

CALCULATION OF BULK VISCOSITY OF TWO-COMPONENT FLUIDS FROM SECH(AT) FORM OF THE TIME CORRELATION FUNCTION

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1. Introduction

To study transport coefficient of one component of classical dense fluids a considerable amount of work has been done during last three decades. Extensive molecular dynamics (MD) simulation [1] studies for hard sphere fluids and Lennard-Jones (LJ) fluids have been undertaken, during this period, to find out the transport properties. But, the transport coefficient in two-component fluids are least understood. All among the transport coefficients the bulk viscosity of fluids which has relevance to the behavior of fluids under rapid loading conditions. In other words, the bulk viscosity can be considered as a measure of the resistance offered by a medium subjected to the forces of compression or expansion. It also plays an important role in the study of the dynamical structure factor. In spite of the importance of bulk viscosity, it has not been studied in detail. To study the transport properties the approach, which has now been more frequently used, is based on the time correlation function (TCF) formalism. A time correlation function is time average of a dynamical variable at two different times. In this approach the transport properties are defined in the form of Green-Kubo integrals of TCFs. To study bulk viscosity by the Green-Kubo method which is expressed [2] as the time integral of the bulk stress auto correlation (BSAC) function. The BSAC function can be calculated by using Mori's memory function approach [2-4] coupled with its sum rules. Recently we have studied bulk viscosity of expanded Rb, it was found that frequency sum-rules of bulk-stress auto correlation function plays an important role in understanding the bulk viscosity of fluid. In the present work we have derived expression of the sum rules of BSAC function and put them in suitable form for numerical calculation. The numerical results have been obtained for the LJ potential near the triple point of Ar-Kr mixture. By putting the numerical results of the sum rules in the expression of viscosity, we obtained the bulk viscosity of Ar-Kr mixture and compared with the computer simulation results.

2. Theory

The bulk viscosity of fluids is given by the Green-Kubo relation

$$\eta_B = \frac{1}{Vk_B T} \int_0^\infty dt S^B(t), \quad (1)$$

where η_B, V, k_B and T represents bulk viscosity, volume of the system, Boltzmann constant and temperature, respectively. The quantity $S^B(t)$ is bulk stress auto correlation function given by

$$S^B(t) = \frac{1}{9} \sum_a \sum_b \langle J^{aa}(t) J^{bb}(0) \rangle, \quad (2)$$

with

$$J^{ab} = \sum_{j=1}^N \left(\frac{p_{ja} p_{jb}}{m} + r_{ja} F_{jb} \right) - \delta_{ab} V \left(P + \frac{dP}{d\bar{E}} (E - \bar{E}) \right), \quad (3)$$

where a and b run over x, y and z . In the above equation N is the total number of particles, included like and unlike species. p_{ja}, r_{ja} and F_{ja} are the a -th component of velocity, position and force, respectively on the j -th particle at time t . The expressions for \bar{E} and PV in terms of the pair potential $u_{ij}(r)$ and pair distribution function $g_{ij}(r)$ between the like and unlike particles are given as

$$\bar{E} = \frac{3}{2} k_B T + \sum_{i,j=1}^2 N_i n_j \int_0^\infty dr r^2 g_{ij}(r) u_{ij}(r), \quad (4)$$

and

$$PV = k_B T - \frac{2\pi}{3} \sum_{i,j=1}^2 N_i n_j \int_0^\infty dr r^3 g_{ij}(r) \frac{du_{ij}(r)}{dr}. \quad (5)$$

The frequency sum rules of $S(t)$ are given by the short time expansion coefficient defined through

$$S(t) = S_0 - S_2 \frac{t^2}{2!} + S_4 \frac{t^4}{4!} \dots, \quad (6)$$

where S_0, S_2 , and S_4 are the zeroth, second and fourth order sum rules of the stress auto correlation function, respectively. The expression for zeroth sum rule is obtained to be

$$S_0^B = \frac{8}{3} (k_B T)^2 + \frac{2\pi}{9} k_B T \sum_{i,j=1}^2 N_i n_j \int_0^\infty dr r^4 g_{ij}(r) (A_{ij} r^2 - B_{ij})$$

$$- 5 \left(V \frac{dP}{d\bar{E}} \right) (k_B T)^2 - (PV)^2 + \left(V \frac{dP}{d\bar{E}} \right)^2 \left(6(k_B T)^2 - \bar{E} \right) + 2PV^2 \left(\frac{dP}{d\bar{E}} \right) \left(E - \frac{3}{2} k_B T \right),$$

where n_i, N_j and $g_{ij}(r)$ are number density of species labeled i , total number of species labeled j and pair correlation function between the particles of species i and j , respectively. In the above expression and what follows, the quantities A, B and C are defined as

$$B_{ij} = \frac{1}{r} \frac{du_{ij}(r)}{dr}, \quad A = \frac{1}{r} \frac{dB_{ij}}{dr}, \quad C = \frac{1}{r} \frac{dA_{ij}}{dr}$$

The second sum rules of BSAC function for the two-component fluids can be calculated from $\dot{J}^{ab}(t)$ as follows:

$$S_2^b(t) = \langle \dot{J}^{aa}(t) \dot{J}^{bb}(t) \rangle_{t=0}. \quad (9)$$

With putting the first time derivative of equation (3) in to the equation (8), the expression for the S_2^B is obtained as

$$\begin{aligned} S_2^B = & \frac{4\pi}{9} (k_B T)^2 \sum_{i,j=1}^2 \frac{N_i n_j}{m_i} \int_0^\infty dr r^2 g_{ij}(r) [(6C_{ij} r^4 + 45A_{ij} r^2 + 45B_{ij}) + r^2 (k_B T)^{-1} (A_{ij} r^2 + B_{ij})] \\ & + \frac{8\pi^2}{9} (k_B T) \sum_{i,j,k=1}^2 \frac{N_i n_j n_k}{m_i} \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3^{ijk}(r, r_1) r^2 r_1^2 r r_1 \beta_1 (A_{ij} A_{ik} r^2 r_1^2 + B_{ij} A_{ik} r_1^2 + B_{ik} A_{ij} r^2 \\ & + B_{ij} B_{ik}), \end{aligned} \quad (10)$$

where g_3^{ijk} is the static triplet distribution function. When the number of particles of one species is equal to zero, the expression given by equations (7) and (10) is reduced to one-component system, which is already known [4]. For calculation of the bulk viscosity from equation (1) we have to calculate $S^B(t)$. The exact calculation of this quantity is not possible yet as it involves the calculation of many body problems. Therefore, we express $S(t)$ as some functional form $F(at)$, such that just two terms in the exact Taylor series expansion of $S(t)$ and that of $F(at)$ are the same. We assume $S(t)$ to be of the form given as

$$S^B(t) = S_0 F\left(t\sqrt{S_2/S_0}\right). \quad (11)$$

For $F(at)$ we use sech(at) form of the time correlation function. This form is derivable [5] from the Mori memory function equation given as

$$\frac{dS}{dt} = - \int_0^\infty M_1(t-\tau) S(\tau) d\tau. \quad (12)$$

Considering $F(at)$ as sech(at) and using equation (1), the expression for bulk viscosity is obtained to be

$$\eta_B = \frac{\pi}{2} (n/k_B T) (S_0^{3/2} / \sqrt{S_2}).$$

3. Results and Discussion

To calculate the bulk viscosity, we compute values of S_0 and S_2 in equation (13). The required inputs for the calculation of sum rules of the (BSAC) function are the interaction potential between

like and unlike species, the static pair correlation function $g_{ij}(r)$ and the triplet correlation function $g_3^{ijk}(r, r_1)$. We consider interaction potential is of Lennard- Jones (LJ) type given as

$$U_{ij} = 4\epsilon_{ij} \left[\left(\sigma_{ij}/r \right)^{12} - \left(\sigma_{ij}/r \right)^6 \right], \quad (14)$$

where i and j are the indices of the two species. For the present work we choose our system as a mixture of Ar-Kr. Therefore, for the above equation the values of ϵ for Ar is $\epsilon_{11} = 120k \times k_B$ and for Kr is $\epsilon_{22} = 167k \times k_B$. The value of interatomic distance for Ar is $\sigma_{11} = 3.405\text{\AA}$ and for Kr is $\sigma_{22} = 3.633\text{\AA}$. The cross-interaction between unlike species are given by the Lorentz-Berthelot mixing rules $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$ and $\epsilon_{12} = \sqrt{\epsilon_{11} \times \epsilon_{22}}$. The number density and temperature of the system are 1.84 grcm^3 and 121.7 K , respectively. We have used MD simulation data of Zhou and Miller [6] for the pair correlation function for two-body contribution. We have used the Gauss quadrature method for evaluation of the numerical integrations. We have calculated the contributions of different interactions separately with the following notation

$$S_{2n} = S_{2n}^{Ar-Ar} + S_{2n}^{Kr-Kr} + S_{2n}^{Ar-Kr}$$

Table 1. Values of zeroth and second sum rules. The units for S_0 and S_2 are 10^{-29} erg^2 and $10^{-3} \text{ erg}^2 \text{ s}^{-2}$, respectively.

Sum rules	Ar-Ar	Kr-Kr	Ar-Kr
S_0	131.64	326.6	381.07
S_2	102.34	218.6	294.74

The results are given in Table 1. Using values of S_0 and S_2 , the value of bulk viscosity obtained for Ar-Kr mixture $\eta_B = 16.45 \times 10^{-4} \text{ gmcm}^{-1} \text{ s}^{-1}$. This value is to be compared with MD simulation value of $\eta_B = 18.5 \times 10^{-4} \text{ gmcm}^{-1} \text{ s}^{-1}$. By putting simulation values of bulk viscosity [1] of pure Ar and Kr, $\eta_B^{Ar} = 9.75$ and $\eta_B^{Kr} = 32.25$, into the linear model which is given as.

$$\eta_B = (1-c)\eta_{Kr} + c\eta_{Ar},$$

we find that the bulk viscosity is 21 in the same units. In above equation c is the concentration of Ar equal to 0.5. Thus we find that linear mixing rule overestimate the bulk viscosity as can be judged by comparing results with simulation studies and our theoretical results. Our theoretical results are more close to the simulation results.

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