

# Longitudinal and bulk viscosities of binary fluid mixtures

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**Abstract.** Expressions for zeroth, second and fourth sum rules of longitudinal and bulk stress auto correlation functions have been derived for binary fluid mixtures. Longitudinal and bulk viscosities of an Ar–Kr mixture have been calculated using Mori’s memory function formalism coupled with the sum rules of longitudinal and bulk stress auto correlation functions. The results obtained are compared with the molecular dynamics simulation. Mass dependence of the longitudinal and bulk viscosities has been studied for different compositions of an isotopic mixture at different densities and temperatures. For very large mass ratio, the longitudinal and bulk viscosities of the isotopic mixture are more dependent on mole fraction than on mass.

**PACS.** 66.20.+d Viscosity of liquids; diffusive momentum transport – 51.20.+d Viscosity, diffusion, and thermal conductivity – 05.60.Cd Classical transport

## 1 Introduction

To study transport coefficients of classical dense fluids, a considerable amount of work has been done during the last four decades resulting in an appreciable progress in the understanding of transport coefficients of pure fluids. Transport properties of binary fluid mixtures have also been of interest to physicists and chemists. Molecular dynamics (MD) simulation studies on mixtures of hard sphere fluids [1], soft sphere fluids [2,3] and Lennard-Jones (LJ) fluids [4–6], have been undertaken to study the transport properties. Among all hydrodynamic transport coefficients, the longitudinal and bulk viscosities of mixtures have been least investigated. The bulk viscosity, which is a measure of the resistance of a medium subject to compression or expansion, has relevance to the behavior of fluids under rapid loading conditions. It also plays an important role in studying the dynamical structure factor, in understanding the attractive intermolecular forces and also acoustic phenomena at the microscopic level. In spite of their importance detailed investigations of the longitudinal and bulk viscosities, have not been possible due to the involved complications. For example they cannot be measured directly by the experiments.

Longitudinal and bulk viscosities can be studied by computer simulation techniques using the Green-Kubo method [7] which expresses them as time integral of the longitudinal and bulk stress auto-correlation (*SAC*) functions. The longitudinal viscosity,  $\eta_l = \frac{4}{3}\eta_s + \eta_B$  ( $\eta_s$  and  $\eta_B$

are shear and bulk viscosities) can also be calculated from the knowledge of shear and bulk viscosities of the system. There are other alternative ways to study the bulk viscosity by computer simulation techniques. First method uses non-equilibrium molecular dynamics and the second has been recently suggested by Okumura and Yonezawa [8]. All methods used to study the bulk viscosity of fluids have provided similar results [8–12]. However, with a few exceptions, considerable deviations between simulations and experimental results [13,14] have been observed [12]. Therefore, though the computer simulation technique provides sufficient information about viscosities, theoretical studies are equally important as these may provide additional information for understanding the involved processes. Theoretically, the bulk viscosity can be calculated by studying the time evolution of the stress auto correlation functions appearing in the Green-Kubo expressions. The stress autocorrelation function can be calculated from knowledge of sum rules coupled with Mori’s memory function approach [7,15,16]. The advantage of this approach is that one can introduce an approximate form [17] of the memory function while preserving a number of properties of the time correlation function. There exist few such theoretical studies [18,19] for the bulk and longitudinal viscosities of pure system like dense inert gases and liquid metals. However, there is no such study available for binary fluid mixtures. Therefore, in the present work, we derive expressions for the zeroth, second and fourth sum rules of the longitudinal and bulk SAC functions for binary fluid mixtures. These expressions are quite general and are

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applicable to any two component system. We have put these expressions in a form suitable for numerical calculations. Numerical results have been obtained for the longitudinal and bulk viscosities of an equimolar Ar–Kr mixture which have been compared with computer simulation data [4].

We have also studied the composition dependence of the longitudinal and bulk viscosities of the modeled mixture wherein particles of the two species have different masses. This study has proved useful in predicting the significant role played by composition over that of ratio of particle masses while preparing a mixture with high viscosity. We have also studied the mass dependence of the longitudinal and bulk viscosity of an isotopic mixture at different thermodynamic states. It is found that the effect of density and temperature on the ratio of viscosities of mixture to that of the pure fluid is more pronounced for the longitudinal viscosity than for the bulk viscosity.

The paper is organised as follows. In Section 2, we present the generalities. Expressions for the sum rules of the bulk stress autocorrelation function for general binary mixtures and for isotopic systems are presented in Section 3. In Section 4, results and the involved discussion have been presented. Section 5 provides a summary and conclusion.

## 2 Generalities

The Green-Kubo expression relates the bulk viscosity of a fluid mixture  $\eta_B$  directly to bulk stress autocorrelation function,  $S^B(t)$  [7]

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

where  $V$ ,  $k_B$  and  $T$  are the volume of the system, the Boltzmann constant and the temperature, respectively. Bulk stress auto correlation (BSAC) function  $S^B(t)$  is defined as

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

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 Cartesian coordinates  $x$ ,  $y$  and  $z$ . In a binary system,  $N = N_1 + N_2$  is the total number of particles with  $N_1$  and  $N_2$  being the number of particles of species 1 and 2. The angular brackets in equation (2) represent ensemble average.  $p_{ja}$ ,  $r_{ja}$  and  $F_{ja}$  are  $a$ th component of velocity, position, and force vectors of the  $j$ th particle, respectively.  $E$  is the total energy of the system. Expressions for the average energy  $\bar{E}$  and pressure  $P$  in terms of the pair potential  $u(r)$  are given by

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

and

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

where  $n_i$ , and  $N_i$  represent the number density and number of particles, respectively, of species  $i$ .  $g_{ij}(r)$  is the partial pair correlation function between particles of the species  $i$  and  $j$ . Alternatively, the bulk viscosity can be calculated from the knowledge of longitudinal viscosity and shear viscosity by using the following Green-Kubo relation [7]

$$\eta_l = \frac{4}{3} \eta_s + \eta_B = \frac{1}{V k_B T} \int_0^\infty dt S^l(t) \quad (6)$$

The longitudinal stress autocorrelation (LSAC) function,  $S^l(t)$ , is defined as

$$S^l(t) = \frac{1}{3} \langle J^{aa}(t) J^{aa}(0) \rangle. \quad (7)$$

These Green Kubo expressions coupled with sum rules of stress auto correlation provide one of the method of calculation of viscosity of liquid mixture.

## 3 Expressions for the sum rules

It has not yet been possible to calculate  $S^{l/B}(t)$  exactly for a system of particles which interact by realistic potentials. Therefore, we study  $LSAC/BSAC$  functions by examining their short time-expansion

$$S_{l/B}(t) = S_0^{l/B} - S_2^{l/B} \frac{t^2}{2!} + S_4^{l/B} \frac{t^4}{4!} \dots, \quad (8)$$

where  $S_0^{l/B}$ ,  $S_2^{l/B}$ , and  $S_4^{l/B}$  are the zeroth, second and fourth order sum rules of the corresponding stress autocorrelation functions, respectively. We present below the results for the  $BSAC$  function and the expressions for the sum rules of the  $LSAC$  function can be obtained in a similar manner and are presented in the Appendix A.

### 3.1 BSAC function

The expression for the zeroth sum rule of the BSAC function can be obtained by putting  $t = 0$  in equation (2) and evaluating the canonical ensemble averages. The expression obtained is given by

$$\begin{aligned} S_0^B &= \frac{8}{3} (k_B T)^2 + \frac{2\pi}{9} k_B T \sum_{i,j=1}^2 N_i n_j \\ &\times \int_0^\infty dr r^4 g_{ij}(r) (A_{ij} r^2 - B_{ij}) \\ &- 5 (V dP/d\bar{E}) (k_B T)^2 - (PV)^2 \\ &+ (V dP/d\bar{E})^2 (6(k_B T)^2 - \bar{E}^2) \\ &+ 2PV^2 (dP/d\bar{E}) \left( \bar{E} - \frac{3}{2} k_B T \right), \end{aligned} \quad (9)$$

In equation (9) and in what follows, we use the following notations

$$B_{ij} = \frac{1}{r} \frac{du_{ij}(r)}{dr}, A_{ij} = \frac{1}{r} \frac{dB_{ij}}{dr}, C_{ij} = \frac{1}{r} \frac{dA_{ij}}{dr}, D_{ij} = \frac{1}{r} \frac{dC_{ij}}{dr}. \quad (10)$$

The derivation of the second sum rule of the BSAC function for binary mixtures requires the calculation of the ensemble average

$$S_2^B = \langle \dot{J}^{aa}(t) \dot{J}^{bb}(t) \rangle_{t=0}, \quad (11)$$

where  $\dot{J}^{bb}(t)$  represents the first time derivative of  $J^{bb}(t)$ . The expression obtained contains correlations upto three particles and can be expressed as

$$S_2^B = S_{22}^B + S_{23}^B. \quad (12)$$

In above equation and in what follows  $S_{nm}$  represents  $m$  body contribution to the  $n$ th sum rule. The expression obtained for  $S_{22}^B$  and  $S_{23}^B$  are, respectively, given as

$$S_{22}^B = \frac{4\pi}{9} (k_B T)^2 \sum_{i,j=1}^2 \frac{N_i n_j}{m_i} \int_0^\infty dr r^2 g_{ij}(r) \times [(6C_{ij}r^4 + 45A_{ij}r^2 + 45B_{ij}) + r^2 (k_B T)^{-1} (A_{ij}r^2 + B_{ij})^2] \quad (13)$$

$$S_{23}^B = \frac{8\pi^2}{9} k_B T \sum_{i,j,k=1}^2 \frac{N_i n_j n_k}{m_i} \int_0^\infty dr \times \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3^{ijk}(\mathbf{r}, \mathbf{r}_1) r^2 r_1^2 r r_1 \beta_1 \times (A_{ij} A_{1ij} r^2 r_1^2 + B_{ij} A_{1ij} r_1^2 + A_{ij} B_{1ij} r^2 + B_{ij} B_{1ij}) \quad (14)$$

where  $g_3^{ijk}(\mathbf{r}, \mathbf{r}_1)$  is the static triplet correlation function. In equation (14) and what follows, the subscript 1 on A and B implies that the argument of the pair potential function  $u(r)$  is changed to  $r_1$ .  $\beta_1$  is the cosine of the angle between the vectors  $\mathbf{r}$  and  $\mathbf{r}_1$ .

The fourth sum rule of the BSAC function is defined as

$$S_4^B = \langle \ddot{J}^{aa}(t) \ddot{J}^{bb}(t) \rangle_{t=0}, \quad (15)$$

where  $\ddot{J}^{aa}(t)$  is the second time derivative of equation (3) with respect to time. The expression for the fourth sum rule  $S_4^B$ , in addition to the pair correlation function, contains triplet and quadruplet distribution functions. The triplet contribution to  $S_4^B$  will be estimated by expression known for pure fluids as explained in the Appendix B. The expression obtained for the fourth sum rule of the BSAC function containing only two-body correlation function is

given by

$$S_{42}^B = \frac{4\pi}{9} (k_B T) \sum_{i,j=1}^2 N_i n_j \frac{1}{4} \left( \frac{1}{m_i} + \frac{1}{m_j} \right)^2 \times \int_0^\infty dr g_{ij}(r) r^2 [18(k_B T)^2 (D_{ij} r^4 + 10C_{ij} r^2 + 15A_{ij}) + k_B T (378B_{ij}^2 + 432A_{ij}^2 r^4 + 612A_{ij} B_{ij} r^2 + 72B_{ij} C_{ij} r^4 + 108A_{ij} C_{ij} r^6 + 6C_{ij}^2 r^8) + 2r^2 (B_{ij} + A_{ij} r^2)^3 - 4B_{ij}^3 r^2]. \quad (16)$$

It is noted that already known expressions of  $S_0^{B/l}$ ,  $S_2^{B/l}$  and  $S_{42}^{B/l}$  for the pure fluids [18,19] can be obtained by setting the number of particles of one of the species equal to zero.

### 3.2 Isotopic system

We consider a binary system in which the two species differ only by their masses. The system has  $N_1$  and  $N_2$  particles of mass  $m_1$  and  $m_2$ , respectively. To study the effect of mass and composition on the longitudinal and bulk viscosities we have first examined the mass dependence of the sum rules. For this purpose we have derived expressions for mass ratio and composition dependence of the sum rules of the *LSAC/BSAC* function by considering the same radial distribution function and interaction potential for the like and unlike species. The zeroth sum rule,  $S_0^{l/B}(m_1, m_2)$  of an isotopic system does not explicitly involve mass and is therefore same as that of the pure fluid i.e.,

$$S_0^{l/B}(m_1, m_2) = S_0^{l/B}(m_1), \quad (17)$$

where  $S_0^{l/B}(m_1)$  is zeroth sum rule of pure fluid. From the equation (17) we observe that  $S_0^{l/B}(m_1, m_2)$  does not depend on the mass and composition of the second species. This implies that mass and composition dependence will come only from the relaxation processes through  $S_2$  and  $S_4$ . Similarly, by taking only masses of two particles different, from equations (13), (14) and (16) we obtain expressions for the mass and composition dependence of the second and fourth sum rules of the *BSAC* functions of isotopic systems. The resulting expressions are expressible in terms of expression for a pure fluid and are given by

$$S_2^{l/B}(m_1, m_2) = \left[ c + (1-c) \frac{m_1}{m_2} \right] S_2^{l/B}(m_1), \quad (18)$$

and

$$S_4^{l/B}(m_1, m_2) = \frac{1}{2} \left[ c(1+c) + (1-c)(2-c) \left( \frac{m_1}{m_2} \right)^2 + 2c(1-c) \frac{m_1}{m_2} \right] S_4^{l/B}(m_1), \quad (19)$$

where  $c = N_1/N$  is the mole fraction of particles with mass  $m_1$ .  $S_2^{l/B}(m_1)$  and  $S_4^{l/B}(m_1)$  are the second and fourth sum rules of *LSAC* and *BSAC* functions which were obtained by Tankeshwar et al. [18]. It also implies that for isotopic fluid mixtures sum rules of shear, bulk and longitudinal stress scales in a similar fashion.

Following the Mori's memory function formalism we obtain approximate expression [19,20] for viscosities in terms of sum rules given as

$$\eta_{l/B} = \sqrt{\frac{2}{\pi}} \frac{n}{k_B T} \left( \frac{(S_0^{l/B})^2}{S_2^{l/B}} \right) \left( \frac{S_4^{l/B}}{S_2^{l/B}} - \frac{S_2^{l/B}}{S_0^{l/B}} \right)^{1/2}, \quad (20)$$

where  $n$  is the total number density. This expression has already been used to study the shear viscosity of pure fluids [19] and binary mixture [20] using sum rules of the transverse stress autocorrelation function. In the present work, we use equation (20) and the corresponding sum rules  $S_0^{l/B}$ ,  $S_2^{l/B}$  and  $S_4^{l/B}$  for the calculation of longitudinal and bulk viscosities of an Ar–Kr mixture and an isotopic system.

## 4 Results and discussion

### 4.1 Ar–Kr system

In order to calculate longitudinal and bulk viscosities of Ar–Kr mixture, we need to compute values for  $S_0^{l/B}$ ,  $S_2^{l/B}$  and  $S_4^{l/B}$ . The required inputs for the calculation of the sum rules of the *LSAC/BSAC* functions are the interaction potential between like and unlike particles, partial static pair correlation functions  $g_{ij}(r)$ , and partial triplet correlation functions. The pair interaction potential, which we use for interaction in Ar–Kr system is the Lennard-Jones potential

$$u_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right], \quad (21)$$

where  $i$  and  $j$  indicate particles of species  $i$  and  $j$ . For interactions between unlike particles,  $\sigma_{12}$  and  $\epsilon_{12}$  are given by the Lorentz-Berthelot mixing rules

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \quad (22)$$

and

$$\epsilon_{12} = (\epsilon_{11} \times \epsilon_{22})^{1/2}. \quad (23)$$

For Ar–Kr system, the values for  $\epsilon$  for the Ar–Ar and the Kr–Kr interactions are taken as  $\epsilon_{11} = 120 K \times k_B$ ,  $\epsilon_{22} = 167 K \times k_B$ , respectively. According to equation (23) the value of  $\epsilon_{12}$  is  $141.56 K \times k_B$ . The interatomic radius for Ar–Ar is 0.3405 nm and for Kr–Kr is 0.3633 nm. This parameter for Ar–Kr is obtained to be 0.3519 nm. We perform calculations for the equimolar mixture of Ar and Kr at the thermodynamic state with the mass density  $=1.84 \text{ g cm}^{-3}$  and the temperature  $=121.7 \text{ K}$ . This thermodynamic state is close to the triple point in the liquid

**Table 1.** Results for the zeroth, second and fourth sum rules of the BSAC function obtained from equation (9), (13), (14) and (16) in units of  $10^{-43} \text{ J}^2$ ,  $10^{-17} \text{ J}^2 \text{ s}^{-2}$  and  $10^{10} \text{ J}^2 \text{ s}^{-4}$ , respectively.

$S_{nm}^B$	Ar–Ar	Ar–Kr	Kr–Kr
$S_0^B$	131.64	381.07	326.60
$S_{22}^B$	102.34	294.74	218.61
$S_{23}^B$	-29.44	-92.09	-48.85
$S_{42}^B$	48.92	96.41	48.19
$S_{43}^B$	-18.6	-30.5	-16.02

**Table 2.** Results for zeroth, second and fourth sum rules of LSAC function obtained from equations (A.2)–(A.4) for the Ar–Kr mixture in units of  $10^{-43} \text{ J}^2$ ,  $10^{-17} \text{ J}^2 \text{ s}^{-2}$  and  $10^{10} \text{ J}^2 \text{ s}^{-4}$ , respectively.

$S_{nm}^l$	Ar–Ar	Ar–Kr	Kr–Kr
$S_0^l$	311.68	804.14	658.00
$S_{22}^l$	197.24	555.47	405.38
$S_{23}^l$	-52.28	-163.7	-85.58
$S_{42}^l$	92.23	180.17	88.29
$S_{43}^l$	-31.3	-51.0	-22.5

region. This thermodynamic state is chosen as molecular dynamics (MD) data for partial pair correlation functions is available only for this state in the literature [5]. In the present work we have taken ideal gas values of  $VdP/d\bar{E}$ ,  $PV$  and  $\bar{E}$  for calculating  $S_0^{l/B}$  as it is expected that the potential-potential contribution dominates [21] near triple point. For the calculation of the triplet contribution to second and fourth sum rules, we have used the superposition approximation as described in the Appendix B. The superposition approximation has been tested [22] for a pure system by performing MD simulations for LJ fluids and it has been found that near the triple point it overestimates the results by only 10 percent.

Numerical integrations have been carried out by using the Gauss quadrature method. Results for the sum rules are given in Tables 1 and 2, where  $S_{nm}^{l/B}$  represents the  $m$  body contribution to the  $n$ th sum rule. In these tables, contributions due to Ar–Ar, Ar–Kr, and Kr–Kr interactions are presented separately. It can be seen from the tables that contributions of triplet correlation functions to second and fourth sum rules is up to 30 percent of the contributions due to static pair correlations.

With results for the sum rules from Table 1, equation (20) yields  $\eta_B = 20.62 \times 10^{-5} \text{ Pa s}$  for the equimolar Ar–Kr mixture. The available computer simulation value [4] is  $18.5 \times 10^{-5} \text{ Pa s}$  for a state very close to the thermodynamic state considered in the present work. For mole fractions  $c = 0.4$  and  $c = 0.6$ , available simulation data [4] for the bulk viscosity are  $\eta_B = 20.5 \times 10^{-5} \text{ Pa s}$  and  $\eta_B = 15.6 \times 10^{-5} \text{ Pa s}$ , respectively. The corresponding theoretical value of the shear viscosity is  $27.87 \times 10^{-5} \text{ Pa s}$  [20]. This yields theoretical value of ratio of bulk to shear viscosity of 0.74 which is in close

agreement with the MD value of 0.78. Using the results for the sum rules from Table 2 in equation (20), we obtain  $\eta_l = 50.0 \times 10^{-5}$  Pa s for the equimolar Ar–Kr mixture. The corresponding computer simulation [4] value is  $49.8 \times 10^{-5}$  Pa s. For composition  $c = 0.4$  and  $c = 0.6$ , available simulation data are  $\eta_l = 56.7 \times 10^{-5}$  Pa s and  $\eta_l = 44.52 \times 10^{-5}$  Pa s, respectively. Thus, we see that our method provides a reasonably good description of bulk and longitudinal viscosities of fluid mixtures as far as the comparison with simulation data. Here, it is important to note that simulation results for the bulk viscosity show poor agreement with experimental data, despite good agreement with other simulation data as has been pointed by Fernandez et al. [12]. Thus present work strengthening the view point that accurate experimental data for bulk viscosity, a property which is difficult to measure experimentally, is not available.

It has been known that many body correlations play important role in predicting the transport coefficients. In order to examine the importance of the triplet correlation in the present case, we have calculated longitudinal and bulk viscosities by neglecting the triplet contributions to second and fourth sum rules. The value of longitudinal and bulk viscosities are  $36.22 \times 10^{-5}$  Pa s and  $15.87 \times 10^{-5}$  Pa s. Therefore, it can be said that many body correlation plays an important role in explaining the large viscosity of a dense system.

There exist mixing rules/empirical models namely linear and exponential models for the prediction of viscosity of binary mixture. In the present work, we also compare our results with predictions of these models and subsequently use these models to compare our results for isotopic fluid wherein no other study is available. According to the linear model [23] viscosity of the mixture,  $\eta_{mix}$ , can be obtained from the following relation

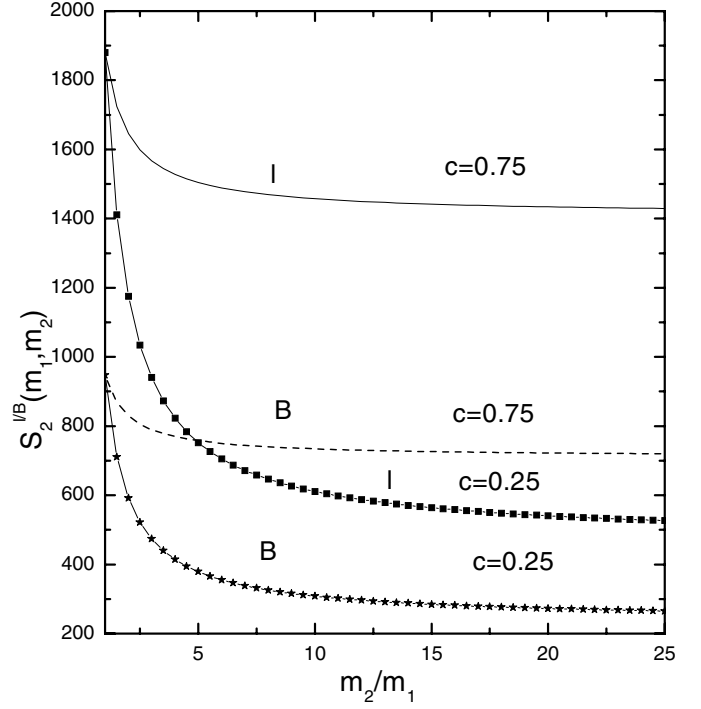
$$\eta_{mix} = (1 - c)\eta_{Kr} + c\eta_{Ar}, \quad (24)$$

where  $c$  is the composition of Ar in Ar–Kr mixture. Using simulation data [4] for pure system i.e.,  $\eta_B^{Ar} = 9.75 \times 10^{-5}$  Pa s and  $\eta_B^{Kr} = 32.2 \times 10^{-5}$  Pa s the bulk viscosity of equimolar mixture is found to be  $21.0 \times 10^{-5}$  Pa s. Using simulation data [4] for pure system i.e.,  $\eta_l^{Ar} = 30.54 \times 10^{-5}$  Pa s and  $\eta_l^{Kr} = 85.0 \times 10^{-5}$  Pa s the value of longitudinal viscosity of equimolar mixture is found to be  $57.7 \times 10^{-5}$  Pa s.

On the other hand, there is a more reliable exponential model [24] which reads

$$\eta_{mix} = \exp[(1 - c)\ln(\eta_{Kr}) + c\ln(\eta_{Ar})]. \quad (25)$$

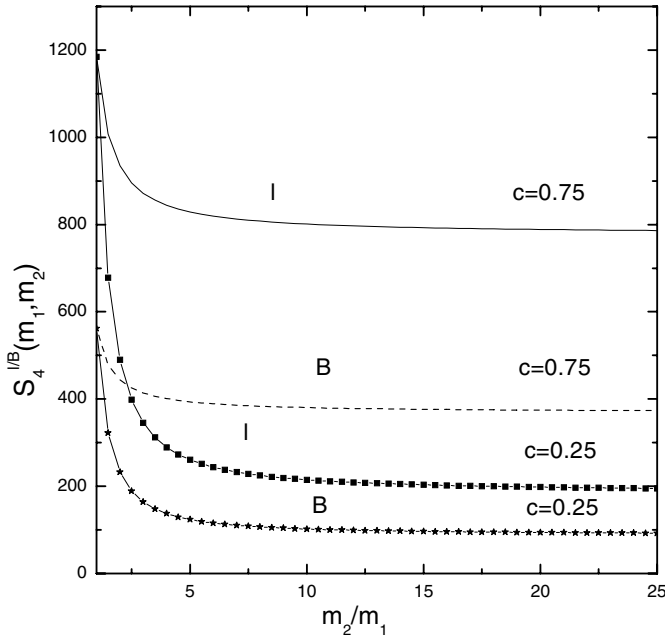
Using simulation data of pure Ar and Kr systems, the results for the longitudinal and bulk viscosities are  $52.7 \times 10^{-5}$  Pa s and  $17.7 \times 10^{-5}$  Pa s, respectively. Thus, we find that equation (25) provided [20] better results than the linear model for the longitudinal viscosity and for the bulk viscosity. Here it may be recalled that equation (25) also provides better results for the shear viscosity of mixtures than equation (24).



**Fig. 1.** Variation of the second sum rule,  $S_2^{l/B}(m_1, m_2)$  as obtained from equation (18) in unit of  $10^{-17} \text{J}^2 \text{s}^{-2}$  of LSAC/BSAC functions of an isotopic system with mass ratio  $m_2/m_1$  of two species at  $c = 0.25$  and  $c = 0.75$ .

## 4.2 Isotopic system

In order to study the bulk viscosity of a binary mixture with same size of particles and same interaction between them, the zeroth, second, and fourth sum rules of BSAC function have been computed numerically for pure Ar system at  $n^* = n\sigma^3 = 0.584$  and  $T^* = k_B T/\epsilon = 1.19$ . The results obtained for pure Ar system for  $S_0^B(m_1)$ ,  $S_2^B(m_1)$  and  $S_4^B(m_1)$  are  $882.01 \times 10^{-43} \text{J}^2$ ,  $947.3 \times 10^{-17} \text{J}^2 \text{s}^{-2}$  and  $562.2 \times 10^{10} \text{J}^2 \text{s}^{-4}$ , respectively. The corresponding results obtained for  $S_0^l(m_1)$ ,  $S_2^l(m_1)$  and  $S_4^l(m_1)$  are  $1640.7 \times 10^{-43} \text{J}^2$ ,  $1880.6 \times 10^{-17} \text{J}^2 \text{s}^{-2}$  and  $1184.3 \times 10^{10} \text{J}^2 \text{s}^{-4}$ , respectively. Mass dependence of second and fourth sum rules is obtained from equations (18), and (19), respectively. The results obtained are shown in Figures 1 and 2 for  $c = 0.25$  and  $0.75$ . It is seen from the figures that with the increase in mass ratio the values of the sum rules start decreasing and this decrease is sharper for small mass ratio and low mole fraction. But for large  $m_2/m_1$  the decrease in values sum rules is very slow. For example for  $c = 0.25$ ,  $S_2^{l/B}$  is almost constant for  $m_2/m_1$  larger than 12 while for  $c = 0.75$  it becomes constant for  $m_2/m_1$  larger than 8. By using these results for the sum rules in equation (20), the variations of the ratio of the viscosity of the mixture to the viscosity of the pure fluid as a function of mass ratio and composition for an isotopic fluid have been obtained and are shown in Figure 3. The solid line in Figure 3 shows variations of the ratio of the viscosities with the mass ratio at two different compositions ( $c = 0.25$  and  $0.75$ ). For



**Fig. 2.** Variation of the fourth sum rule,  $S_4^{l/B}(m_1, m_2)$  as obtained from equation (19) in units of  $10^{10} J^2 s^{-4}$  of LSAC/BSAC functions for an isotopic system with the mass ratio  $m_2/m_1$  of two species at  $c = 0.25$  and  $c = 0.75$ .

the linear model we obtain

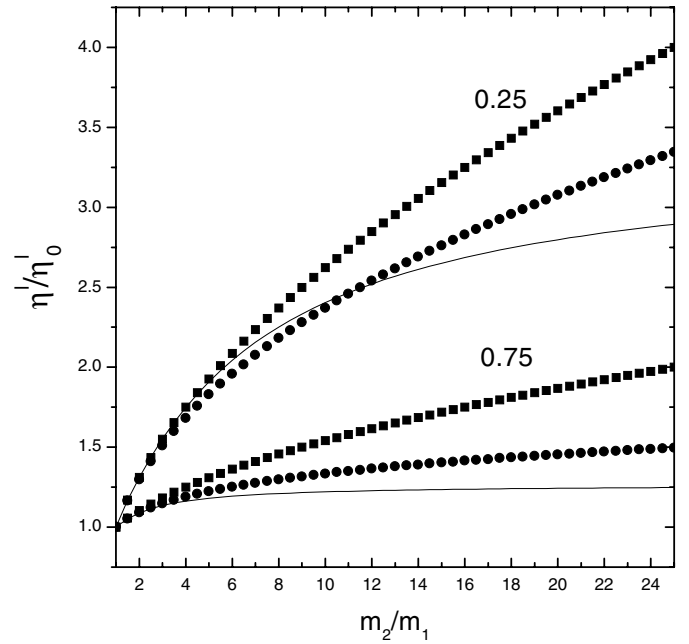
$$\eta_{mix}^{l/B} = \eta_0^{l/B} \left[ c + (1-c) \left( \frac{m_2}{m_1} \right)^{1/2} \right]. \quad (26)$$

On the other hand, for the exponential model we obtain

$$\eta_{mix}^{l/B} = \eta_0^{l/B} \left[ \frac{m_2}{m_1} \right]^{(1-c)/2}. \quad (27)$$

In the above equation  $\eta_0^{l/B}$  is longitudinal/bulk viscosity of pure fluid with mass  $m_1$ . Predictions from equations (26) and (27) are shown in Figure 3 represented by solid squares and circles, respectively. It can be seen from the figure that at  $c = 0.25$ , the prediction of linear model agrees well only for small mass ratios, i.e. for  $\frac{m_2}{m_1} < 4$ . On the other hand, for  $\frac{m_2}{m_1} > 4$ , the predictions of the exponential model are better than those of the linear model. At  $c = 0.75$ , the exponential model predicts better results than the linear model for the entire range of mass ratios. It is also noted that at higher mass ratios i.e. for  $m_2/m_1 > 8$ , the increase in the bulk and longitudinal viscosities with the mass ratio becomes very slow. To examine this large mass ratio effect we consider limiting behavior of equation (20) for large mass ratio

$$\eta^{l/B} = \frac{2n}{\pi k_B T} \left( \frac{(S_0^{l/B})^2}{S_2^{l/B}} \right) \left( \frac{S_4^{l/B}}{S_2^{l/B}} \right)^{1/2}, \quad (28)$$



**Fig. 3.** Variation of the ratio of longitudinal viscosities of an isotopic mixture to that of a pure fluid with mass ratio  $m_2/m_1$  of particles of two species at  $c = 0.25$  and  $c = 0.75$ . Solid squares are results from the linear model and solid circles from the exponential model. The solid lines are results obtained from equation (20).

which for  $c \gg (1-c)m_1/m_2$  reduces to

$$\eta_{mix}^{l/B} = \eta_0^{l/B} \frac{1}{\sqrt{2}} \left( \frac{1+c}{c^2} \right)^{1/2}. \quad (29)$$

This equation implies that a tracer ( $c \simeq 1$ ) does not affect the viscosity of the solvent irrespective of its mass. It further implies that the longitudinal/bulk viscosity of an isotopic mixture is controlled more by molar composition rather than by the ratio of particle masses for large mass ratios. The maximum values that the viscosity can attain for equimolar mixture is  $\sqrt{3}$  times the viscosity of the pure fluid. For  $c = 0.75$  and  $c = 0.25$  these limiting values are  $\sqrt{14/9} = 1.247$  and  $\sqrt{10} = 3.162$ , respectively. These values (shown as horizontal arrows) are in agreement with those observed from the figure. Physically, this implies that when the mass difference is large, transfer of momentum due to sudden compression prefers to take place mainly through lighter particles and as a result the longitudinal/bulk viscosity depends on composition of lighter particles. It can also be seen from Figure 3 that none of the empirical formulae is able to explain this behavior of large mass ratios. There is, to our knowledge, no simulation study to verify these results for isotopic mixtures. However, such studies have been carried out both theoretically and through computer simulations for the self-diffusion coefficients and it was found that heavy tracer particle can have minimum value of self-diffusion which is  $\sqrt{1/2}$  times that of the solvent [25,26]. Here, it is noted that the mass dependence of longitudinal and bulk viscosities is very much similar to that of the shear viscosity

**Table 3.** Results for zeroth, second and fourth sum rules of the LSAC function for pure argon system at six thermodynamic states in units of  $10^{-43} \text{ J}^2$ ,  $10^{-17} \text{ J}^2 \text{ s}^{-2}$  and  $10^{10} \text{ J}^2 \text{ s}^{-4}$ , respectively.

$T^*$	$n^*$	$S_0^l$	$S_2^l$	$S_4^l$
0.73	0.844	1658.015	1004.086	426.537
1.19	0.584	1640.738	1880.594	1184.330
2.56	0.743	7088.385	18463.370	23886.190
3.46	0.500	6275.282	17215.350	29057.180
3.54	0.803	11971.383	45503.990	85383.720
4.45	0.803	16341.481	79322.190	194361.200

**Table 4.** Results for zeroth, second and fourth sum rules of the BSAC function obtained from equations (12)–(14) for pure Ar at six thermodynamic states in units of  $10^{-43} \text{ J}^2$ ,  $10^{-17} \text{ J}^2 \text{ s}^{-2}$  and  $10^{10} \text{ J}^2 \text{ s}^{-4}$ , respectively.

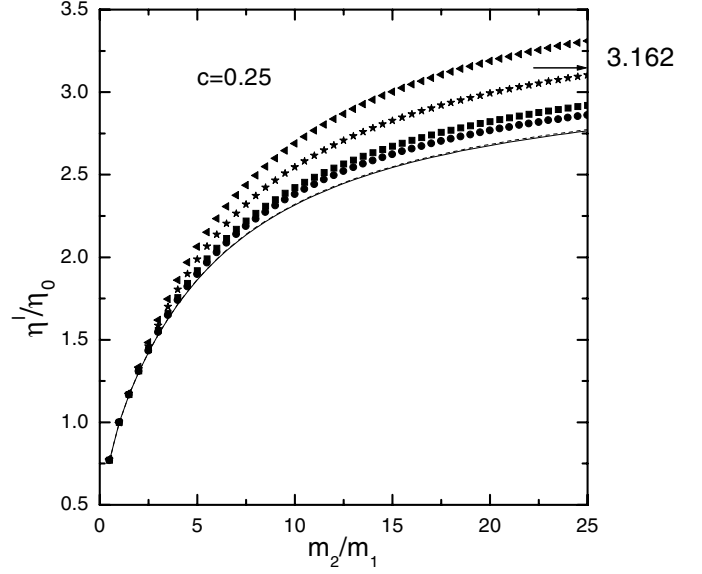
$T^*$	$n^*$	$S_0^B$	$S_2^B$	$S_4^B$
0.73	0.844	943.555	467.609	129.755
1.19	0.584	882.017	947.385	562.271
2.56	0.743	3534.323	10173.163	11352.270
3.46	0.500	3274.432	8733.913	13636.970
3.54	0.803	5244.636	23742.320	48163.190
4.45	0.803	6925.770	45798.540	111246.900

of an isotopic system [20], so that the results presented here for very large mass ratio are equally applicable.

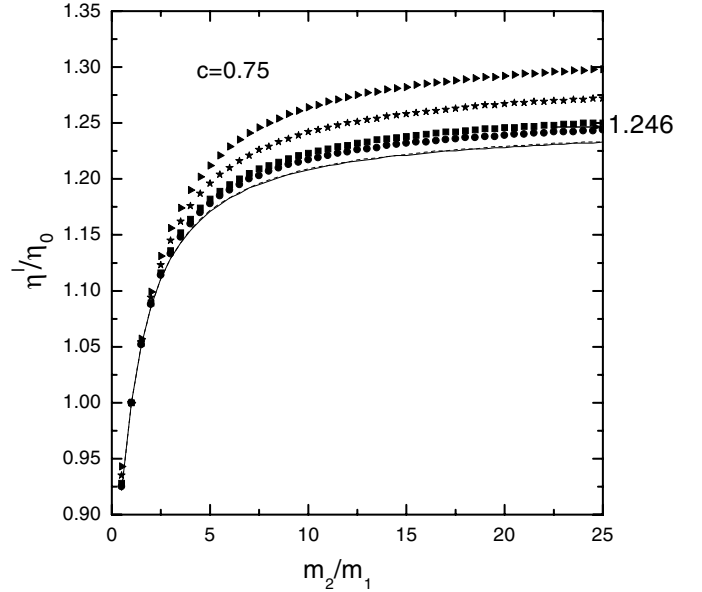
In order to examine whether the above findings depend on the thermodynamic state, we have calculated zeroth, second and fourth sum rules of LSAC and BSAC functions of pure fluid at six thermodynamic states. The results obtained are provided in Tables 3 and 4. The results obtained for  $\eta^l/\eta_0^l$  for  $c = 0.25$  and  $0.75$  are shown in Figures 5 and 6, whereas for  $\eta^B/\eta_0^B$  are shown in Figures 6 and 7. As evident from these figures that the viscosity does not depend on temperature and density for low values of the mass ratio. However, as  $m_2/m_1$  increases, the influence due to thermodynamic states becomes apparent. The value of ratio of viscosity of mixture to viscosity of pure system is found to be lowest for the first thermodynamic state corresponding to  $T^* = 0.73$  and is maximum for the sixth thermodynamic state corresponding to  $T^* = 4.45$ . Here it may be noted that this influence is more evident for longitudinal viscosity than for the bulk viscosity.

## 5 Summary and conclusions

Expressions for the zeroth, second and fourth sum rules of the longitudinal and bulk stress auto correlation functions have been derived for binary mixtures. These expressions have been put in a form suitable for numerical calculations. Numerical results have been obtained for an equimolar Ar–Kr mixture. Longitudinal and bulk viscosities of this mixture have been calculated using Mori’s memory function formalism and the Green-Kubo relation. Our method provides a good description of longitudinal

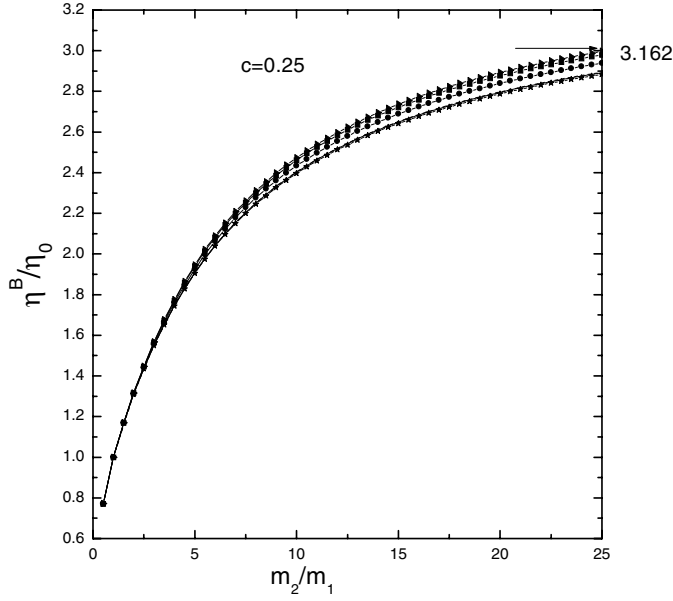


**Fig. 4.** Variation of the ratio of the longitudinal viscosities of an isotopic mixture obtained from equation (20) to that of a pure system with mass ratio of particles of the two species at  $c = 0.25$  for six thermodynamic states. Solid line, dash line, solid square, solid circle, solid star and solid three angle, respectively represent the thermodynamic states given in Table 3 from top to bottom.

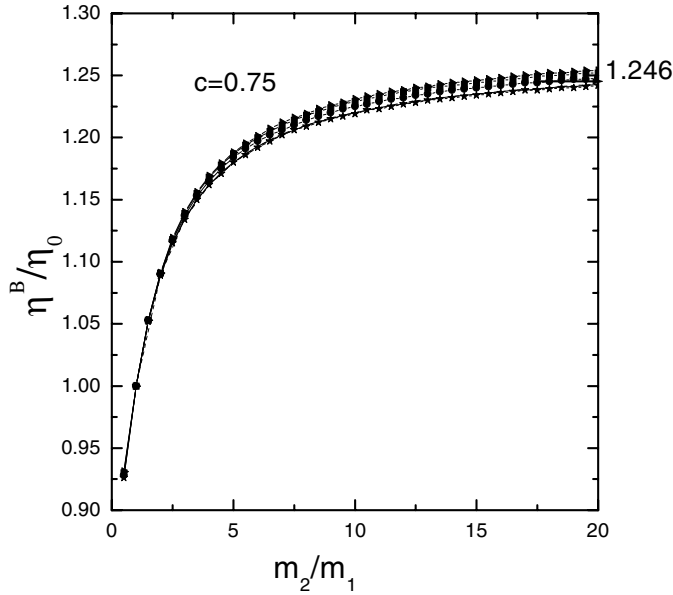


**Fig. 5.** Same as Figure 4 but for  $c = 0.75$ .

and bulk viscosities of fluid mixture as has been judged by comparing our results with that of MD simulation. Further, predictions of the available mixing rules has been compared with present results. We have also studied the mass dependence of longitudinal and bulk viscosities for a modeled mixture in which the two species differ only in their particle masses. It is found that for very high mass ratios viscosity of an isotopic mixture is controlled more by molar composition than by masses. The variation of the ratios of longitudinal and bulk viscosity of an isotopic



**Fig. 6.** Variation of the ratio of the bulk viscosity of an isotopic mixture obtained from equation (20) to that of a pure system, with mass ratio at  $c = 0.25$  for six thermodynamic states. Solid line, dash line, solid square, solid circle, solid star and solid triangle, respectively represent the thermodynamic states given in Table 4 from top to bottom.



**Fig. 7.** Same as Figure 6 but for  $c = 0.75$ .

mixture to those of a pure fluid, with the mass ratio for different compositions have been investigated at six thermodynamic states. It is noted that the dependence is more pronounced for the longitudinal viscosity than for the bulk viscosity.

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## Appendix A: sum rules of LSAC function

The zeroth order sum rule for the LSAC function  $S_0^l$  is defined as

$$S_0^l = \frac{1}{3} \langle J^{aa}(0) J^{aa}(0) \rangle. \quad (\text{A.1})$$

Using equation (3) and evaluating the involved ensemble averages, the expression obtained for  $S_0^l$  after carrying out angular integrations, is given by

$$\begin{aligned} S_0^l = & 4(k_B T)^2 + \frac{2\pi}{15} k_B T \sum_{i,j=1}^2 N_i n_j \\ & \times \int_0^\infty dr r^4 g_{ij}(r) (3A_{ij} r^2 + 5B_{ij}) - 5(VdP/d\bar{E})(k_B T)^2 \\ & - (PV)^2 + (VdP/d\bar{E})^2 (6(k_B T)^2 - \bar{E}^2) \\ & + 2PV^2 (dP/d\bar{E}) \left( \bar{E} - \frac{3}{2} k_B T \right). \end{aligned} \quad (\text{A.2})$$

The expression obtained for the second and fourth sum rules for binary mixture are, respectively, given as

$$\begin{aligned} S_2^l = & \frac{4\pi}{15} (k_B T)^2 \sum_{i,j=1}^2 \frac{N_i n_j}{m_i} \int_0^\infty dr r^2 g^{ij}(r) [(18C_{ij} r^4 \\ & + 165A_{ij} r^2 + 225B_{ij}) + r^2 (k_B T)^{-1} \\ & \times (3A_{ij}^2 r^4 + 5B_{ij}^2 + 6A_{ij} B_{ij} r^2)] \\ & + \frac{8\pi^2}{15} k_B T \sum_{i,j,k=1}^2 \frac{N_i n_j n_k}{m_i} \\ & \times \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3^{ijk}(\mathbf{r}, \mathbf{r}_1) r^2 r_1^2 r r_1 \beta_1 \\ & \times [(A_{ij} r^2 + B_{ij})(A_{1ij} r_1^2 + 5B_{1ij}) + 2\beta_1 A_{ij} A_{1ij} r^2 r_1^2], \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned} S_{42}^l = & \frac{4\pi}{15} (k_B T) \sum_{i,j=1}^2 N_i n_j \frac{1}{4} \left( \frac{1}{m_i} + \frac{1}{m_j} \right)^2 \\ & \times \int_0^\infty dr g_{ij}(r) r^2 [54(k_B T)^2 \\ & \times (D_{ij} r^4 + 10C_{ij} r^2 + 15A_{ij}) + k_B T (1890B_{ij}^2 \\ & + 1504A_{ij}^2 r^4 + 2340A_{ij} B_{ij} r^2 + 216B_{ij} C_{ij} r^4 \\ & + 324A_{ij} C_{ij} r^6 + 18C_{ij}^2 r^8) + 2r^2 (5B_{ij}^3 + 9A_{ij} B_{ij}^2 r^2 \\ & + 9A_{ij}^2 B_{ij} r^4 + 9A_{ij}^3 r^6)]. \end{aligned} \quad (\text{A.4})$$

In addition to the pair correlation function, the exact expression for  $S_4^l$  contains triplet and quadruplet distribution functions. We estimate the triplet contribution to the fourth sum rule from the knowledge of the expression for pure fluids as explained in the Appendix B.

## Appendix B: three body correlation function

For pure fluids there is the superposition approximation for the calculation of triplet contribution. But for a binary mixture there is scarce of knowledge for extending



the superposition approximation for pure fluid. Recently, Kaushal and Tankeshwar [20] proposed the approximation for a binary system given as

$$g_3^{ijj}(\mathbf{r}, \mathbf{r}_1) = g_{ij}(r)g_{ij}(r_1)g_{jj}(|\mathbf{r} - \mathbf{r}_1|)(c + (1 - c)\delta_{ij}), \quad (\text{B.1})$$

where  $c$  and  $1 - c$  are molar compositions of species 1 and 2. This approximation is based on the fact that the correlation between  $i$  and  $j$  species is direct, whereas correlations among the same species is weaker and composition dependent. In the absence of one of the species and also for an isotopic system this approximation reduces to the Kirkwood superposition approximation. The results obtained using this approximation for  $S_{23}^B$  are listed in Table 1. For the triplet contribution to the fourth sum rule of the LSAC/BSAC functions, we have estimated it using the knowledge of the expression for pure system. This method has been explained and successfully tested by Kaushal and Tankeshwar [20]. However, for the sake of completeness, we explain it below for the triplet contribution to second sum rule of the BSAC function. We write  $S_{23}^B$  in reduced units i.e., the length in term of  $\sigma$  and the energy in terms of  $\epsilon$ , so that the integral is dimensionless. In this way, we obtain the expression

$$S_{23}^B = \frac{8\pi^2}{9}k_B T \sum_{i,j=1}^2 \frac{N_i n_i n_j}{m_i} \epsilon_{ij}^2 \sigma_{ij}^4 I_{ij}, \quad (\text{B.2})$$

where  $I_{ij}$  is given by

$$I_{ij} = \int_0^\infty dr^* \int_0^\infty dr_1^* \int_{-1}^1 d\beta_1 g_3^{ijk}(\mathbf{r}, \mathbf{r}_1) r^{*2} r_1^{*2} r^* r_1^* \beta_1 \times (A_{ij}^* A_{1ik}^* r^{*2} r_1^{*2} + B_{ik}^* A_{1ij}^* r_1^2 + A_{ij}^* B_{1ik}^* r^{*2} + B_{ij}^* B_{1ij}^*). \quad (\text{B.3})$$

Here all the quantities are given in reduced units and denoted by the superscript  $\star$ . We assume that the integrand has the same value for all partial triplet correlation functions. This is strictly correct in an isotopic system, but with weighted values in terms of their different potential strength ( $\epsilon$ ) and particle diameter ( $\sigma$ ). Using a similar procedure, the estimate for the triplet contribution to the fourth sum rule is given in Table 1 for the BSAC function and in Table 2 for the LSAC function.

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