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Strong Soret Effect in One Dimension

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We consider a one-dimensional gas of two kinds of particles with different masses interacting through short range interactions. The system exhibits an extreme form of the Soret effect: when the ends of the system are in contact with thermal baths of different temperatures, there is complete separation of the species. We show how this separation can be well described in the Boltzmann approximation and discuss the origin of this odd behavior.

KEY WORDS: Statistical mechanics; off-equilibrium systems; onsager relations.

1. INTRODUCTION

When a binary fluid is subjected to a temperature gradient, the densities ρ_+ and ρ_- of the species become space-dependent in such a way that the relative concentration $\rho_+(x)/\rho_-(x)$ changes along the direction of heat flow. This is the Ludwig–Soret, or Soret effect.[1] That this effect happens does not in itself need an explanation: once the temperature difference takes the system away from equilibrium and breaks translational symmetry, there is no reason why the ratio of concentrations should stay constant.

However, the Soret effect has practical applications in the separation of species,[2] and this requires a quantitative prediction of its magnitude in each case. There have been several analytic approaches to do this for gases,[3] condensed phases,[4] grains in suspension,[5] porous media,[6] etc. (For a review, see ref. 7).

From a purely theoretical point of view the Soret effect is interesting because it cannot in general be discussed in terms of local equilibrium, in

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which a space-dependent local temperature fully accounts for the concentration ratio—as for example the local pressure accounts for the variation of the density in a gas column under gravity. To see this explicitly, we consider here a model belonging to a family of systems for which such a local equilibrium approximation yields strictly zero effect, contrary to observation. They consist of two species of different masses m_+ and m_-, interacting through a pair potential $V(r_i - r_j)$ which does not depend on the particle type (the masses of particles i and j). A short calculation shows that the partition function Z of such a system is of the form:

$$\frac{1}{V} \ln Z(\rho_+, \rho_-, T) = -\rho_+ \ln \rho_+ - \rho_- \ln \rho_- + \frac{d}{2} \rho_+ \ln(m_+ T) + \frac{d}{2} \rho_- \ln(m_- T) - \beta F(\rho, T) \tag{1}$$

where F depends on ρ_+, ρ_- only through their sum $\rho \equiv \rho_+ + \rho_-$, and d is the dimension. Assume now that under heat flow we can divide space in small cells $\delta^d(x)$ with densities $\rho_+(x)$ and $\rho_-(x)$, within which the system is in equilibrium at temperature $T(x)$. The total partition function will then be a product expressions (1) for each cell. If we now maximize it with respect to $\rho_+(x)$ and $\rho_-(x)$ (with fixed number of particles) we get:

$$\begin{aligned} \alpha_+ &= -\frac{1}{T(x)} \frac{\partial F}{\partial \rho}(\rho, T(x)) - \ln(\rho_+) + \frac{d}{2} \ln(m_+) \\ \alpha_- &= -\frac{1}{T(x)} \frac{\partial F}{\partial \rho}(\rho, T(x)) - \ln(\rho_-) + \frac{d}{2} \ln(m_-) \end{aligned} \tag{2}$$

with $\alpha_\pm$ space-independent Lagrange multipliers. Subtracting these equations we get $\rho_+ / \rho_- = \text{constant}$, i.e., no Soret effect.

In this paper we study a very simple one-dimensional model which belongs to the class described above, and has a most extreme form of Soret effect: there is total phase separation even for arbitrarily small temperature differences. The two pure phases are separated by an interface in which species are mixed, its width is a function of the parameters. Although this full separation is not realistic, it is interesting to exhibit a model which, for large sizes, is driven far from equilibrium by an arbitrarily small difference of temperature.

We also study in this model the closely related question of the laws for heat transfer. In regions in which phases are pure this transfer has an anomalous spatial and temperature dependence, just as found in oscillator

chains.[8] Within the interface we show that the behavior becomes the usual Fourier law, as recently found by Dhar[9] in a model similar to the present one, but in which particles are forced to stay mixed.

2. THE MODEL

We shall consider a one dimensional system of length L consisting of N point particles of two species: N_+ heavy and N_- light particles of masses m_+ and m_-, respectively.

Particles interact through an infinitely narrow potential of height V, so that when two particles meet they collide if their center of mass energy

$$E_c = \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}(v_1 - v_2)^2 < V \tag{3}$$

and ignore each other otherwise. The collision between particles conserves energy and momentum:

$$v_1 \longrightarrow v_1' = v_1 + \frac{2m_2}{m_1 + m_2}(v_2 - v_1) \tag{4}$$

$$v_2 \longrightarrow v_2' = v_2 - \frac{2m_1}{m_1 + m_2}(v_2 - v_1) \tag{5}$$

These collision rules are reversible and satisfy detailed balance. Between collisions the particles evolve freely across the system. Particles colliding against the walls $x = 0$ and $x = L$ rebounce with a velocity with random distribution corresponding to thermalisation at temperatures T_c and T_h, respectively:

$$P_\alpha(v)\, dv = \frac{m}{\kappa T_\alpha} v \exp\left(-\frac{mv^2}{2\kappa T_\alpha}\right) dv \qquad \alpha = c, h \tag{6}$$

This guarantees that if $T_c = T_h$ the system equilibrates to the Maxwell distribution.

In fact, only the potential between particles of different species is relevant, since particles of equal mass only exchange their velocities in a collision, which then just amounts to exchanging their labels—a one dimensional peculiarity. As a consequence of this, we can consider this model as having a potential $V(r_i - r_j)$ which is independent of particle type (and hence belongs to the family (1)), and at the same time consider that particles of the same type are transparent to one another, and hence our model is a particular case of the one introduced by Widom and Rowlinson.[10]

3. PHASE SEPARATION

We use a simple molecular dynamics in the simulation, calculating the minimum collision time and letting the system evolve freely between collisions. We perform simulations for different number of densities, and different values of the length ranging from $L = 100$ to $L = 2000$, which allows us to consider finite-size effects.

We have checked that in the equilibrium case (the temperature in both sides of the system are identical) the two species are homogeneously distributed in space and their velocity distribution is Maxwellian. We also have checked that for the case of one type of particles with two different temperatures, the average energy is the one corresponding to an homogeneous temperature $\sqrt{T_c T_h}$. This is because if we consider only one type of particles, in the elastic case the particles simply cross the system without any interaction with other particles and it is easy to verify that the distribution of velocities is just composed of two Maxwellian distributions at different temperatures for particles flying in each direction.

In Fig. 1 we show the evolution of the particles after a long thermalisation time, starting from a configuration with random positions ($L = 100$, $V/T_c = 10$, $T = T_h/T_c = 10$, $m_-/m_+ = 0.2$). We can see that the space is divided in two regions with only a single species, separated by an interface in which both species mix. Away from the interface, because all particles have the same mass, the system can be considered as non-interacting. Hence we have the following picture: the heavy particles collide with the hot wall at $x = L$. They fly unperturbed (modulo relabelings) throughout the the heavy-particle phase, until they meet the first light particles around the interface. After one or more crossings and collisions with light particles, they return to the heavy-particle phase, where they are free again. The same can be said of the light particles on the left.

A simple computation helps clarify what happens in the interface. Consider a system with a light and a heavy particle. Estimating their velocities according to the temperatures of the walls, we have:

- If the light particle is on the left and the heavy one on the right:

$$\langle v_-^2 \rangle \approx \frac{T_c}{m_-} \qquad \langle v_+^2 \rangle \approx \frac{T_h}{m_+}, \tag{7}$$

which gives a typical center of mass energy:

$$2E_{\mathrm{CM}}^{(1)} = \frac{(T_c + T_h)(m_+ + m_-) - (\sqrt{T_c m_-} + \sqrt{T_h m_+})^2}{(m_+ + m_-)}. \tag{8}$$

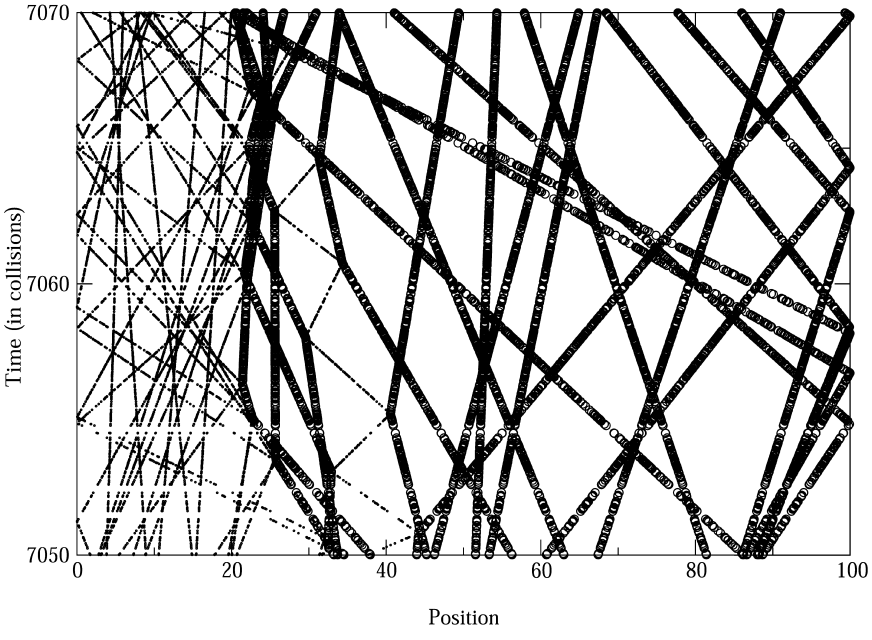

Fig. 1. Plot of the time evolution of the positions of the particles. The large circles correspond to a particles with $m_+ = 1$ while the small ones to a $m_- = 0.2$. The walls are a $T_c(x = 0) = 1$ and $T_h(x = 100) = 10$. The interaction potential is $V = 10$. There are 20 particles of each type.

- If the heavy particle is on the left and the light one on the right:

$$\langle v_-^2 \rangle \approx \frac{T_h}{m_-} \qquad \langle v_+^2 \rangle \approx \frac{T_c}{m_+}, \tag{9}$$

giving the typical precollision center of mass energy:

$$2E_{\mathrm{CM}}^{(2)} = \frac{(T_c + T_h)(m_+ + m_-) - (\sqrt{T_h m_-} + \sqrt{T_c m_+})^2}{(m_+ + m_-)} \tag{10}$$

In fact is easy to show that:

$$A = \frac{2E_{\mathrm{CM}}^{(1)}}{2E_{\mathrm{CM}}^{(2)}} < 1 \qquad \text{if} \quad m_+ > m_-; \qquad T_c < T_h, \tag{11}$$

Hence, we see that the probabilities of collision are not symmetric: while this does not prove that phase separation exists, it gives us the sign of the

effect. Note that there is a similarity with asymmetric exclusion processes,[11] although unlike that case here detailed balance holds in the bulk.

4. INTERFACE

In Fig. 2 we show the time-averaged particle densities $\rho_+(x)$ and $\rho_-(x)$:

$$\rho_\pm(x) = 1/t \lim_{t\to\infty} \int_0^t dt' \sum_{i\in\pm} \delta(x - x_i(t')) \tag{12}$$

for a system with the same parameters as Fig. 1. We see, as before, that the two types of particles are completely separated, but the interface seems much thicker than in Fig. 1. The reason for this discrepancy is simple: the position of the interface fluctuates with time. Upon time-averaging we are actually measuring the instantaneous interface width convoluted with the dispersion in its position.

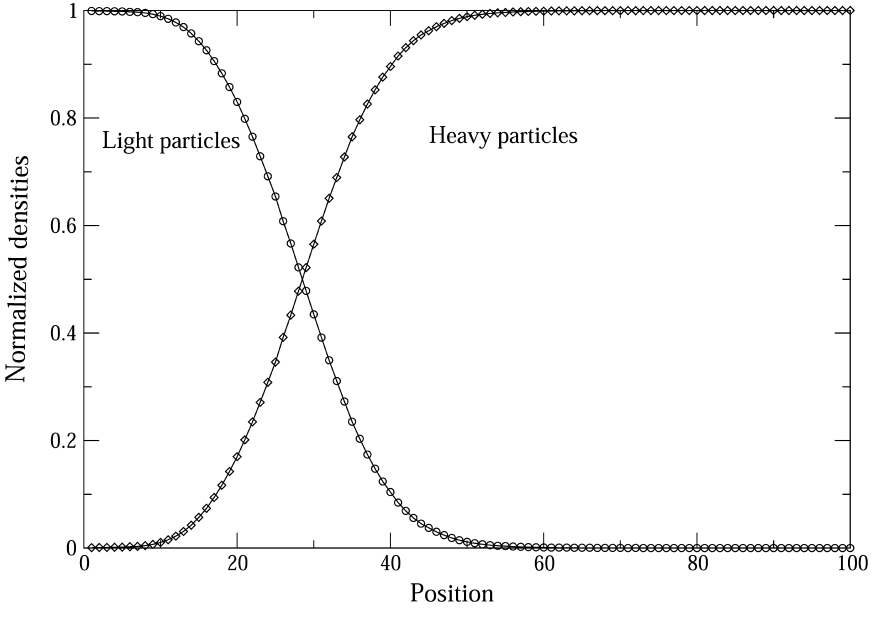

Fig. 2. Plot of the densities ρ_+ and ρ_-. The parameters of the model are the same as in Fig. 1. Data obtained with 100 bins taking measures every 10 collisions during a time corresponding to 500.000 collisions per particle. The diamonds correspond to the heavy particles while the circles correspond to the light ones.

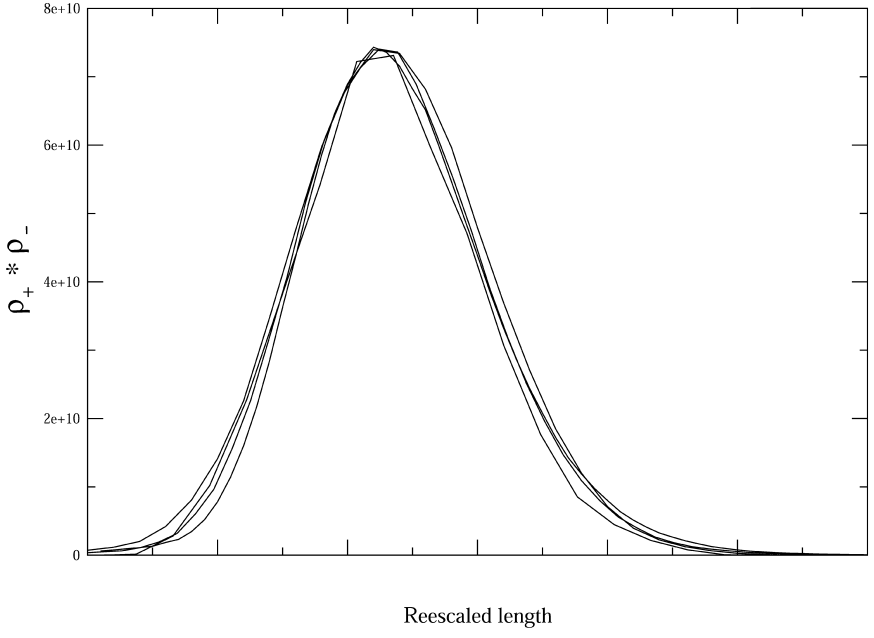

Fig. 3. Plot of the product $\rho_+(x)\,\rho_-(x)$. For different sizes L, centering and rescaling the interface with $\sqrt{L}$. The curves correspond to $L = 100, 200, 400, 800$.

The fluctuations in the position of the interface ΔL scale with the system size L. In Fig. 3 we check the assumption that, just like in an ordinary equilibrium system $\Delta L \propto \sqrt{L}$. In order to do this, we plot the product of densities $\rho_+(x)\,\rho_-(x)$, a quantity that is large only in the interface, for several system sizes and we verify that, indeed, the function scales with $\sqrt{L}$. In Fig. 3 we have considered again the same parameters as in Figs. 1 and 2, and systems lengths from $L = 100$ to $L = 800$. Rescaling the averaged interface with $\sqrt{L}$, the curves collapse.

In Fig. 4 we plot $\rho_+\rho_-$ for a system of length 100 and $V = 10$. On the left figure we vary the temperature of the hot wall keeping the mass ratio constant, while on the right figure we have changed the mass ratio while keeping the temperatures constant. These plots show us the shift in terms of the parameters of the average location of the wall.

As we seen earlier, the time-averaged width of the interface is dominated by the time fluctuations of the wall position, rather than by its instantaneous width. Hence, it is convenient to define a parameter that reflects the mixing of the particles at every time, thus giving a measure of the instantaneous width of the interface. For each heavy particle we count

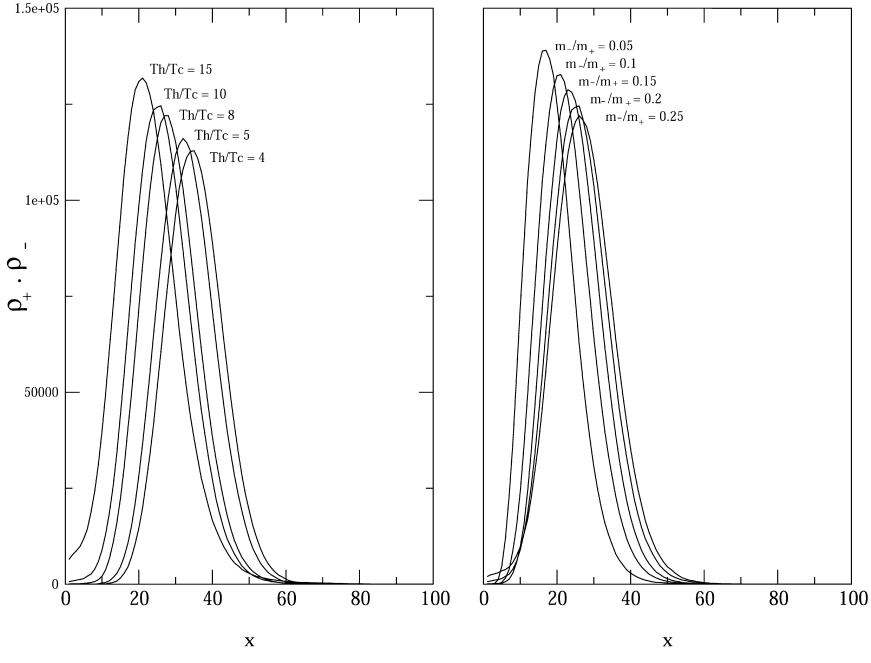

Fig. 4. Product $\rho_+(x)\,\rho_-(x)$ for different values of the parameters. Left: $T_h/T_c = 4$, 5, 8, 10, 15 and $m_-/m_+ = 0.2$. Right: $m_-/m_+ = 0.05$, 0.1, 0.15, 0.2, 0.25 and $T_h/T_c = 10$.

the number q_i $(= 0, 1, 2)$ of its nearest neighbors that are light particles. Our parameter is then:

$$q \equiv \frac{\sum_i^N q_i - 1}{2} \tag{13}$$

For a sharp interface $q = 0$, and for a very mixed system q is of order N. In Fig. 5 we show the frequency distribution of q averaged over many time-steps for various sizes of the system. We see that the averaged distribution of q (which reflects the instantaneous width of the interface) is independent of the system size, as expected. We can hence study how the width changes with the various parameters, in a system-size independent way.

On (a) in Fig. 6 we can see how the sharpness of the interface increases as we decrease the mass ratio. The same effect occurs when we increase the interaction potential (b) or the temperature ratio (c). The physical interpretation of these tendencies is easy to understand. The system is completely mixed when the two thermal walls are at the same temperature. In fact, in this case the asymmetry (11) in the probability of collisions

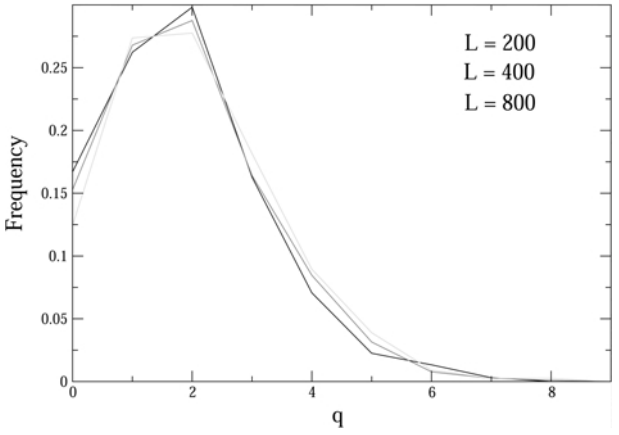

Fig. 5. Check of the size independence of the averaged frequency of q. The parameters are $V/T_c = 5$, $T_h/T_c = 10$, $m_-/m_+ = 0.2$.

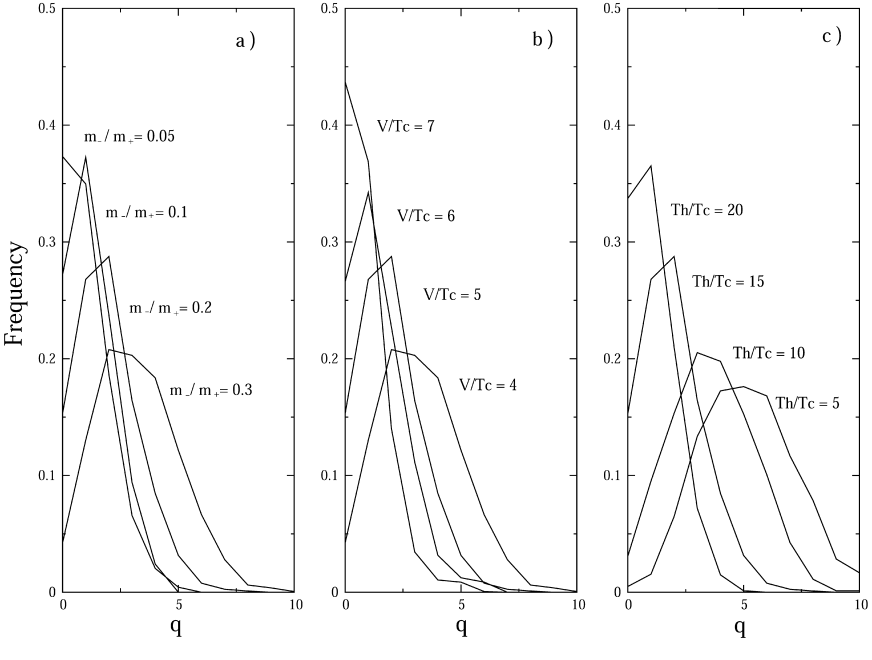

Fig. 6. Dependence of the distribution of q on the parameters. (a) $Th/Tc = 10$, $m_-/m_+ = 0.2$ and $V/T_c = 4$, 5, 6, 7; (b) $Th/Tc = 10$, $V/T_c = 5$ and $m_-/m_+ = 0.05$, 0.1, 0.2, 0.3 (c) $m_-/m_+ = 0.2$, $V/T_c = 5$ and $Th/Tc = 5$, 10, 15, 20.

disappears ($A = 1$), and equilibrium is reached. Obviously if the masses are equal or the interaction potential is zero, the system is also completely mixed because there are no collisions.

We have found no evidence of a threshold in the values below which there is no separation for an infinite system. Indeed, the limit of "mixed particles" (e.g., at equal temperatures or equal masses) is only achieved when the interface length becomes larger than system size.

5. BOLTZMANN EQUATION

Let us now write down a Boltzmann equation for the probability distribution function of the velocities of the particles, and check that it reproduces correctly the phase-separation effect.

We have to deal with two coupled equations:

$$\frac{\partial f(x, v, t)}{\partial t} = -v \frac{\partial f}{\partial x} + \int |v-u| \, \Theta(V - E_c(u, v)) \times (f(x, v', t)\, g(x, u', t) - f(x, v, t)\, g(x, u, t))\, du \tag{14}$$

$$\frac{\partial g(x, v, t)}{\partial t} = -v \frac{\partial g}{\partial x} + \int |v-u| \, \Theta(V - E_c(u, v)) \times (f(x, u', t)\, g(x, v', t) - f(x, u, t)\, g(x, v, t))\, du \tag{15}$$

where $f(x, v, t)$ and $g(x, v, t)$ are the probability distributions for the two types of particles, and $\Theta(x) = 1$ if $x > 0$, and zero otherwise. As usual, u' and v' are velocities the particles should have before the collision in order that the velocities after collision are u and v respectively. These equations must be solved with the adequate boundary conditions (6).

The approximation that is made in Eqs. (14) and (15) is that the correlations between particles are neglected: each particle collision is independent of the collisions the particle has suffered before. More formally, this means that:

$$f_2(x, x', v, v', t) = f(x, v, t)\, f(x', v', t) \tag{16}$$

$$g_2(x, x', v, v', t) = g(x, v, t)\, g(x', v', t) \tag{17}$$

Unfortunately, as far as we know, the system (14) and (15) cannot be solved analytically. We solve it numerically using a stochastic process based on the Bird algorithm[12] which has been proved[13] to converge to the solution of the Boltzmann equation.[14] We have used this algorithm for this system taking into account the point potential.

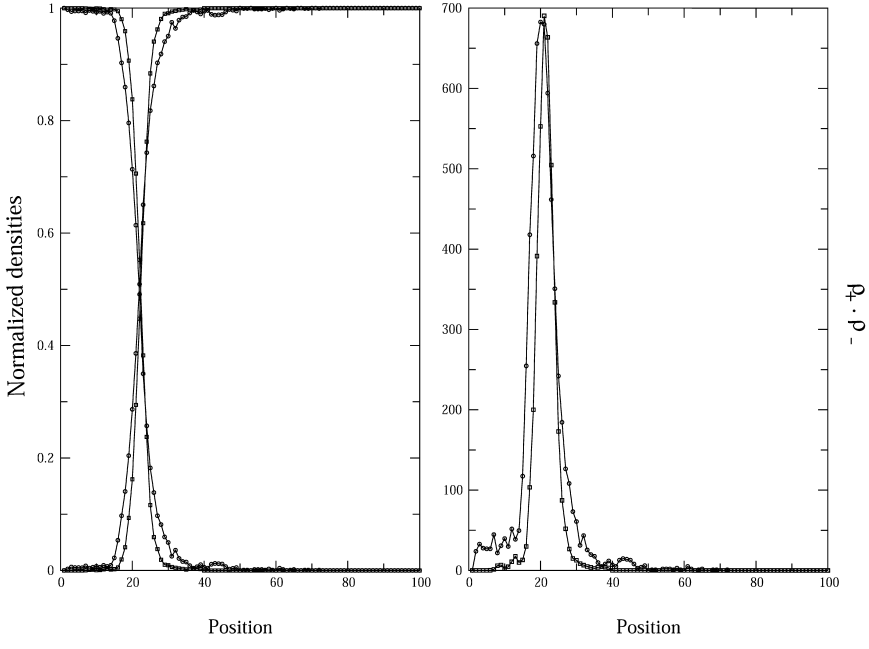

Fig. 7. Left: Densities profiles (left) and $\rho_+(x)\,\rho_-(x)$ (right) for a system of length 100 with 200 particles of each type and $V/T_c = 4$, $m_-/m_+ = 0.2$ and $T_h/T_c = 10$. The squares represent molecular dynamics while the circles the results of the Boltzmann equation.

In Fig. 7 we show the profile of the spatial density of the two types of particles for a system consisting of 200 particles of each type for a potential $V/T_c = 4$, mass ratio $m_+/m_- = 0.2$ and temperature ratio $T_h/T_c = 10$, evolving with the original model. To this we superpose the numerical solution of the Boltzmann equation for the corresponding densities: we can see that the two normalized profiles are almost identical, thus confirming the accuracy of the Boltzmann approximation. We have checked that this good agreement holds for any value of the parameters.

The fact that the Boltzmann equation is a good approximation, at least away from the interface, is easy to understand. As the two species are separated, the most likely situation after a collision is that at least one of the two colliding particles goes freely to its corresponding wall, it loses all memory of the correlation with other particles. Thus, the neglect of the correlations implicit in the Boltzmann equation is a good approximation.

A special note should be made about the interface fluctuations. The Boltzmann equation has a unique solution for every finite length L (it is first order). However, if we were to compute the stability matrix around the solution, we would find that the mode corresponding to translation of the

wall becomes softer as $L \to \infty$. This in turn means that corrections to the Boltzmann approximation become more and more important in that limit, and they yield the wall's fluctuations. (This question becomes more familiar if we bear in mind the analogy with a 2D Ising ferromagnet with the spins on right boundary set to $+1$ and on the left to -1. The Boltzmann equation is analogous to a mean-field solution, which places the interface in the middle, and neglects the fluctuating displacements of the domain wall.)

6. HEAT TRANSPORT—RECOVERY OF LINEAR ENERGY PROFILE AND TEMPERATURE DIFFERENCE DEPENDENCE OF THE CURRENT

In one dimensional systems, the obtention of Fourier's law is still an open question.[15, 17] We shall not study here the size-dependence of the conductivity, but content ourselves with checking the recovery of a uniform energy gradient in the limit of "broad interface."

As mentioned above, this one dimensional model has the peculiarity that particles can be considered non-interacting everywhere except in the interface, where both species mix. This reflects itself in an extremely pathological form of heat transfer: the only spatial gradient in kinetic energy of the particles occurs across the interface, since far from the interface we have a gas of noninteracting particles. It thus seems reasonable, if we wish to recover the usual laws for heat transfer, to place ourself in conditions such that the interface is broader than the sample itself and species are mixed.

In order to study the temperature profile in the interface we have chosen very small temperature differences and species with very similar masses. In Fig. 8 we show the energy profile for a system of length $L = 100$ with 100 particles of each type, with masses $m_+ = 1$ and $m_- = 0.95$, respectively. We plot the energy profile for m_+ for different values of the temperature ratio, $T_h/T_c = 1.05$, 1.10, 1.15, 1.20. We can clearly see that the energy distribution changes linearly along the system, and that it is proportional to the thermal gradient. In fact, the straight lines fitted have all the same slope, indicating that the conductivity in the interface is the same for all cases.

Even in this small gradient case we can see that the mass distribution is not uniform. In fact, the massive particles are located closer to the hottest wall while the lightest ones are closer to the coldest wall, the concentration gradients being uniform. This fact can be seen in Fig. 9, where we have plotted the normalized particle densities for the same case as in Fig. 8 for $T_h/T_c = 1.30$. The error bars for the local energy or density correspond to the estimated variance obtained by computing the r.m.s.d over

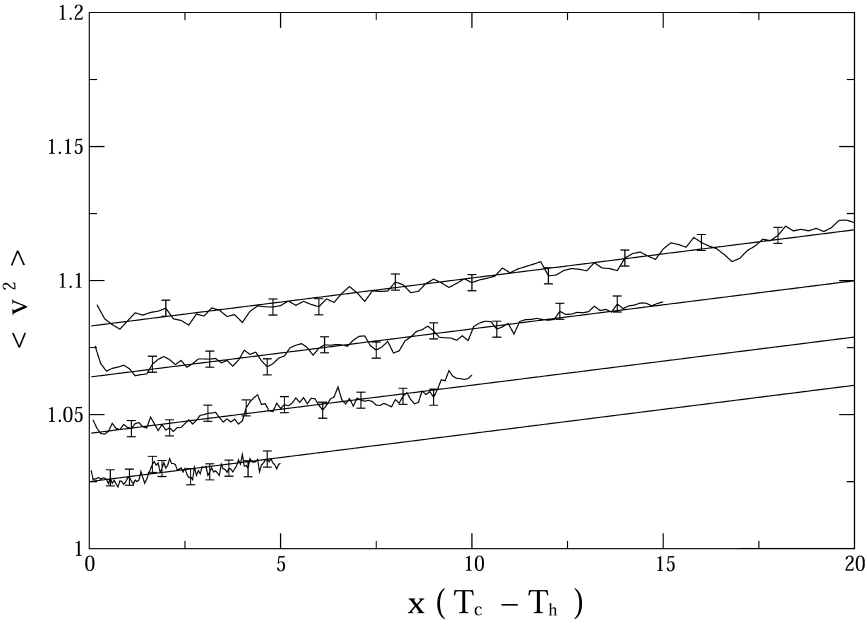

Fig. 8. Plot of the energy profile in function of the temperature ratio along the system for the particles with mass $m_+ = 1$ when the other particles have a mass of $m_- = 0.95$. The length of the system is $L = 100$. The temperature ratios plotted are, from top to bottom, $T_h/T_c = 1.20$, 1.15, 1.10, 1.05. All the fitted lines have the same slope.

several dynamical histories (15 histories were enough to obtain a rough estimate of the errors).

The results above for the broad-interface case are not surprising, in view of the results of Dhar[9] mentioned in the introduction. Note, however, that unlike the present situation, in ref. 9 particles with different masses are never allowed to cross, so the Soret effect is avoided completely.

It can also be seen that for a fixed small thermal gradient, the temperature profile depends linearly on the difference of masses. This fact suggests the possibility of expanding the Boltzmann equation in powers of this parameter and making an estimation of the conductivity for the case in which the masses of the two species are very similar.[16]

7. CONCLUSIONS

In this paper we have numerically solved a model with two types of particles with different masses. We have shown that a thermal gradient is enough to separate completely the two species, at least if the system is large

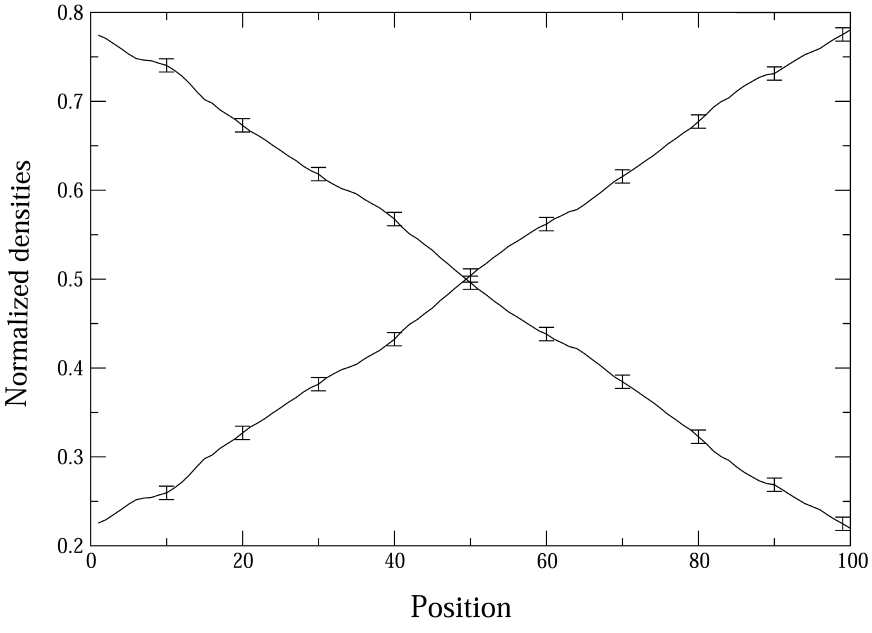

Fig. 9. Plot of the mass profile along the system for the particles with mass $m_+ = 1$ when the other particles have a mass of $m_- = 0.95$. The length of the system is $L = 100$. The temperature ratio considered is $Th/Tc = 1.30$. The curve with positive slope correspond to $m_+ = 1$.

enough to accommodate the interface. The phase separation is due to the collision asymmetry (11) provoked by the thermal gradient applied. For large enough systems, the heavy particles are closer to the hottest wall while the light particles are closer to the coldest one. Between these two regions there is an interface where the two types of particles live together. In the regions occupied by only one type of particles the kinetic energy gradient is zero because the system is a noninteracting gas, so that all the energy density drop is localized in the interface (a finite region of the space). We have also studied the behavior of the interface for different values of the characteristic parameters of the system, showing that its instantaneous width is independent of the system size. By means of a numerical solution of the Boltzmann equation for this systems, we have checked that the total phase separation is also obtained within this approximation [Eqs. (14) and (15)]. We have also investigated the limit of "broad interface," in which the interface is broader than the system itself, and shown that a linear dependence of the heat current on the temperature difference, and a constant gradient of the energy density are recovered in that case.

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