

## Shear viscosity of liquid mixtures: Mass dependence

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The expressions for zeroth, second, and fourth sum rules of the transverse stress autocorrelation function of a two-component fluid have been derived. These sum rules and Mori's memory function formalism have been used to study the shear viscosity of Ar-Kr and isotopic mixtures. It has been found that the theoretical result is in good agreement with the computer simulation result for the Ar-Kr mixture. The mass dependence of shear viscosity for different mole fractions shows that deviation from ideal linear model comes even from the mass difference in two species of the fluid mixture. At higher mass ratio, shear viscosity of the mixture is not explained by any of the empirical models.

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### I. INTRODUCTION

An appreciable progress has been made for studying diffusion, viscosity, and thermal conductivity of one-component fluids. This has become possible only due to the collective efforts of experiments, theoretical studies, and computer simulations. The transport properties of the two-component fluids have also been of interest among the physicists and chemists due to their composition dependence and more recently from the point of view of glass transition. Extensive computer simulation studies have been carried out to investigate transport phenomena in Lennard-Jones fluid [1–3], soft sphere fluid [4], and hard sphere fluid [5] mixtures. The composition dependence of diffusion and shear viscosity has been one of the aims of these studies. The composition dependence of shear viscosity of a binary mixture from theoretical point of view is not yet fully understood. There exist models such as ideal linear model [6] and an exponential model [7] for composition dependence. But it has been found that there are deviations [3] from the predictions of these models. Some microscopic theoretical studies, based on mode coupling approach [8] and kinetic theory approach [9], have also been made. Recently, Mukherjee *et al.* [10] have studied the composition dependence of shear viscosity of modeled binary mixture system. In this modeled system, the two species have the same mass and same size but different interaction strength. It is found that deviations from ideality are enormous in such a system. In fact, in a real system, the two species differ in mass, size, and interaction strength simultaneously. In the present work, we study equimolar Ar-Kr mixture and a composition dependence of shear viscosity of the modeled mixture in which the two species are allowed to have only different masses. Similar studies have been carried out earlier [11,12] for self-diffusion coefficients, predicting weaker mass dependence of self-diffusion in agreement with simulation studies [13,14].

To study the shear viscosity of the mixture, we have used the time correlation function approach coupled with the Mori-Zwanzig memory function formalism. In this approach, memory function is the basic quantity to be determined. The memory function can be calculated microscopically using binary collision [15] and mode coupling theories [16]. Though there already exists a microscopic expression [17]

for the binary contribution, it has been derived only for a one-component system. Alternatively, one can study viscosity coefficient by investigating the short time properties of transverse stress autocorrelation (TSAC) function and modeled memory function. In the present work, we have derived zeroth, second, and fourth sum rules of TSAC function. These expressions are quite general, applicable to any two-component system, and involve partial pair and triplet correlation functions. These sum rules have been computed numerically for equimolar Ar-Kr mixture. The result obtained for shear viscosity is in good agreement with the computer simulation result [1]. In order to investigate the effect of mass on shear viscosity of the mixture, we have studied different compositions for various mass ratios of the two species. It has been found that even the mass difference in the two species leads to deviations from the empirical, linear and exponential models.

The layout of the paper is as follows. In Sec. II, we present theoretical formalism and derivation of expressions for the sum rules of the TSAC function for a general two-component system and an isotopic system. In Sec. III, results and discussion are given. Section IV consists of brief summary and conclusion.

### II. THEORETICAL FORMALISM

The Green-Kubo expression relating transverse stress autocorrelation function  $S(t)$  to viscosity [1] is given by

$$\eta = \frac{1}{k_B T V} \int_0^\infty S(t) dt, \quad (1)$$

where  $k_B$ ,  $T$ , and  $V$  are the Boltzmann's constant, absolute temperature, and volume of the system, respectively. Here,  $S(t)$  is defined as

$$S(t) = \langle J_{xy}(t) J_{xy}(0) \rangle, \quad (2)$$

with

$$J_{xy}(t) = \sum_i^N [m_i v_{iy}(t) v_{ix}(t) + x_i(t) F_{iy}(t)]. \quad (3)$$

In the above equation,  $N(=N_1+N_2)$  is the total number of particles, labeled as 1 and 2.  $x_i(t)$  and  $v_{ix}(t)$  represent  $x$  component of position and velocity of the  $i$ th particle, respectively, at time  $t$ .  $v_{iy}(t)$  and  $F_{iy}(t)$  are, respectively,  $y$  components of velocity and force at time  $t$ . The angular brackets in Eq. (2) represent the ensemble average. The TSAC function  $S(t)$  involves interactions among the like particles and the unlike particles.

It is not yet possible to calculate  $S(t)$  exactly for a system of interacting particles. Therefore, we study the time evolution of the TSAC function by examining its short time properties. The short time expansion of  $S(t)$  is given as

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

where  $S_0$ ,  $S_2$ , and  $S_4$  are called zeroth, second, and fourth sum rules of the stress autocorrelation function, respectively.

## A. Expressions for the sum rules

### 1. Two-component system

The zeroth sum rule of TSAC function [18] is defined as

$$S_0 = \langle J_{xy}(0) J_{xy}(0) \rangle. \quad (5)$$

Using Eq. (3) for  $J_{xy}(0)$  and evaluating the canonical ensemble averages in the above equation, the expression obtained for  $S_0$  is

$$S_0 = N(k_B T)^2 + \frac{k_B T}{2} \sum_{\mu, \nu=1}^2 n_\mu N_\nu \int d\mathbf{r} g^{\mu\nu}(r) x^2 U_{yy}^{\mu\nu}. \quad (6)$$

Here,  $n_\mu$  denotes the number density of species labeled as  $\mu$ .  $g^{\mu\nu}(r)$  is the pair correlation function between the particles of species  $\mu$  and  $\nu$ . In Eq. (6) and what follows, we use the notation

$$U_{\alpha_1, \alpha_2, \dots, \alpha_n}^{\mu\nu}(r) = \frac{\partial^n U^{\mu\nu}(r)}{\partial r_{\alpha_1} \partial r_{\alpha_2} \dots \partial r_{\alpha_n}}, \quad (7)$$

where  $U^{\mu\nu}(r)$ , in the above expression, is the pair potential between the particles of species  $\mu$  and  $\nu$ .  $r_{\alpha_n}$  is  $\alpha_n$ th component of  $\mathbf{r}$ . Clearly, expression for  $S_0$  contains interaction among the like species and the unlike species of the two-component system.

The derivation of the second sum rule of the TSAC function for the two-component fluids requires the calculation of the ensemble average of the product of the time derivative of dynamical variable  $J_{xy}(t)$  at  $t=0$  with itself. It is defined as

$$S_2 = \langle \dot{J}_{xy}(0) \dot{J}_{xy}(0) \rangle, \quad (8)$$

where  $\dot{J}_{xy}$  represents the first time derivative of the dynamical variable  $J_{xy}(t)$  and is given as

$$\dot{J}_{xy}(t) = m \dot{v}_{1x}(t) v_{iy}(t) + 2 v_{ix}(t) F_{iy}(t) + x_i(t) \dot{F}_{iy}(t), \quad (9)$$

where  $\dot{v}_{ix}(t)$  and  $\dot{F}_{iy}(t)$  are the first time derivatives of  $v_{ix}(t)$  and  $F_{iy}(t)$ , respectively. From Eqs. (8) and (9), one expects  $S_2$  to involve four and five particle contributions, however, on use of Yvon theorem one finds that  $S_2$  involves static correlation upto three particles only. The expression obtained after lengthy but simple algebra is given as

$$S_2 = (k_B T)^2 \sum_{\mu, \nu=1}^2 \frac{n_\mu N_\nu}{m_\mu} \int d\mathbf{r} g^{\mu\nu}(r) [7 U_{yy}^{\mu\nu} + 6 x U_{yyx}^{\mu\nu} + (k_B T)^{-1} x^2 (U_{y\alpha}^{\mu\nu})^2] + (k_B T) \sum_{\mu, \nu=1}^2 \frac{N_\mu}{m_\mu} n_\mu n_\nu \times \int \int d\mathbf{r} d\mathbf{r}_1 g_3(\mathbf{r}, \mathbf{r}_1) x x_1 U_{y\gamma}^{\mu\nu} U_{1y\gamma}^{\mu\nu}, \quad (10)$$

where  $g_3(\mathbf{r}, \mathbf{r}_1)$  is the static triplet distribution function. These results for  $S_0$  and  $S_2$  can also be obtained from the second and fourth sum rules of the transverse current correlation function obtained [18] for the two-component system. The fourth sum rule is defined as

$$S_4 = \langle \ddot{J}_{xy}(0) \ddot{J}_{xy}(0) \rangle. \quad (11)$$

The expression for  $S_4$  is expected to involve partial triplet and quadruplet distribution functions in addition to the pair correlation function. In the absence of knowledge of higher-order partial correlation functions, we have restricted evaluation of the expression of the sum rule only upto two-body terms. Triplet contribution to the fourth sum rule has been estimated from the knowledge of the expression for one-component system, as explained in the Appendix. However, we have neglected the four-body contributions to the fourth sum rule as they are quite insignificant [19]. For example, by neglecting four-body contributions in case of one-component system at triple point, the change in the value of viscosity is of the order of 2% for the density and temperature investigated here. The expression for  $S_{42}$  involving only the two-body contributions thus obtained is given as

$$S_{42} = \frac{(k_B T)^2}{2} \sum_{\mu, \nu=1}^2 n_\mu N_\nu \left( \frac{1}{m_\mu} + \frac{1}{m_\nu} \right)^2 \int d\mathbf{r} g^{\mu\nu}(r) \times [9(k_B T) U_{xxy}^{\mu\nu} + 16(U_{y\alpha}^{\mu\nu})^2 + 20(U_{xy}^{\mu\nu})^2 + 15 U_{xx}^{\mu\nu} U_{yy}^{\mu\nu} + 10 x U_{yy\alpha}^{\mu\nu} U_{x\alpha}^{\mu\nu} + 26 x U_{xy\alpha}^{\mu\nu} U_{y\alpha}^{\mu\nu} + 3 x^2 (U_{y\alpha\beta}^{\mu\nu})^2 + (k_B T)^{-1} x^2 U_{y\alpha}^{\mu\nu} U_{y\beta}^{\mu\nu} U_{\alpha\beta}^{\mu\nu}]. \quad (12)$$

From  $S_0$ ,  $S_2$ , and  $S_{42}$ , respectively, given by Eqs. (6), (10), and (12), the already known expressions [19] for the one-component system can be obtained when the number of particles of either species is put equal to zero.

### 2. Isotopic system

We consider here a system in which two species differ only in their masses, with  $N_1$  particles having mass  $m_1$  and  $N_2$  particles having mass  $m_2$ . The study of such a system is important to know the effect of mass and concentration on

shear viscosity. Analytical expressions for the mass and concentration dependence of sum rules of the TSAC function for such an isotopic system are derived by allowing all particles to interact with same pair potential. Substituting  $g_{12}(r) = g_{12}(r) = g_{22}(r)$  in Eq. (6), one finds that

$$S_0 = N(k_B T)^2 + \frac{k_B T}{2} N n \int d\mathbf{r} g(r) x^2 U_{yy}. \quad (13)$$

This implies that  $S_0$  does not depend on mass of the particles and their concentration. Similarly, when the static correlation function and the interaction among all the particles are same, from Eqs. (10) and (12), the mass and concentration dependences of  $S_2(m_1, m_2)$  and  $S_4(m_1, m_2)$ , respectively, are obtained to be

$$S_2(m_1, m_2) = \left[ c + \frac{(1-c)m_1}{m_2} \right] S_2(m_1) \quad (14)$$

and

$$S_{42}(m_1, m_2) = \frac{1}{2} \left[ c(1+c) + (1-c)(2-c) \frac{m_1^2}{m_2^2} + 2c(1-c) \frac{m_1}{m_2} \right] S_{42}(m_1), \quad (15)$$

where  $c = N_1/N$  is the concentration of particles having mass  $m_1$ .  $S_2(m_1)$  and  $S_4(m_1)$  are, respectively, given as

$$S_2(m_1) = \frac{N n (k_B T)^2}{m_1} \times \int d\mathbf{r} g(r) [7U_{yy} + 6xU_{yyx} + (k_B T)^{-1} x^2 (U_{y\alpha})^2] + \frac{N k_B T n^2}{m_1} \int \int d\mathbf{r} d\mathbf{r}_1 g_3(\mathbf{r}, \mathbf{r}_1) x x_1 U_{y\gamma} U_{1y\gamma}, \quad (16)$$

and

$$S_{42}(m_1) = \frac{2N n (k_B T)^2}{m_1^2} \int d\mathbf{r} g(r) [9(k_B T) U_{xxyy} + 16(U_{y\alpha})^2 + 20(U_{x\alpha})^2 + 15U_{xx} U_{yy} + 10x U_{yy\alpha} U_{x\alpha} + 26x U_{xy\alpha} U_{y\alpha} + 3x^2 (U_{y\alpha\beta})^2 + (k_B T)^{-1} x^2 U_{y\alpha} U_{y\beta} U_{\alpha\beta}]. \quad (17)$$

The above expressions for  $S_2(m_1)$  and  $S_{42}(m_1)$  are exactly the second and fourth (two body only) sum rules of the TSAC function of the one-component system [19].

### B. Expression for shear viscosity

To calculate shear viscosity from the expression given in Eq. (1), one requires to know time evolution of the TSAC function  $S(t)$ . The exact evaluation of time evolution is possible only for a simplified description of atomic motion.

Mori has shown, however, that time correlation functions obey [20,21] an equation of motion that determines their time evolution and is given by

$$\frac{dS(t)}{dt} = - \int_0^t M_1(t-\tau) S(\tau) d\tau, \quad (18)$$

where  $M_1(t)$  is the first-order memory function defined as

$$M_1(t) = \langle f_1(t) f_1^*(0) \rangle / \langle |f_1(0)|^2 \rangle, \quad (19)$$

with

$$f_1(t) = \exp(iQ_1 \tilde{L} Q_1 t) Q_1 J. \quad (20)$$

Here  $Q_1$  is the operator projecting into the subspace orthogonal to the variable  $J(t)$  and  $\tilde{L}$  is a Liouville operator. The quantity most required, for the calculation of time evolution of the TSAC function from Mori's equation, is the memory function  $M_1(t)$ . Though there exist ways to calculate  $M_1(t)$  in binary collision approximation [17] and with the mode coupling theory [20,21], the binary part calculations are still not known for the two-component system interacting via continuous interaction potential. On the other hand, several phenomenological forms [22,23] for the calculation of  $M_1(t)$  have been proposed. Following earlier work which has provided [19,23] reasonably good estimates of shear viscosity for the one-component fluid, we choose

$$M_1(t) = a \operatorname{sech}(bt), \quad (21)$$

where  $a = M_1(t=0) = S_2/S_0$  and  $b^2 = (S_4/S_2) - (S_2/S_0)$ , so that  $S(t)$  satisfies sum rules upto the fourth order.

Defining Fourier-Laplace transform as

$$\tilde{S}(\omega) = i \int_0^\infty \exp(i\omega t) S(t) dt, \quad (22)$$

one obtains a relation for the time dependence of  $S(t)$ , given as

$$S(t) = \frac{1}{\pi} \int_0^\infty \cos(\omega t) S''(\omega) d\omega, \quad (23)$$

where  $S''(\omega)$  is the imaginary part of  $\tilde{S}(\omega)$ . Using Green-Kubo expression [Eq. (1)], a general expression for the viscosity has been obtained, which is given by

$$\eta = - \frac{i}{V k_B T} \tilde{S}(\omega=0). \quad (24)$$

Using Eqs. (18), (21), and (24), and writing  $a$  and  $b$  in terms of sum rules, we obtain an expression for the shear viscosity given as

$$\eta = \left( \frac{2}{\pi} \right) \left( \frac{n}{k_B T} \right) \left( \frac{S_4}{S_2} - \frac{S_2}{S_0} \right)^{1/2} \left( \frac{S_0^2}{S_2} \right). \quad (25)$$

TABLE I. Values of sum rules  $S_0$ ,  $S_2$ , and  $S_4$ . The value of  $S_0$  is in the units of  $10^{-43} \text{ J}^2$ ;  $S_{22}$  and  $S_{23}$  are in the units of  $10^{-17} \text{ J}^2 \text{ s}^{-2}$ ; and that of  $S_4$  in the units of  $10^{10} \text{ J}^2 \text{ s}^{-4}$ .

	Ar-Ar	Ar-Kr	Kr-Kr
$S_0$	106.804	289.066	220.316
$S_{22}$	70.948	195.546	140.615
$S_{23}$	-28.065	-107.272	-55.138
$S_{42}$	32.166	63.492	31.201
$S_{43}$	-6.131	-24.247	-4.891

We will use this equation for the calculation of shear viscosity, and expressions of  $S_0$ ,  $S_2$ , and  $S_4$  to study the Ar-Kr and isotopic mixtures.

### III. RESULTS AND DISCUSSION

To calculate shear viscosity from the expression given by Eq. (25), one requires to compute the sum rules  $S_0$ ,  $S_2$ , and  $S_4$ . The zeroth sum rule contains only the two-body terms, whereas the expression for  $S_2$  contains two- as well as three-body terms. After carrying out the angular integrations by using analytical method, the sum rules have been computed numerically. The angularly integrated expressions are given in the Appendix. The numerical computation of the sum rules requires interatomic potential, partial pair, and triplet correlation functions as input. Presently, calculations have been carried out for equimolar mixture of argon and krypton by using simulation data [3] for the partial pair correlation. The interaction potential for such a system is Lennard-Jones potential given as

$$U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (26)$$

In the above expression of the potential, the value of  $\epsilon$  for Ar-Ar is taken as  $\epsilon_{11} = 120 \text{ K} \times k_B$ , whereas for Kr-Kr  $\epsilon_{22} = 167 \text{ K} \times k_B$ . The value of interatomic diameter for Ar-Ar is  $\sigma_{11} = 3.405 \text{ \AA}$  and that for Kr-Kr is  $\sigma_{22} = 3.633 \text{ \AA}$ . For interactions among the unlike particles, we have used  $\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}}$  and  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$ . The mass density and temperature of the system are, respectively, taken as  $1.84 \text{ g cm}^{-3}$  and  $121.7 \text{ K}$ , corresponding to the state where the simulation results for  $g(r)$  are available. This thermodynamic state is close to the triple point. Numerical integrations have been carried out by using the Gauss quadrature method. The triplet contribution to the second and fourth sum rule has been evaluated using the method explained in the Appendix. The values of  $S_0$ ,  $S_{22}$ ,  $S_{23}$ ,  $S_{42}$ , and  $S_{43}$  for Ar-Ar, Ar-Kr, and Kr-Kr are given in Table I. Here  $S_{nm}$  represents  $m$ -body contribution to  $n$ th sum rule. Using the values of  $S_0$ ,  $S_2$ , and  $S_4$  given in Table I, we obtain  $\eta = 22.31 \times 10^{-5} \text{ Pa s}$  for the equimolar Ar-Kr mixture. The corresponding computer simulation value [1] is  $23.6 \times 10^{-5} \text{ Pa s}$  for a system available for  $\rho = 1.91 \text{ gm cm}^{-3}$  and  $T = 120 \text{ K}$ . The available corresponding experimental values [1] at  $c = 0.4$  and  $0.6$  are, respectively,  $27.2 \times 10^{-5} \text{ Pa s}$  and  $21.7 \times 10^{-5} \text{ Pa s}$ . Thus we see that our method provides a

good description of the viscosity of the mixture of fluid as can be judged from the comparison with the experimental/simulation data. This good quantitative agreement is just coincidental as one can see that by different choices of the memory functions, numerical estimates can be varied. For example, using Gaussian memory instead of hyperbolic secant, the results for shear viscosity will be enhanced by about 25%.

The shear viscosity of the Ar-Kr mixture as predicted by the linear relationship [6]

$$\eta_{mixture} = (1-c)\eta_{Kr} + c\eta_{Ar} \quad (27)$$

is  $27.6 \times 10^{-5} \text{ Pa s}$ , which is higher by about 20% than the computer simulation or our theoretical result. Here we have used [1]  $\eta_{Ar} = 15.6 \times 10^{-5} \text{ Pa s}$ ,  $\eta_{Kr} = 39.6 \times 10^{-5} \text{ Pa s}$ . The second relation [7] called exponential model determines shear viscosity of the mixture, given by

$$\eta_{mixture} = \exp[(1-c)\ln \eta_{Kr} + c \ln \eta_{Ar}]. \quad (28)$$

This predicts the value of the shear viscosity of the mixture to be  $24.85 \times 10^{-5} \text{ Pa s}$ , which is closer to the calculated/simulation value than the value predicted by Eq. (28). This finding is in agreement with the earlier investigation [2].

#### Mass and concentration dependence

In order to check the validity of the above linear and exponential models, we will study here a system where the interactions among particles and the size of the particles have been kept same. The sum rules for  $S_0$ ,  $S_2$ , and  $S_4$  given by Eqs. (13), (16), and (17) have been computed numerically for pure Ar system at  $\rho = 1.19 \text{ gm cm}^{-3}$  and  $T = 121.7 \text{ K}$ . The values of  $S_0$ ,  $S_2(m_1)$ , and  $S_4(m_1)$  are  $535.578 \times 10^{-43} \text{ J}^2$ ,  $561.508 \times 10^{-17} \text{ J}^2 \text{ s}^{-2}$ , and  $374.383 \times 10^{10} \text{ J}^2 \text{ s}^{-4}$ , respectively. The mass and concentration dependences of sum rules for the isotopic system are obtained from Eqs. (13), (14), and (15), respectively. The values of the sum rules and Eq. (25) have been used to study the variation of viscosity with the mass and concentration for an isotopic fluid. Figure 1 shows the variation of viscosity with mass ratio at different concentrations ( $c = N_1/N$ ) of particles of mass  $m_1$  for an isotopic fluid. Using the fact that shear viscosity of a pure system varies as a square root of the mass, the mass and concentration dependence of shear viscosity for an isotopic fluid using linear model is then given by

$$\eta = \eta_0 \left[ c + (1-c) \sqrt{\frac{m_2}{m_1}} \right]. \quad (29)$$

Here  $\eta_0$  is the viscosity of one-component system of particles with mass  $m_1$  at  $c = 1$ . The mass and concentration dependence of the shear viscosity for an isotopic fluid according to the exponential model is given as

$$\eta = \eta_0 \left[ \sqrt{\frac{m_2}{m_1}} \right]^{(1-c)}. \quad (30)$$

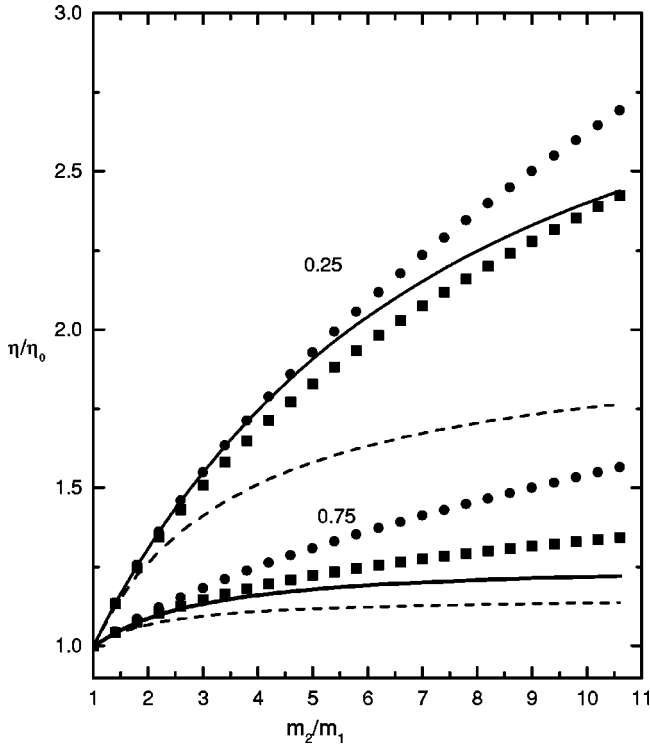


FIG. 1. Variation of the ratio of shear viscosity of an isotopic mixture to the shear viscosity of a one-component system, with mass ratio of two species at  $c=0.25$  and  $0.75$ . Solid circles are results from linear model and solid squares from the exponential model. The solid lines are results from Eq. (25) and dotted lines are results from Eq. (31).

The results obtained from Eqs. (29) and (30) are also shown in Fig. 1. It is seen from the figure that at  $c=0.25$ , the linear model is able to explain the mass dependence but for  $m_2/m_1 < 4$ . At higher mass ratio, the exponential model seems to be better. At  $c=0.75$ , the exponential model predicts better results than linear model but only for small mass ratio. At higher mass ratio ( $>4$ ), there is a significant departure from both the models.

To underline reasons for this deviation, we examine behavior of  $S_2$  and  $S_4$  with changes in the concentration and mass ratio. It is noted that with increase in  $m_2/m_1$ ,  $S_2$  increases linearly but  $S_4$  increases as a square of mass ratio, as is evident from Eqs. (14) and (15). It is also found that  $S_4$  does not follow the linear behavior with increase in concentration, whereas  $S_2$  increases linearly. To analyze the effect of only  $S_4$  on shear viscosity, we also calculate the viscosity using only  $S_0$  and  $S_2$ . The expression obtained for  $\eta$  by assuming that  $S(t) = S_0 \operatorname{sech}(\sqrt{(S_2/S_0)t})$ , is given as

$$\eta = \left(\frac{\pi}{2}\right) \left(\frac{n}{k_B T}\right) \left(\frac{S_0^{3/2}}{\sqrt{S_2}}\right). \quad (31)$$

This for an isotopic system becomes

$$\eta = \eta_0 \left[ c + (1-c) \frac{m_1}{m_2} \right]^{-1/2}. \quad (32)$$

The mass dependence obtained from this relation is also shown in Fig. 1 as dotted line. It can be seen from the figure that by including  $S_4$ , one could improve the mass and concentration dependence of shear viscosity.

#### IV. SUMMARY AND CONCLUSIONS

We have derived expressions for the first three nonvanishing sum rules of the TSAC function, and evaluated them numerically for a two-component system. Using these expressions, coupled with Mori's memory function formalism, we have calculated shear viscosity of equimolar Ar-Kr system. It is found that our approach provides an estimate of shear viscosity close to the computer simulation/experimental data. Further, it is found that the exponential model predicts better results than the linear model in agreement with the earlier investigations. In order to underline the reasons of deviation from the linear model, we have studied the mass and concentration dependence of an isotopic mixture where the interactions among the like and the unlike particles are assumed to be the same. The study of an isotopic system reveals that at large mass ratio there is a considerable deviation from the ideal linear model. Thus, one concludes that deviations from the linear model in a real system can also be attributed to the mass difference in the two species of a mixture. Further, for very large mass ratios there are deviations even from the exponential model. Thus, one finds that two empirical models can be useful only when the two species of a mixture are not very different in their masses.

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#### APPENDIX

The angular integration of the sum rules of the TSAC function is done using the method explained earlier [19]. The angularly integrated expression for zeroth sum rule is given as

$$S_0 = N(k_B T)^2 + \frac{2\pi(k_B T)}{15} \sum_{\mu, \nu=1}^2 n_\mu N_\nu \int_0^\infty dr g^{\mu\nu}(r) r^4 [A_{\mu\nu} r^2 + 5B_{\mu\nu}], \quad (A1)$$

where  $B = (1/r)[\partial U(r)/\partial r]$  and  $A = (1/r)(\partial B/\partial r)$ . The subscripts  $\mu\nu$  on  $A$  and  $B$  imply that interaction is among  $\mu$  and  $\nu$  species of the system. The angularly integrated expression of the two-body contribution to second sum rules is given as

$$S_{22} = (k_B T)^2 \sum_{\mu, \nu=1}^2 \frac{4\pi n_\mu N_\nu}{m_\mu} \int_0^\infty dr g^{\mu\nu}(r) r^2 \left[ 7B_{\mu\nu} + \frac{2}{5} C_{\mu\nu} r^4 + \frac{13}{3} A_{\mu\nu} r^2 + (15k_B T)^{-1} r^2 (A_{\mu\nu}^2 r^4 + 5B_{\mu\nu}^2 + 2A_{\mu\nu} B_{\mu\nu} r^2) \right], \quad (A2)$$

where  $C=(1/r)(\partial A/\partial r)$ . The term containing the three-body distribution function in  $S_2$  is angularly integrated using the addition theorem which finally provides

$$S_{23} = \frac{8\pi^2 k_B T}{15} \sum_{\mu, \nu=1}^2 \frac{N_\mu n_\mu n_\nu}{m_\mu} \int_0^\infty \int_0^\infty dr dr' r^2 r'^2 \times \int_{-1}^{+1} d\xi g_3^{\mu\nu\gamma}(\mathbf{r}, \mathbf{r}') r r' \xi [10B_{\mu\nu} B'_{\mu\nu} + 2A'_{\mu\nu} B_{\mu\nu} r'^2 + 2A_{\mu\nu} B'_{\mu\nu} r^2 + A_{\mu\nu} A'_{\mu\nu} r^2 r'^2 (3\xi^2 - 1)], \quad (\text{A3})$$

where  $\xi$  is cosine of angle between  $\mathbf{r}$  and  $\mathbf{r}'$ . Though there exists superposition approximation for the calculation of triplet contribution in a one-component system, it is not yet clear how to extend it to a two-component system. For a two-component system, atleast two of the three particles belong to the same species. Obviously, the correlation will be concentration dependent. In this way, we propose for a two-component system

$$g_3^{\mu\nu\gamma}(\mathbf{r}, \mathbf{r}') = g_{\mu\nu}(r) g_{\mu\nu}(r') g_{\nu\nu}(|r-r'|) (x_\mu + x_\nu \delta_{\mu\nu}). \quad (\text{A4})$$

In this approximation, we have only taken care of concentration dependence and the possible combination of partial correlations. This approximation reduces to the already known Kirkwood superposition approximation when one of the species is absent, and also for the isotopic system. This approximation is based upon the fact that the correlation between  $\mu$  and  $\nu$  species is direct, whereas correlation among the same species is weaker and concentration dependent. The result obtained using the approximation (A4) is given in Table I.

On the other hand if we write  $S_{23}$  in reduced units, i.e., length in terms of  $\sigma$  and energy in terms of  $\epsilon$ , so the integral involved is dimensionless. The expression thus obtained is given as

$$S_{23} = \frac{8\pi^2 k_B T}{15} \sum_{\mu, \nu=1}^2 \frac{N_\mu}{m_\mu} n_\mu n_\nu \epsilon_{\mu\nu}^2 \sigma_{\mu\nu}^2 I_{\mu\nu}, \quad (\text{A5})$$

where

$$I_{\mu\nu} = \int_0^\infty \int_0^\infty dr^* dr'^* r^{*2} r'^{*2} \int_{-1}^{+1} d\xi g_3^{\mu\nu}(r, r') r^* r'^* \times \xi [10B_{\mu\nu}^* B'^*_{\mu\nu} + 2A'^*_{\mu\nu} B^*_{\mu\nu} (r'^*)^2 + 2A_{\mu\nu}^* B'^*_{\mu\nu} (r^*)^2 + A'^*_{\mu\nu} A^*_{\mu\nu} (r^*)^2 (r'^*)^2 (3\xi^2 - 1)]. \quad (\text{A6})$$

The superscript \* means that the respective quantities are in reduced units. We approximate the integrand to have the same value for all partial triplet correlation function, true in an isotopic system, but with their weighted values in terms of their different strength of potential ( $\epsilon$ ) and atomic size ( $\sigma$ ). The integral  $I_{\mu\nu}$  has been calculated using the superposition approximation. The results obtained for  $S_{23}^{Ar-Ar}$ ,  $S_{23}^{Ar-Kr}$ ,  $S_{23}^{Kr-Kr}$  are  $-24.558 \times 10^{-17} \text{ J}^2 \text{ s}^{-2}$ ,  $-104.460 \times 10^{-17} \text{ J}^2 \text{ s}^{-2}$ , and  $-41.291 \times 10^{-17} \text{ J}^2 \text{ s}^{-2}$ , respectively. These results are comparable with those obtained directly and are given in Table I. Therefore, we estimate triplet contribution to the fourth sum rule in a similar manner and corresponding results are also given in Table I.

The angular integration of the fourth sum rule of the TSAC function involving the two-body distribution function is given as

$$S_{42} = \frac{2\pi(k_B T)^2}{15} \sum_{\mu, \nu=1}^2 n_\mu N_\nu \left( \frac{1}{m_\mu} + \frac{1}{m_\nu} \right)^2 \int_0^\infty dr g^{\mu\nu}(r) r^2 \times [9(k_B T)(D_{\mu\nu} r^4 + 5A_{\mu\nu} + 10C_{\mu\nu} r^2) + 294A_{\mu\nu}^2 r^4 + 465B_{\mu\nu}^2 + 490A_{\mu\nu} B_{\mu\nu} r^2 + 54A_{\mu\nu} C_{\mu\nu} r^6 + 36B_{\mu\nu} C_{\mu\nu} r^4 + r^2(k_B T)^{-1}(A_{\mu\nu}^3 r^6 + 3B_{\mu\nu} A_{\mu\nu}^2 r^4 + 3A_{\mu\nu} B_{\mu\nu}^2 r^2 + 5B_{\mu\nu}^3) + 3C_{\mu\nu}^2 r^8], \quad (\text{A7})$$

where  $D=(1/r)(\partial C/\partial r)$ . Expressions given here are suitable for numerical integration.

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