1}(12,34)C(34,1'2') \\ &= \int d3\,d4\,C(1'2',34)C^{-1}(34,12) \qquad (13)\end{aligned}$$

Recalling the expression (11), it is easy to check that such an inverse is given explicitly by

$$C^{-1}(12,1'2') = \frac{\delta(1-1')\,\delta(2-2')}{n^2 g(\mathbf{r}_1-\mathbf{r}_2)\phi(p_1)\phi(p_2)} \qquad (14)$$

with the restriction that when the potential has a hard core the inverse (14) is defined only for distances $(\mathbf{r}_1-\mathbf{r}_2)$ and $(\mathbf{r}_1'-\mathbf{r}_2')$ greater than the hard-core diameter.

3. TIME-DEPENDENT CORRELATION FUNCTIONS AND EQUATIONS OF MOTION

The TDPDF defined in (2) can be rewritten, in the notation of Section 2, as

$$C(12,1'2';t-t') = \langle\Gamma(1'2',t')\Gamma(12,t)\rangle \qquad (15)$$

It depends only on the time difference because the equilibrium system is assumed to have time-translational invariance. Introducing the Liouville operator L by

$$\begin{aligned}L(1\cdots N) &= \sum_{\alpha=1}^{N} L(\alpha) + \tfrac{1}{2}\sum_{\alpha\neq\beta} L_1(\alpha\beta) \\ iL(\alpha) &= \frac{\mathbf{p}_\alpha}{m}\cdot\frac{\partial}{\partial\mathbf{r}_\alpha} \qquad (16) \\ iL_1(\alpha\beta) &= -\frac{\partial}{\partial\mathbf{r}_\alpha}v(\mathbf{r}_\alpha-\mathbf{r}_\beta)\cdot\left(\frac{\partial}{\partial\mathbf{p}_\alpha}-\frac{\partial}{\partial\mathbf{p}_\beta}\right)\end{aligned}$$

and using Koopman's operator e^{iLt} to express the time-displaced fields in (15), the Laplace transform of the TDPDF,

$$\begin{aligned}&C(12,1'2';z) \\ &\quad = -i\int_0^\infty d(t-t')\{\exp[iz(t-t')]\}C(12,1'2';t-t') \qquad (\operatorname{Im} z>0) \qquad (17)\end{aligned}$$

can be written as

$$C(12, 1'2'; z) = -i\int_0^\infty d(t - t')\,\langle \Gamma(1'2')\{\exp[i(z + L)(t - t')]\}\Gamma(12)\rangle$$
$$= \frac{1}{z}\,C(12, 1'2') - \frac{1}{z}\left\langle \Gamma(1'2')\,\frac{L}{z + L}\,\Gamma(12)\right\rangle \tag{18}$$

Here $C(12, 1'2')$ is the initial value (11) of the TDPDF, with the convention that when time or frequency is not explicitly shown as an argument, the initial value of the correlation function is understood.

Following Mazenko,$^{(7,8)}$ it is possible to show that the effect of the Liouville operator on the field $(12, 1' \cdots N')$ (where the internal variables are now explicitly shown) is to transfer attention from the internal to the external variables, i.e.,

$$L(1' \cdots N')\Gamma(12, 1' \cdots N')$$
$$= -L(12)\Gamma(12, 1' \cdots N') - \int d3\,[L_1(13) + L_1(23)]\Gamma(123, 1' \cdots N') \tag{19}$$

Using this relationship, and introducing a five-point time-dependent correlation function by

$$C(123, 1'2'; z) = \langle \Gamma(1'2')[L/(z + L)]\Gamma(123)\rangle \tag{20}$$

it is easy to rewrite (18) in the form

$$[z - L(12)]C(12, 1'2'; z)$$
$$- \int d3\,[L_1(13) + L_1(23)]C(123, 1'2'; z) = C(12, 1'2') \tag{21}$$

This equation is the first of a hierarchy of exact equations obeyed by each time-dependent correlation function and involving successively higher order ones. Thus, for instance, the derivation leading to (21) can be repeated for $C(12, 1'2'3'; z)$ with the result

$$[z - L(12)]C(12, 1'2'3'; z)$$
$$- \int d3\,[L_1(13) + L_1(23)]C(123, 1'2'3'; z) = C(12, 1'2'3') \tag{22}$$

which involves the six-point correlation function $C(123, 1'2'3'; z)$ and the initial value $C(12, 1'2'3')$. The latter can be evaluated by using the method of Section 2.

In order to ease the notation, an operator format which has already been introduced in the literature$^{(5,7,8)}$ is employed. Briefly stated, it consists in regarding an arbitrary correlation function $C(1 \cdots l, 1' \cdots m'; t)$ as a matrix element $\langle 1 \cdots l | C_{lm}(t) | 1' \cdots m' \rangle$ of an operator acting on a linear vector space. For the present purposes, the vectors of this space are orthonormal in the sense that, e.g.,

$$\langle 1 | 1' \rangle = \delta(1 - 1') \qquad \text{and} \qquad \langle 12 | 1'2' \rangle = \delta(1 - 1')\, \delta(2 - 2') \tag{23}$$

The reason why such a notation is convenient stems from the fact that, in many cases, the only important characteristic of an arbitrary correlation function is the number of particles l and m, which are correlated at two different times.

The l-particle Liouville operator can be handled in an analogous fashion by letting

$$\langle 1 \cdots l | L_{ll} | 1' \cdots l' \rangle = L(1 \cdots l) \langle 1 \cdots l | 1_{ll} | 1' \cdots l' \rangle \tag{24}$$

where 1_{ll} is the appropriate unit operator. Finally, the interaction operators $L_{l,l+1}$ that will be needed here are defined as

$$\langle 1 | L_{12} | 1'2' \rangle = \int d2\, L_1(12) \langle 12 | 1_{22} | 1'2' \rangle \tag{25}$$

and

$$\langle 12 | L_{23} | 1'2'3' \rangle = \int d3\, [L_1(13) + L_1(23)] \langle 123 | 1_{33} | 1'2'3' \rangle \tag{26}$$

With the help of this condensed notation, (21) and (22) can be rewritten as follows:

$$(z - L_{22}) C_{22}(z) - L_{23} C_{32}(z) = C_{22} \tag{27}$$

$$(z - L_{22}) C_{23}(z) - L_{23} C_{33}(z) = C_{23} \tag{28}$$

where again the absence of the argument in a correlation function implies that its static value is understood.

In order to proceed further, (27) is now written as a closed equation for the TDPDF, i.e.,

$$[z - L_{22} - \Sigma_{22}(z)] C_{22}(z) = C_{22} \tag{29}$$

where the memory function $\Sigma_{22}(z)$ has been introduced through the defining relation

$$\Sigma_{22}(z) C_{22}(z) = L_{23} C_{32}(z) \tag{30}$$

As mentioned in Section 1, the advantage of writing the equation of motion for $C_{22}(z)$ in terms of the memory function is that it allows a shift of attention to the latter, which is expected to be a better behaved quantity.

Moreover, by an application of Mazenko's method$^{(8)}$ to the present case it can be shown that these correlation functions have the symmetry properties

$$C_{lm}(z) = -\tilde{C}_{lm}(-z), \qquad C_{lm} = \tilde{C}_{lm} \tag{31}$$

where the tilde denotes the transposed operator. Then, operating on (30) with $(z - L_{22})$ from the right and using (27), (28), and (31), it can be seen that the equation of motion of the TDPDF becomes

$$(z - L_{22})C_{22}(z) - [\Sigma_{22}^{(s)} + \Sigma_{22}^{(c)}(z)]C_{22}(z) = C_{22} \tag{32}$$

where

$$\Sigma_{22}^{(s)} = L_{23}C_{32}C_{22}^{-1} \tag{33}$$

$$\Sigma_{22}^{(c)}(z) = L_{23}[C_{33}(z) - C_{32}(z)C_{22}^{-1}(z)C_{23}(z)]L_{32}C_{22}^{-1} \tag{34}$$

In other words, the memory function can be split into a static (i.e., z-independent) part given by (33), and a collisional part, which describes the dynamics of the system.

Equation (32) is still exact, but a glance at (34) shows that the collisional part of the memory function is rather complicated, since it involves higher order correlation functions. While, in principle, the closure of the hierarchy of equations for the $C_{lm}(z)$ can be done at successively higher order levels, it seems more practical, in a first analysis, to make approximations on the memory function directly in (32). From this point of view, the obvious candidate for a first approximation is the assumption—however crude it might be—that the collisional part of the memory function vanishes. Setting $\Sigma^{(c)} = 0$, we find that Eq. (32) becomes

$$[z - (L_{22} + \Sigma_{22}^{(s)})]C_{22}(z) \simeq C_{22} \tag{35}$$

It is the object of the next section to study this equation in some detail.

4. MEAN FIELD EQUATION FOR THE TDPDF

In order to study the properties of (35) it is convenient to return to the previous notation. This is done by taking matrix elements with $\langle 12|$ and $|1'2'\rangle$ and recalling (23)–(26). The result is that (35) now reads

$$\begin{aligned}[z - L(12)]C(12, 1'2'; z) - \int d3 \cdots d7\, [L_1(13) + L_1(23)] \\ \times C(123, 67)C^{-1}(67, 45)C(45, 1'2'; z) = C(12, 1'2')\end{aligned} \tag{36}$$

As anticipated in Section 1, the combination $(L_{22} + \Sigma_{22}^{(s)})$ can be shown to be independent of the bare potential. There are various methods of showing this, the most straightforward being to work out explicitly each term in (36). This can be done rather easily in the present case, due to the simplicity of the static correlation functions (11)–(14), and hence a few of the intermediate steps are simply outlined. Denoting the second term by $I(12, 1'2'; z)$ and using (11)–(14), the integrations over $d4 \cdots d7$ are easily carried out, with the result

$$I(12, 1'2'; z) = \int d3\,[L_1(13) + L_1(23)]n\phi(p_3)\,\frac{g(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)}{g(\mathbf{r}_1 - \mathbf{r}_2)}\,C(12, 1'2'; z) \tag{37}$$

Recalling the definition (16) for the interaction part of the Liouville operator and using the hierarchy of equations (12) obeyed by $g(\mathbf{r}_1 \cdots \mathbf{r}_l)$, the integration over $d3$ in (37) can also be performed. After some algebra (37) becomes

$$\begin{aligned} I(12, 1'2'; z) = -i\Bigg\{&\left[\frac{1}{\beta}\frac{\partial}{\partial\mathbf{r}_1}\ln g(\mathbf{r}_1 - \mathbf{r}_2) + \frac{\partial}{\partial\mathbf{r}_1}v(\mathbf{r}_1 - \mathbf{r}_2)\right]\cdot\frac{\partial}{\partial\mathbf{p}_1} \\ &- \left[\frac{1}{\beta}\frac{\partial}{\partial\mathbf{r}_1}\ln g(\mathbf{r}_1 - \mathbf{r}_2) + \frac{\partial}{\partial\mathbf{r}_1}v(\mathbf{r}_1 - \mathbf{r}_2)\right]\cdot\frac{\partial}{\partial\mathbf{p}_2}\Bigg\}C(12, 1'2'; z) \end{aligned} \tag{38}$$

On the other hand, the two-particle Liouville operator appearing in the first term of (36) is, by definition,

$$L(12) = -i\left(\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{r}_1} + \frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial\mathbf{r}_2}\right) + i\frac{\partial}{\partial\mathbf{r}_1}v(\mathbf{r}_1 - \mathbf{r}_2)\cdot\left(\frac{\partial}{\partial\mathbf{p}_1} - \frac{\partial}{\partial\mathbf{p}_2}\right) \tag{39}$$

Thus, as a glance at (38) and (39) reveals, the bare potential disappears when the two pieces are combined, and instead, if the mean force potential (12)

$$W^{(2)}(\mathbf{r}_1 - \mathbf{r}_2) = -(1/\beta)\ln g(\mathbf{r}_1 - \mathbf{r}_2) \tag{40}$$

is introduced, (36) can be rewritten in the compact form

$$[z - \tilde{L}(12)]C(12, 1'2'; z) = C(12, 1'2') \tag{41}$$

Here the renormalized two-particle Liouville operator $\tilde{L}(12)$ is defined as

$$i\tilde{L}(12) = \frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{r}_1} + \frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial\mathbf{r}_2} - \frac{\partial}{\partial\mathbf{r}_1}W^{(2)}(\mathbf{r}_1 - \mathbf{r}_2)\cdot\left(\frac{\partial}{\partial\mathbf{p}_1} - \frac{\partial}{\partial\mathbf{p}_2}\right) \tag{42}$$

corresponding to the renormalized two-body Hamiltonian

$$\tilde{H}(12) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + W^{(2)}(\mathbf{r}_1 - \mathbf{r}_2) \tag{43}$$

It is interesting to show how the approximate equation (41) relates to the Oppenheim–Bloom theory. As (41) shows, the TDPDF evolves according to

$$C(12, 1'2'; t) = \{\exp[-it\tilde{L}(12)]\}C(12, 1'2') \tag{44}$$

Using the initial value (11) and noticing that

$$(\beta/2\pi m)^3\exp[-\beta\tilde{H}(12)] = \phi(p_1)\phi(p_2)g(\mathbf{r}_1 - \mathbf{r}_2) \tag{45}$$

we can rewrite (44) in the following form:

$$C(12,1'2';t) = n^2\left(\frac{\beta}{2\pi m}\right)^3\{\exp[-\beta\tilde{H}(12)]\}\{\exp[-it\tilde{L}(12)]\}\,\delta(1-1')\,\delta(2-2')$$

$$= \left(\frac{n}{y}\right)^2\frac{\zeta^2}{h^6}\int d\bar{1}\,d\bar{2}\,\{\exp[-\beta\tilde{H}(\bar{1}\bar{2})]\}\,\delta(1-\bar{1})\,\delta(2-\bar{2})$$

$$\times\{\exp[-it\tilde{L}(\bar{1}\bar{2})]\}\,\delta(\bar{1}-1')\,\delta(\bar{2}-2') \qquad (46)$$

where the activity

$$y = \zeta(2\pi m/\beta h^2)^{3/2} \qquad (47)$$

has been introduced and h is Planck's constant. Since C is time-reversal invariant, integration of both sides over the momentum variables in Eq. (46) gives

$$G(\mathbf{r}_1\mathbf{r}_2,\mathbf{r}_1'\mathbf{r}_2';t) \equiv \int d\mathbf{p}_1\,d\mathbf{p}_2\,d\mathbf{p}_1'\,d\mathbf{p}_2'\,C(12,1'2';t)$$

$$= \left(\frac{n}{y}\right)^2\frac{\zeta^2}{h^6}\int d\bar{1}\,d\bar{2}\,\{\exp[-\beta\tilde{H}(\bar{1}\bar{2})]\}\,\delta(\mathbf{r}_1-\bar{\mathbf{r}}_1)\,\delta(\mathbf{r}_2-\bar{\mathbf{r}}_2)$$

$$\times\{\exp[it\tilde{L}(\bar{1}\bar{2})]\}\,\delta(\mathbf{r}_1'-\mathbf{r}_1)\,\delta(\mathbf{r}_2'-\mathbf{r}_2) \qquad (48)$$

A familiar cluster expansion$^{(13)}$ can now be utilized to derive the low-density expression for G. With $(n/y)^2 \simeq 1$, $n \simeq (2\pi m/\beta h^2)^{3/2}\zeta$, and $W^{(2)}(\mathbf{r}_1-\mathbf{r}_2) \simeq v(\mathbf{r}_1-\mathbf{r}_2)$, Eq. (48) becomes

$$G(\mathbf{r}_1\mathbf{r}_2,\mathbf{r}_1'\mathbf{r}_2';t) = n^2\{\exp[-\beta v(\mathbf{r}_1-\mathbf{r}_2)]\}\int d\bar{\mathbf{p}}_1\,d\bar{\mathbf{p}}_2\,\phi(\bar{p}_1)\phi(\bar{p}_2)$$

$$\times\{\exp[itL(\mathbf{r}_1\mathbf{r}_2,\bar{\mathbf{p}}_1\bar{\mathbf{p}}_2)]\}\,\delta(\mathbf{r}_1'-\mathbf{r}_1)\,\delta(\mathbf{r}_2'-\mathbf{r}_2) \qquad (49)$$

which coincides with Eq. (37) of Oppenheim and Bloom.$^{(1)}$ Therefore the present theory of the TDPDF, as described by Eq. (41), reduces to the *starting* point of the Oppenheim–Bloom theory in the low-density limit.

Finally, it is also easy to check that the free-particle limit is correctly reproduced. In order to see this, notice that when $v(\mathbf{r}_1-\mathbf{r}_2) = 0$, Eq. (41) reduces to

$$\left[z + i\left(\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{r}_1} + \frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial\mathbf{r}_2}\right)\right]C_0(12,1'2';z)$$

$$= n^2\phi(p_1)\phi(p_2)\,\delta(1-1')\,\delta(2-2') \qquad (50)$$

or, in the CM and relative coordinate system,

$$\left[z + i\left(\frac{\mathbf{p}_c}{M}\cdot\frac{\partial}{\partial\mathbf{r}_c} + \frac{\mathbf{p}}{\mu}\cdot\frac{\partial}{\partial\mathbf{r}}\right)\right]C_0(z)$$

$$= n^2\phi_M(p_c)\phi_\mu(p)\,\delta(\mathbf{r}_c'-\mathbf{r}_c)\,\delta(\mathbf{p}_c'-\mathbf{p}_c)\,\delta(\mathbf{r}'-\mathbf{r})\,\delta(\mathbf{p}'-\mathbf{p}) \qquad (51)$$

where $(\mathbf{r}_c, \mathbf{p}_c)$ refers to the center-of-mass motion and $(\mathbf{r}, \mathbf{p})$ refers to the relative coordinates and momentum, defined by the transformation

$$\mathbf{r}_1 = \mathbf{r}_c + \tfrac{1}{2}\mathbf{r}, \qquad \mathbf{p}_1 = \tfrac{1}{2}\mathbf{p}_c + \mathbf{p}$$
$$\mathbf{r}_2 = \mathbf{r}_c - \tfrac{1}{2}\mathbf{r}, \qquad \mathbf{p}_2 = \tfrac{1}{2}\mathbf{p}_c - \mathbf{p}$$

and $\phi_M(p_c)$ and $\phi_\mu(p)$ are the absolute Maxwellians for mass $M = 2m$ and $\mu = m/2$, respectively. Of course, $C_0(z)$ is the free-particle value of $C(z)$.

The solution of Eq. (51) is easily found to be

$$\begin{aligned} C_0(t) &= n^2\phi_M(p_c)\,\delta(\mathbf{p}_c' - \mathbf{p}_c)\,\delta\left[\mathbf{r}_c - \left(\mathbf{r}_c' + \frac{\mathbf{p}_c}{M}t\right)\right] \\ &\quad \times \phi_\mu(p)\,\delta(\mathbf{p}' - \mathbf{p})\,\delta\left[\mathbf{r} - \left(\mathbf{r}' + \frac{\mathbf{p}}{\mu}t\right)\right] \end{aligned} \tag{52}$$

which, after integration over the momentum variables, gives

$$G_0(\mathbf{r}_c' - \mathbf{r}_c, \mathbf{r}' - \mathbf{r}; t) = n^2\left(\frac{M}{|t|}\right)^3 \phi_M\left[\frac{M}{t}(\mathbf{r}_c' - \mathbf{r}_c)\right]\left(\frac{\mu}{|t|}\right)^3 \phi_\mu\left[\frac{\mu}{t}(\mathbf{r}' - \mathbf{r})\right] \tag{53}$$

This result is identical to Eq. (41) of Oppenheim and Bloom.(1)

5. CONCLUDING REMARKS

A classical, renormalized theory has been presented for the TDPDF, which is a quantity of interest in certain problems of nonequilibrium statistical mechanics such as NMR(1,3) and collision-induced absorption.(4) The renormalization of the collisional effects is built into the theory from the beginning by expressing the equation of motion for the TDPDF in terms of the memory function of the system [cf. Eq. (32)]. This is done along the lines of recent work by Mazenko,(7,8) which has proven to be very successful in the analysis of more familiar many-body properties such as the Van Hove correlation function.

Then, as a first approximation, the case in which the collisional part of the memory function is negligible has been considered, resulting in an equation of motion for the TDPDF [Eq. (41)], which is expressed simply in terms of the renormalized two-body Liouville operator. Thus, in this approximation, the free-streaming of the two correlated particles is modified by the presence of the mean field, much in the same fashion as the Zwanzig modification of the Vlasov equation for the singlet distribution function. In the low-density limit contact is also made with the starting point of the Oppenheim–Bloom theory, and the free-particle case is trivially shown to be the same.

The description of the TDPDF afforded by the mean field approximation seems interesting enough to deserve further study, including a more detailed comparison with the CAA approximation and experiment. In particular, the solution of Eq. (41) can be found by taking advantage of the fact that the eigenfunctions of the two-body Liouville operator are known.(11) However, the calculation is far from trivial and rather lengthy. It also involves some mathematical subtleties which appear to be interesting enough to warrant a more detailed analysis than could be presented here. For these reasons such a study will be reported in a separate paper.

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