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Inhomogeneous hard rod systems: comparison of theoretical and numerical results

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Abstract. The exact dynamics of a system of N hard rods of different masses and the Boltzmann equation for an infinitely extended mixture of two kinds of hard rods are used to derive formulae for the equilibrium velocity distributions, the collision frequency and the velocity autocorrelation function to first order in time. These formulae and a symmetry relation for the self-diffusion coefficients of a binary mixture are used to discuss some of the results of the molecular dynamics simulations performed recently by Marro and Masoliver.

1. Introduction

For many years one-dimensional systems of hard rods have been studied to discuss fundamental problems of (classical) statistical mechanics (see Kasperkovitz and Reisenberger 1985a, Boldrighini 1984, Hiroike 1983, Piasecki 1983, Gevois and Pomeau 1976, de Pazzis 1971). These systems were also used to compare exact theoretical results with those obtained from computer simulations (Haus and Raveché 1978, Bishop and Berne 1974). In most of these investigations all masses were assumed to be equal; only a few papers dealt with systems containing different masses (Boldrighini *et al* 1985, Eder *et al* 1984, Marro and Masoliver 1985a, b, Masoliver and Marro 1983). In a recent series of papers Marro and Masoliver reported on molecular dynamics simulations for binary mixtures of hard rods from which they deduced propositions on the collision frequency, the relaxation of the initial velocity distribution to an equilibrium distribution, short- and long-time behaviour of the single-particle velocity autocorrelation functions for particles of each species, and (approximate) self-diffusion constants.

The purpose of this paper is to compare their findings with theoretical results, as far as they can be deduced from the exact (deterministic) dynamics of the system or its Boltzmann description. These results concern the equilibrium velocity distribution, the collision frequency, the derivatives of the normalised velocity autocorrelation functions at $t = 0$ and a symmetry relation for the self-diffusion constants of a binary mixture. The corresponding formulae are stated in § 2. In § 3 we contrast the theoretical results with the numerical results of Marro and Masoliver and discuss possible reasons for disagreement where it occurs. Our conclusions are summarised in § 4.

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2. Theoretical results

The system under consideration consists of N mass points m_i moving in one dimension. These particles are assumed to move freely until two of them, say those labelled by i and $i+1$, collide with each other. In such an event the initial velocities of the two collision partners, v_i and v_{i+1}, are suddenly changed into

$$v_i' = \frac{m_i - m_{i+1}}{m_i + m_{i+1}} v_i + \frac{2m_{i+1}}{m_i + m_{i+1}} v_{i+1} \tag{2.1}$$

$$v_{i+1}' = \frac{2m_i}{m_i + m_{i+1}} v_i - \frac{m_i - m_{i+1}}{m_i + m_{i+1}} v_{i+1} \tag{2.2}$$

where $v_i > v_{i+1}$ and hence $v_i' < v_{i+1}'$. That is, the mass points are impenetrable and interact through hard core collisions ('hard rods'). We assume that the distance of two particles is limited by a length L ('volume') and that the furthest particles, labelled by 1 and N, interact like nearest neighbours. This can be interpreted in several ways, e.g. by assuming the particles to move on a ring. It is easily seen that the centre of mass moves freely. This trivial part of the motion can be separated from the relative motion but this is of importance for small systems only.

It has been shown that systems where all the masses are equal ('homogeneous systems') are integrable (Kasperkovitz and Reisenberger 1985a, b). This means that the evolution is not ergodic on the whole energy surface but only on tiny fractions of it (strictly speaking, subsets of measure zero). These are the 'invariant tori' or 'smallest stationary ensembles' characterised by N conserved quantities. Since two particles only exchange their velocities in a collision if their masses are equal one may choose the set of initial velocities as these conserved quantities.

There are strong indications that 'inhomogeneous' systems where at least two different finite masses are allowed to collide are ergodic (Foidl 1987), provided that $N > 3$ (for the peculiarities of the three-particle system see, e.g., Rabouw and Ruijgrok (1981) and Richens and Berry (1981)). In the following we shall adopt the ergodic hypothesis for these systems, i.e. we shall interpret expectation values calculated with a microcanonical ensemble as time averages for initial conditions belonging to the same energy. Obviously such an interpretation is not allowed for the homogeneous systems where the smallest stationary ensemble determined by the initial condition has to be used instead.

The quantities we are interested in are the following:

(i) the velocity distribution function, i.e. the fraction of particles which are expected to have a velocity lying in $(v, v+dv)$;

(ii) the average number of collisions of pair $i, i+1$ and the collision frequency derived from it; and

(iii) the velocity autocorrelation function to first order in time.

The velocity distribution is the expectation value

$$f_Z(v) = \frac{1}{N} \sum_i \langle \delta(v_i - v) \rangle_Z \tag{2.3}$$

where Z indicates the ensemble over which the observable is averaged. This label contains the fixed parameters $N, L, m_1, \ldots, m_N$, and the labels E (total energy) or $\{u_i\}$ (set of initial velocities) if the ensemble is constant in time. In any case the average

is formed over all configurations. If $c_{i,i+1}(\tau|V, X)$ = number of collisions of the pair $i, i+1$ within the time interval $(0, \tau)$, if the initial conditions are given by $V = (v_1, v_2, \ldots, v_N)$ and $X = (x_1, x_2, \ldots, x_N)$, then the collision frequency of this pair is

$$\nu_Z^{i,i+1}(\tau) = \left\langle \frac{c_{i,i+1}(\tau|V, X)}{\tau} \right\rangle_Z. \tag{2.4}$$

Note that this quantity is independent of τ if Z is constant in time, i.e. if the ensemble is the closure of one or more orbits in phase space. For these ensembles the collision frequency

$$\nu_Z = \frac{1}{N} \sum_i \nu_Z^{i,i+1} = \frac{1}{t_{0,Z}} \tag{2.5}$$

defines a timescale $t_{0,Z}$. (Note that the frequency (2.5) is one half of the commonly used collision frequency $N^{-1} \Sigma_i \nu_Z^i$, $\nu_Z^i = \nu_Z^{i-1,i} + \nu_Z^{i,i+1}$). The value $t_{0,Z}$ can be used to scale time-dependent expectation values like the velocity autocorrelation function

$$\Phi_Z^i(t) = \langle v_i v_{i,t}[V, X] \rangle_Z. \tag{2.6}$$

For a non-stationary ensemble where initially the velocities are fixed by some vector $U = (u_1, u_2, \ldots, u_N)$ while all configurations are equally probable the expectation values of (2.3), (2.4) and (2.6) are

$$f_U(v) = \frac{1}{N} \sum_j \delta(v - u_j) \tag{2.7}$$

$$\lim_{\tau \to 0} \nu_U^{i,i+1}(\tau) = [(N-1)/L](u_i - u_{i+1})_+ \tag{2.8}$$

and

$$\Phi_U^i(t) = u_i^2 + \frac{2(N-1)}{L} u_i \left(\frac{m_{i-1}}{m_i + m_{i-1}} [(u_{i-1} - u_i)_+]^2 - \frac{m_{i+1}}{m_i + m_{i+1}} [(u_i - u_{i+1})_+]^2 \right) t + O(t^2) \tag{2.9}$$

where

$$(z)_+ = \tfrac{1}{2}(z + |z|). \tag{2.10}$$

From these equations the microcanonical expectation values are obtained by averaging over all vectors U belonging to the energy E. The corresponding functions for the homogeneous system follow from equations (2.7)-(2.9) if one sets $m_i = m$ and averages over all permutations of the initial velocities u_j (Kasperkovitz and Reisenberger 1985a, b, c). It is obvious that the velocity distribution function depends only on the magnitudes of the masses m_i while the total collision frequency and the velocity autocorrelation function depend on the mass distribution at hand, i.e. on the whole sequence $m_1, m_2, \ldots, m_N$ or part of it. If the masses are assigned to the particles at random one has to average ν_E and $\Phi_E^i(t)$ over all possible mass distributions.

In the following we consider the thermodynamic limit of a binary mixture of masses m_a and m_b where the concentrations

$$N_s/N = c_s \qquad s = a, b \tag{2.11}$$

the density

$$N/L = n \tag{2.12}$$

and the energy per particle

$$E/N = \varepsilon = \tfrac{1}{2}k_B T \tag{2.13}$$

approach finite values. For this system the microcanonical expectation values are as follows:

$$f_\varepsilon(v) = c_a f_\varepsilon^a(v) + c_b f_\varepsilon^b(v) \tag{2.14}$$

$$f_\varepsilon^s(v) = \left(\frac{m_s}{4\varepsilon\pi}\right)^{1/2} \exp\left(-\frac{m_s v^2}{4\varepsilon}\right) \tag{2.15}$$

$$\nu_\varepsilon = n\left(\frac{\varepsilon}{\pi}\right)^{1/2}\left[c_a^2\left(\frac{2}{m_a}\right)^{1/2} + 2c_a c_b\left(\frac{1}{m_a}+\frac{1}{m_b}\right)^{1/2} + c_b^2\left(\frac{2}{m_b}\right)^{1/2}\right] \tag{2.16}$$

$$\Phi_\varepsilon(t) = c_a \Phi_\varepsilon^a(t) + c_b \Phi_\varepsilon^b(t) \tag{2.17}$$

$$\begin{aligned} \Phi_\varepsilon^a(t) &= \Phi(\varepsilon, n, c_a, c_b, m_a, m_b, t) \\ \Phi_\varepsilon^b(t) &= \Phi(\varepsilon, n, c_b, c_a, m_b, m_a, t) \end{aligned} \tag{2.18}$$

$$\Phi(\varepsilon, n, c_1, c_2, m_1, m_2, t) = \frac{2\varepsilon}{m_1}\left\{1 - 4n\left(\frac{2\varepsilon}{\pi m_1}\right)^{1/2}\left[c_1 + c_2\left(\frac{2m_2}{m_1+m_2}\right)^{1/2}\right]t + O(t^2)\right\}. \tag{2.19}$$

Since (2.18) is valid for all times it follows from Kubo's formula that the self-diffusion constants D^a and D^b are functionally related by

$$\begin{aligned} D^a &= D(\varepsilon, n, c_a, c_b, m_a, m_b) \\ D^b &= D(\varepsilon, n, c_b, c_a, m_b, m_a) \end{aligned} \tag{2.20}$$

where $D(z_1, \ldots, z_6)$ is the same function in both equations.

According to the ergodic hypothesis we interpret the quantities (2.14), (2.16), and (2.17) or (2.19) for $m_a \neq m_b$ as time averages for fixed initial conditions (V, X). This means, for instance, that the function

$$(\tau N)^{-1} \sum_i c_{i,i+1}(\tau | V, X)$$

averaged over all mass distributions, should tend to (2.16) for $\tau \to \infty$ if E is the total energy calculated from the initial velocities V. Likewise, the quantities (2.14) and (2.17) should be the average of the observables $N^{-1}\Sigma_i \delta(v_{it'}[V, X] - v)$ and $v_{it'}[V, X]_{v_i(t'+t)}[V, X]$, respectively, taken over the infinite time interval $0 \leq t' \leq \tau$, $\tau \to \infty$, and all possible mass configurations.

It is interesting to compare these time averages over infinite time intervals ($\tau \to \infty$) with the corresponding averages over very short times ($\tau \to 0$). For fixed initial conditions (V, X) the abovementioned observables are highly irregular functions of time. To obtain smooth functions it is sufficient to average these observables over all configurations X. This spatial averaging has no influence on the time average for $\tau \to \infty$ since the energy E does not depend on the positions. Therefore, if we specify the initial velocities $v_i = u_i$ and perform the necessary average over the possible mass distributions, we can use equations (2.7)-(2.9) to get some insight into the way these time averages depend on the length of the time interval considered. To this end we now assume that initially one half of the particles have velocities $+c$ and the other half $-c$, the signs being randomly distributed. The order of the signs and the mass distribution are irrelevant for the velocity distribution

$$f_{\{\pm c\}}(v) = \tfrac{1}{2}[\delta(v-c) + \delta(v+c)] \tag{2.21}$$

but the corresponding averages have to be performed to obtain the desired collision frequency and the velocity autocorrelation function.

$$\lim_{\tau\to 0} \nu_{\{\pm c\}}(\tau) = \tfrac{1}{2}nc \qquad c>0 \tag{2.22}$$

$$\Phi_{\{\pm c\}}(t) = c_a\Phi^a_{\{\pm c\}}(t) + c_b\Phi^b_{\{\pm c\}}(t) = c^2[1-2nct+\mathrm{O}(t^2)]. \tag{2.23}$$

Like the quantities (2.21) and (2.22), the linear term of the function (2.23) is independent of the masses although the corresponding terms of the constituents

$$\Phi^a_{\{\pm c\}}(t) = c^2\left[1-2nc\left(c_a + c_b\frac{2m_b}{m_a+m_b}\right)t+\mathrm{O}(t^2)\right] \tag{2.24}$$

and $\phi^b_{\{\pm c\}}(t)$ (obtained by exchanging a and b in equation (2.24)) depend on the mass ratio m_a/m_b and the concentrations c_a and c_b.

All these considerations apply for inhomogeneous systems only. If all masses are equal equations (2.7)-(2.9) have to be averaged over all permutations of initial velocities to obtain the time averages. For the initial conditions considered here one obtains once more the right-hand sides of equations (2.21)-(2.23). However the interpretation is now different: these quantities are now the time averages over an infinite time interval for fixed initial conditions, whereas before the time interval was infinitesimal and the observables were averaged over all possible initial configurations.

It is interesting to note that the results for the collision frequencies and the velocity autocorrelation functions, equations (2.16) and (2.19), and (2.22) and (2.24), respectively, may also be obtained from the Boltzmann equation. For $h^a(v, t|v_0)$, the velocity distribution of an a particle at time t that evolves from the initial distribution

$$h^a(v, 0|v_0) = \delta(v-v_0) \tag{2.25}$$

the Boltzmann equation is

$$\frac{\partial h^a(v, t|v_0)}{\partial t} = -P^a(v_0)h^a(v, t|v_0) + \int W^a(v_0\to v_1)h^a(v, t|v_1)\,\mathrm{d}v_1. \tag{2.26}$$

In this equation the velocity-dependent collision rate

$$P^a(v_0) = \int W^a(v_0\to v_1)\,\mathrm{d}v_1 \tag{2.27}$$

and the transition probability (Eder and Lackner 1984)

$$W^a(v_0\to v_1) = n|v_1-v_0|\left[c_af^a(v_1) + c_b\left(\frac{m_a+m_b}{2m_b}\right)^2 f^b\left(\frac{m_a+m_b}{2m_b}v_1 - \frac{m_a-m_b}{2m_b}v_0\right)\right] \tag{2.28}$$

where the functions $f^s(s=a, b)$ describe the velocity distribution of the collision partners. The collision frequency for the a species follows from (2.27) as

$$\nu^a = \tfrac{1}{2}\int P^a(v_0)f^a(v_0)\,\mathrm{d}v_0 \tag{2.29}$$

where the factor $\frac{1}{2}$ takes into account that in (2.28) and (2.27) the collisions of the test particles with both neighbours are counted while the definition of ν given before in equation (2.5) refers to one (randomly selected) pair only. The corresponding velocity autocorrelation function is given by

$$\Phi^a(t) = \int\int vv_0h^a(v, t|v_0)f^a(v_0)\,\mathrm{d}v\,\mathrm{d}v_0. \tag{2.30}$$

This function is obtained up to first order in t if

$$h^a(v, t|v_0) = \delta(v - v_0) + t[-P^a(v_0)\delta(v - v_0) + W^a(v_0 \to v)] + O(t^2) \quad (2.31)$$

is inserted into the integral (2.20). Formulae for the b species are obtained by interchanging a and b everywhere.

If the functions f^s are the equilibrium distributions (2.15) then

$$\nu_\varepsilon^a = n\left(\frac{\varepsilon}{\pi}\right)^{1/2}\left[c_a\left(\frac{2}{m_a}\right)^{1/2} + c_b\left(\frac{1}{m_a}+\frac{1}{m_b}\right)^{1/2}\right] \quad (2.32)$$

and

$$\nu_\varepsilon = c_a\nu_\varepsilon^a + c_b\nu_\varepsilon^b \quad (2.33)$$

coincides with (2.16). If the distributions f_ε^a and f_ε^b are used in (2.28), (2.27) and (2.30), this integral may be carried out to yield (2.19) with $m_1 = m_a$, $m_2 = m_b$. If the initial distribution (2.21) is used instead of f_ε^a and f_ε^a one obtains

$$\nu_{\{\pm c\}}^a = \tfrac{1}{2}nc \quad (2.34)$$

and $\Phi_{\{\pm c\}}^a(t)$ as given by equation (2.24).

It should be noted that the integrated form of the Boltzmann equation at $t = 0$, equation (2.31), can be derived from exact dynamics of the (finite) system by averaging over all mass distributions and performing the thermodynamic limit. This explains why the exact results listed above can also be derived from a Boltzmann description of the system.

3. Comparison with molecular dynamics simulations

We now compare our theoretical results with the corresponding data of the computer simulations performed by Marro and Masoliver (1985a, b) and Masoliver and Marro (1983). The parameters of the binary mixture studied by these authors are

$$N = L = 1000 \quad (3.1)$$

$$m_a = 1 \qquad m_b = \mu \qquad 1 \leqslant \mu \leqslant 50 \quad (3.2)$$

$$c_a = c_b = \tfrac{1}{2} \quad (3.3)$$

and

$$c = 1. \quad (3.4)$$

The particles with mass $m_a = 1$ were selected at random and so were the particles with initial velocity $+1$.

One topic studied extensively by Marro and Masoliver is the relaxation of the initial velocity distribution

$$f_0(v) = \tfrac{1}{2}[\delta(v-1) + \delta(v+1)] \quad (3.5)$$

to an equilibrium distribution $f_{eq}(v)$ if $\mu > 1$. An irreversible approach to a distribution which is constant in time would contradict Poincaré's recurrence theorem; but it can be expected that within sufficiently long periods of observation the instantaneous distribution of the velocities deviates only slightly from some function $f_{eq}(v)$ for most of the time. This function can then be identified with the time average of the instantaneous velocity distribution, a quantity already considered in the theoretical analysis of § 2.

In all their investigations Marro and Masoliver assume that $f_{eq}(v)$ is one single Gaussian. This is a strange assumption for several reasons.

(i) The authors observed equipartition of energy (Masoliver and Marro 1983). Together with the assumed form of $f_{eq}(v)$ this would imply that $f^a_{eq}(v)$ and $f^b_{eq}(v)$, the equilibrium distributions for the two species, are different non-Gaussian functions the sum of which is a Gaussian. This would call for further explanation, because it is at variance with the usual assumption that in equilibrium all components of a (three-dimensional) gas mixture have Maxwell-Boltzmann velocity distributions with mass-dependent mean-square velocities (Chapman and Cowling 1970).

(ii) Marro and Masoliver calculate the kurtosis

$$k = \langle v^4 \rangle / \langle v^2 \rangle^2 - 3 \tag{3.6}$$

for the experimentally observed distributions f^{MD}_{eq} (here and later on the MD refers to the molecular dynamics simulations of Marro and Masoliver). The values k^{MD} ranging from -0.49 to 3.08 (see table 1) strongly indicate that fitting $f^{MD}_{eq}(v)$ to a single Gaussian, for which $k = 0$, is highly questionable.

Table 1. Standard deviation(s), kurtosis and Boltzmann's H function for equilibrium (= time averaged) velocity distributions.

	μ									
	1.01	1.03	1.05	1.2	2	5	8	10	30	50
σ_a^{TH}	1.0025	1.0075	1.0124	1.049	1.225	1.73	2.12	2.35	3.94	5.05
σ_b^{TH}	0.9975	0.9927	0.9880	0.957	0.866	0.77	0.75	0.74	0.72	0.71
σ^{TH}	1.0000	1.0001	1.0003	1.004	1.061	1.34	1.59	1.74	2.83	3.61
α^{MD}	1.0009	1.0009	1.0014	1.006	1.006	1.33	1.57	1.70	2.54	2.96
k^{TH}	0.0001	0.0007	0.0018	0.025	0.33	1.33	1.81	2.01	2.63	2.77
k^{MD}	−0.49	−0.38	−0.09	−0.09	0.28	1.31	1.70	2.10	2.61	3.08
$-H^{TH}_{eq}$	1.42	1.42	1.42	1.42	1.48	1.68	1.82	1.89	2.26	2.43
$-H^{MD}_{eq}$	0.37	0.37	0.37	0.37	0.37	0.39	0.41	0.41	0.44	0.44

(iii) To illustrate the approach to equilibrium Marro and Masoliver also calculated Boltzmann's H function,

$$H = \int f(v) \ln f(v) \, dv \tag{3.7}$$

for the time-dependent velocity distributions. The limiting value H_{eq} is obtained for the stationary distribution $f_{eq}(v)$. If this is a Gaussian with standard deviation σ then

$$-H_{eq} = \ln \sqrt{2\pi e} + \ln \sigma. \tag{3.8}$$

A linear dependence of $-H^{MD}_{eq}$ on $\ln \sigma^{MD}$ has actually been observed (Marro and Masoliver 1985, figure 2) but the limit found for $\sigma^{MD} \to 1$ is ~ 0.37 instead of $\ln \sqrt{2\pi e} \sim 1.42$ and the slope is ~ 0.07 instead of 1. This is a hint that the approximation of $f_{eq}(v)$ by a single Gaussian is inappropriate or that the runs are too short to extract equilibrium properties.

According to the considerations of § 2 the equilibrium distribution for $\mu > 1$ should be (cf equations (2.14) and (2.15))

$$F_\varepsilon(v) = \tfrac{1}{2}[G_\mu(v) + G_{1/\mu}(v)] \tag{3.9}$$

$$G_\mu(v) = \frac{1}{[\pi(1+\mu)]^{1/2}} \exp\left(-\frac{v^2}{1+\mu}\right) \tag{3.10}$$

where the energy per particle has been chosen as

$$\varepsilon = E/N = \tfrac{1}{4}(1+\mu) \tag{3.11}$$

because of equations (3.1)-(3.4). The standard deviations of the two Gaussians are

$$\sigma_a = [\tfrac{1}{2}(1+\mu)]^{1/2} \qquad \sigma_b = [\tfrac{1}{2}(1+\mu^{-1})]^{1/2}. \tag{3.12}$$

From equations (3.9) and (3.10) one obtains by elementary integration the standard deviation

$$\sigma = \langle v^2 \rangle = \tfrac{1}{2}(2+\mu+\mu^{-1})^{1/2} \tag{3.13}$$

and the kurtosis

$$k = 3\left(\frac{1-\mu}{1+\mu}\right)^2. \tag{3.14}$$

The evaluation of equation (3.7) for $f = F_\varepsilon$ has to be done numerically.

Table 1 shows the values of σ, k and $-H_{eq}$, obtained from theory (superscript TH) and molecular dynamics simulation (superscript MD). The standard deviations σ^{TH} and σ^{MD} are seen to agree for $\mu \leqslant 10$, but for larger mass ratios the wide spread of the velocities of the light particles has either not been reached experimentally or not been properly taken into account. The differences are more pronounced for the kurtosis which according to equation (3.14) should always be positive. The negative values of k^{MD} for $\mu \leqslant 1.2$ indicate that the runs for these mass ratios have been too short to allow a calculation of equilibrium properties. These negative values show a strong resemblance of the initial distribution (3.5) for which $k = -2$. This fact becomes more pronounced as the mass ratio tends to 1. This reflects a fact already pointed out by Marro and Masoliver: if the masses are almost equal the inhomogeneous (ergodic) system very much resembles a homogeneous (integrable) one even for long observation times. On the other hand, k^{MD} and k^{TH} agree well for larger mass ratios. Finally, the most dramatic differences between theory and computer simulation show up in Boltzmann's H function, where $-H_{eq}^{MD}$ shows the same tendency as $-H_{eq}^{TH}$ (monotonically increasing with μ) but is smaller by one order of magnitude. Since $-H_{eq} = -\infty$ for the initial distribution, as can be seen by approximating the distribution (3.5) by a sequence for which the integral (3.7) can be calculated, the small values of $-H_{eq}^{MD}$would suggest that *all* runs were too short to yield reliable results for all equilibrium properties of interest. This is a point which has to be clarified by further investigations.

Another quantity that can be compared is the collision frequency. For $\mu > 1$ one obtains from equations (3.1)-(3.3) and (2.16),

$$\nu_\varepsilon = \frac{1}{8\sqrt{\pi}}[(2+2\mu)^{1/2} + 2(2+\mu+\mu^{-1})^{1/2} + (2+2\mu^{-1})^{1/2}] \tag{3.15}$$

while for $\mu = 1$ and the initial velocities ± 1 one finds

$$\nu_{\{\pm 1\}} = \tfrac{1}{2} \tag{3.16}$$

(cf equation (2.22)). This is *not* the limit of equation (3.15) for $\mu \to 1$ which is $\pi^{-1/2} \sim 0.56$. The discontinuity of the collision frequency, obtained as the time average for two hard rod systems with identical initial conditions but mass ratios $\mu = 1$ and $\mu > 1$, respectively, reflects the qualitative differences between integrable and ergodic systems. In table 2 the values of $t_0 = \nu^{-1}$ of Marro and Masoliver (1985b) are contrasted with their counterparts (3.15) and (3.16).

Table 2. Inverse collision frequency.

	μ										
	1	1.01	1.03	1.05	1.2	2	5	8	10	30	50
t_0^{MD}	2.0	1.97	1.86	1.79	1.77	1.68	1.36	1.16	1.07	0.65	0.50
t_0^{TH}	2.0	1.773	1.773	1.772	1.766	1.684	1.366	1.171	1.080	0.687	0.546

The theoretical values agree with the molecular dynamics data over a wide range ($1.05 \leq \mu \leq 10$). However, for $\mu \to 1$ the measured time unit t_0^{MD} tends to 2, the inverse of the limit

$$\lim_{\tau \to 0} \nu_{\{\pm 1\}}(\tau) = \tfrac{1}{2} \tag{3.17}$$

which is obtained for all runs starting with the velocity distribution (3.5), independently of the mass ratio μ. This is one more hint that the evolution of the 'nearly integrable' systems with $\mu \leq 1.2$ should have been followed for much longer times. One might object that equation (2.22), which yields the frequency (3.17), has been derived by averaging over all positions and all permutations of the initial velocities ± 1. But Marro and Masoliver (1985b) and Masoliver and Marro (1983) state that their results are practically independent of the initial conditions. If the collision frequency $\nu_{V,X} = (N\tau)^{-1} \Sigma_i c_{i,i+1}(\tau | V, X)$ is really (practically) independent of the initial configuration X then averaging over X does not change this quantity (essentially) and its limit for $\tau \to 0$ should be calculable by means of (2.8). The collision frequency $\nu(+0)$ would then be a function of the random variables u_i which here assume the values ± 1 with probability $\frac{1}{2}$. The expectation value of $\nu(+0)$ for this distribution is just $\frac{1}{2}$, as given in equation (3.17). The corresponding standard deviation is ~ 0.02 which would explain why the collision frequency for short times is practically independent of the distribution of the initial velocities ± 1. Note that it is not necessary to make an assumption on how $\nu_{V,X}(\tau)$ depends on the initial positions, once the ergodic hypothesis has been accepted. But this, of course, concerns only the collision frequency $\nu(\tau)$ for large observation times τ.

For medium mass ratios ($2 \leq \mu \leq 10$) where Marro and Masoliver observe the fastest decay of the initial velocity distribution (3.5) their collision frequencies are in excellent agreement with the theoretical values. A systematic deviation from these values occurs again for $\mu \geq 10$, but now in the opposite direction. These deviations may be related to the presence of heavy masses and the special initial conditions chosen here. Consider, for instance, the time $t_1 = n = 1$ after which two neighbouring particles would have collided just once if they had opposite velocities and were initially a distance $L/N = n^{-1} = 1$ apart. Taking into account the initial distribution of the velocities and equations (2.1) and (2.2) for $m_b = \mu \gg 1 = m_a$ we expect that at this moment nearly all the heavy

and ~75% of the light particles still have velocities of magnitude ~1 while ~25% of the light particles have been accelerated to velocities near ±3. Repeating the argument we would expect that after a time $t_2 = 2n = 2$ the magnitude $|v|$ would still be ~1 for the heavy particles, but $|v| \sim 1$ only for ~67% of the light particles, $|v| \sim 3$ for ~27%, and $|v| \sim 5$ for ~6% of them. The heavy particles will, of course, slow down to their thermal velocity, e.g. $|v| \sim 0.6$ for $\mu = 50$, but this will not happen before sufficiently many fast light particles are present. In the initial stage of the evolution the light particles will have to be, on average, much faster than in equilibrium, as can be seen from an example: to slow down a rod of mass $m_b = 50$ from $v_b = 1$ to $v_b' = 0.6$ the light rod of mass $m_a = 1$ must have a velocity of magnitude $|v_a| \sim 9.2$ which is much larger than the equilibrium value $|v_a| \sim 4$. The initial creation of fast particles entails a rapid increase of the collision frequency $\nu(\tau)$ from its initial value $\nu(+0) = 0.5$. Moreover, if the arguments given above hold true, $\nu(\tau)$ will first overshoot its equilibrium value $\nu(\infty) = \nu_\varepsilon$. Consequently, if the observation time τ is not long enough, the measured collision frequency will be too large (and hence t_0 too small) compared to the time average for $\tau = \infty$, and this effect will increase with the mass ratio μ.

The next quantity we want to discuss is the slope of the normalised velocity autocorrelation function at $t = 0$ which is of interest for Langevin-type approximations

$$\psi(t) \sim \exp(-t/\tau) \tag{3.18}$$

which describe the Ornstein-Uhlenbeck process. For the homogeneous system Lebowitz and Sykes (1972) calculated the function for even N, assuming that initially half of the particles have velocity $+c$ and the other half $-c$. Their result for $c = 1$, $n = 1$ and $N \to \infty$ is

$$\psi_{\{\pm 1\}}(t) = \exp(-2t) \tag{3.19}$$

so that the slope at $t = 0$ is equal to -2. This result follows also from (2.9). For the inhomogeneous systems we see from equations (2.19), (3.1), (3.2) and (3.11) that the derivatives of Ψ_ε^a and Ψ_ε^b are given by the formulae

$$-\frac{\partial}{\partial t}\Psi_\gamma^a(t)_{|t=0} = (\tau_{a,\gamma})^{-1} = d_\gamma(\mu) \tag{3.20}$$

$$-\frac{\partial}{\partial t}\Psi_\gamma^b(t)_{|t=0} = (\tau_{b,\gamma})^{-1} = d_\gamma(\mu^{-1}) \tag{3.21}$$

with $\gamma = \varepsilon$ and

$$d_\varepsilon(\mu) = \left(\frac{2}{\pi}\right)^{1/2}[(1+\mu)^{1/2} + (2\mu)^{1/2}]. \tag{3.22}$$

For the non-stationary distribution with the random velocities ±1, $\gamma = \{\pm 1\}$, one finds for the derivatives (3.20) and (3.21) with

$$d_{\{\pm 1\}}(\mu) = \frac{1+3\mu}{1+\mu} \tag{3.23}$$

(cf equation (2.24)).

In their numerical investigations Marro and Masoliver calculated the function

$$\Phi_{V,X}^a(t) = \sum_i^{(a)} \Phi_{V,X}^i(t) \tag{3.24}$$

where

$$\sum_i^{(a)} = \text{sum over all particles with mass } m_i = m_a \tag{3.25}$$

and

$$\Phi^i_{V,X}(t) = v_{i,0}[V, X]v_{i,t}[V, X] \tag{3.26}$$

$v_{i,t'}[V, X]$ being the velocity of particle i at time t' if the initial velocities and positions are given by V and X, respectively. The function (3.24) is neither a time average nor the average over a stationary ensemble. Comparison with the velocity autocorrelation functions defined in § 2 is therefore only possible if one accepts Marro and Masoliver's claim that the function (3.24) is practically independent of X, the initial configuration of the particles. Each of the functions (3.26) could therefore be averaged over X to yield a function that is, to first order in time, given by equation (2.9) with $u_i = v_i$. For the mixture considered here we may then argue as before and replace the linear term depending on the initial distribution of the velocities ± 1 and masses 1 and μ, respectively, by its average. The resulting derivative is given by equation (3.23) which differs significantly from the time average (3.22) expected for $\mu > 1$. Quite the same arguments hold for the second constituent of the mixture. Table 3 shows for both species the theoretical values of the derivative, $(\tau_\varepsilon^{\mathrm{TH}})^{-1}$ and $(\tau_{\{\pm 1\}}^{\mathrm{TH}})^{-1}$, and the values $(\tau^{\mathrm{MD}})^{-1}$ obtained from tables 1 and 2 of Marro and Masoliver (1985b). Note that these τ values were obtained by fitting the functions $\Phi^s_{V,X}(t)/\Phi^s_{V,X}(0)$, $s = a, b$, within a region $0 \leq t \leq t_0$ to exponentials (3.18).

Table 3. Theoretical relaxation times of the velocity autocorrelation function and those obtained by computer simulations (Marro and Masoliver 1985b).

	μ										
	1	1.01	1.03	1.05	1.2	2	5	8	10	30	50
$(\tau_{a,\varepsilon}^{\mathrm{TH}})^{-1}$	2.26	2.27	2.28	2.30	2.42	2.98	4.48	5.59	6.21	10.62	13.68
$(\tau_{a,\{\pm 1\}}^{\mathrm{TH}})^{-1}$	2.00	2.00	2.01	2.02	2.09	2.33	2.67	2.78	2.82	2.94	2.96
$(\tau_a^{\mathrm{MD}})^{-1}$	2.00	1.52	1.57	1.67	1.73	2.03	4.62	4.33	4.94	4.23	4.09
$(\tau_{b,\varepsilon}^{\mathrm{TH}})^{-1}$	2.26	2.25	2.23	2.22	2.11	1.78	1.38	1.25	1.19	1.02	0.97
$(\tau_{b,\{\pm 1\}}^{\mathrm{TH}})^{-1}$	2.00	2.00	1.99	1.98	1.91	1.67	1.33	1.22	1.18	1.06	1.04
$(\tau_b^{\mathrm{MD}})^{-1}$	2.00	1.81	1.91	1.80	1.74	1.51	1.40	1.38	1.26	1.07	0.93

The disagreement of the theoretical and numerical results is obvious. Apart from $\mu = 1$ the values of $(\tau^{\mathrm{MD}})^{-1}$ and $(\tau_{\{\pm 1\}}^{\mathrm{TH}})^{-1}$ are of comparable magnitude for $\mu = 2$ only where they still differ by 13% (light particles) and 10% (heavy particles), respectively. The differences between $(\tau^{\mathrm{MD}})^{-1}$ and $(\tau_{\{\pm 1\}})^{-1}$, which are especially marked for the lighter constituent of the mixture, indicate that averaging the velocity autocorrelation function (3.26) over all particles of the same kind may smoothen the functional dependence on the initial positions but it is insufficient to completely get rid of it. The sum in definition (3.24) makes plausible why it is immaterial which random sequences of masses and signs of the particle velocities have been used in the computer experiment, but even this assertion cannot be proved before the functions $\Phi^i_{V,X}(t)$ are explicitly known.

The discrepancy of the observed derivatives $(\tau^{MD})^{-1}$ and the expected time averages $(\tau_\epsilon^{TH})^{-1}$ is, on the average, even greater; the relative agreement for $\mu = 5$ could be related to the fast relaxation of the initial distribution for this mass ratio (see also Dickman 1985). This is not surprising because the velocity autocorrelation function (3.24) has neither been averaged over different time origins nor over several initial states with the same energy. Moreover, as has been pointed out before and is also evident from the average distribution of the velocities, equations (3.7) and (3.8), the set of initial velocities considered here is very atypical, especially for $\mu \gg 1$. Deviations from the theoretical values are therefore the larger the more the masses differ. It is, however, interesting to note that for $1 < \mu \leqslant 2$ and $\mu \geqslant 30$ the observed values $(\tau^{MD})^{-1}$ are closer to the 'initial' values $(\tau_{\{\pm 1\}}^{TH})^{-1}$ than to the time averages $(\tau_\epsilon^{TH})^{-1}$. This shows once more that these systems are similar to integrable ones over long periods while those with $2 \leqslant \mu \leqslant 10$ reveal ergodic behaviour much sooner.

The only overall agreement between the theoretical and the numerical results reduces to the following qualitative statement. The slope of the light particle's velocity autocorrelation function decreases monotonically with increasing mass ratio μ; for the heavy particles the slope increases monotonically. Theoretically the one slope decreases without limit whereas the other one tends to a finite limit for $\mu \to \infty$.

Finally, let us comment on the mass dependence of the self-diffusion constants D^a and D^b. Marro and Masoliver (1985b) found that their approximate self-diffusion constants $\bar{D}^a$ and $\bar{D}^b$ fitted well to relations of the form

$$D^s = \alpha_s + \beta_s z(m_a, m_b) \qquad s = a, b \tag{3.27}$$

where α_s, β_s are numerical constants and $z(m_a, m_b)$ is the reduced mass $m_a m_b/(m_a + m_b)$. This would be compatible with equation (2.20) if $\alpha_a = \alpha_b$ and $\beta_a = \beta_b$ but Marro and Masoliver found

$$\alpha_a^{MD} = 0.79 \qquad \alpha_b^{MD} = 0.07 \qquad \beta_a^{MD} = -0.61 \qquad \beta_b^{MD} = 0.82. \tag{3.28}$$

It might be that in their original fit the variable was

$$z(m_a, m_b) = \mu/(1+\mu) \tag{3.29}$$

which later on was interpreted as reduced mass because of (3.2). If we consider μ as the mass ratio m_a/m_b then (2.20) and (3.27) imply the following relations between the numerical constants:

$$\beta_a + \beta_b = 0 \tag{3.30}$$

$$\beta_a - \beta_b = -2(\alpha_a - \alpha_b). \tag{3.31}$$

While (3.31) is well satisfied by the parameters (3.28) and the signs of β_a^{MD} and β_b^{MD} are different, as required by (3.30), their magnitudes differ considerably. We therefore think that relation (3.27) with $z(m_a, m_b)$ given by (3.29) should be modified so that it satisfies the general symmetry requirements, irrespective of whether this is an approximate law or a rigorous one.

4. Conclusion

In § 2 we first stated for a binary mixture of hard rods formulae for the equilibrium velocity distribution, the collision frequency and the velocity autocorrelation function

to first order in time. In § 3 our theoretical results were compared with the corresponding numerical results obtained from molecular dynamics simulations for mixtures of 1000 (500+500) rods with mass ratios $\mu = m_b/m_a$ varying from 1 to 50 (Marro and Masoliver 1985a, b, Masoliver and Marro 1983). The results of this comparison and our conclusions are the following.

(i) Contrary to the assumption of Marro and Masoliver the equilibrium velocity distribution is not one single Gaussian but the superposition of two Maxwell-Boltzmann distributions whose differences become more apparent as μ increases.

(ii) The equilibrium values of Boltzmann's H function both decrease with μ but the values calculated by Marro and Masoliver are smaller than those obtained by theory by one order of magnitude. Since the origin of this discrepancy is not clear further investigations are needed to clarify this point.

(iii) The collision frequencies agree well over a wide range of mass ratios ($1.2 \leqslant \mu \leqslant 10$) but the deviations for nearly homogeneous systems ($\mu \leqslant 1.2$) and those containing very heavy particles ($\mu \geqslant 30$) indicate that the runs performed by Marro and Masoliver were too short to extract equilibrium properties (= time averages).

(iv) For the derivative of the velocity autocorrelation function at $t = 0$ agreement was only found for the mass ratio $\mu = 5$ for which the fastest relaxation of the initial velocity distribution has been observed in the computer experiment. For mass ratios $\mu < 5$ and $\mu > 5$ the derivatives obtained numerically differ considerably from the theoretical values, especially the value for the light particles, which is 77% of the theoretical one for $\mu = 1.01$ and only 30% for $\mu = 50$. As for the collision frequency it may be conjectured that these deviations result from the interplay of the slow relaxation of these systems and the peculiar initial conditions used in the molecular dynamics simulation.

(v) We finally concluded from general considerations that the dependence of the self-diffusion constant D^a and D^b on the masses m_a and m_b cannot be of the form given by Marro and Masoliver. Even if the mass-dependent variable $m_a m_b/(m_a + m_b)$ is reinterpreted as $\mu/(1+\mu)$, the numerical constants have to be modified so that D^a and D^b satisfy a symmetry relation that follows from the definition of these constants.

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