Mutual Diffusion and Bulk Viscosity Coefficients of Binary Dense Hard Sphere Mixtures: Kinetic Theory and Molecular Dynamics Calculations

C. Hoheisel[a]; G. Stell[b]

[a] Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany [b] Department of Chemistry, State University New York, Stony Brook, New York, USA

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MUTUAL DIFFUSION AND BULK VISCOSITY COEFFICIENTS OF BINARY DENSE HARD SPHERE MIXTURES: KINETIC THEORY AND MOLECULAR DYNAMICS CALCULATIONS

C. HOHEISEL

*Theoretische Chemie, Ruhr-Universität Bochum,
Universitätsstrasse 150, D-W-4630 Bochum, Germany.*

and

G. STELL

*Department of Chemistry, State University New York,
Stony Brook, New York 11794, USA.*

Bulk viscosity and mutual coefficients of hard sphere (HS) mixtures predicted by kinetic theory are compared with molecular dynamics (MD) results. While for the mutual diffusion only the isotopic 2-component system is considered, for the bulk viscosity, both isotopic and systems composed of differently sized HS's are investigated. The results are interesting in two respects:

i) for the isotopic mixture, value and concentration dependence of the mutual diffusion coefficient given by kinetic theory agree well with the 'exact' MD data.

ii) for mixtures composed of differently sized particles, kinetic theory predicts slightly higher bulk viscosity compared with the MD data, but gives correct trends for the concentration dependence.

KEY WORDS: Transport coefficients, isotopic mixtures.

1 INTRODUCTION

In a recent study[1] we compared kinetic theory and molecular dynamics (MD) computation results for all the thermal transport coefficients of the 1-component Lennard-Jones liquid. While the diffusion coefficient appeared to be in reasonable agreement, the bulk viscosity was much too high as predicted by kinetic theory.

It was therefore tempting to study also a dense 2-component system in order to examine whether kinetic theory is capable of predicting the composition dependence of transport coefficients correctly. For Lennard-Jones mixtures, there exist no data for thermal transport coefficients predicted by kinetic theory. However, dense hard-sphere (HS) mixtures have extensively been studied by kinetic theory[2,3]. Consequently we perform here our comparisons for the mutual diffusion and the bulk viscosity of HS mixtures.

Although the mutual coefficient D_{12} has been calculated for various kinds of HS model mixtures by kinetic theory, we consider here only the isotopic mixture. The reason is the awkward thermodynamic factor that is needed for the determination of the diffusion coefficient, when nonideal mixtures are taken into account. An accurate evaluation of the thermodynamic factor by MD computations requires an enormous computational effort which should be avoided.

For thermodynamically ideal, isotopic mixtures the thermodynamic factor is unity, and therefore these systems are best suited for comparisons.

On the other hand, computation of the bulk viscosity coefficient, η_v, involves no such thermodynamic factor. Hence this quantity can be compared without difficulties.

2   COMMENTS ON THE CALCULATIONS

2.1   Kinetic theory

Both for the calculation of the mutual diffusion coefficient, D_{12}, and the bulk viscosity coefficient, η_v, we refer to a modified version of the standard Enskog theory. Details of this approach have been given in Ref. 2,4 for D_{12} and for η_v in Ref. 5,6. Repetition is here unnecessary. One remark on the bulk viscosity coefficient may however be in order. Detailed investigation of kinetic theoretical approximations reveals two contributions to this transport coefficient:

$$\eta_k^{kin} = \eta_{k1}^{kin} + \eta_{k2}^{kin},$$

where η_{k1}^{kin} represents a small correction to the dominant η_{k2}^{kin} part. However, as the η_{k2}^{kin}-term appears to be closer to the exact MD results, we present this term only in the following relevant tables and figures.

2.2   Molecular dynamics computations

Basic aspects and details of our equilibrium molecular dynamics computations have been given in a recent report[7]. Here we restrict ourselves to some advice concerning the actual computations for the hard sphere system. Further technical details of the runs are summarized in Table 1. We performed the calculations for the hard soft sphere (HSS) mixture using a soft sphere pair potential with exponents $n = 36$ (36-SS) and $n = 24$ (24-SS) rather than for the HS system. We showed in a recent work how well the n-SS system approximates the genuine HS system for computation of thermal transport coefficients[8].

For the comparison of MD and kinetic theoretical results we chose a medium density range, for which we know that kinetic theory applies fairly well.

The MD values for D_{12} and η_v given in the tables have a statistical uncertainty of 8 and 15 per cent, respectively. The curves presented in the figures are graphically smoothed.

Table 1 Technical details of the MD computations.

A MD runs

	η_v	D_{12}
Number of particles (N)	32	108
Integration time step	10^{-14} s	10^{-14} s
Number of steps per run	$18 \cdot 10^5$	$65 \cdot 10^4$
Number of runs	3–4	4–6
Computation time per 10^3 steps	1.3 s	6.2 s
Ensemble		$NVEp$

$(V:$ volume:
$E:$ total energy;
$p:$ total momentum)

B Pair potential (HSS)

$u(r) = \varepsilon(r/\sigma_{12})^n$
$n = 24$ for determination of η_v
$n = 36$ for determination of D_{12}
$\varepsilon k_B^{-1} = 120$ K (k_B Boltzmann constant)
$\sigma_{12} = 3.405$ Å

C Reduced units

$$n^* = \frac{N}{V} \sigma_{12}^3$$

$$T^* = T k_B/\varepsilon$$

Table 2 States considered for the model mixtures.

State	n^*	T^*
1	0.191	1
2	0.500	1
3	0.600	1
4	0.696	1

Table 3 Binary model mixtures*.

Model	$\dfrac{m_1}{m_2}$	m_1 (a.u.)	$\dfrac{\sigma_{11}}{\sigma_{22}}$	σ_{11} (Å)	Comment
A	5	66.58	1	3.405	isotopic
B	2	53.27	0.8	3.027	
C	1.2	43.58	0.8	3.027	

* $m_{12} = \frac{1}{2}(m_1 + m_2) = 39.95$ a.u.
$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) = 3.405$ Å.

Table 4 Mutual diffusion coefficient calculated by kinetic theory and computed by MD for model mixture A.

x_1	D_{12}^{MD*}		D_{12}^{MD**}	
Mole fraction)	$(10^{-4} \ cm^2 \ s^{-1})$			
0.1	1.16	(0.87)	1.52	(1.25)
0.2	1.12	"	1.61	"
0.3	1.16	"	1.52	"
0.4	1.07	"	1.62	"
0.5	1.01	"	1.62	"

* State 3.
** State 2; numbers in parenthesis from kinetic theory.

3 MODEL MIXTURES

Three different model mixtures have been considered for the studies. The state points are summarized in Table 2, and the potential parameters and the particle masses are given in Table 3.

Mixture model A represents an isotopic 2-component system, for which the mass ratio, m_1/m_2, of the component particles is 5. As we have already stated in the introduction, this system embodies a thermodynamically ideal mixture, and thus thermodynamic factors are unity. System A is therefore well suited for the investigation of diffusion processes, though this type of mixture shows admittedly no very interesting features[9].

The mixture models B and C contain particles of different volume, and hence have more interesting properties. In particular, the particles of component 2 are smaller by about a factor 2. Throughout, we consider here *additive* 'hard soft spheres', for which the interaction diameter of unlike spheres is given by the mean of the diameters of the like spheres.

4 RESULTS AND DISCUSSION

4.1 Mutual diffusion

For model mixture A, we compare MD results and kinetic theoretical predictions of the mutual diffusion coefficient D_{12} in Figure 1. The MD results have been graphically smoothed, while the kinetic theory values stem from Eq. (7) of the work of Kincaid et al.[3] For the chosen densities, the kinetic theory gives values only about 10% lower than the exact ones. Furthermore, the mole fraction dependence of the diffusion coefficient is predicted in exact agreement with MD data. This means, that for the isotopic mixture of the considered mass ratio, the diffusion coefficient is independent
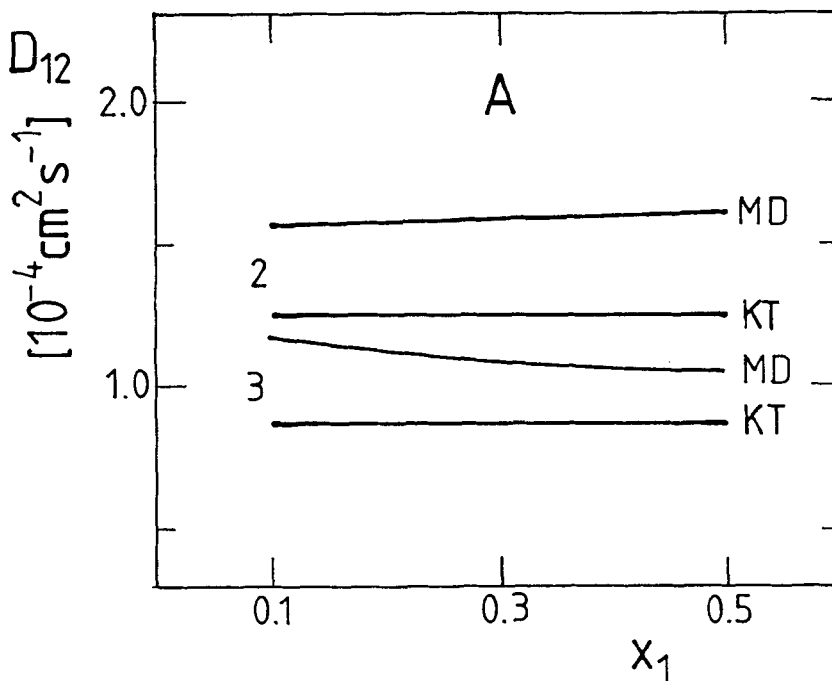
Figure 1 Composition dependence of the mutual diffusion coefficient of the isotopic mixture A computed by MD and predictecd by kinetic theory (Eq. (7) of Ref. 3). $T^* = 1$, $n^* = 0.5$ (2); $n^* = 0.6$ (3).

of the composition. The fact is well known from investigations of Lennard-Jones mixtures ([10] p. 250).

It appears that kinetic theory predicts, in the first Enskog approximation, slightly too low diffusion coefficients, which is in complete agreement with earlier findings of Alder and coworkers[11] for the self-diffusion coefficient of the pure HS fluid at the densities considered.

Higher Enskog approximations should improve agreement of MD and kinetic theoretical calculations, as is shown in the work of Kincaid *et al.*[3] In view of these results we believe that the kinetic theory results for the diffusion in 3-component mixtures given in Ref. 3 should agree well with exact MD data. MD computations for 3-component systems are presently being performed.

4.2 Bulk viscosity

Good agreement is found for the bulk viscosity coefficient, η_v, calculated by the 'K-version' of kinetic theory introduced by one of the authors and collaborators[5,6,12]. The kinetic theory results and the 'exact' MD values can be compared in Figure 2 and Table 5.

Considering first the isotopic mixture A, we notice the excellent agreement of kinetic theory and MD for the composition dependence of η_v presented in Figure 2.
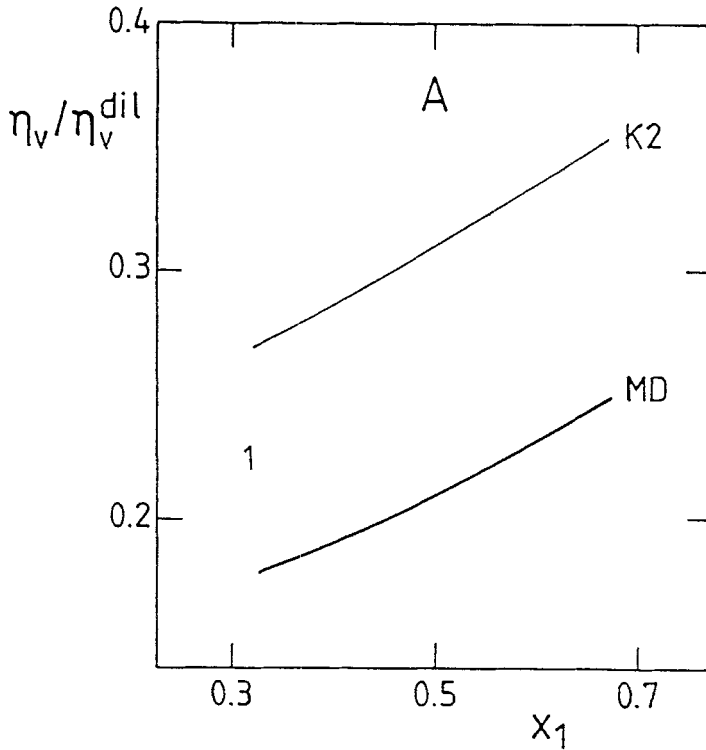
Figure 2 Composition dependence of the bulk viscosity of the isotopic mixture A computed by MD and predicted by kinetic theory (K2). $T^* = 1$, $n^* = 0.191$ (1).

Table 5 Bulk viscosity coefficient calculated by kinetic theory and computed by MD.

Model	State	x_1	η_v/η_v^{dil*} MD	η_v/η_v^{dil*} K2
A	1	0.34	0.192	0.268
		0.44	0.192	0.293
		0.56	0.221	0.324
		0.66	0.245	0.351
B	4	0.34	4.33	13.7
		0.44	4.08	11.6
		0.56	3.59	9.5
		0.66	3.33	8.2
C	4	0.34	3.77	12.8
		0.44	3.39	10.8
		0.56	2.90	8.6
		0.66	2.70	7.2

$$* \, \eta_v^{dil} = \frac{5}{16} \sqrt{\frac{m_2 k_B T}{\pi \sigma_{22}^4}}$$

This discrepancy vanishes, however, when the exact HS system is considered rather than the 24-SS fluid. From ref. (8) we can conclude that the MD η_v-values of the genuine HS fluid exceed those of the 24-SS fluid by about 35%. So kinetic theory predicts practically exact results for η_v of the isotopic HS mixture.

The results for the systems B and C which are gathered together in Table 5 confirm what we have found for the isotopic mixture. While the kinetic theoretical η_v-values exceed the MD values by about a factor of two, the trends are correctly reflected by the theory. In particular, the higher mass ratio of system B with respect to system A leads to slightly enhanced η_v-values of system B relative to A. This tendency is well accounted for by kinetic theory.

The difference between the MD and kinetic theory η_v-values stems primarily from the fact, that we performed the MD for the 24-SS fluid rather than the HS fluid. Using again the results of ref. (8), we are enabled to estimate reliably the growth of η_v going from the 24-SS fluid to the genuine HS system. For the considered densities, we find an increase of the MD values between 50% and 100%. This brings theoretical and computed values in reasonable agreement.

5 FINAL REMARKS

It has been shown that the current version of kinetic theory (RET) accounts correctly for the diffusion process in binary mixtures. Concentration dependence and absolute value predicted by RET agree well with exact MD results.

Good agreement exists also for the value and composition dependence of the bulk viscosity of isotopic mixtures predicted by kinetic theory and computed by MD. For non-ideal mixtures, the bulk viscosity is slightly too high predicted by kinetic theory in comparison with MD data. On the other hand, the composition dependence of η_v is exactly predicted by the theory.

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