

Cluster expansion for the coherent and incoherent dynamic structure factors in simple classical liquids

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A cluster expansion is obtained for the coherent and incoherent dynamic structure factors in the case of a simple classical dense fluid. The expansion is useful in the case of fluids where the hard-core repulsive part of the interaction plays an important role. The first term in the expansion is given by the dynamic structure factor of a noninteracting system. The second term is obtained by solving the dynamics of a two-particle system with initial positions given by the pair-correlation function for the full system and initial velocities given by a Maxwellian distribution. The third term is obtained by solving the dynamics of a three-particle system, etc. Keeping only the first two terms, the effect of repeated binary collisions on the dynamic structure factor is studied in the case of a hard-core fluid and a Lennard-Jones (6,12) fluid with liquid-argon parameters. The results are compared with neutron-scattering experiments.

I. INTRODUCTION

The coherent and incoherent dynamic structure factors $S(k, \omega)$ and $S_s(k, \omega)$ of simple liquids have been obtained from both molecular dynamics¹ and neutron scattering experiments.² However, a first-principle calculation of these quantities is not yet available. Most of the theories are based on either the solution of a kinetic equation such as the Boltzmann equation, which is the method pioneered by Nelkin and co-workers,³ or the calculation of memory functions, which were introduced by Zwanzig⁴ and Mori.⁵ Recently Mazenko⁶ has developed a fully renormalized kinetic theory. There also have been attempts⁷ to construct the dynamic structure factor $S(k, \omega)$ from some known and (hopefully) simpler functions of k and ω .

In the present paper we follow a different approach in calculating the dynamic structure factors. We develop a cluster-expansion scheme for both $S(k, \omega)$ and $S_s(k, \omega)$. The first term is the dynamic structure factor of a free gas. The second term arises due to the binary collisions between the atoms in the liquid. This term is obtained by solving the dynamics of a two-particle system with their initial relative positions given by the equilibrium radial distribution function $g(r)$ of the liquid and their initial velocities given by the Maxwellian distribution. The third term involves the dynamics of a three-body system

and the three-particle equal-time correlation function.

This scheme is useful for hard-core and hard-core-like systems at any density. Keeping only the first two terms in the cluster expansion, we study the effect of binary collisions in the liquid at high densities due to the hard repulsive cores of the atoms by calculating $S(k, \omega)$ and $S_s(k, \omega)$. Since it is straightforward to solve for the dynamics of a two-particle system with the aid of a computer, we have calculated the dynamic structure factors using both the Lennard-Jones (LJ) (6, 12) potential with liquid-argon parameters and the hard-core potential with a suitably chosen diameter.⁸ In Sec. II we present the cluster-expansion scheme and in Sec. III we give the details of computation and discuss the results. Using Schofield's¹⁰ prescription for quantum corrections we make a comparison with neutron scattering results.

II. CLUSTER EXPANSION

In this section we shall derive the cluster-expansion scheme for the dynamic structure factors using linear-response theory. The starting point is a classical equivalent of the Kubo formula for the density-density response function $K(k, \omega)$ derived by Ron⁹ for a system of N particles contained in a volume V :

$$K(\vec{k}, \omega) = \frac{N}{V^{N+1}} \int d\vec{p}_1, \dots, d\vec{p}_N \sum_{\vec{k}_1, \dots, \vec{k}_N} \sum_i \langle \vec{k} \dots 0 \mid \frac{1}{L-\omega} \mid \vec{k}_1, \dots, \vec{k}_N \rangle \times \bar{F}(\vec{k}_1, \dots, \vec{k}_i - \vec{k}, \dots, \vec{k}_N) \vec{k} \cdot \frac{\partial G}{\partial \vec{p}_i}(\vec{p}_1, \dots, \vec{p}_N). \quad (1)$$

Here L is the standard N -particle Liouville operator. $\bar{F}(\vec{k}_1, \dots, \vec{k}_l, -\vec{k}, \dots, \vec{k}_N)$ is the Fourier transform of $F(\vec{r}_1, \dots, \vec{r}_N)$, where

$$F(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{Z} \exp\left(-\beta \sum_{j < k} \Phi(|\vec{r}_j - \vec{r}_k|)\right). \quad (2)$$

Z is the partition function and $\Phi(r)$ is the interaction potential. $G(\vec{p}_1, \dots, \vec{p}_N)$ is the canonical distribution function for the N -momenta. The fluctuation-dissipation¹⁰ theorem relates $S(k, \omega)$ and $K(k, \omega)$:

$$S(k, \omega) = (m\bar{v}^2/2\pi\rho) [\text{Im} K(k, \omega)/\omega], \quad (3)$$

where ρ is the density of the liquid and $\bar{v} = (2k_B T/m)^{1/2}$ is the thermal velocity of the atoms in the liquid. In Eq. (1), if the summation over l is removed by setting $l = 1$, we obtain $S_s(k, \omega)$, the incoherent dynamic structure factor. In the rest of the paper we discuss only the general case since $S_s(k, \omega)$ can be obtained by setting $l = 1$.

High-frequency expansion¹¹ for the density-density response function and large-wave-vector expansion for the dynamic structure factor¹² have been known for some time. However, such expansions are not useful in the case of dense liquids with hard-core repulsive interaction. Using a model potential

$$\Phi(r) = \epsilon(a/r)^n \quad (4)$$

one sees^{12, 13} that these expansions diverge term by term in the limit $n \rightarrow \infty$ (in this limit the interaction becomes hard core). The two-particle

terms involving the pair correlation function diverge much faster than the three-particle terms involving three-particle correlation functions and the three-particle terms diverge much faster than the four-particle terms, etc. In the present paper we propose to sum the most divergent terms and obtain a cluster expansion for the dynamic structure factor. Such a cluster expansion is useful for hard-core and hard-core-like systems. This is equivalent to using a cluster expansion¹⁴ for the operator $(L - \omega)^{-1}$ in Eq. (1), i.e.,

$$\begin{aligned} \frac{1}{L - \omega} &= \frac{1}{L_0 - \omega} + \sum_{i < j} \left(\frac{1}{L_0 + L_I(ij) - \omega} - \frac{1}{L_0 - \omega} \right) \\ &+ \text{term involving three particles} + \dots \end{aligned} \quad (5)$$

Such expansions have been used in the literature for deriving the memory functions and kinetic equations.¹⁵ In the present paper we shall restrict ourselves to keeping only the first two terms and study the effect of binary collisions on the dynamic structure factor. The two-term cluster expansion reproduces all the terms involving the free-particle and the two-particle contributions in both large- ω or large- k expansions previously mentioned. Neglecting the three-particle term introduces an error of the order $1/\omega^6$ or $1/k^4$ in $S(k, \omega)$.

Using Eqs. (1) and (5) we obtain a cluster expansion for $K(k, \omega)$. Keeping only the first two terms we have

$$\begin{aligned} K(k, \omega) &= \frac{N}{V^{N+1}} \int d\vec{p}_1, \dots, d\vec{p}_N \sum_{\vec{k}_1, \dots, \vec{k}_N} \sum_i \left\langle \vec{k} \dots 0 \left| \frac{1}{L_0 - \omega} \right| \vec{k}_1, \dots, \vec{k}_N \right\rangle \\ &\times \bar{F}(\vec{k}_1, \dots, \vec{k}_i, -\vec{k}, \dots, \vec{k}_N) \vec{k} \cdot \frac{\partial G(\vec{p}_1, \dots, \vec{p}_N)}{\partial \vec{p}_i} \\ &+ \frac{N}{V^{N+1}} \int d\vec{p}_1, \dots, d\vec{p}_N \sum_{\vec{k}_1, \dots, \vec{k}_N} \sum_i \left\langle \vec{k} \dots 0 \left| \left(\sum_{i < j} \frac{1}{L_0 + L_I(ij) - \omega} - \frac{1}{L_0 - \omega} \right) \right| \vec{k}_1, \dots, \vec{k}_N \right\rangle \\ &\times \bar{F}(\vec{k}_1, \dots, \vec{k}_i, -\vec{k}, \dots, \vec{k}_N) \vec{k} \cdot \frac{\partial G(\vec{p}_1, \dots, \vec{p}_N)}{\partial \vec{p}_i}. \end{aligned} \quad (6)$$

In the first term the matrix elements of the operator $1/(L_0 - \omega)$ are easily evaluated. To study the second term we write

$$\sum_{i < j} \left(\frac{1}{L_0 + L_I(ij) - \omega} - \frac{1}{L_0 - \omega} \right) = \sum_{i < j} \left(-\frac{1}{L_0 - \omega} L_I(ij) \frac{1}{L_0 - \omega} + \dots \right). \quad (7)$$

Each $L_I(ij)$ involves an operator $(\partial/\partial \vec{p}_i - \partial/\partial \vec{p}_j)$ operating on everything to the right. We now introduce complete sets of plane-wave states between various operators. Then the matrix ele-

ment of operator $1/(L_0 - \omega)$ on the left involves only \vec{p}_1 . Doing integrations over momenta, only those terms with $i = 1$ survive. Using the restriction on j we replace $\sum_{i < j}$ by $N-1$ and set $j = 2$. Thus,

$$\sum_{i < j} \left(\frac{1}{L_0 + L_I(ij) - \omega} - \frac{1}{L_0 - \omega} \right) = (N-1) \left(\frac{1}{L_0 + L_I(12) - \omega} - \frac{1}{L_0 - \omega} \right). \tag{8}$$

Then we write $L_0 = L_0(1) + L_0(2) + L'_0$ where $L'_0 = \sum_{i=3}^N L_0(i)$ and noting the fact that L'_0 commutes with $L_I(12)$, we evaluate $K(k, \omega)$,

$$\begin{aligned} K(k, \omega) &= \frac{N}{V^2} \int d\vec{p}_1 \sum_{\vec{k}_1} \left\langle \vec{k} \left| \frac{1}{-(i/m)\vec{p}_1 \cdot \partial / \partial \vec{r}_1 - \omega} \right| \vec{k}_1 \right\rangle \bar{F}(\vec{k}_1 - \vec{k}) \vec{k} \cdot \frac{\partial G(\vec{p}_1)}{\partial \vec{p}_1} \\ &+ \frac{N(N-1)}{V^3} \int d\vec{p}_1 d\vec{p}_2 \sum_{\vec{k}_1 \vec{k}_2} \left\langle \vec{k}, 0 \left| \frac{1}{L_0(1) + L_0(2) + L_I(12) - \omega} - \frac{1}{L_0(1) + L_0(2) - \omega} \right| \vec{k}_1 \vec{k}_2 \right\rangle \\ &\times \left(\bar{F}(\vec{k}_1 - \vec{k}, \vec{k}_2) \frac{\partial G(\vec{p}_1, \vec{p}_2)}{\partial \vec{p}_1} \cdot \vec{k} + \bar{F}(\vec{k}_1, \vec{k}_2 - \vec{k}) \frac{\partial G(\vec{p}_1, \vec{p}_2)}{\partial \vec{p}_2} \cdot \vec{k} \right). \end{aligned} \tag{9}$$

Equation (9) can be written as

$$K(k, \omega) = K_0(k, \omega) + [K_1(k, \omega) - K_1^0(k, \omega)]. \tag{10}$$

Clearly $K_0(k, \omega)$ and $K_1^0(k, \omega)$ are related to the free-particle response functions and $K_1(k, \omega)$ is related to the two-particle response function. Using the fluctuation-dissipation theorem and Eq. (10) we write

$$S(k, \omega) = S_0(k, \omega) + [S_1(k, \omega) - S_1^0(k, \omega)]. \tag{11}$$

After a simple calculation we obtain

$$S_0(k, \omega) = (1/\pi^{1/2} k v) e^{-\omega^2/k^2 v^2} \tag{12}$$

and

$$S_1^0(k, \omega) = S_0(k, \omega) \rho \int g(r) d^3r, \tag{13}$$

where we have used the fact that

$$\rho \int g(r) d^3r = N - 1. \tag{14}$$

Now $S_1(k, \omega)$ is calculated as follows: $K_1(k, \omega)$ can be very easily written as

$$\begin{aligned} K_1(k, \omega) &= \frac{N(N-1)}{V} \int d\vec{p}_1 d\vec{p}_2 \int d\vec{r}_1 d\vec{r}_2 e^{-i\vec{k} \cdot \vec{r}_1} \\ &\times \frac{1}{L_{12} - \omega} \sum_{i=1,2} e^{i\vec{k} \cdot \vec{r}_i} F(\vec{r}_1, \vec{r}_2) \vec{k} \cdot \frac{\partial G}{\partial \vec{p}_i}(\vec{p}_1, \vec{p}_2), \end{aligned} \tag{15}$$

where

$$\begin{aligned} F(\vec{r}_1, \vec{r}_2) &= \frac{1}{Z} \int \exp \left(-\beta \sum_{i < j} \Phi(|\vec{r}_i - \vec{r}_j|) \right) d\vec{r}_3 \cdots d\vec{r}_N \\ &= g(|\vec{r}_2 - \vec{r}_1|)/V^2. \end{aligned} \tag{16}$$

Using the antisymmetry of the imaginary part of $K(k, \omega)$ and the fluctuation-dissipation theorem, it is easily shown that

$$\begin{aligned} S_1(k, \omega) &= -\frac{N-1}{V^2} \frac{1}{\pi} \int_0^\infty dt \frac{\sin \omega t}{\omega} \\ &\times \int d\vec{p}_1 d\vec{p}_2 \int d\vec{r}_1 d\vec{r}_2 e^{-i\vec{k} \cdot \vec{r}_1} e^{-iL_{12}t} \\ &\times \sum_i e^{i\vec{k} \cdot \vec{r}_i} \frac{i\vec{k} \cdot \vec{p}_i}{m} g(|\vec{r}_2 - \vec{r}_1|) G(\vec{p}_1, \vec{p}_2). \end{aligned} \tag{17}$$

Here we might recall that the incoherent dynamic structure factor is given by the $l = 1$ term.

Since $e^{-iL_{12}t}$ is a time-evolution-operator equation, (17) can be evaluated from a knowledge of the trajectories of the two-particle system. Using Liouville theorem it is easily shown that

$$\begin{aligned} S_1(k, \omega) &= -\frac{N-1}{V^2} \frac{1}{\pi} \int_0^\infty dt \frac{\sin \omega t}{\omega} \\ &\times \int d\vec{p}_1 d\vec{p}_2 \int d\vec{r}_1 d\vec{r}_2 e^{-i\vec{k} \cdot \vec{r}_1} \\ &\times \sum_{i=1,2} e^{i\vec{k} \cdot \vec{r}_i(t)} \frac{i\vec{k} \cdot \vec{p}_i(t)}{m} \\ &\times g(|\vec{r}_2(t) - \vec{r}_1(t)|) G(\vec{p}_1(t), \vec{p}_2(t)), \end{aligned} \tag{18}$$

where $\vec{r}_i(t)$ and $\vec{p}_i(t)$ ($i = 1, 2$) are the coordinates and momenta of the two particles at time t given that at $t = 0$, $\vec{r}_i(0) = \vec{r}_i$ and $\vec{p}_i(0) = \vec{p}_i$ ($i = 1, 2$). Using the center-of-mass and relative-coordinate system and taking the limit $N/V = \rho$ as $N \rightarrow \infty$ and $V \rightarrow \infty$, we obtain

$$\begin{aligned} S_1(k, \omega) &= -\frac{1}{\pi} \int_0^\infty dt \frac{\sin \omega t}{\omega} \int d\vec{r} d\vec{p} \rho g(r(t)) G(p(t)) \\ &\times \frac{d}{dt} [e^{-k^2 v^2 t^2/8} (e^{-i\vec{k}[\vec{r}(t) - \vec{r}]/2} \\ &+ e^{i\vec{k}[\vec{r}(t) + \vec{r}]/2})], \end{aligned} \tag{19}$$

where

$$G(p(t)) = \frac{1}{(2m^2 \bar{v}^2 \pi)^{3/2}} e^{-p^2(t)/2m^2 \bar{v}^2}. \quad (20)$$

Thus the calculation of $S(k, \omega)$ reduces to the calculation of the trajectories for various initial configurations with distributions of the initial relative coordinate given by the radial distribution function of the full system and the initial relative velocities given by a Maxwellian distribution.

Using the binary-collision cluster expansion for $S(k, \omega)$ we easily check that the second and fourth moments are reproduced exactly. The two-particle and free-particle terms occurring in all the higher moments are also reproduced exactly. In the limit of dilute systems when $g(r) \sim e^{-\beta\Phi(r)}$ the three-particle effects are negligible and hence $S(k)$ is also reproduced correctly. However, for dense systems $S(k)$ is correct only up to order $1/k^2$ and the error is of the order $1/k^4$. Thus, $S(k)$ approaches unity for large k .

In the present paper we have obtained a cluster-expansion scheme which is useful even in the case of hard-core potentials and has much wider applicability than the conventional large- k or large- ω expansion. It also isolates the effect of binary collisions and thus, we hope, will lead to a better understanding of the dynamics in simple liquids.

In Sec. III we present the results of the two-term cluster expansion.

III. RESULTS

Using the spherical symmetry of the interaction potential, the integration over the angles of the initial relative position $r(0)$ with respect to the wave vector k (taken to be in Z direction) is carried out immediately, thus reducing the number of numerical integrations to be performed in Eq. (19). Standard numerical integration procedures are used for the integrations over time and the magnitude of the initial relative position with suitable step size. The Gaussian-quadrature methods are used for the integrations over the magnitudes of the relative momenta and the angles the relative momentum vector makes with the initial relative position. The number of points required to obtain precise values of $S(k, \omega)$ depend on the k value chosen. These parameters are chosen in each case by trial until the values of $S(k, \omega)$ do not vary at least to the third significant figure. The $S(k, \omega)$ thus obtained gives a second moment exact within 1%. The fourth moment in the case of LJ potential compares with the exact value within 1 to 5% in the wave-vector range of 2 to 12 \AA^{-1} .

For both the LJ potential and the hard-sphere potential we have used the corresponding radial distribution function obtained from molecular-

TABLE I. List of typical parameters used in the computation of the dynamic structure factors in liquid argon (where r.u. stands for reduced units).

Wave vector	13.69 r.u.
Number of initial relative position used	200
Step size of the initial position	0.04 r.u.
Number of initial velocities in Gauss-Hermite integration	8
Number of angles the initial relative velocity makes with initial relative position used in Gauss-Legendre integration	12
Step size used in time fourier transform	0.032 r.u.
Time step used in integrating the equation of motion	0.016 r.u.
Exact second moment	2.79 r.u.
Calculated second moment	2.80 r.u.
Exact fourth moment (coherent)	37.02 r.u.
Calculated fourth moment (coherent)	34.88 r.u.
Exact fourth moment (incoherent)	39.89 r.u.
Calculated fourth moment (incoherent)	37.85 r.u.

dynamics computations.¹⁶

Having chosen the initial configuration, we solve Newton's equation of motion using the prescription of Verlet and Levesque.¹⁷ The time step of integration is chosen small enough so that we obtain an accurate trajectory for the times corresponding to the decay time of the integrand in Eq. (19). This can be written as

$$-\frac{1}{\pi} \int \frac{\sin \omega t}{\omega} B(k, t) dt,$$

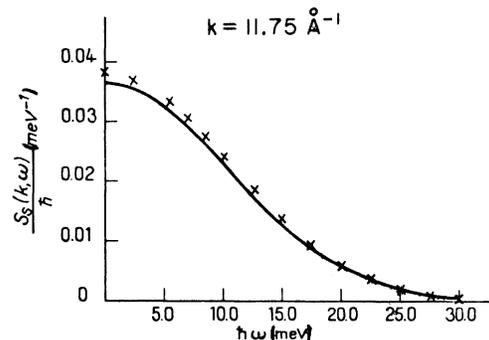


FIG. 1. Plot of $S_s(k, \omega)/\hbar$ vs $\hbar\omega$ at $k=11.75 \text{ \AA}^{-1}$. The crosses indicate the perfect-gas values.

where

$$B(k, t) = \rho \int d\vec{r}(0) \left\{ \int d\vec{p}(0) F(\vec{r}(0), \vec{p}(0), t) \right. \\ \times \frac{d}{dt} \left[e^{-k^2 \bar{v}^2 t^2 / 8} (e^{-i(\vec{k}/2)[\vec{r}(t) - \vec{r}(0)]} \right. \\ \left. \left. + e^{i(\vec{k}/2)[\vec{r}(t) + \vec{r}(0)]} \right) \right] \\ \left. - \frac{1}{2} k^2 \bar{v}^2 t e^{-k^2 \bar{v}^2 t^2 / 4} g(|\vec{r}(0)|) \right\}$$

and

$$B(k, t) \rightarrow 0 \text{ as } t \rightarrow \infty.$$

The condition for the time step of integration requires small step size for small values of wave vector and large step size for large wave vectors. For the case of hard-sphere potentials the calculation of the trajectory is much simpler and we refer the reader to the literature for details.¹⁸

All the calculations are carried out using an IBM 370-165 machine for the case of liquid argon with density of 0.844 and at a temperature of 0.722 in reduced units. For these parameters neutron scattering data are available so that a direct comparison is possible.¹⁹ In Table I we list the various typical parameters for the case of a wave vector of 4.0 Å⁻¹ or 13.62 reduced units.

Even though the theory predicts all ω behavior for large k, a direct comparison with experiments is not possible due to the lack of available data. In Fig. 1 we present a plot of S_s(k, ω) vs ω for a

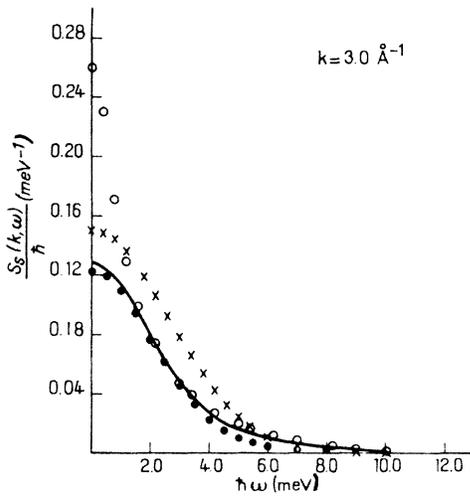


FIG. 2. Plot of S_s(k, ω)/ħ vs ħω at k=3.0 Å⁻¹. The crosses denote perfect-gas values; the circles denote the experiment; the dots denote the present calculation with the hard-sphere model; and the full line denotes the present calculation with the Lennard-Jones (6, 12) potential.

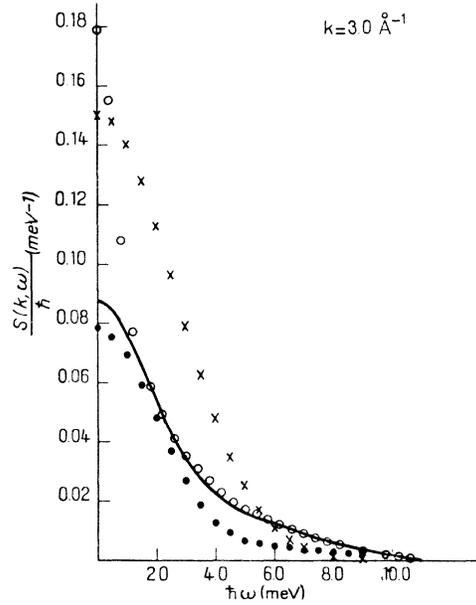


FIG. 3. Plot of S(k, ω)/ħ vs ħω at k=3.0 Å⁻¹. Symbols are the same as in Fig. 2.

large wave vector of 11.75 Å⁻¹. The free gas and the LJ curves approach one another showing the relatively minor importance of the binary collisions in the large-k regime.

For very small wave vectors the theory is valid only for a very large ω where the data are not known precisely or not available. The interesting region is the intermediate values of the wave vec-

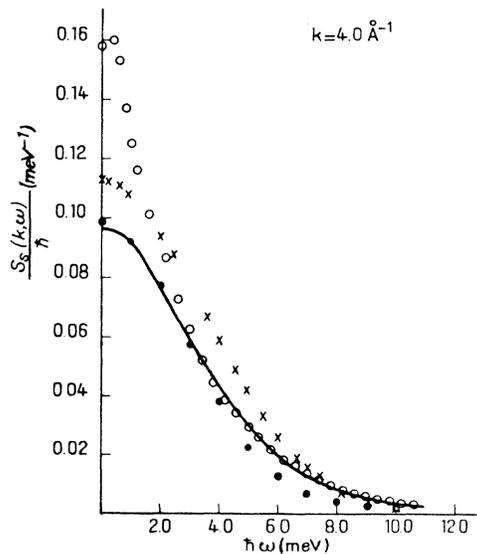


FIG. 4. Plot of S_s(k, ω)/ħ vs ħω at k=4.0 Å⁻¹. Symbols are the same as in Fig. 2.

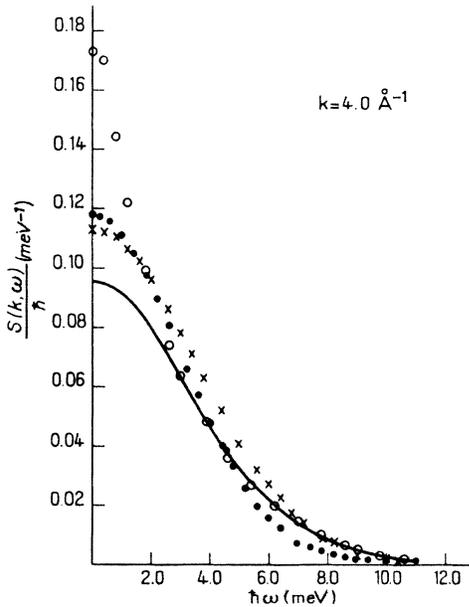


FIG. 5. Plot of $S(k, \omega)/\hbar$ vs $\hbar\omega$ at $k=4.0 \text{ \AA}^{-1}$. Symbols are the same as in Fig. 2.

tor (2 to 4.4 \AA^{-1}) where the high-frequency behavior predicted by the theory can be directly compared to the experiments. In Figs. 2 to 5 we have plotted $S_s(k, \omega)$ and $S(k, \omega)$ vs ω for typical wave vectors of 4.0 and 3.0 \AA^{-1} . In the same plots we have shown the free-gas behavior, experimental results, and the calculations based on the hard-sphere potential. The agreement between the LJ curve and the experiments is very good from ~ 3 to 10.6 meV . At lower frequencies the cluster expansion breaks down and is not useful. The long tail of the hard-sphere model is characteristic of the discontinuous potential. This can be seen more clearly in Fig. 6 where we present $\omega^2 S(k, \omega)$ vs ω . Thus the hard-sphere model seems to be inadequate to describe the high-frequency behavior of $S(k, \omega)$.

Instead of presenting a multitude of curves, we merely point out that the dynamic structure factor

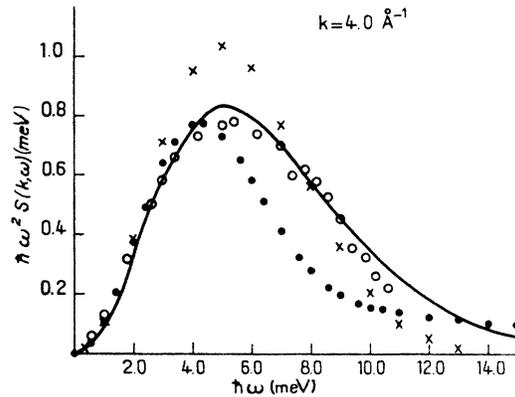


FIG. 6. Plot of $\hbar\omega^2 S(k, \omega)$ vs $\hbar\omega$ at $k=4.0 \text{ \AA}^{-1}$. Symbols are the same as in Fig. 2.

in simple classical liquids can be calculated from first principles in a wide range of (ω, k) values using the cluster-expansion scheme without any adjustable parameters. This scheme also brings out the fact that an analytic potential is too "soft" to describe the repulsive core effects in liquids and the hard-core potential is too "hard" to describe the high-frequency behavior of the dynamic structure factor. This approach complements other attempts²⁰ to extend the region of validity in the $\omega - k\bar{v}$ plane and is useful in understanding the basic dynamical processes in simple classical liquids.

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