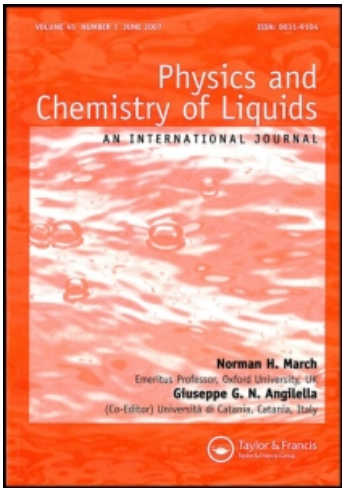
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Derivation of memory function from its equation of motion

Shaminder Singh[a]; Sunita Srivastava[a]; C. N. Kumar[a]; K. Tankeshwar[a]
[a] Department of Physics, Panjab University, Chandigarh - 160 014, India

Online publication date: 13 May 2010

To cite this Article Singh, Shaminder , Srivastava, Sunita , Kumar, C. N. and Tankeshwar, K.(2003) 'Derivation of memory function from its equation of motion', Physics and Chemistry of Liquids, 41: 6, 567 — 574
To link to this Article: DOI: 10.1080/00319100310001613001
URL: http://dx.doi.org/10.1080/00319100310001613001

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Physics and Chemistry of Liquids
Vol. 41, No. 6, December 2003, pp. 567–574

Taylor & Francis
Taylor & Francis Group

DERIVATION OF MEMORY FUNCTION FROM ITS EQUATION OF MOTION

SHAMINDER SINGH, SUNITA SRIVASTAVA,
C.N. KUMAR and K. TANKESHWAR*

Department of Physics, Panjab University, Chandigarh – 160 014, India

(Received 12 April 2003)

Downloaded At: 07:48 28 January 2011

A new form of Memory Function (MF) appearing in the Mori's formalism has been derived using plausible approximations. In addition to the fact that present form of MF satisfies sum-rules upto sixth order, it has special characteristic of presence of one more adjustable parameter. It is also found that the present form of MF behaves as $\mathrm{sech}^{\nu}(bt)$ under suitable conditions. The utility of the present MF is exemplified by studying time evolution of velocity auto correlation function and transport coefficients of Lennard–Jones fluids.

Keywords: Memory function; Diffusion; Viscosity; Thermal conductivity

1. INTRODUCTION

A considerable amount of work has been carried out in recent years to study the time evolution of Time-Correlation Functions (TCFs) and transport coefficients of fluids. The TCFs can be studied theoretically through Mori's equation [1–3]. The role of Mori's Memory Function (MF) formalism in the study of transport and dynamical properties of fluids is of considerable importance as it allows to avoid difficult calculations of the exact TCF for a given realistic system. The exact calculation of TCF is impossible for a fluid as it involves a many-body problem. So reduction of the problem of studying TCF to the calculation of the appropriate MF is an important step in the theoretical analysis of atomic motion in fluids. Since the exact microscopic calculation of MF is not yet feasible, in general, a simple approximation to the MF can be made which preserves a number of important properties of TCF irrespective of the approximation introduced for MF. Therefore, quite a few number of phenomenological forms [4–10] of MF have been proposed in the past. These include functions like Gaussian [2], simple exponential, square of hyperbolic secant and hyperbolic secant [4–6] to evaluate the transport coefficients of classical Lennard–Jones (LJ) fluids.

*Corresponding author.

ISSN 0031-9104 print: ISSN 1029-0451 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/00319100310001613001

We have recently proposed a MF [11], which was found to yield quite satisfactory results for the calculation of transport coefficients over a wide range of densities and temperatures. The form of MF was a function of density and temperature of the system, which we derived from Mori's equation itself by proposing a plausible ansatz for the third order MF. Following a similar procedure, we now put forward a new form of MF in the present work. The resulting form of the MF satisfies the first six sum-rules. This new form of the MF in addition to satisfying sum-rules up to sixth order has an additional parameter. The utility of the presently derived MF has been exemplified by studying the time development of Velocity Auto-Correlation Function (VACF) and self-diffusion coefficient of LJ fluids. The results obtained have been compared with Molecular Dynamics (MD) Simulation results [12,14]. To determine the shear viscosity, η, and thermal conductivity, λ, of the fluids with the knowledge of sum-rules [4] up to fourth order only, we apply similar approximations at one stage lower in Mori's continued fraction. This, instead of providing an expression for the MF, directly yields a functional form of the TCF. This functional form has been used to calculate η and λ of LJ fluids. The results are compared with non-equilibrium MD results [12].

The lay out of the article is as follows: in Section 2 we present the derivation of the new form of the MF. In Section 3, the results are discussed.

Downloaded At: 07:48 28 January 2011

2. THEORY

Transport coefficients can be written as a time integral of an appropriate TCF with the help of a Green–Kubo relation given as

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

where κ represents any transport coefficient, $C(t)$ is an appropriate TCF and K is some thermodynamic quantity. In particular, κ would represent the self-diffusion coefficient when $C(t)$ represents the VACF, and κ shall represent shear viscosity and thermal conductivity when $C(t)$ is the transverse Stress Auto-Correlation (TSC) function and Energy Current Density (ECD) correlation function, respectively. Mori's equation of motion which determines the evolution of a given TCF, $C(t)$ is given as

$$\frac{dC(t)}{dt} + \int_0^t M_1(t-\tau)C(\tau)\, d\tau = 0, \tag{2}$$

where $M_1(t)$ is the first order MF. The $M_1(t)$ satisfies an equation similar to Eq. (1) i.e.,

$$\frac{dM_1(t)}{dt} + \int_0^t M_2(t-\tau)M_1(\tau)\, d\tau = 0. \tag{3}$$

Writing $M_2(t)$ in terms of $M_3(t)$ in the same way as that in Eq. (2) and using it in the time derivative of Eq. (2) we obtain

$$\frac{d^2M_1(t)}{dt^2} + \delta_2 M_1(t) + \int_0^t M_3(t-\tau)\frac{dM_1(\tau)}{d\tau}\,d\tau = 0, \tag{4}$$

with $\delta_2 = M_2(0)$. This equation is still an exact relation. Now we make use of an approximation to write $M_3(t-\tau)$ as a product of two functions of t and τ.

$$\begin{aligned} M_3(t-\tau) &\to M_3(t)f(M_1(\tau)) \\ &= M_3(t)\frac{M_1^{\alpha}(\tau)}{M_1^{\alpha}(0)} \end{aligned} \tag{5}$$

This approximation is exact for $\tau = 0$ and provides a correction to Markovian approximation for $\tau < t$. Writing $M_3(t-\tau)$ as a product of two functions implies that for a function even in time, coupling between t and τ is ignored, which may be good approximation for a system where long time dynamics is not all that significant. Using Eqs. (4) and (5) we obtain the following expression

$$\ddot{M}_1(t) + \delta_2 M_1(t) + M_3(t)\frac{(M_1^{\alpha+1}(t) - M_1^{\alpha+1}(0))}{(\alpha+1)M_1^{\alpha}(0)} = 0. \tag{6}$$

We further assume the following form of $M_3(t)$

$$M_3(t) = A\frac{M_1^{\alpha+2}(t)}{M_1^{\alpha+2}(0)} + B\frac{M_1(t)}{M_1(0)}. \tag{7}$$

This approximation is similar to ideas used in super cooled liquids and glass transition theory based on feedback phenomenon [13]. From Eqs. (6) and (7) we obtain

$$\ddot{M}_1(t) + \left(\delta_2 - \frac{B}{\alpha+1}\right)M_1(t) + \frac{(B-A)M_1^{\alpha+2}(t)}{(\alpha+1)M_1^{\alpha+1}(0)} + \frac{AM_1^{2\alpha+3}}{(\alpha+1)M_1^{2\alpha+2}(0)} = 0. \tag{8}$$

One of the solution of this equation is given by

$$M_1(t) = \frac{M_1(0)(1+\gamma)^{1/(\alpha+1)}}{(1+\gamma\cosh(kt))^{1/(\alpha+1)}}, \tag{9}$$

where

$$k = [(\alpha+1)(B - \delta_2(\alpha+1))]^{1/2},$$

$$\gamma = \frac{\delta_2}{B - \delta_2(\alpha+2)},$$

Downloaded At: 07:48 28 January 2011

and

$$B = \frac{\delta_2(\alpha+2)(\alpha+3) - \delta_3}{(\alpha+1)},$$

which is true for α not equal to -1. In above equations and what follows, δ_n are related to sum-rules of the corresponding TCF through following relations

$$\delta_0 = C_0, \quad \delta_1 = \frac{C_2}{C_0}, \quad \delta_2 = \frac{C_4}{C_2} - \frac{C_2}{C_0}, \quad \delta_3\delta_2 = \frac{C_6}{C_2} - \left(\frac{C_4}{C_2}\right)^2,$$

where C_0, C_2, C_4 and C_6 are zeroth, second, fourth and sixth order sum-rules of corresponding TCF, $C(t)$, respectively. Equation (9) is a new form of MF and satisfies sum-rules exactly upto sixth order and still has an additional parameter α. Thus the parameter α will not affect the short time properties of the TCF.

For $\gamma = 1$ the Eq. (9) reduces to the following expression

$$M_1(t) = \delta_1 \mathrm{sech}^{\nu}\left(\sqrt{\frac{\delta_2}{\nu}}t\right), \tag{10}$$

with $\nu = 2/(\alpha+1)$. This is the form of MF derived by us [11] earlier. Further for $\alpha = 1$, Eq. (9) reduces to the expression gives as

$$M_1(t) = \frac{M_1(0)(1+\gamma)^{1/2}}{[1+\gamma\cosh(kt)]^{1/2}}, \tag{11}$$

with

$$k = (8\delta_2 - \delta_3)^{1/2},$$

and

$$\gamma = \frac{2\delta_2}{6\delta_2 - \delta_3}.$$

It may be noted that for $\delta_3 = 4\delta_2$, γ becomes unity and Eq. (11) provides an expression of $M_1(t)$ given as

$$M_1(t) = \delta_1 \mathrm{sech}\left(\sqrt{\delta_2}t\right). \tag{12}$$

Thus the MF, given by Eq. (9) can be thought of as modification over MF given by Eqs. (10) and (12), which have been frequently used. The MF given by Eq. (9) has an advantage over Eqs. (10) and (12), as it has an additional parameter α.

Downloaded At: 07:48 28 January 2011

In order to study time dependence of $C(t)$, we use the Fourier–Laplace transform $\tilde{C}(\omega)$ of $C(t)$ which can be written as

$$\tilde{C}(\omega) = -\frac{C(t=0)}{\omega + \tilde{M}_1(\omega)}, \tag{13}$$

where $\tilde{M}_1(\omega)$ is the Fourier–Laplace transform of $M_1(t)$. The expression for $C(t)$ in terms of its spectral function, $f(\omega) = 2\tilde{C}''(\omega) = 2\int_0^\infty C(t)\cos(\omega t)\,dt$ is given as

$$C(t) = \frac{1}{\pi}\int_0^\infty \cos(\omega t) f(\omega)\,d\omega. \tag{14}$$

Using definition of $f(\omega)$ and Eq. (13) we can write the expression of $C(t)$ given as

$$C(t) = \frac{2}{\pi}\int_0^\infty \frac{\tilde{M}_1''(\omega)\cos(wt)}{(\omega + \tilde{M}_1'(\omega))^2 + (\tilde{M}_1''(\omega))^2}\,d\omega, \tag{15}$$

where $\tilde{M}_1'$ and $\tilde{M}_1''$ are real and imaginary parts of Fourier–Laplace transform of $M_1(t)$ and are, respectively, given as

$$\tilde{M}_1'(\omega) = -\delta_1(1+\gamma)^{1/(\alpha+1)}\int_0^\infty \frac{\sin(\omega t)}{(1+\gamma\cosh(kt))^{1/(\alpha+1)}}\,dt, \tag{16}$$

and

$$\tilde{M}_1''(\omega) = \delta_1(1+\gamma)^{1/(\alpha+1)}\int_0^\infty \frac{\cos(\omega t)}{(1+\gamma\cosh(kt))^{1/(\alpha+1)}}\,dt. \tag{17}$$

The Green–Kubo expression for the self-diffusion coefficients can be written in terms of zero frequency Fourier–Laplace transform of $M_1(t)$ as

$$D = \frac{k_B T}{m}\frac{1}{\tilde{M}_1''(0)}. \tag{18}$$

We calculate $\tilde{M}_1''(0)$ from Eq. (17), the expression thus obtained for self-diffusion coefficients is given by

$$D = \frac{k_B T}{m}\frac{k}{I\,\delta_1(1+\gamma)^{1/(\alpha+1)}}, \tag{19}$$

where

$$I = \int_0^\infty (1+\gamma\cosh(x))^{-1/(\alpha+1)}dx,$$

and k_B is Boltzmann constant.

In order to calculate shear viscosity, η and thermal conductivity, λ we follow the same procedure but at one step lower than in the case diffusion coefficients. We now

Downloaded At: 07:48 28 January 2011

apply conditions given by Eqs. (5) and (7) at Eq. (2) instead of at Eq. (3). This is due to the fact that sum-rules of TSC and ECD functions are known only up to fourth order. Thus we obtain an expression of η and λ given as

$$\eta = \frac{n\,\delta_0(1+\gamma)^{1/(\alpha+1)} I}{k\,k_B\,T}, \tag{20}$$

and

$$\lambda = \frac{n\,\delta_0(1+\gamma)^{1/(\alpha+1)} I}{k\,k_B\,T^2}, \tag{21}$$

where γ and k are now given as

$$\gamma = \frac{\delta_1}{B - \delta_1(\alpha+2)},$$

$$k = [(\alpha+1)(B - \delta_1(\alpha+1))]^{1/2},$$

with

$$B = \frac{\delta_1(\alpha+2)(\alpha+3) - \delta_2}{(\alpha+1)}.$$

We shall use these expressions to calculate shear viscosity and thermal conductivity of LJ fluids.

Downloaded At: 07:48 28 January 2011

3. RESULTS AND DISCUSSION

In order to study the multifarious advantages of the MF derived in the present work, we have investigated time development of VACF and transport coefficients of LJ fluids. In addition to the fact that present MF satisfies exactly the first six sum-rules, it has special characteristic of presence of a parameter α, which gives us freedom to study the behaviour of VACF for different values of α. The results obtained for VACF for $\alpha = 0.1$, 1.0, 2.0, 5.0 and 10.0 are shown in Fig. 1 near the triple point of LJ fluids ($n^* = n\sigma^3 = 0.85$ and $T^* = k_B T/\epsilon = 0.778$, where σ and ϵ are the parameters of LJ potential). The MD results are also depicted in Fig. 1 as solid circles. It can be seen from the figure that time development of $C(t)$ varies significantly with variation in α. However, short time behaviour is essentially same as guided by the sum-rules. The self-diffusion coefficient $D^*(= D(m/\epsilon\sigma^2)^{1/2})$ which is area under the curve for $\alpha = 0.1$, 1.0, 2.0, 5.0 and 10.0 are, respectively, 0.0444, 0.0429, 0.0407, 0.0355 and 0.0322. The MD value of D^* is 0.0335. Thus we see that the effect of α on self diffusion is not as significant as in the variation of $C(t)$.

We have also studied shear viscosity and thermal conductivity by using expressions (20) and (21). The results obtained for shear viscosity, $\eta^*(= \eta\sigma^2(m\epsilon)^{-1/2})$ and thermal conductivity, $\lambda^*(= (\lambda\sigma^2/k_B)(m/\epsilon)^{1/2})$ at few thermodynamic states are shown in Figs. 2 and 3, respectively along with MD results. It is found that our results are reasonably good for $\alpha = 3$.

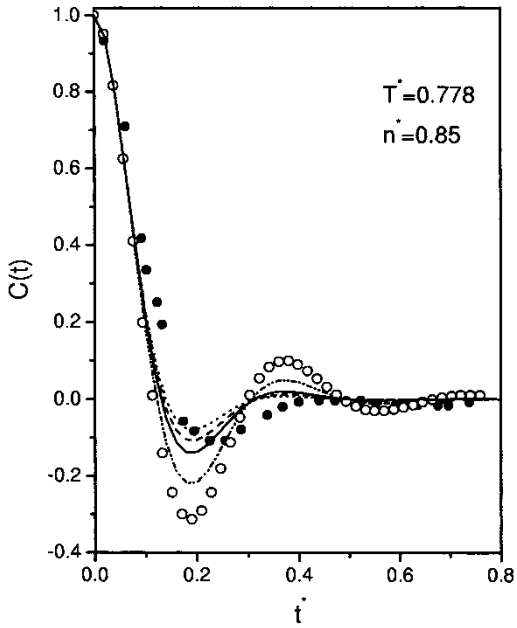


FIGURE 1 Variation in $C(t)$ with $t^* = t(\epsilon/m\sigma^2)^{1/2}$ for different values of α. Solid circles represent the MD results. Dotted line, dashed line, solid line, dash dot line and open circles represent the variation of $C(t)$ for $\alpha = 0.1$, 1.0, 2.0, 5.0 and 10.0 respectively.

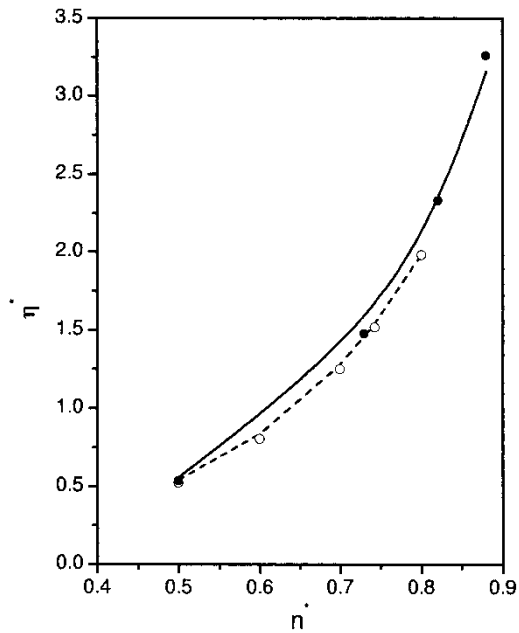


FIGURE 2 Variation in shear viscosity, η^* with density, n^*. Solid line represents our results and solid circles represent the MD results at $T^* = 1.06$. Dashed line represents our results and open circles are MD results at $T^* = 1.84$.

Downloaded At: 07:48 28 January 2011

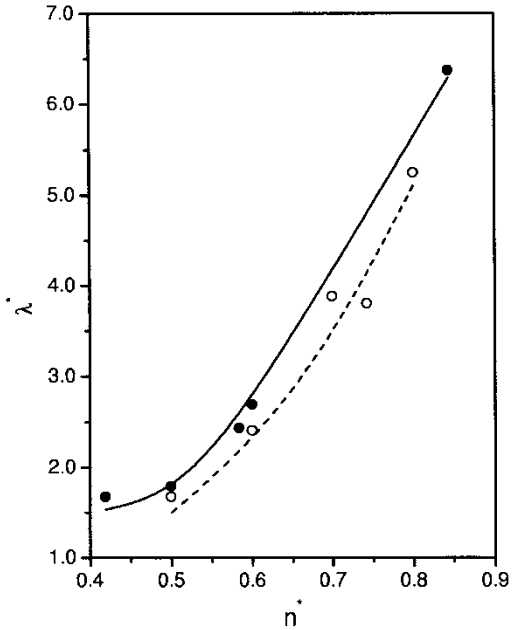


FIGURE 3 Variation in thermal conductivity, λ^* with density, n^*. Solid line represents our results and solid circles represent the MD results at $T^* = 1.23$. Dashed line represents our results and open circles are MD results at $T^* = 1.81$.

Thus we see that the MF presented here has advantage of an additional parameter α, which effects intermediate and long time behaviour of the time evolution of a TCF. Such a model is expected to be more useful for investigating line shape of coherent and incoherent scattering functions of fluids.

Downloaded At: 07:48 28 January 2011

References

[1] H. Mori (1958). *Phys. Rev.*, **112**, 1829.
[2] J.P. Boon and S. Yip (1980). *Molecular Hydrodynamics*. McGraw-Hill, New York.
[3] W. Götze (1991). In: J.P. Hansen, D. Levesque and J. Zinn-Justin (Eds.), *Liquids, Freezing and Glass Transition*. Elsevier Science, North Holland.
[4] K. Tankeshwar, K.N. Pathak and S. Ranganathan (1987). *J. Phys. C: Solid State Phys.*, **20**, 5749; *ibid* (1988). **21**, 3607; *ibid* (1989). **1**, 6181; *ibid* (1990). **2**, 5891.
[5] K. Tankeshwar, G.S. Dubey and K.N. Pathak (1988). *J. Phys. C: Solid State Phys.*, **21**, L811.
[6] D. M. Heyes and J.G. Powles (1990). *Mol. Phys.*, **71**, 781.
[7] U. Balucani, V. Tognetti and R. Vallauri (1979). *Phys. Rev.*, **A 19**, 177.
[8] K. Tankeshwar and K.N. Pathak (1995). *J. Phys.: Condens. Matter*, **7**, 5729.
[9] M.H. Lee (1996). *J. Phys.: Condens. Matter*, **8**, 3755.
[10] K. Tankeshwar and K.N. Pathak (1994). *J. Phys.: Condens. Matter*, **6**, 591.
[11] Singh Shaminder, C.N. Kumar and K. Tankeshwar (2002). *Mod. Phys. Lett.*, **B 16**, 739.
[12] D.M. Heyes (1983). *J. Chem. Soc. Faraday Trans.*, **2**, 79, 1741; *ibid* (1984). **80**, 1363.
[13] R.L. Jacobs (1986). *J. Phys.*, **C19**, L119.
[14] L.L. Lee and T.H. Chung (1982). *J. Chem. Phys.*, **77**, 4650.