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Mori's Memory Function Formalism and Shear Viscosity

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Abstract – Memory function appearing in the Mori's memory function formalism has been used to evaluate the Shear viscosity of Lennard - Jones (LJ) fluids. The functional form of this memory function depends upon the thermodynamic state and at the same time it may be mentioned that the memory function is derivable from a equation of motion for the development of time correlation function (TCF). The results so obtained are compared with Molecular Dynamics simulation results.

Keywords: Shear Viscosity, Transport Coefficient, Sum Rules, Time Correlation Function, Molecular Dynamics Simulation, Fluid

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INTRODUCTION

In past four decades a considerable progress has been made to provide more and more accurate microscopic theories for the prediction of transport coefficients of fluids like shear viscosity. One of the approach which has been extensively used is through the time evolution of the time correlation function. The exact calculation of time correlation function for all times is not possible for a fluid, particles of which are interacting via realistic interaction potential, as it involves the solution of many body system. Therefore, in the past Mori's equation[1] of motion has been used. The Mori's equation reduces the problem of calculation of TCF to a problem of calculation of memory function which appears in the equation of motion. Though, there exists microscopic expression for the memory function, its exact evaluation is again not possible. Therefore the approximations based on mode coupling approach and kinetic theory have been employed in the past. These microscopic approaches have not yet been coupled with microscopic expressions for the two particle's contribution to TCF.

The second approach is to choose more and more appropriate phenomenological form of the memory function. In the past memory function like gaussian, simple exponential, hyperbolic secant and square of hyperbolic secant have been used to predict transport coefficients of classical fluids. It has been noticed, in all these attempts, that none of phenomenological function corresponding to gaseous and liquid state of the system predicts transport coefficients with uniform accuracy over complete range of densities and temperatures. Therefore, search for functional form of memory function which changes its form with density and temperature, a form of memory function[2] which satisfy these properties. In this paper the functional form of memory function and frequency sum rules of transverse stress correlation function are used to calculate shear viscosity of LJ fluids over a wide range of density and temperature. The results obtained are in good agreement with the computer simulation results.

THEORY

Transport coefficients can be written as time integral of appropriate time correlation function in terms of Green Kubo relation given by

$$\tau = K \int_0^\infty C_2(t)dt \qquad (1)$$

where τ is representing any transport coefficients, C(t) is an associated time correlation function and K is some thermodynamic quantity. For example τ will be self-diffusion coefficient when C(t) is TCF of velocity of a tagged particle. Mori's equation of motion which determines the time evolution of C(t) is given as

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

where $M_1(t)$ is first order memory function. The $M_1(t)$ satisfies an equation similar to equation

(2) i.e.,

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

Writing $M_2(t)$ in terms of $M_3(t)$ in a same way as that in equation (3) and using it in the time derivative of equation (3) we obtain

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

With $\delta_2 = M_2(0)$. This equation is still an exact relation. Using some plausible approximation for third order memory function we obtain an equation which is given as

$$\ddot{M}_1(t) = M_1(t)\left(\frac{\delta_3}{\alpha+1} - \delta_2\right) - \frac{\delta_3}{\alpha+1}\frac{M_1^{\alpha+2}(t)}{M_1^{\alpha+1}(0)} \qquad (5)$$

Here α is some constant to be determined and $\delta_3 = M_3(0)$. The Solution of this equation is given by

$$M_{1(t)} = \delta_1 \operatorname{sech}^{\nu}\left(\sqrt{\frac{\delta_2}{\nu}}\,t\right), \qquad (6)$$

with

$$\nu = \frac{2}{(\alpha+1)} = \frac{2\delta_2}{\delta_3 - 2\delta_2} \qquad (7)$$

This is new form of memory function which we shall be using. Here the parameter ν which is related to sum rules which in turn depends upon density and temperature. This will determine the functional form of memory function. Here, it may be noted that for very large value of ν this memory function exactly reproduces the gaussian model, whereas for $\nu=1$ and 2 it represents hyperbolic secant form and square of hyperbolic secant form of memory function.

The memory function given by equation (6) combined with equation (1) and (2) provide an expression for the transport coefficient given as

$$\tau = K\frac{\sqrt{\delta_2}}{\delta_1\sqrt{\nu}\int_0^{\infty}\operatorname{sec}h^{\nu}(x)dx} \qquad (8)$$

These δ_n are related to sum rule of corresponding TCF upto $2n^{th}$ order. On the other hand if the same procedure is used at one step before i.e. at equation (2) instead of equation (3) we obtain expression of transport coefficient given as

$$\tau = K\frac{\delta_0}{\sqrt{\delta_1}}\sqrt{\nu}\int_0^{\infty}\operatorname{sec}h^{\nu}(x)dx \qquad (9)$$

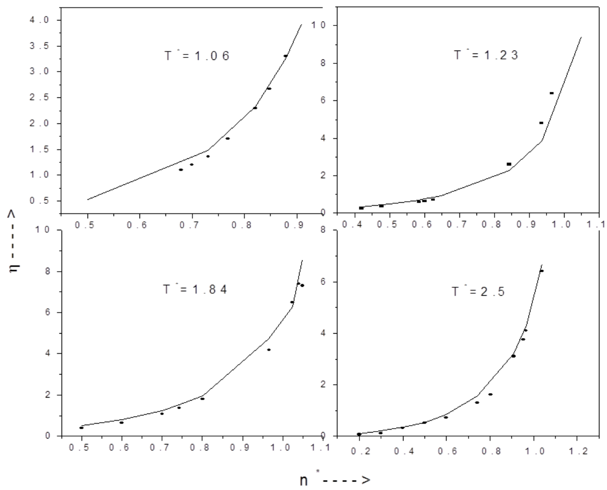

Fig.1: Variation of shear viscosity(reduced units) vs reduced density for four reduced temperatures. Full curves –our results. Dots are simulation results.

RESULTS AND DISCUSSION

The expressions discussed above can be used to calculate the appropriate transport coefficients with the use of frequency sum rules at various temperatures and densities of the fluid. The numerical results for the sum rules transverse stress correlation (TSC) function are already available[3]. Using these results for sum rules of TSC function and equation (9) with $K=1/Vk_BT$, where V is volume, k_B Boltzmann constant and T is temperature.

The shear viscosity η^* $(=\eta\sigma^2(m\varepsilon)^{-1/2})$ for different value of T^* $(=k_BT/\varepsilon)$ and $n^*(=n\sigma^3)$ is calculated. The comparison of results with the computer simulation results are shown in Fig.1, where solid dots represent simulation results of Heyes[4] and lines represent results calculated by using the above formalism . It is seen from the figure the agreement is quite good. Here it may be noted that for all these densities and temperatures ν has been found to be less than one.

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