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Dynamical structure factor of dense gases

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The space-time memory function associated with the dynamical structure factor is expressed in terms of current-current and density-current correlation functions. We then apply the binary-collision expansion to evaluate these correlation functions. In this approximation, we include exactly all the effects of a single collision between a pair of particles. The dynamical structure factor is then evaluated from the memory function and compared with the neutron scattering data on dense krypton gas. The agreement is very good even for wave numbers below the first diffraction peak in the structure factor, indicating that the spatial correlations are included in this theory.

I. INTRODUCTION

It is well known that the dynamical properties and the transport properties of a physical system are embodied in time correlation functions (TCF). The theoretical problem of studying these functions is basically that of describing the dynamical properties of a many-body system. The time evolution of the TCF can be expressed in terms of a space-time memory function[1] and thus the problem reduces to the calculation of an appropriate memory function. The memory function has in it all the contributions to the dynamics of a many-body system—free streaming, uncorrelated and correlated binary collisions, and higher-order collisions.

In previous papers,[2] we have applied the technique of binary-collision expansion (BCE)[3] to evaluate the space-time memory function and from that the time-correlation function of interest. In this approximation, we consider exactly all the effects of a single collision between a pair of particles. Since the BCE is applied to the memory function, this should lead to an improved approximation relative to the direct expansion of the correlation function. In other words, higher-order terms in density do appear in TCF (with not exactly the correct coefficients), even though the memory function is expanded only to first order in the density. It should also be noted that the full two-particle static correlations are included in this theory through the use of the exact pair-distribution function. An added feature of this formalism is that it is an explicitly *ab initio* calculation and is valid for any intermolecular potential. The only inputs required are the pair-distribution function and the intermolecular potential. Of course the results of this simple model will show increased deviation from experimental results for longer times especially as the density approaches liquid density wherein the effects of correlated binary collisions and higher-order collisions cannot be neglected.

In this paper, we use this technique to evaluate the density correlation function, $S(q,\omega)$, and compare our results with the experimental neutron scattering data.[4] Until this experiment, the only data available on $S(q,\omega)$ were at the triple point and our theory will not be valid at such high densities. However, the recent data[4] are at moderate densities ($n\sigma^3=0.482$ and 0.628) and it will be of interest to study the role of binary collisions in the time decay of the density correlation function. In addition, the line-shape data has indicated a potential related effect implying that the hard-sphere Enskog kinetic equation[5] which has been found to be valid up to quite high densities (by comparison with simulation results[6]) is not the appropriate kinetic equation. A comparable kinetic equation for continuous potentials is still lacking. In our theory, we do look into the dynamics of the intermolecular collisions using a continuous (Lennard-Jones) potential.

In Sec. II, we formulate the problem and apply BCE to the appropriate correlation functions that appear in the memory function. In Sec. III, we present the results of our calculation and compare them with the experimental and molecular dynamics results. It is seen that our results agree with the experimental values, for $q \gtrsim 1$ Å^{-1}, especially at the lower density.

II. MEMORY FUNCTION FORMALISM

The time evolution of the intermediate coherent scattering function $F(q,t)$, defined by

$$F(q,t)=\langle \rho_{-q}(0)e^{iLt}\rho_q(0)\rangle=\langle \rho_{-q}(0)\rho_q(t)\rangle \tag{1}$$

is governed by the Mori-Zwanzig equation[1]

$$\frac{\partial F}{\partial t}=-\int_0^t d\tau M(q,t-\tau)F(q,\tau)\ , \tag{2}$$

where $M(q,t)$ is the space-time memory function defined by

$$M(q,t)=\langle \dot\rho_{-q}(0)e^{iLQt}\dot\rho_q(0)\rangle\langle \rho_{-q}(0)\rho_q(0)\rangle^{-1}\ . \tag{3}$$

Here

$$\rho_q=\frac{1}{\sqrt{N}}\sum_{j=1}^{N}e^{i\vec{q}\cdot\vec{R}_j}$$

is the particle density, N is the total number of particles, L is complete Liouville operator, q is the wave vector, and $Q=1-P$ where

$$P=|\rho_q(0)\rangle\langle\rho_q(0)|\,\langle\rho_{-q}(0)\rho_q(0)\rangle^{-1}$$

is the projection operator. $\langle \cdots \rangle$ denotes an equilibrium ensemble average and the dot denotes derivative with respect to time. The static structure factor $S(q)$ is defined as

$$S(q)=\langle \rho_{-q}(0)\rho_q(0)\rangle \; . \tag{4}$$

In terms of the Laplace transform variable z, Eqs. (2) and (3) transform to

$$\tilde{F}(q,z)=\frac{S(q)}{z+\tilde{M}(q,z)} \tag{5}$$

with

$$\tilde{M}(q,z)=\left\langle \dot{\rho}_{-q}(0)\frac{1}{z-iLQ}\dot{\rho}_q(0)\right\rangle [S(q)]^{-1} \; . \tag{6}$$

The time dependence of the memory function is rather complicated, being governed, not by $\exp(iLt)$ but by $\exp(iLQt)$. However, the operator Q can be eliminated using the identity

$$\frac{1}{z-iLQ}=\frac{1}{z-iL}-\frac{1}{z-iLQ}iLP\frac{1}{z-iL} \; . \tag{7}$$

We then get

$$\tilde{M}(q,z)=\frac{\tilde{J}(q,z)/S(q)}{1+\tilde{C}(q,z)/S(q)} \; , \tag{8}$$

where

$$\begin{aligned} \tilde{J}(q,z)&=\left\langle \dot{\rho}_{-q}(0)\frac{1}{z-iL}\dot{\rho}_q(0)\right\rangle \; , \\ \tilde{C}(q,z)&=\left\langle \rho_{-q}(0)\frac{1}{z-iL}\dot{\rho}_q(0)\right\rangle \; . \end{aligned} \tag{9}$$

Note that in eliminating the projection operator Q, we have introduced two correlation functions, the longitudinal current $\tilde{J}$, and the cross correlation between density and current, $\tilde{C}$.

We then get the dynamical structure factor $S(q,\omega)$ by noting that

$$S(q,\omega)=\frac{1}{\pi}\mathrm{Re}\tilde{F}(q,z=-i\omega) \tag{10}$$

$$=\frac{1}{\pi}\frac{M'(q,\omega)S(q)}{(M')^2+(\omega-M'')^2} \tag{11}$$

with

$$M'(q,\omega)+iM''(q,\omega)=\frac{J'(q,\omega)+iJ''(q,\omega)}{1+C'(q,\omega)+iC''(q,\omega)} \; , \tag{12}$$

where

$$\begin{aligned} \tilde{J}(q,z=-i\omega)&=J'(q,\omega)+iJ''(q,\omega) \\ &=\int_0^{\infty} J(q,t)e^{i\omega t}dt \end{aligned} \tag{13}$$

and a similar expression for C' and C''.

So far the formulation is exact. Our approximation consists of evaluating $J(q,t)$ and $C(q,t)$ using the first two terms of the binary-collision expansion.[3] The basic formula of BCE is

$$\frac{1}{z-iL}\simeq\frac{1}{z-iL_0}+\frac{1}{2}\sum_{j,k}\left[\frac{1}{z-iL_0-iL_{jk}}-\frac{1}{z-iL_0}\right]+\cdots \; . \tag{14}$$

Here $L=L_0+\sum L_{jk}$ with

$$\begin{aligned} L_0&=-i\sum_j \frac{\vec{P}_j}{m}\cdot\frac{\partial}{\partial\vec{R}_j}=\sum_j L_0(j) \; , \\ L_{jk}&=i\frac{\partial\phi}{\partial\vec{R}_j}\cdot\left[\frac{\partial}{\partial\vec{P}_j}-\frac{\partial}{\partial\vec{P}_k}\right] \; , \end{aligned} \tag{15}$$

where ϕ is the two-body potential and $(\vec{R}_j,\vec{P}_j)$ are the phase-space coordinates of particle j of mass m. The first term of this expansion yields the free-streaming contribution and the second term represents exactly all the effects of a single binary collision. Defining the free-particle and binary-collision contributions by subscripts 0 and 1, respectively, we have

$$\begin{aligned} J(q,t)&\cong J_0(q,t)+nJ_1(q,t) \; , \\ C(q,t)&\cong C_0(q,t)+nC_1(q,t) \; , \end{aligned} \tag{16}$$

where

$$\begin{aligned} J_0(q,t)&=-\frac{d^2}{dt^2}\left[\exp-\frac{q^2v_0^2t^2}{4}\right] \; , \\ C_0(q,t)&=\frac{d}{dt}\left[\exp-\frac{q^2v_0^2t^2}{4}\right] \; , \end{aligned}$$

where $v_0^2=2k_BT/m$, T being the temperature.

The expressions for $J_1(q,t)$ and $C_1(q,t)$ are complicated and are therefore given in the Appendix, wherein the calculation of $J(q,t)$ in BCE is outlined. Thus once we obtain $J(q,t)$ and $C(q,t)$, we use Eqs. (13), (12), and (11) to get $S(q,\omega)$. It should be noted that the only inputs required to calculate $J_1(q,t)$ and $C_1(q,t)$ [Eqs. (A9) and (A12)] are the pair-distribution function $g(r)$ and the interatomic potential $\phi(r)$. Thus our theory has no arbitrary parameters. It can be easily checked that this approximation satisfies the zeroth, second, and fourth moments exactly.

It should be noted that the expansions of $J(q,t)$ and $C(q,t)$ are only up to first order in density. However, Eqs. (8) and (5) indicate that the density expansion of $S(q,\omega)$ will have terms of all orders in density. In addition, since our theory uses the exact $g(r)$, this will also contribute terms of higher order in density. This implies that higher-order collisions, more than the single binary collision between a pair of particles, are somewhat included in our theory. Of course the coefficients of the higher-order terms are not correct.

From Eqs. (11)–(13), it can be easily seen that $S(q,\omega=0)$ turns out to be indeterminate. However, the limit of $S(q,\omega)$ as ω approaches zero, is very well defined. By working out the small-ω behavior of the correlation functions involved, it can be shown that

$$S(q,\omega=0)=2\frac{\delta}{\alpha}S(q)\ , \tag{17}$$

where

$$\delta=\int_0^\infty tC(q,t)dt$$

and

$$\alpha=\int_0^\infty tJ(q,t)dt\ .$$

For discussion purposes, it will be instructive to recast the Zwanzig-Mori equation (5) in the form

$$\chi(q,z)=\frac{\chi_0(q,z)}{1-\psi(q,z)\chi_0(q,z)}\ , \tag{18}$$

where $\chi(q,z)$ is the density response function and $\chi_0(q,z)$ is the free-particle response function. The polarization potential $\psi(q,z)$ is then given by

$$\psi(q,z)=k_BT\left[\left[1-\frac{1}{S(q)}\right]-\omega\left[\frac{1}{M(q,z)}-\frac{1}{M_0(q,z)}\right]\right]\ . \tag{19}$$

The static part of $\psi(q,z)$ describes the mean-field effects and the frequency-dependent part describes the dynamical events.

III. RESULTS AND DISCUSSION

The two density states we have analyzed using our theory are $n\sigma^3=0.482$ and 0.628 at a temperature of $T^*\equiv k_BT/\epsilon=1.47$ with $\sigma=3.57$ Å and $\epsilon/k_B=202$ K. These are the thermodynamic states for which the experimental data have been published.[4] The higher density is about 75% of the liquid density. The binary-collision contributions $J_1(q,t)$ and $C_1(q,t)$ are evaluated using Lennard-Jones as the interatomic potential. For such a potential, $g(r)$ can be generated for any thermodynamic state using the optimized cluster theory.[7] This $g(r)$ agrees remarkably well with the molecular dynamics result[8] and the static-structure factor $S(q)$ is in very good agreement with the experimental values[4] except for very low wave vectors at the lower density.

As before,[2] the multidimensional integrals occurring in $J_1(q,t)$ and $C_1(q,t)$ [Eqs. (A9) and (A12)] are performed through importance sampling Monte Carlo methods[9] and the Verlet algorithm[10] is used to evaluate $\vec{r}(t)$ and $\vec{p}(t)$. For reasons of practicality, we cut off the r integration at $r=2.25\sigma$. A typical number of initial configurations taken to evaluate the integral is 60 000. By computing the imaginary part of the integral, which should be exactly zero, we estimate that the errors involved in evaluating the integral is around 5%.

In Fig. 1 we have plotted the full width at half maximum (FWHM) of the dynamical structure factor $S(q,\omega)$ as a function of the wave vector q. In Fig. 1(a) $n^*=0.482$ and in Fig. 1(b) $n^*=0.628$. The solid line is a smooth curve drawn through the experimental points[4] and crosses are the results of our theory. It is seen that our theory yields results that are in good agreement with the experimental values up to $q\sim1.2$ Å^{-1} at the lower density. At the higher density some deviation from the experimental results are seen for $q<1.6$ Å^{-1}. In Fig. 2, $S(q,\omega=0)/S(q)$, as obtained from Eq. (17), is plotted as a function of q for the two densities. Here again the solid line is a smooth curve through the experimental points and the crosses are the results of our theory. The agreement between our theory and the experimental values is very similar to that seen in Fig. 1. For values of q less than about 1 Å^{-1}, the numerical results for $J_1(q,t)$ and $C_1(q,t)$ start exhibiting an oscillation which reflects as a side peak in $S(q,\omega)$. This seems to suggest that this simple binary-collision theory breaks down for $q<1$ Å^{-1}. Hence we have not plotted any points in Figs. 1 and 2 for such values of q.

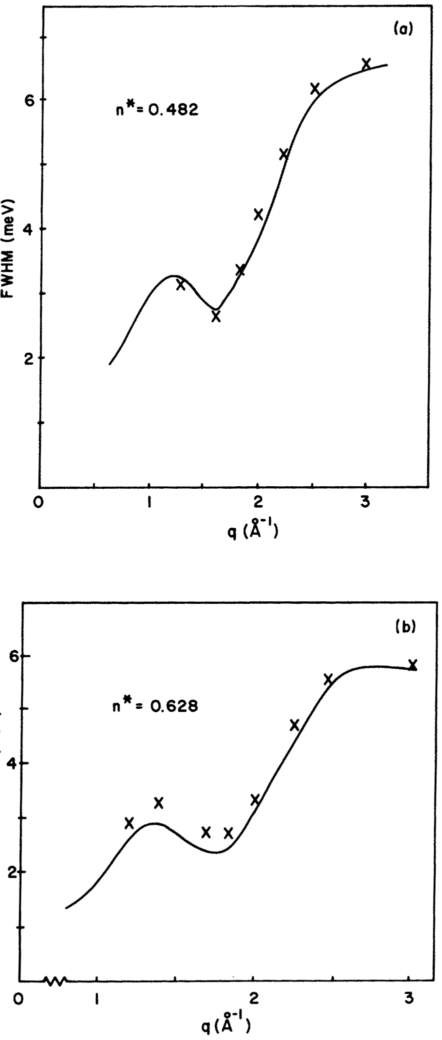

FIG. 1. Full width at half maximum (FWHM) of $S(q,\omega)$ as a function of q for two density states (a) $n^*=0.482$ and (b) $n^*=0.628$. Experimental result is the solid line and our results are denoted by crosses.

However, it should be noted that the behavior in the vicinity of the first diffraction peak, which occurs for $q\sim1.8$ Å^{-1}, is very well explained by our theory. Spatial correlations play an important role in this region and this has been taken into account in our theory as was noted in

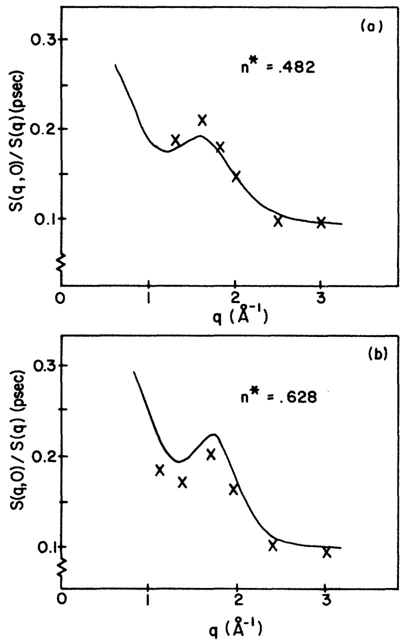

FIG. 2. Scattering law $S(q,\omega)/S(q)$ for zero energy transfer as a function of q for (a) $n^*=0.482$ and (b) $n^*=0.628$. The solid line is the experimental result and the crosses denote our results.

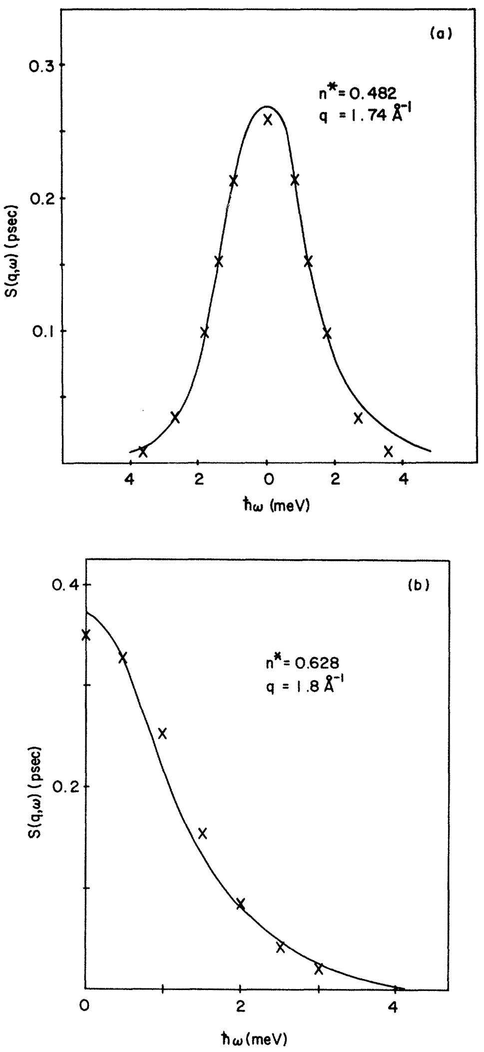

FIG. 3. Scattering law $S(q,\omega)$ as a function of energy transfer $\hbar\omega$ for (a) $n^*=0.482$, $q=1.74$ Å^{-1}, and (b) $n^*=0.628$, $q=1.8$ Å^{-1}. The solid line is the experimental result and the crosses denote our results.

Eq. (19). The FWHM, obtained from our theory clearly shows the de Gennes narrowing behavior which arises from strong spatial correlations. This narrowing behavior was not perceptible when a BCE directly on $S(q,\omega)$ was attempted.[11]

In Fig. 3, we have plotted $S(q,\omega)$ for a value of q near the first diffraction peak for both the densities. This provides an overall picture of the validity of our theory. It can be seen that at the lower density, the agreement is very good except around $\omega=0$. The experimental curve, shown by the solid line, is not symmetrical about $\omega=0$ while our theory will of course be an even function of ω. The agreement at the higher density, even though not as good as at the lower density, is sufficient enough to have confidence to apply our theory for such states.

As was pointed out in Sec. II, we have calculated the first two terms in the density expansion of the current correlation function and the density-current correlation function. In other words, in the equation $J(q,\omega) = J_0(q,\omega)+nJ_1(q,\omega)+\cdots$ we have obtained exact expressions for J_0 and J_1 (and similarly for C_0 and C_1), which are valid for all q and ω. Since we have incorporated only the effects of a single binary collision, this expansion is a short-time expansion and hence has only limited validity as a representation of $J(q,\omega)$. The region of (q,ω) space for which we expect reasonable results will depend on the density—the lower the density, the greater the (q,ω) space.

However, we have calculated the density correlation function $S(q,\omega)$ through the memory function which has in it the above density expansions and hence in this representation we have a density expansion for $S(q,\omega)$ to all orders in density, even though the coefficients of terms of order n^2 and higher are not exact. Such a procedure has increased the region of validity quite significantly.

Since the region of validity depends on q and density, the parameter often used is $(ql)^{-1}$, where l is the mean free path. If $ql > 1$, the system is characterized by free streaming and uncorrelated binary collisions. As ql decreases, correlated and collective collisions become important and finally the hydrodynamic effects. For the density states we have investigated, we can thus make some qualitative comments about the validity of our theory in different ranges of the momentum transfer. For $q < \frac{1}{2}q_0$, where q_0 is the position of the first diffraction peak of structure factor $S(q)$, the collective modes and hydrodynamic effects start playing an important role. Our theory, being still only an extended binary-collision approximation, will exhibit increased deviations from experimental values for such q values. For $\frac{1}{2}q < q \lesssim q_0$, spatial correlations and binary collisions play important roles and the present theory is able to account for the $S(q,\omega)$ spectrum in this region very well. For q greater than q_0 the system can be adequately described by a short-time expansion theory such as binary-collision approximation.

The very good agreement of the results of our theory with experimental values for q around q_0 is one of the features of this formalism. This is due to the fact that our theory has in it some of the effects of higher-order binary collisions and also those of mean field. Any extensions of the theory to low values of q ($\lesssim 1$ Å^{-1}) or to liquid densities will require proper inclusion of correlated collisions. In conclusion, a simple binary-collision theory, in which a particle encounters only one collision, when applied to evaluate the space-time memory function associated with the density correlation function, is able to account for a very significant portion of the spectrum of the density correlation function at moderate densities.

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APPENDIX: BINARY COLLISION EXPANSION OF $J(q,t)$

From the definition of $\tilde{J}(q,z)$ [Eq. (9)] and the BCE formula [Eq. (14)]. We have

$$\begin{aligned}\tilde{J}_0(q,z)&=\left\langle\dot{\rho}_{-q}\frac{1}{z-iL_0}\dot{\rho}_q\right\rangle ,\\ \tilde{J}_1(q,z)&=\left\langle\dot{\rho}_{-q}\sum\left[\frac{1}{z-iL_0-iL_{jk}}-\frac{1}{z-iL_0}\right]\dot{\rho}_q\right\rangle .\end{aligned}\tag{A1}$$

In the time domain, we have for the free-streaming part,

$$J_0(q,t)=\frac{1}{Z}\frac{1}{N}\int d\vec{R}_1\cdots d\vec{R}_N\exp(-\beta U)\prod_{j=1}^{N}G(P_j)d\vec{P}_j\sum_l -i\vec{q}\cdot\frac{\vec{P}_l}{m}e^{-i\vec{q}\cdot\vec{R}_l}\sum_k i\vec{q}\cdot\frac{\vec{P}_k}{m}e^{i\vec{q}\cdot\vec{R}_k^{0}(t)} ,\tag{A2}$$

where $\beta=1/k_BT$, U is the potential, $G(P_j)$ is the normalized Maxwellian, Z is the configurational partition function, and $\vec{R}_k^{0}(t)\equiv e^{iL_0t}\vec{R}_k=\vec{R}_k+(\vec{P}_k/m)t$, the ideal gas propagation.

In (A2), only the terms $k=l$ will contribute, yielding

$$\begin{aligned}J_0(q,t)&=\int\left[\frac{\vec{q}\cdot\vec{P}_1}{m}\right]^2\exp\left[i\vec{q}\cdot\frac{\vec{P}_1t}{m}\right]G(P_1)d\vec{P}_1\\ &=-\frac{d^2}{dt^2}\int\exp\left[i\vec{q}\cdot\frac{\vec{P}_1t}{m}\right]G(P_1)d\vec{P}_1\\ &=-\frac{d^2}{dt^2}\exp(-q^2v_0^2t^2/4)\end{aligned}\tag{A3}$$

with $v_0^2=2k_BT/m$. For the binary-collision contribution, we have

$$\begin{aligned}nJ_1(q,t)=\frac{1}{N}\frac{1}{Z}\int d\vec{R}_1\cdots d\vec{R}_N\exp(-\beta U)\prod_{j=1}^{N}G(P_j)d\vec{P}_j\frac{N(N-1)}{2}\sum_l -i\vec{q}\cdot\frac{\vec{P}_l}{m}e^{-i\vec{q}\cdot\vec{R}_l}\\ \times\left\{\exp\left[i\left[\mathscr{L}_{12}+\sum_{j=3}^{N}L_0(j)\right]t\right]-e^{iL_0t}\right\}\\ \times\sum_k i\vec{q}\cdot\frac{\vec{P}_k}{m}e^{i\vec{q}\cdot\vec{R}_k} ,\end{aligned}\tag{A4}$$

where $\mathscr{L}_{12}=L_0(1)+L_0(2)+L_{12}$ is the two-body propagator.

When the summations involved are performed, only terms involving particles 1 and 2 remain, yielding

$$nJ_1(q,t)=\frac{N-1}{V^2}\int d\vec{R}_1d\vec{R}_2g(r)\prod_{j=1}^{2}G(P_j)d\vec{P}_j\left[\frac{\vec{q}\cdot\vec{P}_1}{m}e^{i\vec{q}\cdot\vec{R}_1}\sum_{k=1}^{2}\left[\vec{q}\cdot\frac{\vec{P}_k(t)}{m}e^{i\vec{q}\cdot\vec{R}_k(t)}-\vec{q}\cdot\frac{\vec{P}_k}{m}e^{i\vec{q}\cdot\vec{R}_k^{0}(t)}\right]\right] ,\tag{A5}$$

where $\vec{R}_k(t)=e^{i\mathscr{L}_{12}t}\vec{R}_k$ and similarly for $\vec{P}_k(t)$. Here $g(r)$ is the pair-distribution function with $r=|\vec{R}_1-\vec{R}_2|$ and defined through

$$g(r)=\frac{1}{ZV^2}\int d\vec{R}_3\cdots d\vec{R}_N \exp(-\beta U)\ , \tag{A6}$$

where V is the volume.

Going over to the center-of-mass coordinates

$$\begin{aligned}&\vec{R}=\tfrac{1}{2}(\vec{R}_1+\vec{R}_2),\ \ \vec{P}=\vec{P}_1+\vec{P}_2\ ,\\ &\vec{r}=\vec{R}_1-\vec{R}_2,\ \ \vec{P}=\vec{P}_1-\vec{P}_2\ ,\end{aligned} \tag{A7}$$

we get after the trivial integration over $\vec{R}$,

$$\begin{aligned}nJ_1(q,t)=n\int d\vec{r}\,g(r)\Bigg[&M(P)M(p)d\vec{P}d\vec{p}\,\tfrac{1}{4}\exp\left[i\vec{q}\cdot\frac{\vec{P}}{2m}t\right]\\ &\times[E(q,r,r(t))A(q,p,P,p(t))-E(q,r,-r(t))A(q,p,P,-p(t))]-J_0(q,t)\Bigg]\ ,\end{aligned} \tag{A8}$$

where

$$E(q,r,r(t))=\exp[i\vec{q}\cdot(\vec{r}-\vec{r}(t))/2]$$

and

$$A(q,p,P,p(t))=[(\vec{q}\cdot\vec{P})-(\vec{q}\cdot\vec{p})][(\vec{q}\cdot\vec{P})-(\vec{q}\cdot\vec{p}(t))]\ .$$

The P integration can then be performed yielding

$$nJ_1(q,t)=n\int d\vec{r}\,g(r)\{d\vec{p}M(p)\exp(-q^2v_0^2t^2/8)[E(q,r,r(t))B(q,p,p(t))-E(q,r,-r(t))B(q,p,-p(t))]-J_0(q,t)\}\ , \tag{A9}$$

where

$$B(q,p,p(t))=D_0-D_1\frac{\vec{q}}{2m}\cdot(\vec{p}+\vec{p}(t))+\frac{1}{4m^2}(\vec{q}\cdot\vec{p})(\vec{q}\cdot\vec{p}(t))$$

with

$$D_0=\frac{q^2v_0^2}{4}\left[1-\frac{q^2v_0^2t^2}{4}\right] \tag{A10}$$

and

$$D_1=\frac{q^2v_0^2t}{4}\ ,$$

$$M(P)=\frac{1}{(2\pi m^2v_0^2)^{3/2}}\exp\left[-\frac{p^2}{2m^2v_0^2}\right]$$

is a normalized Maxwellian.

A similar procedure yields

$$C_0(q,t)=\frac{d}{dt}\exp\left[-\frac{q^2v_0^2t^2}{4}\right] \tag{A11}$$

and

$$nC_1(q,t)=n\int d\vec{r}\,g(r)\{M(p)d\vec{p}\exp(-q^2v_0^2t^2/8)[E(q,r,r(t))T(q,p(t))-E(q,r,-r(t))T(q,-p(t))]-C_0(q,t)\}\ , \tag{A12}$$

where

$$T(q,p(t))=\frac{-q^2v_0^2t}{4}-\frac{i\vec{q}\cdot\vec{p}(t)}{2m}\ .$$

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[1] R. Zwanzig, in *Lectures in Theoretical Physics,* edited by W. Brittin (Wiley, New York, 1961), Vol. 3; H. Mori, Prog. Theor. Phys. 33, 423 (1965).

[2] S. Ranganathan, M. Rao, and S. Yip, Phys. Lett. 74A, 180 (1979); T. J. Fletcher and S. Ranganathan, Can. J. Phys. 61, 926 (1983); S. Ranganathan, Can. J. Phys. 61, 1655 (1983).

[3] R. Zwanzig, Phys. Rev. 129, 486 (1963).

[4] P. Egelstaff *et al.*, Phys. Rev. A 27, 1106 (1983).

[5] J. W. Dufty, M. J. Lindenfeld, and G. E. Garland, Phys. Rev. A 24, 3212 (1981).

[6] S. Yip, W. E. Alley, and B. J. Alder, J. Stat. Phys. 27, 201 (1982).

[7] S. Sung and D. Chandler, J. Chem. Phys. 56, 4989 (1972).

[8] R. Bansal, W. Bruns, K. N. Pathak, and S. Ranganathan (to be published).

[9] J. M. Hammersley and D. C. Handicomb, *Monte Carlo Methods* (Methuen, London, 1975).

[10] L. Verlet, Phys. Rev. 159, 98 (1967).

[11] S. Ranganathan and K. N. Pathak, Phys. Rev. A 29, 972 (1984).