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On the Memory Functions in Simple Classical Liquids

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The relation between the two memory function formalisms for correlation functions in classical liquids is discussed. It is found that the kinetic equation formalism of Duderstadt and Akcasu with a simple exponential memory function can account for the double Gaussian form of the memory function in the generalized-hydrodynamics approach. The former therefore gives reasonably good results for the coherent scattering function $\tilde{S}(k, \omega)$, as is shown for the case of liquid Rb at 315 K in the range $1.25 \leqslant k \leqslant 5.5\ \text{Å}^{-1}$.

KEY WORDS: Memory function; classical liquids; kinetic equation; generalized hydrodynamics; dynamical structure factor.

1. INTRODUCTION

Two memory function formalisms(1) have been developed for the analysis of time correlations in classical liquids. One is based on the non-Markovian kinetic equation of the form

$$\begin{aligned}\frac{\partial}{\partial t} F(\mathbf{k}, \mathbf{v}, \mathbf{v}', t) &- i\mathbf{k}\cdot\mathbf{v}F(\mathbf{k}, \mathbf{v}, \mathbf{v}', t) \\ &+ i\mathbf{k}\cdot\mathbf{v}M(\mathbf{v})nC(k) \int F(\mathbf{k}, \mathbf{v}, \mathbf{v}', t)\, d\mathbf{v} \\ &= -\int_0^t dt' \int d\mathbf{v}''\varphi(\mathbf{k}, \mathbf{v}, \mathbf{v}'', t - t')F(\mathbf{k}, \mathbf{v}'', \mathbf{v}', t')\end{aligned} \tag{1}$$

for the correlation function $F(\mathbf{k}, \mathbf{v}, \mathbf{v}', t)$ of density fluctuations in phase space and time.(2–7) The other is based on the generalized hydrodynamics(8–12) and the continued fraction representation of the form(11–14)

$$\tilde{F}(k, s) = S(k)\left(s + \frac{\omega_0^2(k)}{s + [\omega_l^2(k) - \omega_0^2(k)]\tilde{M}(k, s)}\right)^{-1} \tag{2}$$

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for the Laplace transform of the space–time density correlation function $\tilde{F}(k, s)$. Here, $\tilde{M}(k, s)$ is the memory function associated with the longitudinal current correlations.

Both of the formalisms are exact, and the first-principles calculation of the memory functions is rather difficult.(6,7,9,14) The usefulness of the formalisms therefore depends entirely on the choice of a suitable mathematical form for the memory functions, or, alternatively, on selecting a set of appropriate dynamical variables for which the Markovian description is valid.[2] Lebowitz *et al.*(3) and Duderstadt and Akcasu(4) used the ansatz

$$\varphi(\mathbf{k}, \mathbf{v}, \mathbf{v}', t) = W(k, t)\varphi(\mathbf{k}, \mathbf{v}, \mathbf{v}', 0) \tag{3}$$

The latter authors assumed for the memory function $W(k, t)$

$$W(k, t) = \exp[-\alpha(k)t] \tag{4}$$

with

$$\alpha(k) = \alpha(0)[1 + (k/k_0)^2] \tag{5}$$

and proposed a modeled kinetic equation (MKE), which contains a free constant parameter k_0. Despite being such a simple model, the MKE was found to give a good result for the current correlation functions in liquid Ar.(4) Jhon and Forster(6) pointed out and remedied the defect that the MKE fails for small k and ω because of the incorrect hydrodynamic limit of the assumption (3).

The memory function in the continued fraction (CF) formalism, on the other hand, has been shown by Rahman to consist, in the hydrodynamic limit, of two parts arising from dissipations due to viscosity and heat diffusion.(11) He thus assumed a double Gaussian form for the memory function $M(k, t)$ (in time domain). Kahol *et al.*(13) analyzed the experimental(15) and molecular-dynamics(16) data on the dynamical structure factor $S(k, \omega)$ of liquid Rb, showing that the double Gaussian memory function gives quite good agreement with the data in the range $0.174 \leqslant k \leqslant 3.5$ Å^{-1}, while a single Gaussian form is sufficient for $k \gtrsim 3.5$ Å^{-1}.

The purpose of the present paper is to discuss the relation between the MKE formalism and the CF formalism. We note here that the memory function $M(k, t)$ in the CF formalism contains the effect of the free-particle motion, which gives no contribution to the memory function $W(k, t)$ in the MKE. We may therefore expect a simpler form for $W(k, t)$ than for $M(k, t)$ to obtain a result of the same quality. This is an advantage of the kinetic equation approach, in which various microscopic processes are treated explicitly and separately, in contrast to the hydrodynamic approach. Our

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[2] If such a "complete" set of the dynamical variables is found, it is easy to determine the memory function. See, e.g., Refs. 7 and 9.

numerical calculation will be restricted in this paper to liquid Rb in the range of wave numbers 1.25–5.5 Å^{-1}, where the experimental data of Copley and Rowe are available.(12) In this region of relatively large wave numbers, the MKE is expected to be valid, and we shall not consider in this paper the memory function of Jhon and Forster.(6) The assumption (5) in the MKE is, however, too simple to account for a marked k dependence of the relaxation time (see Fig. 1). We shall therefore treat $\alpha(k)$ as a free parameter.

In Section 2 we shall relate the MKE to the CF representation (2) and find the memory function $\tilde{M}(k, s)$ that corresponds to the exponential one in the MKE. The parameter $\alpha(k)$ is determined through the quantity $\tilde{M}(k, s = 0)$, which can be interpreted as a generalized relaxation time and is given experimentally by the value of $\tilde{S}(k, \omega)$ at $\omega = 0$. In Section 3 it is found that the memory function $M(k, t)$ in time domain behaves like a double Gaussian. The MKE with the simple exponential memory function therefore takes good account of the two distinct decays of $M(k, t)$ found in the CF approach, and gives a good representation of the experimental data on $\tilde{S}(k, \omega)$. Section 4 is devoted to a discussion of the results.

2. MEMORY FUNCTION IN LAPLACE DOMAIN

In this section we shall relate the MKE to the CF representation to find the memory function $\tilde{M}(k, s)$, and then discuss the relaxation time $\tilde{M}(k, 0)$ to determine the parameter $\alpha(k)$.

2.1. Relation Between the Two Formalisms

The relation can be found if we construct from the MKE an equation for the longitudinal current correlation function, and thus find the memory function $M(k, t)$ associated with the current correlations. Equivalently, this can be done in Laplace domain by solving the MKE and by comparing the result for the density correlation function $\tilde{F}(k, s)$ with the CF representation (2). The MKE can be solved analytically,(3,6) and $\tilde{F}(k, s)$ is given by Eq. (8.17) of Ref. 3, which we rewrite in the following form:

$$\tilde{F}(k, s) = S(k)[s + \tilde{L}'(k, s)]^{-1} \tag{6}$$

where

$$\tilde{L}'(k, s) = [1 - nC(k)]b(k, s)/a(k, s) \tag{7}$$

$$b(k, s) = 1 - s\tilde{\chi}(k, s) \tag{8}$$

$$a(k, s) = s^{-1}\{1 - [1 - s\tilde{W}(k, s)k^{-2}A(k)]b(k, s)\} \tag{9}$$

Here, $S(k)$ is the static structure factor, n the number density, $C(k)$ the direct correlation function,

$$\tilde{\chi}(k, s) = e^{\kappa^2}\kappa^{-2(z+\kappa^2)}\gamma(z + \kappa^2, \kappa^2)/\zeta(s) \tag{10}$$

$$\tilde{W}(k, s) = [s + \alpha(k)]^{-1}$$

$$A(k) = nC(k)k^2 - m\beta\Omega_k{}^2$$

$$\Omega_k{}^2 = \frac{n}{m}\int \cos(kz)g(r)\frac{\partial^2 v(r)}{\partial z^2}\,d\mathbf{r} \tag{11}$$

$$\zeta(s) = \Omega_0{}^2\tilde{W}(k, s), \qquad z = s/\zeta(s), \qquad \kappa^2 = k^2/m\beta\zeta^2(s)$$

where m is the mass of an atom, and $\beta = (k_{\mathrm{B}}T)^{-1}$, T being the temperature. In (10), $\gamma(z + \kappa^2, \kappa^2)$ is the incomplete γ function, and in (11), $g(r)$ is the pair distribution function and $v(r)$ the pair potential.

The large-s behavior of $\tilde{\chi}(k, s)$ is found to be

$$\tilde{\chi}(k, s) \sim \frac{1}{s} - \frac{k^2}{m\beta}\frac{1}{s^3} + \frac{k^2}{m\beta}\left(\frac{3k^2}{m\beta} + \Omega_0{}^2\right)\frac{1}{s^5} - \frac{k^2}{m\beta}\Omega_0{}^2\alpha(k)\frac{1}{s^6} + \cdots \tag{12}$$

from which we see that the memory function $\tilde{L}'(k, s)$ can be written as

$$\tilde{L}'(k, s) = \omega_0{}^2(k)\tilde{L}(k, s) = \omega_0{}^2(k)\{s + [\omega_l{}^2(k) - \omega_0{}^2(k)]\tilde{M}(k, s)\}^{-1} \tag{13}$$

where the memory functions $\tilde{L}(k, s)$ and $\tilde{M}(k, s)$ are normalized such that $s\tilde{L}(k, s) \to 1$ and $s\tilde{M}(k, s) \to 1$ for $s \to \infty$, or in time domain

$$L(k, t = 0) = M(k, t = 0) = 1 \tag{14}$$

In (13), $\omega_0{}^2(k)$ and $\omega_l{}^2(k)$ defined by

$$\omega_0{}^2(k) = k^2/m\beta S(k) \tag{15}$$

$$\omega_l{}^2(k) = 3k^2/m\beta + \Omega_0{}^2 - \Omega_k{}^2 \tag{16}$$

are the ratio of the second and zeroth moments of the coherent scattering function $\tilde{S}(k, \omega) = \pi^{-1}\,\mathrm{Re}\,\tilde{F}(k, i\omega)$, and that of the fourth and second moments, respectively. Equation (14) is obvious since the MKE formalism correctly satisfies the zeroth-, second-, and fourth-moment sum rules. Comparing the correlation function $\tilde{F}(k, s)$ given by (6), (7), and (13) with (2), we see that the MKE gives the following memory function for the longitudinal current correlations:

$$\tilde{M}(k, s) = \frac{1}{\omega_l{}^2(k) - \omega_0{}^2(k)}\left(\frac{k^2}{m\beta}\frac{a(k, s)}{b(k, s)} - s\right) \tag{17}$$

which is not simply the Laplace transform of an exponential or Gaussian function. The inverse Laplace transformation will be carried out in the next section to see the behavior of the memory function in time domain. We now determine the unknown parameter $\alpha(k)$.

2.2. Relaxation Time

To find a convenient method of determining $\alpha(k)$, we consider the area under the curve $M(k, t)$,

$$\tau(k) = \int_0^\infty M(k, t)\, dt = \tilde{M}(k, s = 0) \tag{18}$$

which can be interpreted as a relaxation time so long as $M(k, t)$ does not take large, negative values or oscillate strongly. Note that the relaxation time $\tau(k)$ is defined without specifying a mathematical form of $M(k, t)$, and can be found experimentally from the $\tilde{S}(k, 0)$ value through the relation

$$\tilde{S}(k, 0) = [S(k)(\omega_l^2 - \omega_0^2)/\pi\omega_0^2]\tau(k) \tag{19}$$

We see from (19) that two memory functions with the same relaxation time result in the agreement of $\tilde{S}(k, \omega)$ at $\omega = 0$. In the case of the memory function (17), we have

$$\tau(k) = \frac{1}{\alpha(k)}\left\{1 + \frac{\Omega_0^2}{\omega_l^2 - \omega_0^2}[J(\kappa) - 1] - \frac{k^2 v_0^2}{\omega_l^2 - \omega_0^2}\right\} \tag{20}$$

where

$$J(\kappa) = e^{\kappa^2}\kappa^{2(1-\kappa^2)}\gamma(\kappa^2, \kappa^2) \qquad \text{and} \qquad v_0^2 = 2/m\beta$$

Although the MKE is not a good approximation at small ω, we determine, as a convenient method,(5) the parameter $\alpha(k)$ such that the relaxation time (20) coincides with the experimental one. We have evaluated the experimental relaxation time using the results for $\tilde{S}(k, 0)$ and $S(k)$ of Copley and Rowe on liquid Rb at 315 K. The experimental results for the fourth moment of $\tilde{S}(k, \omega)$ are unreliable,(12) and use has been made of the analytical expression of $\omega_l(k)$ given by Hubbard and Beeby,(17) with the parameters chosen to be $\omega_E^2 = \Omega_0^2 = 36.84\ \text{psec}^{-2}$ and $r_0 = 4.4048$ Å.(18,16) The results are shown in Fig. 1. We have also plotted in Fig. 1 the relaxation time (20) with the assumption (5) for $\alpha(k)$, where $\alpha(0) = 5.96\ \text{psec}^{-1}$ has been determined from the known value of the shear viscosity, $\eta_s = 6.7 \times 10^{-3}$ P.(18) It is seen that the assumption (5) fails to describe the k dependence of the experimental relaxation time. The relaxation time (20) has a lower limit

$$\tau_\infty(k) = \tfrac{1}{2}\pi^{1/2}kv_0/(\omega_l^2 - \omega_0^2) \tag{21}$$

corresponding to $\alpha(k) \to \infty$. In this limit the MKE reduces to the linearized Vlasov equation studied by Nelkin and Ranganathan.(19) The relaxation time $\tau_\infty(k)$ has also been plotted in Fig. 1. If the experimental relaxation time lies below $\tau_\infty(k)$, the relaxation time (20) cannot be made to coincide with the experimental one. This occurs for $k \geqslant 4.5$ Å^{-1} except at $k = 5.0$ Å^{-1}. For

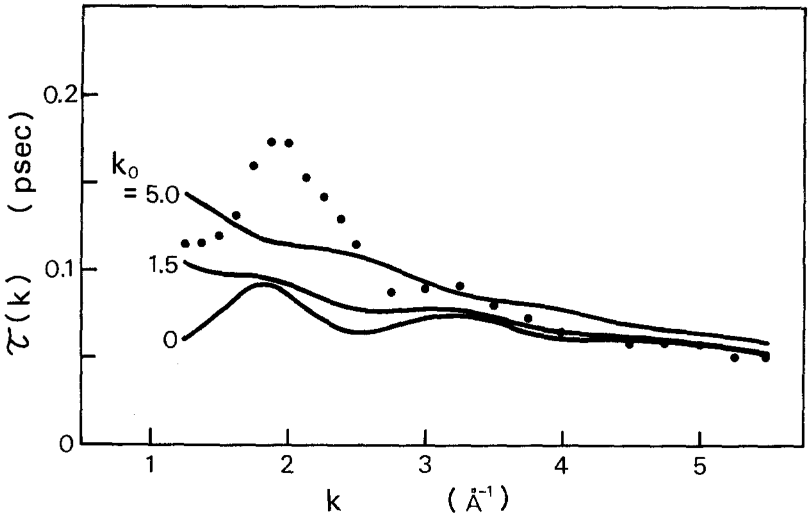

Fig. 1. The relaxation time $\tau(k)$ for liquid Rb at 315 K. The dots denote the experimental results of Copley and Rowe,(15) as obtained from Eq. (19). The solid curves show $\tau(k)$ defined by Eq. (20) with the assumption (5) for $\alpha(k)$ with three values of k_0 (in Å^{-1}). The curve for $k_0 = 0$ represents the collisionless limit, Eq. (21).

Table I. Wave Number Dependence of the Parameters[a]

k, Å^{-1}	$\tau(k)$, psec	$\tau'(k)$, psec	$\alpha(k)$, psec^{-1}	$y(k)$
1.25	0.1146	0.1669	8.50	0.795
1.50	0.1190	0.1691	7.61	0.694
1.75	0.1596	0.1635	4.12	0.561
2.0	0.1725	0.1813	3.42	0.517
2.5	0.1150	0.1472	6.64	0.552
3.0	0.0895	0.0928	9.33	0.390
3.5	0.0804	0.0815	10.4	0.295
4.0	0.0646	0.0647	38.0	0.319
4.5	0.0602	0.0588	∞	—
5.0	0.0570	—	284	0.202
5.5	0.0510	—	∞	—

[a] $\tau(k)$ is the experimental relaxation time shown in Fig. 1; $\tau'(k)$ is calculated from Eq. (18) for the double Gaussian memory function of Kahol *et al.*(13); $\alpha(k)$ is determined by Eq. (20) with the experimental relaxation time $\tau(k)$; and $y(k)$ is defined by Eq. (23).

such a large k the mean field treatment is valid, and we put $\alpha(k) = \infty$. The values of $\alpha(k)$ thus determined are listed in Table I.

3. NUMERICAL RESULTS

We now proceed to calculate the memory function $M(k, t)$ in time domain. We have seen that $M(k, t)$ is normalized to unity at $t = 0$ and decays to zero as $t \to \infty$ [see (18), where $\tau(k)$ is finite]. The short-time behavior of $M(k, t)$ is of interest here, since it gives some idea of whether $M(k, t)$ behaves like a Gaussian or an exponential. From the asymptotic expansion (12) it follows that

$$M(k, t) = 1 - y(k)\alpha(k)t + \cdots \tag{22}$$

The initial decay rate $\alpha(k)$ of the original memory function $W(k, t)$ is thus converted to $y(k)\alpha(k)$, where

$$y(k) = 1 - k^2v_0^2/(\omega_l^2 - \omega_0^2) \tag{23}$$

By virtue of the inequality

$$\omega_l^2 - \omega_0^2 \geqslant k^2v_0^2 \geqslant 0 \tag{24}$$

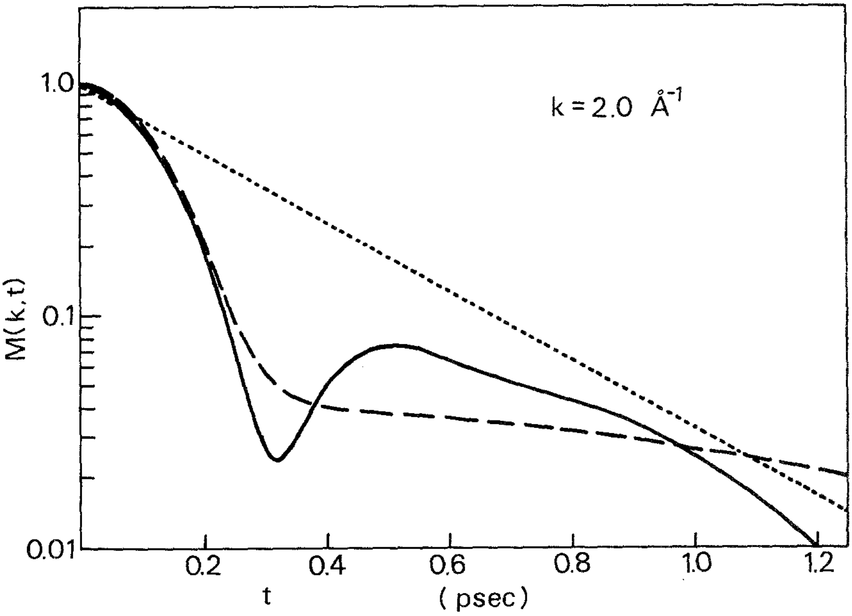

Fig. 2. The memory function $M(k, t)$ (solid line) at $k = 2.0$ Å^{-1}, corresponding to the exponential memory function (dotted line) in the MKE. The double Gaussian memory function (dashed line) of Kahol *et al.*[13] is shown for comparison.

which has been proved by Kugler [see Eq. (B6) of Ref. 5], we see that $0 \leqslant y(k) \leqslant 1$. Also, we easily see that $y(k) \rightarrow 0$ for $k \rightarrow \infty$, and that $y(k) \simeq 1$ at $k = 0$ since the longitudinal sound velocity(20) $C_3 = \lim_{k\rightarrow 0} \omega_l(k)/k$ and the isothermal sound velocity $C_T = v_0/[2S(0)]^{1/2}$ are much larger than v_0. The memory function $M(k, t)$ therefore decays initially like a Gaussian for large k and an exponential for small k. The values of $y(k)$ in the case of liquid Rb are given in Table I.

An analytical calculation of the inversion integral of $\tilde{M}(k, s)$ seems difficult because of the complicated s dependence of $\tilde{M}(k, s)$, and we have carried out a numerical integration. The result for $k = 2.0$ Å^{-1} is plotted in Fig. 2. The original exponential memory function in the MKE and the double

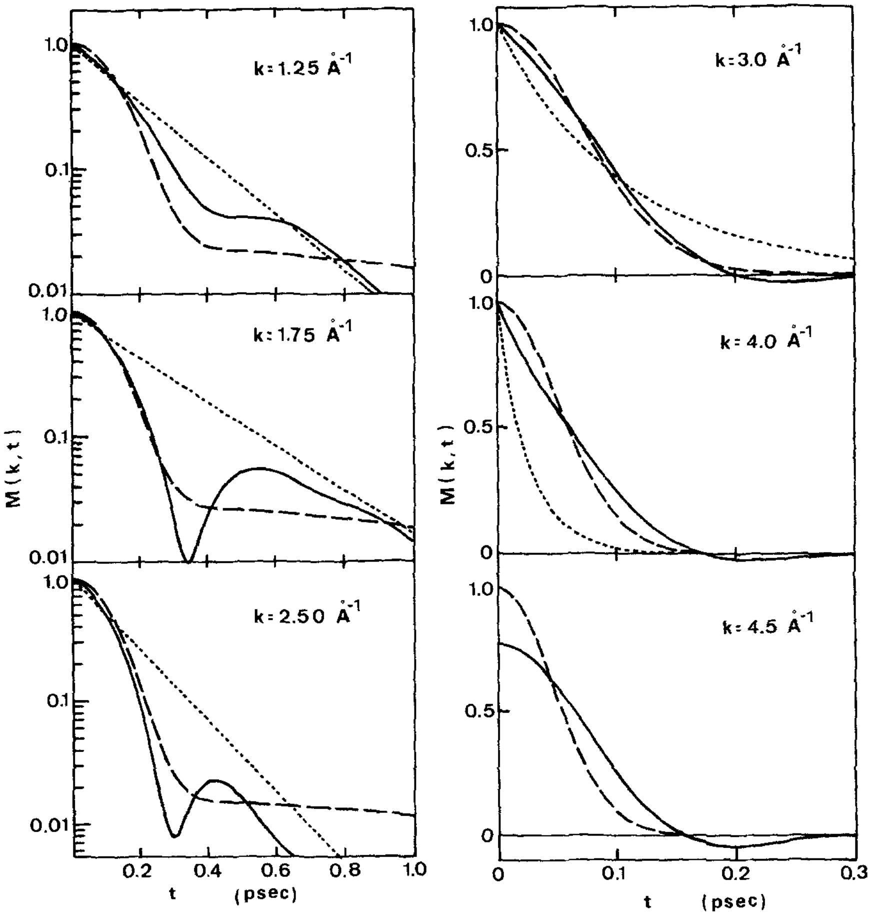

Fig. 3. Same as Fig. 2, for other values of k. The solid line for $k = 4.5$ Å^{-1} is the result of the collisionless approximation.

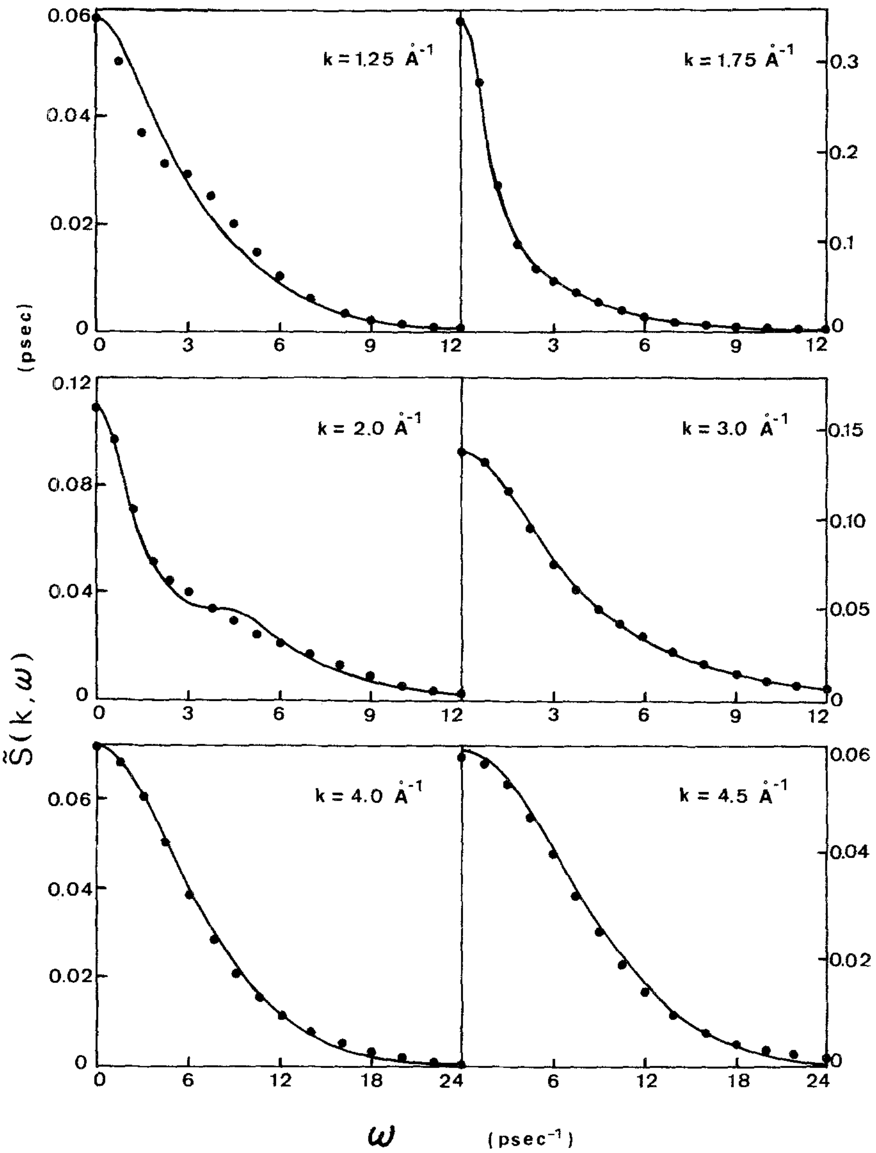

Fig. 4. Symmetrized scattering function $\tilde{S}(k, \omega)$ for liquid Rb as a function of ω. The solid lines are the results of the MKE with the parameter $\alpha(k)$ given in Table I. The dots denote the experimental data of Copley and Rowe.[15]

Gaussian memory function given by Kahol *et al.*(13) have also been shown for comparison. A striking qualitative similarity of $M(k, t)$ to the double Gaussian memory function is seen; that is, $M(k, t)$ exhibits two distinct decays, an initial, Gaussian-like fast decay followed by a much slower one. It should be mentioned that the relaxation times of the two memory functions are not in agreement, as seen in Table I[3]; the quantitative comparison is therefore meaningless.

Similar results have been found for other values of k, as shown in Fig. 3. As k increases, the memory effect in the MKE becomes less important; the memory function $M(k, t)$ then becomes nearly Gaussian, again in good qualitative agreement with the result of Kahol *et al.*(13) The memory function at $k = 4.5$ Å^{-1} is the result of the collisionless limit. In this limit the fourth-order sum rule is violated, and $M(k, 0) = (kv_0)^2/(\omega_l^2 - \omega_0^2) \neq 1$.

To see the validity of the memory functions obtained above, we have calculated the scattering function $\tilde{S}(k, \omega)$, and compared with the experimental results of Copley and Rowe for the symmetrized scattering function. As seen in Fig. 4, the agreement is reasonably good, showing that the MKE takes good account of the effects of the two distinct decays of $M(k, t)$. The structure(15) in the experimental result at $k = 2.0$ Å^{-1} is seen to be somewhat exaggerated. A qualitative disagreement is seen at $k = 1.25$ Å^{-1}, where the structure is missing from the present result; the memory function $M(k, t)$ in this case is not very different from the exponential one. This seems to indicate the inadequacy of the simple exponential memory function (4) in the MKE.[4]

4. DISCUSSION

It has been shown that the MKE with the exponential memory function can account for the double Gaussian decay of the memory function $M(k, t)$ in the CF formalism. The reason for this is that, although the MKE is a single-relaxation-time model, the Vlasov terms also contribute to the memory function $M(k, t)$. At large k's, the memory term is unimportant and the Vlasov terms give rise to a nearly Gaussian decay of $M(k, t)$. At smaller k's their effects are mixed together in $M(k, t)$ to exhibit the two distinct decays. This mixing has been seen in (20) for the relaxation time and in (22) for the initial decay of $M(k, t)$. For k smaller than about 1.3 Å^{-1} (in the case of liquid Rb), the simple exponential model (4) seems inadequate. For much smaller k

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[3] The reason for this is that the values of $\tilde{S}(k, \omega = 0)$ in Ref. 13 do not agree with experiment, and also that in Ref. 13, Rahman's molecular-dynamics data are used for $S(k)$ and $\omega_l(k)$.

[4] The discrepancy is not due to the incorrect hydrodynamic limit of the MKE; heat conduction effects are important only for $k \lesssim 0.35$ Å^{-1}, as seen from the recent work by Sjögren and Sjölander.(21) It is therefore desirable to examine the MKE in the range $0.35 \lesssim k \lesssim 1.2$ Å^{-1} with sufficiently accurate data of $S(k)$, $\omega_l(k)$, and $S(k, \omega)$.

($k \lesssim 0.35$ Å^{-1}), the assumption (3) breaks down and the memory function of Jhon and Forster(6) should be used.

The fact that the exponential memory function gives good results is worth noting, since it suggests that the memory effect arises from a certain well-defined physical quantity, which has been made hidden in the kinetic equation (1) by the projection method. The parameter $1/\alpha(k)$ can be interpreted in terms of the proper lifetime (or a relaxation time) of this physical quantity. In a previous paper(7) we have considered zero sound as a hidden quantity to derive a kinetic equation of the form (1). The memory effect arises in this case from the finite duration of the collision between atoms that occurs through the intermediary of zero sound. The relaxation time of the memory function is thus of the order of magnitude of the lifetimes of the zero-sound waves, which has been found to be 1–0.1 psec; this is consistent with the values of $\alpha(k)$ found in the present paper. The kinetic equation derived in the previous paper, however, does not give the correct fourth moment, and an improvement of the theory is now under consideration. Searches for such a hidden variable are very much in demand to calculate the memory function from first principles and to better understand the dynamical behavior of simple classical liquids.

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