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Generalized Linear Trajectory Approximations and the Constant Acceleration Approximation*

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The evaluation of correlation functions by means of approximation of the time evolution operator is discussed. It is shown that different approximations may be obtained depending upon the particular factorization of the equilibrium distribution function in the averages to be computed. With the approximation of free particle dynamics, generalized linear trajectory approximations for correlation functions are obtained. The circumvention in the generalized approximation of the separation of the intermolecular potential employed in the linear trajectory approximation introduced by Helfand is discussed. For low density, it is demonstrated that the constant acceleration approximation introduced by Bloom and Oppenheim is exactly equivalent to a generalized linear trajectory approximation. An explicit expression for the deviation of the constant acceleration approximation result from the exact correlation function expression is obtained. The differences between the constant acceleration and generalized linear trajectory approximations at higher densities are discussed.

I. INTRODUCTION

A variety of relaxation and line-shape experiments is currently being interpreted in terms of time correlation functions of the general form

$$C(t)=\langle\rho_{\text{eq}}JJ(t)\rangle$$
$$=\langle\rho_{\text{eq}}J\exp(iLt)J\rangle. \tag{1.1}$$

Here J is a dynamical variable, ρ_{eq} the initial equilibrium distribution function, and L the Liouville time evolution operator of the system. The angular bracket denotes an integration over the positions $\mathbf{R}^N$ and momenta $\mathbf{P}^N$ of the N-particle system.[1] Attention will be restricted here to conditions appropriate to a canonical ensemble so that

$$\rho_{\text{eq}}=[\langle\exp(-\beta H)\rangle]^{-1}\exp(-\beta H), \tag{1.2}$$

where H is the Hamiltonian of the system and $\beta=(kT)^{-1}$.

For most fluid systems the evaluation of $C(t)$ is not possible and one must resort to approximations. In one class of these approximations the Liouville operator is separated into two parts,

$$L=L_0+L', \tag{1.3}$$

and the evolution operator is decomposed according to the operator identity

$$\exp(iLt)=\exp(iL_0t)+\int_0^t ds\exp[iL_0(t-s)]iL'\exp(iLs). \tag{1.4}$$

The correlation function $C(t)$ is approximated by

$$C_0(t)=\langle\rho_{\text{eq}}J\exp(iL_0t)J\rangle \tag{1.5}$$

and the remainder term

$$C_R(t)=\int_0^t ds\langle\rho_{\text{eq}}J\exp[iL_0(t-s)]iL'\exp[iLs]J\rangle \tag{1.6}$$

is neglected in the hope that it is a small correction to $C_0(t)$. Under favorable circumstances, according to the separation of L, the approximate correlation function $C_0(t)$ can be explicitly evaluated and be considered an adequate estimate for $C(t)$.

The purpose of this paper is threefold. First it will be shown that the approximation procedure just described is a special case of a more general approximation scheme. This general scheme does not depend on any particular choice of separation of L into L_0 and L'. Second, a particular separation of L that has been referred to in the literature as the linear trajectory approximation[2–5] (LTA) is examined. In this approximation, introduced by Helfand,[2] L_0 is taken to include only the free streaming motion of the particles,

$$iL_0=\sum_{i=1}^N\frac{\mathbf{P}_i}{m}\cdot\nabla_{\mathbf{R}_i}, \tag{1.7}$$

while the interaction Liouville operator is

$$iL'=-\sum_{i=1}^N\nabla_{\mathbf{R}_i}U\cdot\nabla_{\mathbf{P}_i}, \tag{1.8}$$

where $U(\mathbf{R}^N)$ is the intermolecular potential. The general scheme we consider suggests a wider range of generalized linear trajectory approximations (GLTA).

We direct our main discussion to the relationship of the generalized linear trajectory approximation to the "constant acceleration approximation" introduced by Bloom and Oppenheim[6–8] to evaluate certain correlation functions arising in nuclear magnetic relaxation. Bloom and Oppenheim applied the CAA approximation in two steps. First, in the equations of motion for the particles it is assumed that the initial force on each particle does not change with time. Second, in the course of their calculation a symmetrization is introduced (consistent with the assumption of constant acceleration) between the positions of the particles at time t and at the initial time. Because the CAA approximation of Bloom and Oppenheim involves both a short time expansion and symmetrization, it has proven difficult to identify and evaluate the correction terms to the CAA. *We demonstrate that for low density the CAA is exactly equivalent to a generalized linear trajectory approximation and explicitly identify the terms excluded from the exact expression by the CAA*. An assessment of the CAA is of some importance. The CAA has proved useful in interpreting experimental nuclear magnetic relaxation measurements in gases[9,10] and may be employed to interpret other relaxation measurements such as microwave line broadening. For higher densities there is a difference between the CAA and the GLTA (generalized linear trajectory approximations); the sources of this discrepancy are discussed.

II. THE GENERAL APPROXIMATION SCHEME

The equilibrium distribution function ρ_{eq} is an eigenfunction of the exact Liouville operator with eigenvalue zero. Due to this fact and the special form of the canonical distribution function Eq. (1.2), the correlation function $C(t)$ may be exactly expressed as

$$C(t)=<\rho_{eq}{}^{(1-j)}J\exp(iLt)J\rho_{eq}{}^{(j)}\rangle, \qquad (2.1)$$

where j is some number between zero and one. If the Liouville operator is now separated according to Eq. (1.3) and use is made of the operator identity Eq. (1.4), one finds

$$C(t)=C_0{}^{(j)}(t)+C_R{}^{(j)}(t), \qquad (2.2)$$

where

$$C_0{}^{(j)}(t)=\langle\rho_{eq}{}^{(1-j)}J\exp(iL_0t)J\rho_{eq}{}^{(j)}\rangle \qquad (2.3)$$

and

$$C_R{}^{(j)}(t)=\int_0^t ds$$
$$\times\langle\rho_{eq}{}^{(1-j)}J\exp[iL_0(t-s)]iL'\exp[iLs]J\rho_{eq}{}^{(j)}\rangle. \qquad (2.4)$$

The important point to note is that since ρ_{eq} is not necessarily an eigenfunction of the approximate Liouville operator L_0, every different choice of j will result in a different correlation function $C_0{}^{(j)}(t)$, when $iL_0\rho_{eq}\neq 0$. Hence, if $C(t)$ is approximated by $C_0{}^{(j)}(t)$, each choice of j will yield a different result. In the past the approximation procedure adopted has always corresponded to the choice of j equal to zero, according to Eq. (1.5) (cf. Sec. III). Here a much wider range of generalized approximations is suggested according to Eq. (2.3).

In Eq. (2.1) only one type of separation of ρ_{eq} is presented. Clearly more general separations are also possible. For simplicity, attention will be restricted to the special choice $j=\frac{1}{2}$ that results in a symmetric form for $C_0{}^{(j)}(t)$. Criteria for the choice of j that results in the "best" approximation of $C(t)$ by $C_0{}^{(j)}(t)$ will not be examined here.

We also limit the present discussion to the Liouville operator decomposition Eqs. (1.7) and (1.8) so that dynamics are approximated by free particle motion. With this choice, restrictions must be imposed upon the form of J. In particular, J must vanish for large interparticle distances in order for $C_0(t)$ and/or its time integral to exist.

III. LINEAR TRAJECTORY APPROXIMATION

In this section, we discuss the relationship between the GLTA and the LTA, which has been employed in recent years in the approximation of correlation functions. This approximation has recently been extended to general hydrodynamic transport coefficients.[4] As an example, we consider the force correlation function

$$A(t)=\langle\rho_{eq}\mathbf{F}_1\cdot\mathbf{F}_1(t)\rangle$$
$$=\langle\rho_{eq}{}^{1/2}\mathbf{F}_1\cdot[\exp(iLt)\mathbf{F}_1\rho_{eq}{}^{1/2}]\rangle, \qquad (3.1)$$

where $\mathbf{F}_1$ is the total force on a particle in a fluid,[2-5]

$$\mathbf{F}_1=\sum_{i=2}^{N}\mathbf{F}_{1i}.$$

The analysis of $A(t)$ proceeds by a division of the force into hard and soft terms $\mathbf{F}_1{}^H$ and $\mathbf{F}_1{}^S$, corresponding to the same division of the intermolecular potential. With neglect of cross correlations,[2-5] $A(t)$ may be written as

$$A(t)=\langle\rho_{eq}\mathbf{F}_1{}^H\cdot\mathbf{F}_1{}^H(t)\rangle+\langle\rho_{eq}\mathbf{F}_1{}^S\cdot\mathbf{F}_1{}^S(t)\rangle$$
$$=A_H(t)+A_S(t). \qquad (3.2)$$

Hard-sphere mechanics is used to compute $A_H(t)$ (see, however, Ref. 4). The LTA enters the analysis by the retention in the soft-force correlation $A_S(t)$ of only the contribution of the free particle dynamics [cf. Eqs. (1.4) and (1.7)]. Thus, in the LTA, $A_S(t)$ takes the form Eq. (2.3) with $j=0$:

$$A_S(t)=\langle\rho_{eq}\mathbf{F}_1{}^S\cdot[\exp(iL_0t)\mathbf{F}_1{}^S]\rangle. \qquad (3.3)$$

Detailed discussion of the potential division and the LTA may be found in Refs. 2–5.

In the GLTA, *no* separation of forces is made and $A(t)$ is approximated as in Eqs. (2.2) and (1.7) for $j=\frac{1}{2}$ as

$$A_0(t)=\langle\rho_{eq}{}^{1/2}\mathbf{F}_1\cdot[\exp(iL_0t)\mathbf{F}_1\rho_{eq}{}^{1/2}]\rangle. \qquad (3.4)$$

From Eqs. (3.4), (3.1), and (2.1), it is evident that in the GLTA, the full evolution operator is replaced by the free particle operator when acting upon the combination $(\mathbf{F}_1\rho_{eq}{}^{1/2})$. This feature partially mitigates the apparent severity of the approximation of free particle dynamics. Along the true configuration space trajectories $\mathbf{R}^N(t)$, the force $\mathbf{F}_{1i}$ vanishes for large separations $|\mathbf{R}_{1i}(t)|$ and $\rho_{eq}{}^{1/2}$ vanishes for $|\mathbf{R}_{1i}(t)|$ on the order of and less than the repulsive core of the potential. Along the approximate free particle linear trajectories, $(\mathbf{F}_{1i}\rho_{\mathrm{eq}}^{1/2})$ exhibits behavior of the same nature. In particular, in the region of overlap of the hard cores, $\{\exp(iL_0t)[\mathbf{F}_{1i}\rho_{\mathrm{eq}}^{1/2}]\}$ vanishes. This behavior is guaranteed in the LTA by the prior division into hard and soft forces.[11]

In the present article, we focus on the consequences of the GLTA in low-density systems, where the results may be compared with the predictions of the CAA.

IV. CONSTANT ACCELERATION APPROXIMATION

Bloom and Oppenheim[6] have introduced the CAA in the evaluation of time integrals of certain intermolecular correlation functions $S(t)$ of the form Eq. (1.1) with $J=|\mathbf{R}_{12}|^{-n}Y_{lm}(\Omega_{12})$. Here $Y_{lm}(\Omega_{12})$ denotes a spherical harmonic of the solid angle Ω_{12} of the intermolecular vector $\mathbf{R}_{12}$ with a lab-fixed axis. A detailed account of the utilization of this approximation in nuclear magnetic relaxation theory may be found in Refs. 6–10.

The analysis of these authors proceeds in terms of the time-dependent pair distribution function (TDPDF)

$$\begin{aligned} h(\mathbf{R}^2, \mathbf{R}'^2, t) &= N(N-1)\int d\mathbf{P}^N d\mathbf{R}^n \rho_{\mathrm{eq}}(\mathbf{R}^N, \mathbf{P}^N) \\ &\qquad \times \exp(iLt)\delta(\mathbf{R}'^2-\mathbf{R}^2) \\ &= N(N-1)\int d\mathbf{P}^N d\mathbf{R}^n d\mathbf{R}'^n \rho_{\mathrm{eq}}^{1/2}(\mathbf{R}^N, \mathbf{P}^N) \\ &\qquad \times \exp(iLt)\delta(\mathbf{R}'^N-\mathbf{R}^N)\rho_{\mathrm{eq}}^{1/2}(\mathbf{R}'^N, \mathbf{P}^N), \end{aligned} \tag{4.1}$$

where $n=N-2$. $S(t)$ may be written in terms of the TDPDF as

$$\begin{aligned} S(t) &= (N-1)\langle[\rho_{\mathrm{eq}}^{1/2}J(\mathbf{R}_{12})]\exp(iLt)[\rho_{\mathrm{eq}}^{1/2}J(\mathbf{R}_{12})]\rangle \\ &= N^{-1}\int d\mathbf{R}^2 d\mathbf{R}'^2 J(\mathbf{R}^2)J(\mathbf{R}'^2)h(\mathbf{R}^2, \mathbf{R}'^2, t). \end{aligned} \tag{4.2}$$

By an analysis of first form of Eq. (4.1), Bloom and Oppenheim[6] have shown that according to the CAA, the TDPDF in the low-density limit is

$$h_C^{(0)}(\mathbf{R}^2, \mathbf{R}'^2, t) = \rho^2[g_0(\mathbf{R}^2)g_0(\mathbf{R}'^2)]^{1/2}\gamma_1(t)\gamma_2(t), \tag{4.3}$$

where $g_0(\mathbf{R}^2)=\exp[-\beta U(R_{12})]$ is the low-density equilibrium pair distribution function (PDF). The time dependence of the TDPDF enters via the factors

$$\begin{aligned} \gamma_j(\mathbf{R}_j'-\mathbf{R}_j, t) &= \gamma_j(t) \\ &= (m\beta/2\pi t^2)^{3/2} \\ &\qquad \times \exp[-(m\beta/2t^2)(\mathbf{R}_j'-\mathbf{R}_j)^2]. \end{aligned} \tag{4.4}$$

We first direct attention to the evaluation of Eq. (4.1) for $h(t)$ in the GLTA for low-density systems and demonstrate the equivalence of this result to Eq. (4.3). For simplicity, we here pass to the low-density limit of Eq. (4.1) prior to employing the GLTA. The direct low-density expansion of the GLTA form of Eq. (4.1) is presented in the Appendix.

In the low-density limit, the exact TDPDF involves only the dynamics and statistics of two particles and may be obtained by a straightforward application of standard cluster expansion techniques[12] as

$$\begin{aligned} h^{(0)}(t) &= \rho^2\int d\mathbf{P}^2[\phi(\mathbf{P}^2)g_0(\mathbf{R}^2)] \\ &\qquad \times \exp[iL_2(\mathbf{R}^2, \mathbf{P}^2)t]\delta(\mathbf{R}'^2-\mathbf{R}^2). \end{aligned} \tag{4.5}$$

In Eq. (4.5), $\phi(\mathbf{P}^2)$ is the product of normalized Maxwellian distributions of particles 1 and 2 and L_2 is the full Liouville operator for the two-particle system. As the bracketed term in Eq. (4.5) is a function only of $H_2(\mathbf{R}^2, \mathbf{P}^2)$, the Hamiltonian of the two-particle system, and $iL_2H_2=0$, Eq. (4.5) may be rewritten exactly as

$$\begin{aligned} h^{(0)}(t) &= \rho^2\int d\mathbf{P}^2[\phi(\mathbf{P}^2)g_0(\mathbf{R}^2)]^{1/2}\exp[iL_2(\mathbf{R}^2, \mathbf{P}^2)t] \\ &\qquad \times \delta(\mathbf{R}'^2-\mathbf{R}^2)[\phi(\mathbf{P}^2)g_0(\mathbf{R}'^2)]^{1/2}. \end{aligned} \tag{4.6}$$

The corresponding low-density correlation function is thus

$$\begin{aligned} S^{(0)}(t) &= (N-1)\int d\mathbf{R}^2 d\mathbf{P}^2[\phi(\mathbf{P}^2)g_0(\mathbf{R}^2)]^{1/2}J(\mathbf{R}^2) \\ &\qquad \times \exp[iL_2t][\phi(\mathbf{P}^2)g_0(\mathbf{R}'^2)]^{1/2}J(\mathbf{R}'^2)\delta(\mathbf{R}^{1/2}-\mathbf{R}^2) \\ &= N^{-1}\int d\mathbf{R}^2 d\mathbf{R}'^2 J(\mathbf{R}^2)J(\mathbf{R}'^2)h^{(0)}(\mathbf{R}^2, \mathbf{R}'^2, t). \end{aligned} \tag{4.7}$$

If we now apply the separation Eqs. (1.4), (1.7), and (1.8) to Eq. (4.6), we obtain in the GLTA

$$\begin{aligned} h_0^{(0)}(t) &= \rho^2\int d\mathbf{P}^2\phi(\mathbf{P}^2)[g_0(\mathbf{R}^2)g_0(\mathbf{R}'^2)]^{1/2} \\ &\qquad \times \exp[iL_0(\mathbf{R}^2, \mathbf{P}^2)t]\delta(\mathbf{R}'^2-\mathbf{R}^2)\delta(\mathbf{R}'^2-\mathbf{R}^2) \\ &= \rho^2[g_0(\mathbf{R}^2)g_0(\mathbf{R}'^2)]^{1/2}\gamma_1(t)\gamma_2(t), \end{aligned} \tag{4.8}$$

where we have used the identity

$$\int d\mathbf{P}_j\phi(\mathbf{P}_j)\exp[(\mathbf{P}_j/m)\cdot\nabla_{R_j}t]\delta(\mathbf{R}_j'-\mathbf{R}_j) = \gamma_j(t). \tag{4.9}$$

Equation (4.8) is identical to the CAA result Eq. (4.3).

As previously noted, Bloom and Oppenheim[6] introduced the CAA in two steps: (1) approximation of dynamics by the assumption of forces constant in time and (2) subsequent symmetrization in $\mathbf{R}^2$ and $\mathbf{R}'^2$ (consistent with the CAA) to satisfy symmetry requirements evident in the second line of Eq. (4.7). The *net* result of these procedures is free particle dynamics (momenta constant in time) with modified equilibrium DF's. In the GLTA as applied in Eqs. (4.8) and (4.7), symmetry requirements are automatically satisfied and the assumption of linear trajectories explicitly revealed.

One may easily show that, at low density, the identity between the CAA and GLTA is maintained for time-dependent DF's for any number of particles.

The remainder term, which is due solely to the deviation from free particle dynamics in $h^{(0)}(t)$, is given by

$$h_R^{(0)}(t)=\rho^2\int_0^t ds\int d\mathbf{P}^2[\phi(\mathbf{P}^2)g_0(\mathbf{R}^2)]^{1/2}$$
$$\times\exp\{iL_0(\mathbf{R}^2,\mathbf{P}^2)[t-s]\}\times iL'(\mathbf{R}^2,\mathbf{P}^2)$$
$$\times\exp\{iL_2(\mathbf{R}^2,\mathbf{P}^2)s\}\delta(\mathbf{R}'^2-\mathbf{R}^2)[\phi(\mathbf{P}^2)g_0(\mathbf{R}'^2)]^{1/2},\tag{4.10}$$

where L' is the interaction part of the two-particle Liouville operator. Bloom and Oppenheim[6] have employed the result Eq. (4.8) in Eq. (4.7) to obtain the CAA value of the time integral

$$\hat{S}^{(0)}\equiv\int_0^\infty dtS^{(0)}(t).$$

We may now obtain an explicit expression for the difference, $\hat{S}_R^{(0)}$, between the exact and CAA results for $\hat{S}^{(0)}$. By substitution of Eq. (4.10) into Eq. (4.7), one may show by standard methods[12] that

$$\hat{S}_R^{(0)}=-\rho\lim_{\epsilon\to 0}\{\int d\mathbf{P}^2\phi^{1/2}(\mathbf{P}^2)\langle 0\,|\,[J(\mathbf{R}^2)g_0^{1/2}(\mathbf{R}^2)]$$
$$\times G_0VT_{12}G_0[J(\mathbf{R}^2)g_0^{1/2}(\mathbf{R}^2)]\,|\,0\rangle\phi^{1/2}(\mathbf{P}^2)\}.\tag{4.11}$$

The binary collision operator T_{12} is defined in terms of the Laplace transforms $G_0(\epsilon)$ and $G_2(\epsilon)$ of $\exp(iL_0t)$ and $\exp(iL_2t)$, respectively, as

$$G_2=G_0-G_0T_{12}G_0.\tag{4.12}$$

The angular closed brackets in Eq. (4.11) denote a spatial average over $\mathbf{R}^2$.

The preceding GLTA analysis may be extended to the case where J depends on momentum *in addition* to relative position. This important case has been considered in the CAA by Oppenheim, Bloom, and Torrey[9] in connection with nuclear relaxation in ^{129}Xe gas. One then obtains the CAA result of these authors and the correction to this approximation.

Next we discuss the difference between the GLTA and the CAA for $h(t)$ at arbitrary density. Similar considerations apply to time-dependent DF's that involve more than two particles. The GLTA expression for $h(t)$ is from Eqs. (4.1) and (1.4)

$$h_0(t)=Z_N^{-1}[N(N-1)]\int d\mathbf{P}^Nd\mathbf{R}^n\phi(\mathbf{P}^N)$$
$$\times\exp[-\tfrac{1}{2}\beta U(\mathbf{R}^2,\mathbf{R}^n)]$$
$$\times\{\exp(iL_0t)\exp[-\tfrac{1}{2}\beta U(\mathbf{R}'^2,\mathbf{R}^n)]\delta(\mathbf{R}'^2-\mathbf{R}^2)\},\tag{4.13}$$

where $Z_N=\int d\mathbf{R}^N\exp(-\beta U)$. In order to obtain the CAA result, we neglect the dynamics of particles $3\cdots N$, so that

$$h_0(t)\cong Z_N^{-1}[N(N-1)]\gamma_1(t)\gamma_2(t)$$
$$\times\int d\mathbf{R}^n\exp\{-\tfrac{1}{2}\beta[U(\mathbf{R}^2,\mathbf{R}^n)+U(\mathbf{R}'^2,\mathbf{R}^n)]\},\tag{4.14}$$

where we have used Eq. (4.9). With neglect of terms of order of the square of the force (an assumption explicitly made in the CAA), we obtain

$$h_0(t)\cong Z_N^{-1}[N(N-1)]\gamma_1(t)\gamma_2(t)$$
$$\times\int d\mathbf{R}^n\exp\{-\beta[U(\mathbf{R}^N)+\tfrac{1}{2}(\mathbf{R}_1'-\mathbf{R}_1)\cdot\boldsymbol{\nabla}_{\mathbf{R}_1}U(\mathbf{R}^N)$$
$$+\tfrac{1}{2}(\mathbf{R}'_2-\mathbf{R}_2)\cdot\boldsymbol{\nabla}_{\mathbf{R}_2}U(\mathbf{R}^N)]\}.\tag{4.15}$$

Equation (4.15) has been shown[7] to reduce to the general CAA result for arbitrary density,

$$h_C(t)=\rho^2\gamma_1(t)\gamma_2(t)[g(\mathbf{R}^2)g(\mathbf{R}'^2)]^{1/2},\tag{4.16}$$

with neglect of terms of order of the square of the force.

From this discussion, it is clear that at higher densities the GLTA and the CAA will differ. The explicit difference between the GLTA and the CAA to first order in the density, $h_0^{(1)}$ and $h_C^{(1)}$, respectively, is given in the Appendix. There are two important differences at higher density. First, the CAA neglects the dynamics of all but two particles while the GLTA includes linear trajectories for all particles. Second, the CAA requires the neglect of gradients and powers of the forces.

APPENDIX

Here we obtain the first density correction to the low density form of the TDPDF Eq. (4.8) in the GLTA. The expression for $h(t)$, Eq. (4.1), is not conveniently analyzed in terms of standard low-density expansion methods[12,13] as the usual equilibrium reduced distribution functions do not naturally enter the analysis. Here we sketch an alternate derivation which is based upon van Kampen's product expansion of equilibrium distribution functions and partition functions.[14]

With the identity Eq. (4.9), the momentum integrations in Eq. (4.1) may be performed. The terms involving only particles one and two are then extracted from the remaining space integrals to obtain

$$h_0(t)=\gamma_1(t)\gamma_2(t)[g_0(\mathbf{R}^2)g_0(\mathbf{R}'^2)]\psi_{12}(t).\tag{A1}$$

The quantity $\psi_{12}(t)$ is $(N-2\equiv n)$

$$\psi_{12}(t)=\rho^2[V^2Z_n(\beta)/Z_N(\beta)]\{\int d\mathbf{R}^nd\mathbf{R}'^nP(\mathbf{R}^n,\mathbf{R}'^n)$$
$$\times\prod_{j\geq 3}^{N}\gamma_j(t)[g_0(R_{1j})g_0(R_{2j})g_0(R_{1j}')g_0(R_{2j}')]^{1/2}\}$$
$$\equiv\rho^2[V^2Z_n(\beta)/Z_N(\beta)]\Pi(t),\tag{A2}$$

where

$$P(\mathbf{R}^n,\mathbf{R}'^n)=Z_n^{-1}(\beta)\exp\{-\tfrac{1}{2}\beta[U(\mathbf{R}^n)+U(\mathbf{R}'^n)]\}\tag{A3}$$

is a "symmetrized" distribution function for n particles. Here $Z_n(\beta)$ and $U(\mathbf{R}^n)$ are the configuration integral and potential energy of the n-particle system $3\cdots N$.

Each of the two bracketed terms in Eq. (A2) is a function of ρ. In order to obtain the lowest-order (ρ^2) result, we replace all configuration integrals by their zero-density value $Z_n=V^n$ and in the space integrations neglect all interactions of the n particles. Writing

$$\psi_{12}(t)=\rho^2[\psi_{12}^{(0)}(t)+\rho\psi_{12}^{(1)}(t)+\cdots], \tag{A4}$$

we then obtain $\psi_{12}^{(0)}(t)=1$ so that with Eq. (A1) we recover the low-density CAA result Eq. (4.8).

In order to compute the first density correction $\psi_{12}^{(1)}(t)$, we require each of the two bracketed terms in Eq. (A2) correct to first order in ρ. This result for the ratio $[V^2Z_n/Z_N]$ has been obtained by van Kampen.[14] To obtain the space integral term $\Pi(t)$ correct to order ρ, we note that neglect of the effects of the interaction among the n particles in $P(\mathbf{R}^n, \mathbf{R}'^n)$ reduces $\Pi(t)$ to a spatial average of the n-fold product in Eq. (A2). This average may be expressed as the product of n equivalent factors,

$$\Pi^{(1)}(t)=\{V^{-1}\int d\mathbf{R}_3 d\mathbf{R}_3'\gamma_3(t) \times[g_0(R_{13})g_0(R_{23})g_0(R_{13}')g_0(R_{23}')]^{1/2}\}^n, \tag{A5}$$

which includes only the effects of a typical third particle. As inclusion of the n-particle mutual interaction in $P(\mathbf{R}^n, \mathbf{R}'^n)$ introduces at least four-particle contributions (and thus higher-order ρ corrections) to $\Pi(t)$, Eq. (A5) will yield $\Pi(t)$ correct to $O(\rho)$.

$\Pi^{(1)}(t)$ may be evaluated by an application of van Kampen's method,[14] and with the aid of van Kampen's result[14] for $[V^2Z_n/Z_N]$ correct to $O(\rho)$ and Eq. (A2), the density correction $\psi_{12}^{(1)}(t)$ may be obtained by straightforward calculation. $\psi_{12}^{(1)}(t)$ may then be employed in Eq. (A1) to obtain the TDPDF in the GLTA, correct to $O(\rho^3)$, $h_0^{(1)}(t)$, as

$$h_0^{(1)}(t)=\rho^2[g_1(\mathbf{R}^2)g_1(\mathbf{R}'^2)]^{1/2}\gamma_1(t)\gamma_2(t) +\rho^3[g_0(\mathbf{R}^2)g_0(\mathbf{R}'^2)]^{1/2}\gamma_1(t)\gamma_2(t)[A_1+A_2(t)]. \tag{A6}$$

The first term in Eq. (A6) is the CAA result[6] which includes the equilibrium PDF's correct to $O(\rho)$. The remaining terms in Eq. (A6) are

$$A_1=\tfrac{1}{2}\int d\mathbf{R}_3[G(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)-G(\mathbf{R}_1', \mathbf{R}_2', \mathbf{R}_3)]^2, \tag{A7}$$

which is the deviation from the CAA equilibrium PDF dependence in Eq. (A6) and

$$A_2(t)=-\frac{\beta}{4m}\int_0^t dss\int d\mathbf{R}_3 d\mathbf{P}_3\phi(\mathbf{P}_3)G(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \times\mathbf{F}_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)\cdot\left[\exp\left(\frac{\mathbf{P}_3}{m}\cdot\nabla_{\mathbf{R}_3}s\right) \times G(\mathbf{R}_1', \mathbf{R}_2', \mathbf{R}_3)\mathbf{F}_3(\mathbf{R}_1', \mathbf{R}_2', \mathbf{R}_3)\right], \tag{A8}$$

which includes the effect of free particle motion of a third particle. In Eqs. (A7) and (A8),

$$G(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)=[g_0(R_{13})g_0(R_{23})]^{1/2}, \tag{A9}$$

and $\mathbf{F}_3$ is the force exerted on particle 3 by particles 1 and 2. The terms (A7) and (A8), when employed in Eqs. (A6) and (4.2), are formally of the order of the square of the forces and thus discarded in the CAA.

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[1] Classical systems are discussed here explicitly. The major points apply to quantum systems as well with appropriate modification of notation.

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