PHYSICAL REVIEW E VOLUME 54, NUMBER 4 OCTOBER 1996

Time correlation functions of classical fluids: A self-consistent approach

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(Received 4 March 1996)

The hierarchy of the Mori-Zwanzing continued fraction representation has been studied by expressing the memory function in terms of its lower-order memory function. The short-time behavior of the memory function is exactly incorporated through sum rules by scaling its lower-order memory function. This scheme provides a self-consistent evaluation of the memory function and hence of the time correlation function. Expressions obtained for transport coefficients have been found to be exactly the same as those obtained by Joslin and Gray [Mol. Phys. **58**, 789 (1986)]. The approach has been applied to study the velocity autocorrelation function of the Lennard-Jones fluids and a good agreement with molecular dynamics data is obtained for dense fluids. [S1063-651X(96)11709-8]

PACS number(s): 51.10.+y, 66.10.−x

I. INTRODUCTION

The time correlation function (TCF) is a fundamental quantity for the study of transport properties of a fluid state of matter, as all the macroscopic transport coefficients can be related to the TCF of an appropriate variable through the Green-Kubo formulas. At present, sufficient information is available about time evolution of various TCFs. This has been possible because of the combined efforts made by performing neutron scattering experiments, computer simulations, and theoretical calculations. Theoretically, TCFs are generally evaluated using Mori's equation of motion which expresses the TCF in terms of first order memory function (MF). Application of Mori's equation of motion [1] to first order MF will express its time evolution in terms of the second order MF. Following this procedure, one can generate a chain of non-Markovian type coupled equations. This approach, in fact, reduces the problem of the calculation of TCF to the calculation of any of the MF. However, this formalism [2,3] has an advantage that one can develop phenomenological theories [4,5] for the calculation of MF and can still preserve some of the exact properties of the TCF. Microscopically, if one expresses the MF as a sum of the binary collision contribution and a term reflecting the long-time behavior, the latter part can be calculated using the kinetic theory [6] or the mode coupling [5] approximation whereas, the first term can be obtained microscopically by the method recently developed by Pathak, Ranganathan, and Johnson [7]. During the last decade, many researchers [8–10] have replaced the second term by its TCF itself or the quadratic of it or their linear combinations. This procedure has its relevance in the study of supercooled liquids and glass transitions. More recently, the third stage MF has been written [11] as a linear combination of first and second order MFs and the TCF itself. In the present work, we propose to express the $(n+1)$th stage MF in terms of the nth stage MF alone. The short-time contribution to MF is taken care of by scaling the nth stage MF through the use of sum rules. Thus this will avoid expressing the MF as a sum of two terms which are important at two different time scales. Our approach provides a self-consistent evaluation of the MF and, hence, of the TCF. Expressions obtained for the generalized transport coefficients have been found to be exactly the same as those obtained by Joslin and Gray (JG) [12] by employing a different kind of approach. Here, it may be mentioned that in the JG approach one can not determine the time dependence of the TCF.

The procedure proposed here has been applied to the study of the velocity autocorrelation function (VACF) of Lennard-Jones (LJ) fluids at a few densities and temperatures. It is found that our method provides a good agreement with the computer simulation results for the time development of VACF of dense fluids.

The paper is organized as follows: In Sec. II the theoretical formalism is presented. Results and discussion are given in Sec. III, and the conclusion in Sec. IV.

II. THEORETICAL FORMALISM

The generalized transport coefficient τ can be written as a time integral of an appropriate time correlation function $C(t)$ through the Green-Kubo relation [2] which is given as

$$\tau = K\int_0^\infty C(t)dt, \tag{1}$$

where K is a thermodynamic constant. The time evolution of $C(t)$ can be obtained by using Mori's [1] equation of motion given as

$$\frac{\partial}{\partial t}C(t) = -\int_0^t M_1(t-t')C(t')dt', \tag{2}$$

where $M_1(t)$ is the first order MF. In order to calculate $C(t)$ from the above equation the fundamental theoretical quantity to be calculated is $M_1(t)$. The calculation of $M_1(t)$ is a complicated task due to the appearance of a projection operator in its definition. However, it follows from the procedure used in deriving Eq. (2) that $M_1(t)$ also satisfies an equation similar to Eq. (2). A generalization of this procedure leads to

$$\frac{\partial}{\partial t} M_n(t) = -\int_0^t M_{n+1}(t-t')M_n(t')dt', \quad n=1,2,3,\ldots, \tag{3}$$

where $M_n(t)$ is the nth order MF. We define the Fourier-Laplace transform $\widetilde{C}(\omega)$ of $C(t)$ as

$$\widetilde{C}(\omega) = i\int_0^\infty dt\ \exp(i\omega t)C(t). \tag{4}$$

Taking the Fourier-Laplace transform of Eqs. (2) and (3), we obtain the continued fraction representation of $\widetilde{C}(\omega)$ given as

$$\widetilde{C}(\omega) = -\frac{C(t=0)}{\omega+\widetilde{M}_1(\omega)}, \tag{5a}$$

$$\widetilde{M}_n(\omega) = -\frac{\delta_n}{\omega+\widetilde{M}_{n+1}(\omega)}, \quad n=1,2,3,\ldots, \tag{5b}$$

where $\delta_n = M_n(t=0)$, are called Mori coefficients which are related to the frequency sum rules (up to $2n$th order) of the spectral function of the time correlation function. In order to calculate $\widetilde{C}(\omega)$ from Eq. (5) it is necessary to close the continued fraction at some stage. One of the procedures to close the hierarchy is to choose a phenomenological form for the lower-order MFs $[M_1(t)$ or $M_2(t)]$. Secondly, one can develop approximate microscopic theories within the kinetic or mode coupling approaches. In these approaches, the MF is expressed as a sum of two parts: the first part reflecting the short-time behavior and the second dominating at longer times. Recently, it has been shown [11] that the third order MF may be expressed as a linear combination of its lower-order MFs and the time correlation function itself. In the present work, we propose to write the $(n+1)$th stage MF in terms of the scaled nth stage MF only. This certainly reduces the number of variables required to study the time evolution of TCF. Our proposal is given as

$$M_{n+1}(t) = A_n M_n(\alpha_n t), \tag{6}$$

where A_n and α_n are the two parameters to be determined. Equation (6) also implies that the functional form of the MF at two adjacent stages is the same at any time. For example, if $M_n(t)$ is exponential in time then Eq. (6) implies that $M_{n+1}(t)$ is also exponential in time, though with a different decay constant.

The parameter A_n is easily calculable from Eq. (6) at $t=0$ and we obtain

$$A_n = \frac{M_{n+1}(t=0)}{M_n(t=0)} = \frac{\delta_{n+1}}{\delta_n}. \tag{7}$$

The Taylor series expansion of any MF $[M_n(t)]$ is given as [13]

$$M_n(t) = \delta_n\left(1-\frac{t^2\delta_{n+1}}{2!}+\cdots\right). \tag{8}$$

Using this equation for the expansion of Eq. (6) on both sides and comparing the coefficients of t^2, we obtain

$$\alpha_n = \left\{\frac{\delta_{n+2}}{\delta_{n+1}}\right\}^{1/2}. \tag{9}$$

Thus we see that Eq. (6) incorporates Mori coefficients up to δ_{n+2} and, hence, it satisfies the sum rules of TCF up to $(2n+4)$th order. Taking the Fourier-Laplace transform of Eq. (6), we obtain

$$\widetilde{M}_{n+1}(\omega) = iA_n\int_0^\infty M_n(\alpha_n t)\exp(i\omega t)\ dt. \tag{10}$$

After a change of variable in the integral in the above equation, we obtain

$$\widetilde{M}_{n+1}(\omega) = \frac{A_n}{\alpha_n} M_n(\omega/\alpha_n). \tag{11}$$

Substituting the above equation in (5b), we obtain

$$\widetilde{M}_n(\omega) = -\frac{\delta_n}{\omega+(A_n/\alpha_n)\widetilde{M}_n(\omega/\alpha_n)}. \tag{12}$$

Equation (12) can be solved self-consistently for $\widetilde{M}_n(\omega)$. Once $\widetilde{M}_n(\omega)$ is determined, $\widetilde{C}(\omega)$ is readily calculable from Eq. (5a). Using Eqs. (1) and (4), one can obtain the relation

$$\tau^{(n)} = -iK\widetilde{C}(0), \tag{13}$$

where n is the stage where approximation (6) is to be employed. From Eqs. (5) and (13) we obtain $\tau^{(n)}$ for two adjacent stages of continued fraction given as

$$\tau^{(2n-1)} = iK\frac{\delta_0\delta_2\cdots\delta_{2n-2}}{\delta_1\delta_3\cdots\delta_{2n-3}\widetilde{M}_{2n-1}(0)}, \quad n>1 \tag{14}$$

$$\tau^{(2n-2)} = iK\frac{\delta_0\delta_2\cdots\delta_{2n-2}\widetilde{M}_{2n-2}(0)}{\delta_1\delta_3\cdots\delta_{2n-3}}, \quad n>1\,. \tag{15}$$

Equation (12) at $\omega=0$ provides

$$\widetilde{M}_n(0) = i\delta_n\left\{\frac{\delta_{n+2}}{\delta_{n+1}^3}\right\}^{1/4}. \tag{16}$$

Substituting Eq. (16) in Eqs. (14) and (15), we obtain

$$\tau^{(2n-1)} = \pi^{(2n)}\left\{\frac{1}{\delta_{2n+1}\delta_{2n}}\right\}^{1/4} \tag{17}$$

and

$$\tau^{(2n-2)} = \pi^{(2n)}\left\{\frac{\delta_{2n-1}}{\delta_{2n}^3}\right\}^{1/4}, \tag{18}$$

where

$$\pi^{(2n)} = K\frac{\delta_0\delta_2\cdots\delta_{2n}}{\delta_1\delta_3\cdots\delta_{2n-1}}. \tag{19}$$

Expressions (17) and (18) can be used to calculate the transport coefficients by knowing the frequency sum rules of the spectral function of $C(t)$. Here, it may be noted that Eqs.

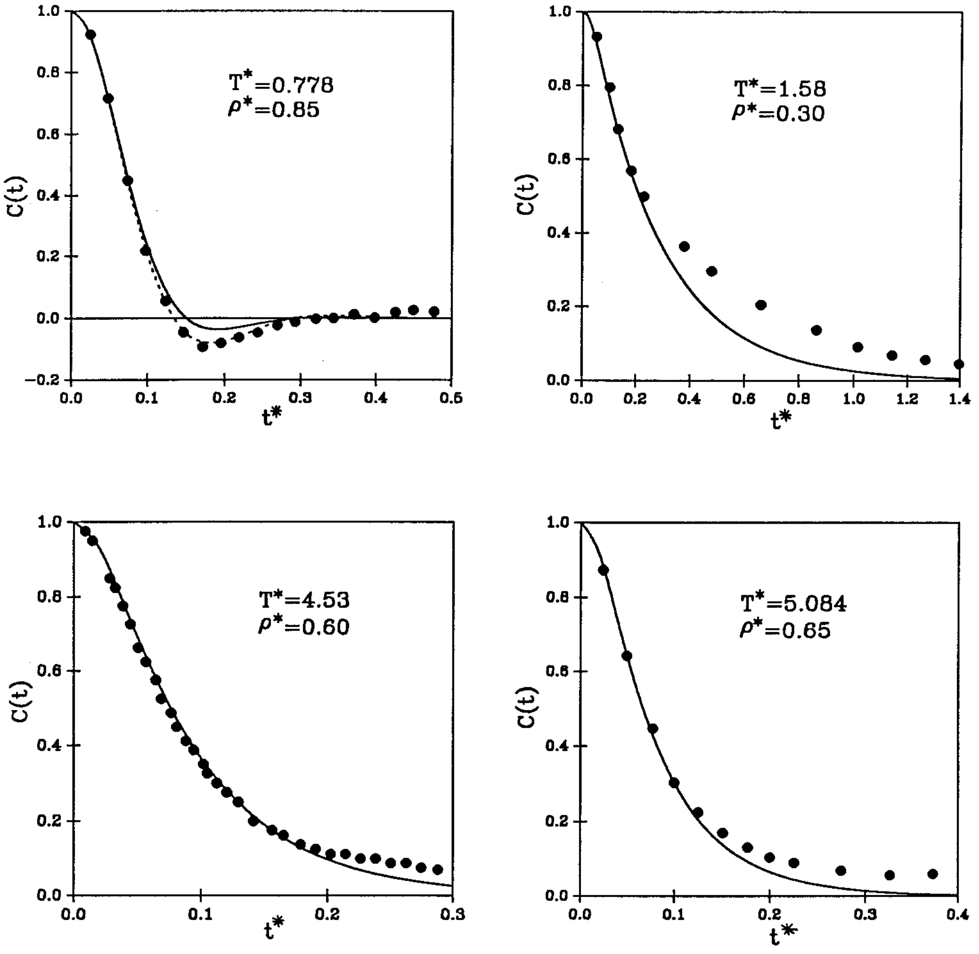

FIG. 1. Variation of the normalized VACF $c(t)$ with time $t^\star = t(\varepsilon/m\sigma^2)^{1/2}$ obtained for four thermodynamic states of LJ fluids. Solid lines are our results, whereas full circles represent MD data. The dotted line is the result obtained when δ_n are taken from MD simulations.

(17) and (18) are exactly the same as those obtained by JG by taking the geometric mean of the transport coefficients obtained at two adjacent stages of the continued fraction. However, unlike in our method, in the JG approach one was not able to obtain the time dependence of the correlation function. The procedure developed above is quite general and can be applied to calculate any space-time correlation function of the fluid by knowing the frequency sum rules. Exact expressions for the sum rules up to sixth order of the VACF and up to fourth order for the stress and energy current density autocorrelations are now available in the literature [14]. These involve pair potential and the static correlation functions up to five particles. The three and higher static correlation contributions to the sum rules have been expressed in terms of pair contributions by using low-order decoupling approximations. It is noted that the use of decoupling approximations does not introduce any significant error in the numerical estimates of the sum rules, as has been judged by comparing the results with the computer simulation evaluation of sum rules of the VACF [14], stress correlation function [14], and current correlation functions [15,16], except at the triple point. In fact, it is the availability of the sum rules which makes the formalism useful.

III. RESULTS AND DISCUSSION

Since we know δ_n up to $n=3$ for the VACF from theory [14] as well as from computer experiments [17] for the LJ fluids, so in this section we use the formalism developed above to calculate the time development of VACF for the case when $n=1$ which sets

$$M_2(t) = A_1 M_1(\alpha_1 t). \tag{20}$$

Writing $\widetilde{M}_1(\omega) = \widetilde{M}_1'(\omega) + i\widetilde{M}_1''(\omega)$, we obtain from Eq. (12)

$$\widetilde{M}_1'(\omega) = -\frac{\delta_1\left\{\omega + \dfrac{A_1}{\alpha_1}\widetilde{M}_1'(\omega/\alpha_1)\right\}}{\left[\omega + \dfrac{A_1}{\alpha_1}\widetilde{M}_1'(\omega/\alpha_1)\right]^2 + \left[\dfrac{A_1}{\alpha_1}\widetilde{M}_1''(\omega/\alpha_1)\right]^2}, \tag{21}$$

$$\widetilde{M}_1''(\omega) = \frac{\delta_1\left\{\dfrac{A_1}{\alpha_1}\widetilde{M}_1''(\omega/\alpha_1)\right\}}{\left[\omega + \dfrac{A_1}{\alpha_1}\widetilde{M}_1'(\omega/\alpha_1)\right]^2 + \left[\dfrac{A_1}{\alpha_1}\widetilde{M}_1''(\omega/\alpha_1)\right]^2}. \tag{22}$$

The two parameters A_1 and α_1 are determined from Eqs. (7) and (9) with δ_n taken from our earlier work [14]. Equations (21) and (22) are solved simultaneously in a self-consistent manner as follows: By choosing an initial guess for $\widetilde{M}_1'(\omega/\alpha_1)$ and $\widetilde{M}_1''(\omega/\alpha_1)$ we calculate $\widetilde{M}_1'(\omega)$ and $\widetilde{M}_1''(\omega)$ from Eqs. (21) and (22), respectively. $\widetilde{M}_1'(\omega/\alpha_1)$

and $\widetilde{M}''_1(\omega/\alpha_1)$ are then calculated by using a spline interpolation, as α_1 in the present case is always greater than 1. The results thus obtained are used to generate a new set of $\widetilde{M}'_1(\omega)$ and $\widetilde{M}''_1(\omega)$. The process is repeated until the two successive iterations yield the same results within a tolerance of 0.01%. Further, it is noted that the final results for $\widetilde{M}'_1(\omega)$ and $\widetilde{M}''_1(\omega)$ do not depend on the initial guess for these and the solution was obtained after about 25 iterations for the densities and temperatures investigated here. Defining the power spectrum of VACF $f(\omega)$ as

$$f(\omega)=2\widetilde{C}''(\omega)=2\int_0^\infty \cos(\omega t)C(t)dt, \tag{23}$$

with

$$\widetilde{C}''(\omega)=\frac{\widetilde{M}''_1(\omega)}{\{\omega+\widetilde{M}'_1(\omega)\}^2+\{\widetilde{M}''_1(\omega)\}^2}. \tag{24}$$

The VACF can be obtained from $f(\omega)$ as

$$C(t)=\frac{1}{\pi}\int_0^\infty \cos(\omega t)f(\omega)d\omega. \tag{25}$$

Results obtained for normalized $c(t)$ for four thermodynamic states are shown in Fig. 1 as solid lines. The solid circles represent the molecular dynamics (MD) results of Lee and Chung [17]. It can be seen from Fig. 1 that our results are in reasonably good agreement with the simulation data for the four thermodynamic states which are chosen to represent a wide range of fluid. It is seen that our results show backscattering effects at triple point ($T^*=k_Bt/\varepsilon=0.778$ and $\rho^*=\rho\sigma^3=0.85$, where σ and ε are two parameters of the LJ fluid). The agreement of our results (shown as a dotted line) with MD data of $c(t)$ is further improved if we use the MD values of δ_n at triple point. Here, it may be noted that our theoretical calculations of δ_n involve the use of superposition and a low order decoupling approximation for the triplet and quadruplet correlation functions, respectively, which have been found to show maximum deviation from MD values near the triple point. Further, it can be noted from Fig. 1 that our approach provides $c(t)$ in close agreement with the simulation results only up to $t^*=0.2$. It implies that our method does not predict the correct higher order sum rules particularly for gases. In order to see the behavior of MF obtained in our method, we plot normalized $M_1(t)$ in Fig. 2 near the triple point. The MD results of Kushick and Berne [18] are shown there as solid circles. The dotted line is the result when sum rules are taken from the MD data. From Fig. 2, it can be seen that the agreement with the MD data and the dotted line is very good. Thus our method provides an interpretation of MD results for both $M_1(t)$ and $c(t)$ near the triple point.

For dilute gas one expects $c(t)$ to decay exponentially, as the molecular chaos approximation is valid for dilute gases; therefore the corresponding first order MF is a δ function in time. However, our method assumes that the functional form of the two adjacent MFs are the same, which is clearly not the case for very dilute gas. This implies that our approach is not suitable for the evaluation of self-diffusion coefficients of very dilute gases. It was found in our earlier work [14] that the deviation of the calculated self-diffusion coefficient from the computer simulation data increases with a decrease in density. Thus we conclude that our approach is quite successful in predicting the time dependence of TCF and, hence, for the self-diffusion coefficient of the dense fluids only. The values of the shear viscosity and thermal conductivity obtained from this procedure, which provides the same expressions for transport coefficients as obtained by JG, are also found to be in reasonable agreement over a wide range of fluid as had earlier been reported in our work [14] and in the work of Heyes and Powles [19].

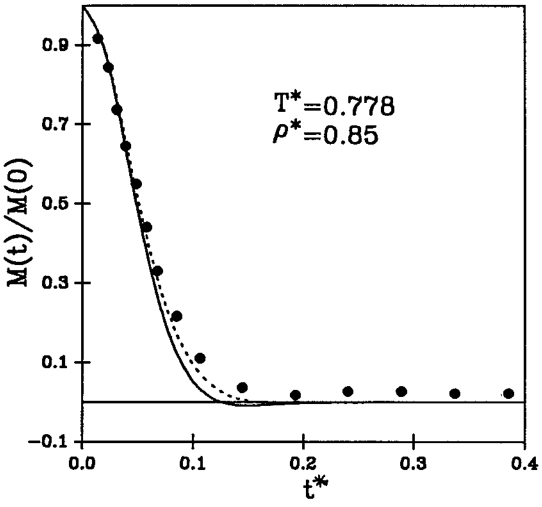

FIG. 2. Variation of the normalized MF with time $t^*=t(\varepsilon/m\sigma^2)^{1/2}$. Solid lines are our results, whereas full circles represent MD results. The dotted line is the result when δ_n are taken from MD simulations.

IV. CONCLUSION

In this paper we have proposed a method of expressing the MF in terms of its lower order MF. The short-time behavior is taken care of by scaling the lower-order MF whereas, the long-time behavior of the two adjacent MFs has been assumed to be similar. This provides a self-consistent evaluation of the MF and, hence, of the TCF. The scaling parameter is determined so as to satisfy the sum rules of the spectral function of the TCF. The intermediate and long-time behaviors are determined self-consistently. Thus the method avoids writing the MF as a sum of two terms, which are important at two different time scales. Here, it may be noted that recently Larsson [20] has argued that the binary collision term reflecting short-time dynamics may not be separable from the recollision term which is important only at long times. However, at present there exists no work in which both contributions have been calculated microscopically for fluids interacting via the continuous interaction potential and, hence, needs more investigation.

Expressions obtained for transport coefficients are found to be exactly the same as those obtained by JG by employing a different approach. In addition to this, our approach is suitable for determining the time development of any space-time correlation function by knowing the corresponding sum rules which require interatomic potential as only input. As an application, the results are obtained for the time development of the VACF and MF. It is found that our approach provides a good interpretation of the MD data, except near the critical point of the LJ fluids.

ACKNOWLEDGMENTS

R.K.S. and R.K.M. gratefully acknowledge financial assistance from the University Grants Commission, New Delhi. We are extremely grateful to Professor K. N. Pathak for useful suggestions and discussions.

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