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On the relaxation of the translational energy in binary mixtures of dense hard sphere systems

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Abstract

Recently derived analytical equations for the relaxation time characteristic for the equilibration of translational energies in binary mixtures of dense gases possessing different masses and temperatures are verified by molecular dynamics simulations. Such comparisons for translational collision numbers describing the average number of collisions of one particle during the relaxation time are also presented. Even for a large ratio of masses fairly good agreement between the theoretical results and those from molecular dynamics simulations is obtained.

1. Introduction

The theory of the relaxation of translational energy in dilute gases has been analyzed by Sather and Dahler [1], Morse [2], Malkin [3] and Shizgal [4]. Such a theory has also been developed for dilute binary gaseous systems composed of nonreacting, in Ref. [5], and chemically reacting hard spheres in Ref. [6]. The analytical results obtained from Refs. [5,6] have been compared with the results of Monte Carlo computer simulations performed with an application of the Nanbu-Babovsky [7-9] method. Recently, basing on the Enskog equation [10], we have generalized [5,6] to the case of dense systems [11] also performing molecular dynamics simulations [12,13] and comparing analytical and numerical results for the case of spheres possessing the same masses. In this Letter we present molecular dynamics simulations for spheres having different masses and compare them with the results following from the theoretical analytical equations [11]. Since the equilibrium pair correlation function is also used far from equilibrium this generalization is not straightforward.

2. Analytical theory

In this Letter we use formulae derived in Ref. [11]. To compare analytical and numerical results we define the relaxation time τ

$$\frac{\mathrm{d}(T_\mathrm{A}-T_\mathrm{eq})}{\mathrm{d}t} = -\frac{1}{\tau}(T_\mathrm{A}-T_\mathrm{eq}), \tag{1}$$

where t denotes the time. T_eq is the equilibrium temperature related to the temperatures of components A and B by

$$(n_\mathrm{A}+n_\mathrm{B})T_\mathrm{eq} = n_\mathrm{A}T_\mathrm{A} + n_\mathrm{B}T_\mathrm{B}. \tag{2}$$

The relaxation time τ can be calculated using the expression

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$$\tau = \frac{3}{16}\frac{(m_A+m_B)^2}{m_A m_B}\frac{1}{(n_A+n_B)d_{AB}^2\chi_{AB}} \times \left[2\pi k_B\left(\frac{T_A}{m_A}+\frac{T_B}{m_B}\right)\right]^{-1/2}, \tag{3}$$

where m_A and m_B are the masses of spheres, d_{AB} is the arithmetic average of their diameters. n_A, n_B, T_A, T_B denote the number densities and temperatures, respectively, k_B is the Boltzmann constant and χ_{AB} is the radial distribution function at the point of contact of the colliding spheres. In the case of equal diameters $d_A = d_B = d$, which we examine in the present Letter, this function can be obtained from the Carnahan-Starling equation [14]

$$\chi = \frac{1-\eta/2}{(1-\eta)^3}, \tag{4}$$

where η is the packing fraction for equal-sized spheres

$$\eta = \frac{\pi}{6}nd^3. \tag{5}$$

Deriving Eq. (3) the traditional Enskog equation could be used because of the spatially uniform system under consideration [11]. The relaxation time τ calculated from Eq. (3) can be compared with τ^{sim} obtained from the simulations and expressed by

$$\tau^{\text{sim}} = t\left(\ln\frac{(T_A-T_{\text{eq}})_{t=0}}{(T_A-T_{\text{eq}})_t}\right)^{-1}. \tag{6}$$

The quantity Z, which describes the average number of collisions of a sphere of type A during the relaxation time, is another quantity useful for comparisons between analytical theoretical and 'experimental' simulation results

$$Z = \tau[N_{AB}]/n_A, \tag{7}$$

where $[N_{AB}]$ is the collision frequency in a dense system expressed by

$$[N_{AB}] = 2\chi_{AB}n_A n_B d_{AB}^2\left[2\pi k_B\left(\frac{T_A}{m_A}+\frac{T_B}{m_B}\right)\right]^{1/2}. \tag{8}$$

As can be seen from Eqs. (3) and (8), the collision number Z can be calculated by

$$Z = \frac{3}{8}\frac{(m_A+m_B)^2}{m_A m_B}\frac{n_B}{n_A+n_B}. \tag{9}$$

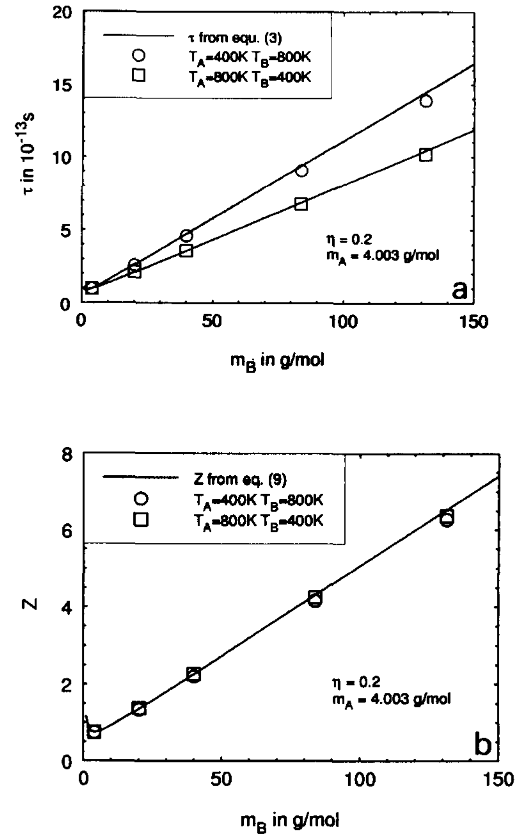

Fig. 1. (a) The relaxation time τ and (b) the collision number Z as a function of masses m_B for the packing fraction $\eta = 0.2$. Simulation results are represented by squares and circles. Corresponding theoretical results calculated from Eq. (3) and Eq. (9) are drawn with solid lines.

The collision number Z can also be calculated from simulations by

$$Z^{\text{sim}} = \tau^{\text{sim}}[N_{AB}]/n_A. \tag{10}$$

To calculate Z^{sim} we use τ^{sim} obtained from simulations and $[N_{AB}]$ which, as we have checked by simulations, can be evaluated with good accuracy from Eq. (8). Thus, we can compare τ with τ^{sim} as well as Z with Z^{sim}.

3. Molecular dynamics simulations

In order to have good statistics we performed 500000 independent runs with the system described. Our system consisted of 54 spheres A and 54 spheres

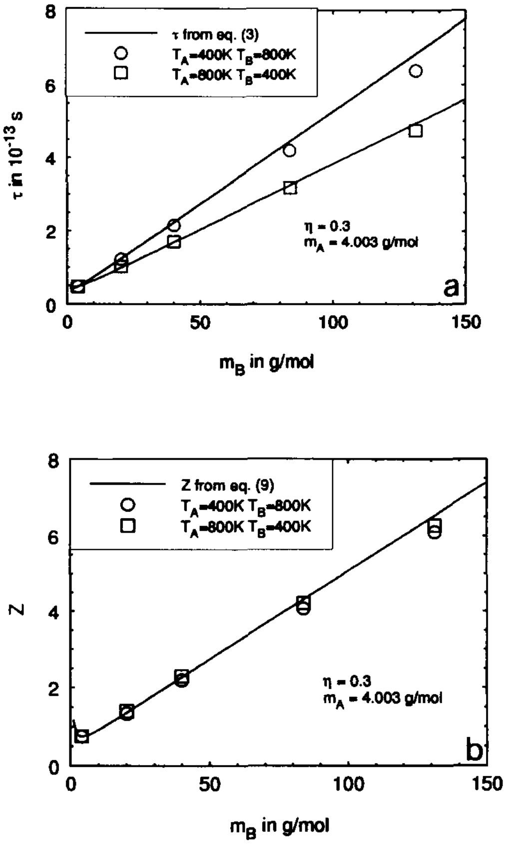

Fig. 2. (a) The relaxation time τ and (b) the collision number Z as a function of masses for the packing fraction $\eta = 0.3$. The representation is as in Fig. 1.

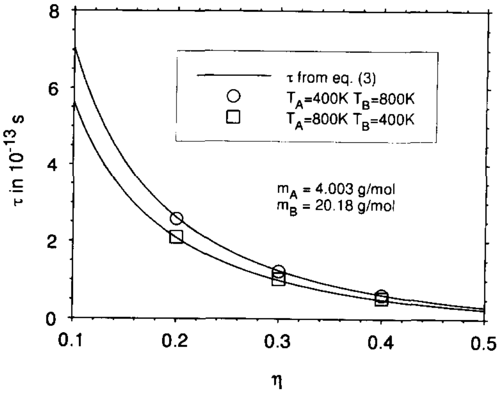

Fig. 3. The relaxation time τ as a function of the packing fraction η. Simulation results are shown by small squares and circles. Theoretical results calculated from Eq. (3) are drawn with solid lines.

B. A comparison of tests with particle numbers 108 and 2916 showed no differences in the quantities of interest except at low densities [11].

Therefore, we have chosen a relatively small particle number and a large number of observed relaxation runs since the computational effort increases more than linearly with increasing particle number.

The spheres belonging to each subsystem were chosen at random so that ideal mixing could be assumed. The diameters of spheres A and B were equal to 3.5 Å and the temperatures of subsystems A and B to $T_A = 800$ K, $T_B = 400$ K at time $t = 0$. Therefore, the equilibrium temperature was $T_{eq} = 600$ K. In connection with our MD runs the 'temperatures' are to be understood in the same way as explained in Ref. [11]. Out of equilibrium they are strictly mean kinetic energies given in temperature units assigning a kinetic energy of $k_BT/2$ to each degree of freedom. The good agreement between theoretical and simulation results justifies the practical usefulness of such quantities for our purpose. We restrict the use of these quantities on the problems under consideration here and do not assume a general validity of this definition of the temperature. We have chosen the size of the molecular dynamics box so that the packing fraction η was 0.2, 0.3 and 0.4, respectively. We performed the simulations over a time period equal to 0.1 ps. The average over 500000 independent runs was taken in the evaluations of the results. This enabled us to obtain for $t = 0$ the temperatures T_A, T_B and T_{eq} with accuracy better than 0.1 K.

Although the diameters of the hard spheres are not equal to those corresponding to the noble gases we introduce the atomic masses of the noble gases He, Ne, Ar, Kr, Xe just to have some typical masses. Fig. 1 shows (a) the relaxation time τ and (b) the collision numbers Z as a function of the mass m_B obtained from computer simulations and from the theoretical expression (Eq. (3) and Eq. (9)) for the packing fraction $\eta = 0.2$. The mass of component A is equal to 4.003 g/mol and the masses of component B are 4.003, 20.18, 39.95, 83.80 and 131.3 g/mol, respectively. For the initial temperatures the cases $T_A = 800$ K, $T_B = 400$ K and $T_A = 400$ K, $T_B = 800$ K are compared. As we can observe, the agreement between the theoretical and numerical results is best if the masses do not differ too much. Fig. 2 shows the same quantities as Fig. 1 but for the packing fraction $\eta = 0.3$. In Fig. 3 the relaxation time τ obtained from computer

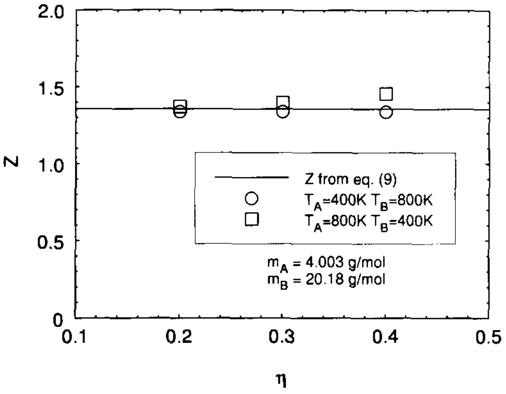

Fig. 4. The collision number Z as a function of the packing fraction η. Results are represented in the same way as in Fig. 3. The constant theoretical value (see Eq. (9)) is represented by a solid straight line.

simulations and from the theoretical expression (Eq. (3)) are shown. In order to analyze the density dependence we have performed simulations for the packing fractions η equal to 0.2, 0.3 and 0.4, respectively. For these simulations we have chosen $m_A = 4.003$ g/mol and $m_B = 20.18$ g/mol and we examined again the cases (1) $T_A = 800$ K and $T_B = 400$ K and (2) $T_A = 400$ K and $T_B = 800$ K. The dependence of the collision numbers Z on the packing fraction η for the same subsystems is shown in Fig. 4.

It would not be effective to extend these MD simulations to lower densities. Since the minimum image convention is used [12,13] artefacts appear if the mean free path and the edge length of the MD box are of the same order of magnitude. Therefore, the MD box must be much larger for lower densities. Unfortunately, for a given density the particle number increases with the third power of the edge length of the MD box. Instead of this large computational effort it seems to us to be more reasonable to extend our direct Monte Carlo simulations of the Boltzmann equation [5] to the case of different masses. Such methods are better suited for the treatment of dilute systems than MD.

The results for $\eta = 0.4$ represent a dense system.

4. Discussion

From the results presented in Figs. 1–4 we see that for the packing fraction η in the range from 0.2 to 0.4 the agreement between theory and simulation results is relatively good. We have obtained differences between the simulation 'experimental' results and the theoretical results in the range from 1 to 5%.

It should be emphasized that this accuracy is worse than that in the case of subsystems with equal masses [11]. This can be understood if we take into consideration that in the system composed of subsystems A and B containing the spheres characterized by the same masses and diameters the nonequilibrium effects need not be large. In this case, although the temperatures T_A and T_B are different, the total system can attain quickly a velocity distribution function near the equilibrium one. Therefore, the correlation function χ (Eq. (3)) obtained from the Carnahan–Starling approach [14], valid for equilibrium, can be a good approximation for χ in the nonequilibrium state in this case. For the systems characterized by different masses, during the timescale corresponding to the relaxation process, the velocity distribution function is still far from the equilibrium state and the role of nonequilibrium effects is more important.

It should be emphasized that the translational energy relaxation plays an important role in the analysis of nonequilibrium effects appearing during a chemical reaction process [15,16,18]. As the values of collisional numbers (Figs. 1b and 2b) and relaxation times for the translational energy are in the same range as such values for rotational energy relaxation [17] these processes can be coupled in the case of molecules. For such comparisons one should take into consideration that the collision number Z_E (describing the energy relaxation, see Ref. [11])) is two times larger than Z.

To summarize, for dense systems composed of two subsystems consisting of hard spheres possessing different temperatures and masses the agreement between the theoretical results for the relaxation times and collision numbers (obtained within our theoretical formalism) and corresponding 'experimental' results obtained in this Letter from molecular dynamical computer simulations is fairly good.

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