Binary-collision effects on density fluctuations of dense gases

S. Ranganathan and K. N. Pathak*
Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario K7L 2W3, Canada
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A dynamical theory of simple fluids which incorporates exactly all the effects of a single binary collision is used to study the dynamic structure factor $S(q,\omega)$ for Lennard-Jones fluids. The comparison of our results with those of recent neutron inelastic-coherent-scattering experiments of dense krypton gas indicates that $S(q,\omega)$ is sensitive to the details of the interatomic potential even in moderately dense gases.

Recent measurements of the dynamical structure factor $S(q,\omega)$ of dense krypton gas through neutron inelastic scattering experiments[1] have revealed significant deviations from hard-sphere kinetic theory[2] and molecular dynamics results[3] even at lower densities. This suggests that the attractive part of the pair potential plays an important role in determining the dynamics of density fluctuations. Very recently, molecular dynamics simulations have been carried out using a Lennard-Jones potential[4] and these confirm that the line shape of $S(q,\omega)$ is sensitive to the details of intermolecular interactions in a dense gas. A dynamical theory[5] which incorporates the static correlations of a Lennard-Jones potential while still approximating the dynamics through generalized Enskog theory has not improved to any great extent the discrepancies. This implies that we have to look into the dynamics of the intermolecular collisions using a realistic pair potential.

In this Brief Report, we look into the dynamics of a binary collision in a Lennard-Jones potential and apply the binary-collision expansion[6] (BCE) to evaluate the dynamic structure factor $S(q,\omega)$. In this expansion, the first term is just the ideal gas result and the second term incorporates exactly all the effects of a single binary collision between a pair of particles. The third term will incorporate binary-collision events between three-particles and involve a three particle correlation function. We shall include only the first two terms of the expansion. Such an expansion has been used to evaluate the correlation function, either directly[7] or through the memory function[8,9] using the Mori formalism and the results indicate that such a procedure is able to account for a very significant portion of the observed spectrum.

The density-density correlation function is defined as

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

where

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

is the density of a system of N particles and

$$L=\sum_{j=1}^{N}L_0(j)+\sum_{j,k}L_{jk}$$

is the complete Liouville operator. Here L_0 is the kinetic contribution to L and L_{jk} is the potential contribution. $\langle\cdots\rangle$ denotes an equilibrium ensemble average. In terms of the Laplace transform variable z, we have

$$\tilde{F}(q,z)=\left\langle\rho_{-q}\left|\frac{1}{z-iL}\right|\rho_q\right\rangle \ . \tag{2}$$

We now apply the binary-collision expansion to Eq. (2). The basic formula of BCE[6] is

$$\frac{1}{z-iL}=\frac{1}{z-iL_0}+\sum_{j,k}\left(\frac{1}{z-iL_0-iL_{jk}}-\frac{1}{z-iL_0}\right)+\cdots \ . \tag{3}$$

The first term involves no collisions while the second term involves just one collison between a pair of particles j and k. Thus if we write

$$F(q,t)\simeq F_0(q,t)+[F_1(q,t)-F_1^0(q,t)] \tag{4}$$

then we have

$$F_0(q,t)=\langle e^{-i\vec{q}\cdot\vec{R}_1}[e^{i\vec{q}\cdot\vec{R}_1^0(t)}+(N-1)e^{i\vec{q}\cdot\vec{R}_2^0(t)}]\rangle \tag{5}$$

and

$$F_1(q,t)=(N-1)\langle e^{-i\vec{q}\cdot\vec{R}_1}[e^{i\vec{q}\cdot\vec{R}_1(t)}+e^{i\vec{q}\cdot\vec{R}_2(t)}]\rangle \ , \tag{6}$$

$$F_1^0(q,t)=(N-1)\langle e^{-i\vec{q}\cdot\vec{R}_1}[e^{i\vec{q}\cdot\vec{R}_1^0(t)}+e^{i\vec{q}\cdot\vec{R}_2^0(t)}]\rangle \ . \tag{7}$$

$\vec{R}_1(t)$ and $\vec{R}_2(t)$ are determined only through two-particle dynamics, i.e., $\vec{R}_1(t)=\exp(i\mathcal{L}_{12}t)\vec{R}_1(0)$ where $\mathcal{L}_{12}=L_0(1)+L_0(2)+L_{12}$. $\vec{R}^0(t)=\exp(iL_0t)\vec{R}(0)=\vec{R}(0)+\vec{P}t/m$ corresponds to an ideal gas. The equilibrium ensemble average can be worked out to be

$$\langle\theta\rangle=\frac{1}{V^2}\int d\vec{R}_1\,d\vec{R}_2\,d\vec{P}_1\,d\vec{P}_2\,g(\vec{R}_1,\vec{R}_2)M(P_1)M(P_2)\theta \ , \tag{8}$$

where $g(\vec{R}_1,\vec{R}_2)$ is the pair distribution function depending only on $r=|\vec{R}_1-\vec{R}_2|$, defined by

$$\frac{g(r)}{V^2}=\frac{\int d\vec{R}_3\cdots d\vec{R}_N\,e^{-\beta U}}{\int d\vec{R}_1\cdots d\vec{R}_N\,e^{-\beta U}} \ , \tag{9}$$

where U is the potential and V is the volume. $M(P_1)$ is the normalized Maxwellian.

Going over to the center-of-mass and relative coordinates

defined through

$$\vec{R}=\tfrac{1}{2}(\vec{R}_1+\vec{R}_2),\quad \vec{P}=\vec{P}_1+\vec{P}_2\ ,$$
$$\vec{r}=\vec{R}_1-\vec{R}_2,\quad \vec{p}=\vec{P}_1-\vec{P}_2\ , \tag{10}$$

we get, after performing $\vec{P}$ and $\vec{R}$ integration,

$$F_0(q,t)=\left[1+n\int d\vec{r}\,g(r)e^{i\vec{q}\cdot\vec{r}}\right]\exp\left[-\frac{q^2v_0^2t^2}{4}\right]\ , \tag{11}$$

$$F_1(q,t)=n\int d\vec{r}\,d\vec{p}\,g(r)G(p)\exp\left[-\frac{q^2v_0^2t^2}{8}\right]\times\left[\exp\left[\frac{i}{2}\vec{q}\cdot[\vec{r}-\vec{r}(t)]\right]+\exp\left[\frac{i}{2}\vec{q}\cdot[\vec{r}+\vec{r}(t)]\right]\right]\ , \tag{12}$$

$$F_1^0(q,t)=n\int d\vec{r}\,g(r)(1+e^{i\vec{q}\cdot\vec{r}})\exp\left[-\frac{q^2v_0^2t^2}{4}\right]\ , \tag{13}$$

where

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

with $v_0^2=2k_BT/m$, and n is the number density. It should be noted that the second term in $F^0(q,t)$ [Eq. (11)] cancels with the second term in $F_1^0(q,t)$ [Eq. (13)]. Thus the dynamics of the two-particle system is solved with their initial relative positions weighted by the pair distribution function $g(r)$ and their initial velocities weighted by a Maxwellian distribution $G(p)$. It can be easily checked that this approximation of $F(q,t)$ satisfies the zeroth, second, and fourth moments exactly.

This theory is an *ab initio* calculation and thus has no arbitrary parameters. The only inputs required are $g(r)$ and the two-particle dynamics. The integration in Eq. (12) is performed through importance sampling Monte Carlo integration[10] and the Verlet algorithm[11] is used to evaluate $\vec{r}(t)$ and $\vec{p}(t)$. The interatomic potential used is the Lennard-Jones potential for which $g(r)$ can be generated for any thermodynamic state using the optimized cluster theory.[12] We have cut off the r integration at $r=2.25\sigma$. By computing the imaginary part of the integral, which should be zero, we conclude that the errors involved in evaluating the integral are between 5% and 10%. The dynamical structure factor $S(q,\omega)$ is then obtained from $F(q,t)$ [Eq. (4)],

$$S(q,\omega)=\frac{1}{\pi}\int_0^\infty F(q,t)\cos(\omega t)\,dt\ . \tag{14}$$

In Fig. 1 we have plotted the full width at half maximum (FWHM) of $S(q,\omega)$ as a function of the wave number q. The solid line curve is the experimental result[1] while the ideal gas result (straight line) is given as a reference. The circles are the results of our calculations. The density in Fig. 1(a) is $n^*=n\sigma^3=0.482$ and in Fig. 1(b) is 0.628. The temperature in both cases is $T^*=k_BT/\epsilon=1.47$. Here we have used $\sigma=3.57$ Å and $\epsilon=202$ K as the parameters for krypton. It is seen that the results of our binary-collision theory are in reasonable agreement with the experimental values at the lower density while at the higher density which is about 75% of the triple point density, the agreement is not as good. The simple binary-collision theory applied directly to the correlation function will show increased deviation from the experimental results as the density increases. Higher-order correlated and uncorrelated collisions have to be included to give good results at high densities. The mean-field effects which are dominant for higher densities

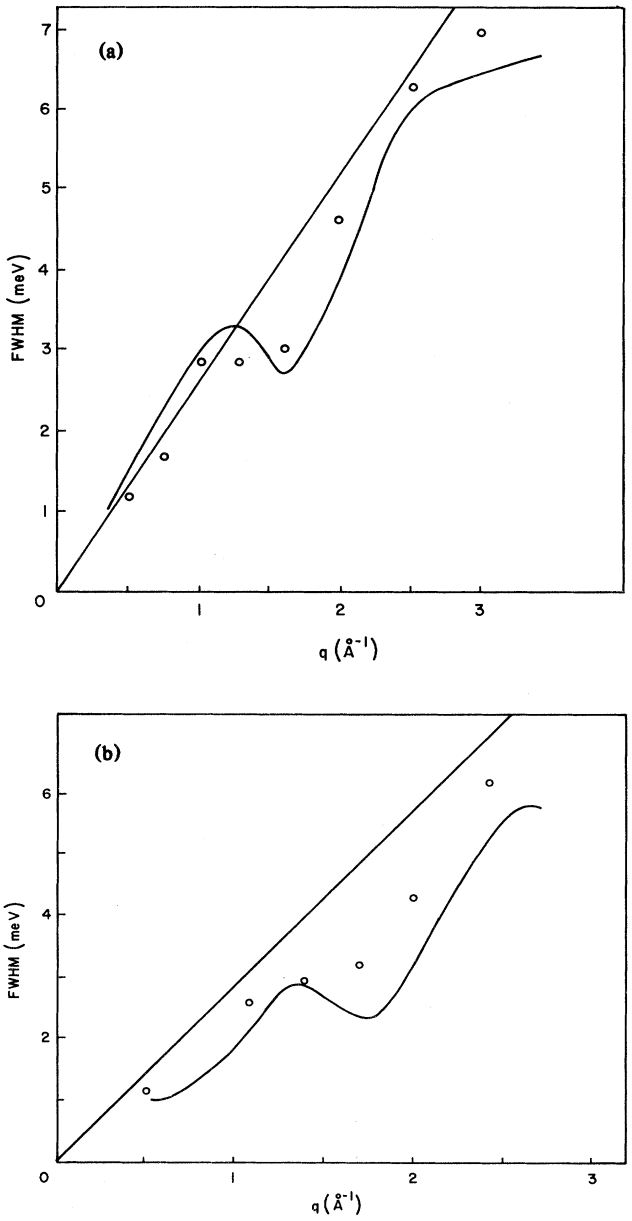

FIG. 1. FWHM of $S(q,\omega)$ for density (a) $n=0.0106$ Å^{-3}; (b) $n=0.0138$ Å^{-3}. Circles: present theory; full line: a smooth line through the experimental points; straight line: perfect gas.

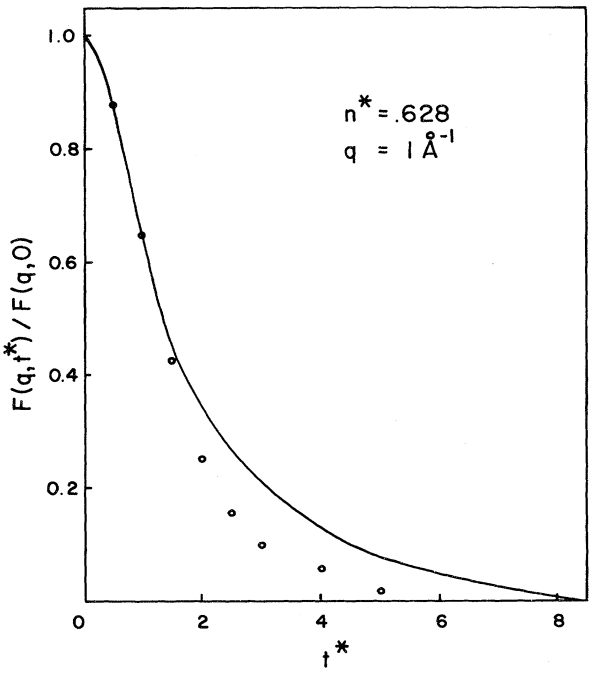

FIG. 2. Variation of $F(q,t^*)$ with dimensionless time t^*. Here $n^*=0.628$, $T^*=1.47$, and $q=1$ Å^{-1}. The solid line is the MD result. The circles represent our results.

and around $q \sim q_0$,[13] where q_0 is the position of the first diffraction peak of the static structure factor, have not been included in our theory and this explains some of the deviations of our results around $q \sim q_0$.

To get an idea of binary-collision effects on density fluctuations, we have plotted, in Fig. 2, $F(q,t^*)$ for the higher density $n^*=0.628$ and $q=1$ Å^{-1} as a function of dimensionless time $t^*=t/\tau$, where $\tau^2=m\sigma^2/48\epsilon$. For krypton, $t^*=1$ corresponds approximately to 3.65×10^{-13} sec. The solid line is the MD (molecular dynamics) result[4] while the results of our calculations are denoted by circles. It is seen that even at this higher density, the BCE theory agrees with MD results up to $t^*\sim1.5$. The difference between our results and the MD values can be directly attributed to third- and higher-order particle dynamics which will introduce correlated collisions.

The general trend of agreement between our results and experimental values indicates that the attractive part of the potential is important even at lower densities and it is the dynamics of particles in such a potential which should be included in any theory of density fluctuations of even moderately dense gases.

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*Permanent address: Department of Physics, Panjab University, Chandigarh 160014, India.

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