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# A molecular dynamics study of the equilibrium relaxation for inhomogeneous systems

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Using the method of molecular dynamics, we have analysed the relaxation towards equilibrium of an inhomogeneous and isolated system whose constituent particles interact through a Lennard-Jones potential. The initial velocity distribution is of the type leading to the overpopulation effect observed by Tjon. The initial particle number density is uniform but there is a kinetic energy gradient. It has been observed that the tendency to homogeneization of the kinetic energy induces the presence of a gradient in density, in such a way that successive inhomogeneities show up in both quantities, till equilibrium is finally reached. Furthermore, we observe an overpopulation effect for low and high speeds, analogous to the one reported in a previous work. The time scale characterizing the relaxation of the velocity distribution function is much smaller than that of the tendency of the system towards homogeneity.

## 1. INTRODUCTION

Tjon [1], in 1979, numerically solved the Boltzmann equation for a two-dimensional system with maxwellian interactions. Taking some special initial conditions, he found an overpopulation effect at high speeds for homogeneous and isotropic systems. Later, Alexanian and Hauge [2] suggested a criterion to discern the initial conditions giving rise to the effect discussed by Tjon.

Recent molecular dynamics studies [3] seem to indicate the existence of a Tjon effect in real systems. Furthermore, an overpopulation effect in the region of low speeds have been observed, at approximately the same values of time at which the Tjon effect shows up.

The system simulated in [3] was spatially homogeneous, just like the systems studied theoretically with the Boltzmann equation [4]. Our aim in this paper is to study the relaxation towards equilibrium of an inhomogeneous system, starting from an initial distribution of velocities of the type leading to the Tjon effect. In this way, we intend to study the mutual influence between the tendency of the system towards homogeneity and the relaxation of the velocity distribution function.

We present the results of a molecular dynamics simulation of an isolated and inhomogeneous system whose particles interact with a Lennard-Jones potential. Initially, there are only two speeds in the system : a fraction of particles moves with speed $v_\alpha$ and the rest with $v_\beta$. The initial velocity distribution is isotropic. The initial inhomogeneity is generated by distributing spatially the particles

with either one speed or the other, in such a way that the initial kinetic energy has a linear gradient along a given direction but the particle number density is uniform.

## 2. Initial conditions

We consider a system of $N=864$ particles with periodic boundary conditions in the three directions. We take $2l=12$ layers of equal thickness. Layers $j$ and $2l-j$ are considered as totally equivalent because of our boundary conditions. From now on, both layers will be labelled by the same common index $j$. For instance, the index $j=6$ refers to the two central layers of the twelve layers considered in the system.

The initial velocity distribution corresponding to the $j$th layer is isotropic and has the form considered in [3], namely

$$f_j(v\,;\,0)=\frac{N}{l}\,[c_j\delta(v-v_\alpha)+(1-c_j)\delta(v-v_\beta)], \tag{2.1}$$

where

$$c_j=\frac{v_\beta^2-2K_j(0)/m}{v_\beta^2-v_\alpha^2}. \tag{2.2}$$

$K_j(t)$ indicates the kinetic energy per particle at time $t$ in the $j$th layer, and $m$ is the mass of each particle. The normalization of the distribution (2.1) is

$$\int_0^\infty dv f_j(v\,;\,0)=\frac{N}{l}, \tag{2.3}$$

$$\int_0^\infty dv\tfrac{1}{2}mv^2 f_j(v\,;\,0)=\frac{N}{l}K_j(0). \tag{2.4}$$

We take $(k_B T_0/m)^{1/2}$ as velocity unit, $k_B$ being the Boltzmann constant and $\frac{3}{2}k_B T_0$ is the initial kinetic energy per particle of the whole system.

We are interested in the simulation of a system with an initial linear gradient in the kinetic energy per particle. In our case

$$\frac{1}{m}K_j(0)=\tfrac{3}{2}+\gamma\left(j-\frac{1+l}{2}\right), \tag{2.5}$$

where $\gamma$ characterizes the strength of the gradient. We have taken into account that, in terms of reduced units,

$$l^{-1}\sum_{j=1,\,l}K_j(0)/m=\tfrac{3}{2}.$$

Actually, the initial kinetic energy is not a continuous function of the position due to the splitting of the system in layers. Substitution of (2.5) into (2.2) yields

$$c_j=\frac{v_\beta^2-3+\gamma(1+l-2j)}{v_\beta^2-v_\alpha^2}. \tag{2.6}$$

According to (2.1), $c_j$ represents the probability, in the $j$th layer, of finding a particle with speed $v_\alpha$. Therefore, $0\leqslant c_j\leqslant 1$. Inserting this condition in (2.6), we find that

$$\gamma\leqslant\frac{\min\,(3-v_\alpha^2,\,v_\beta^2-3)}{l-1}. \tag{2.7}$$

In our simulation, the particles are initially distributed in a f.c.c. structure. We generate the velocity distribution (2.1) with the $c_j$s given by (2.6) by assigning three random numbers to each particle. One of them determines the speed of the particle ($v_\alpha$ or $v_\beta$) and the other two its direction [3]. We have studied the cases corresponding to the following pairs of values $(v_\alpha, v_\beta)$: (1, 2), (1, 3), (1, 4), and (1, 5). In all our experiments, the number density is $\rho = 0{\cdot}60\ \sigma^{-3}$, the parameter $T_0 = 3{\cdot}00\ \epsilon/k_B$, and the time step chosen for the integration of the equations of motion is $h = 0{\cdot}032\ (m\sigma^2/48\epsilon)^{1/2}$, $\epsilon$ and $\sigma$ being the parameters of the Lennard–Jones potential. We assign to $\gamma$ the maximum value allowed by expression (2.7) in each case.

Some comments about the way of generating the initial state of the system are needed. It is clear that different sets of random numbers lead to different initial velocities of the particles (i.e. different microstates). Actually, one should consider a sufficiently large number of initial microstates and average the results over them. Nevertheless, this is beyond our present computational possibilities. We have only considered several microstates corresponding to one of the studied macrostates, i.e., corresponding to the same initial distribution of velocities. The results are analogous to the ones of figure 1 in [3]. Therefore, they are not reproduced here. The velocity distribution shows dispersions which can be estimated as between 5 and 20 per cent, depending upon the region of speeds considered. In any case, we expect that when using a coarse grained description, the results obtained with a microstate are significant to characterize the evolution of the macrostate.

We have considered an initial configuration of the f.c.c. type and one could wonder whether this fact affects the time evolution of the system. Analysis of the results shows that the system has totally forgotten its initial structure for times $t \gtrsim 20\ h$. We shall see that the destruction of the initial structure is related precisely to an abrupt transformation of kinetic energy into potential energy. For both reasons, the results for very short times are not significant. In any case, one of the main goals of the present paper is to study the influence of the initial inhomogeneities on the effect of overpopulation, and, in the study of the homogeneous case of [3], it was also admitted that the particles were initially distributed according to a f.c.c. lattice.

## 3. Results

Since the simulated system is considered to be isolated, its total energy must remain constant. In figure 1, we have plotted the kinetic energy per particle $K(t)$ and the total energy per particle $E(t)$ for the whole system, as functions of time for the pair $v_\alpha = 1$, $v_\beta = 3$. The total energy does indeed remain practically constant. The kinetic energy decreases initially, due to the initial spatial localization of the particles, until it reaches a final value about which it oscillates [5].

Let us recall that the initial density of the system is homogeneous (in the sense that there are the same number of particles $N/l = 144$ in each layer), but the kinetic energy per particle has a linear gradient. The system is isolated and therefore it must evolve in time towards a spatially homogeneous equilibrium state. Thus, we are going to study the time evolution of the kinetic energy per particle $K_j(t)$ and of the number of particles $n_j(t)$ in each layer. These quantities are plotted for the pair $(v_\alpha, v_\beta) = (1, 2)$ in figure 2 and for $(v_\alpha, v_\beta) = (1, 5)$ in

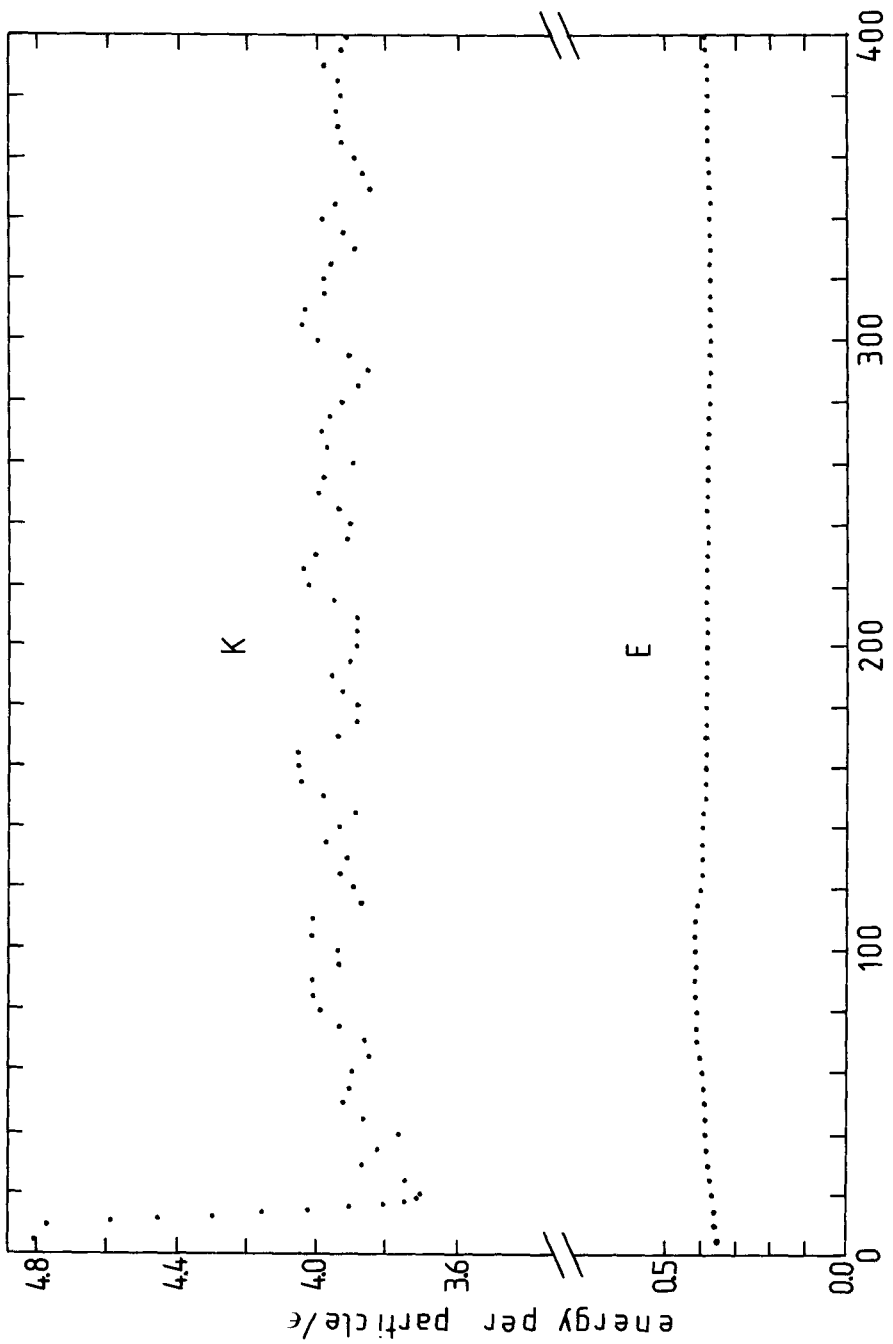


Figure 1. Time evolution of the total energy per particle ($E$) and the kinetic energy per particle ($K$) for the case $v_x = 1$, $v_\beta = 3$.

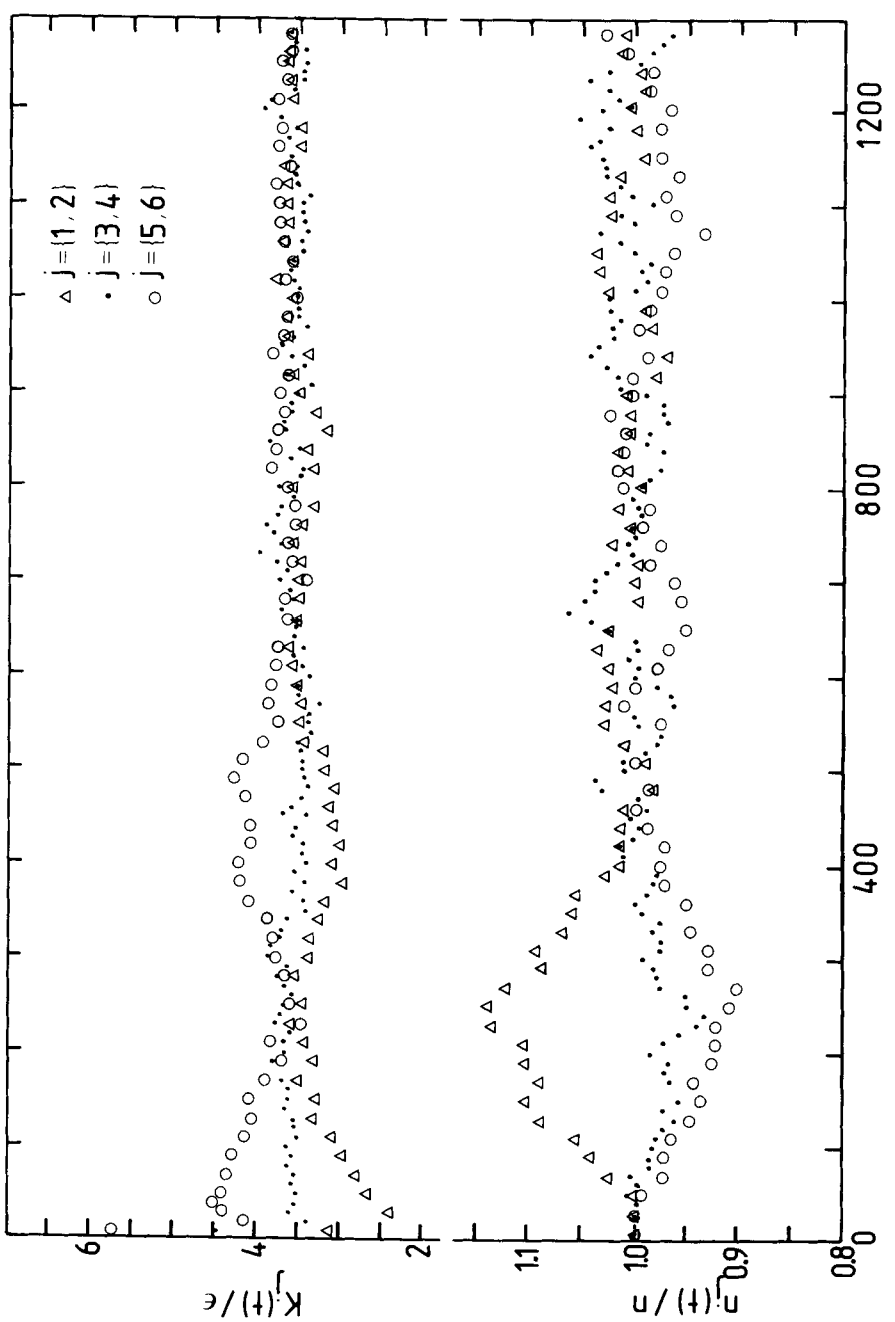


Figure 2. Time evolution of $K_j(t)$ and $n_j(t)/n$ for the case $(v_\alpha, v_\beta)=(1,2)$; $K_j(t)$ is the kinetic energy per particle in the layer $j$, $n_j(t)$ is the number of particles in the layer $j$, and $n=N/(l/2)$ is its average value.

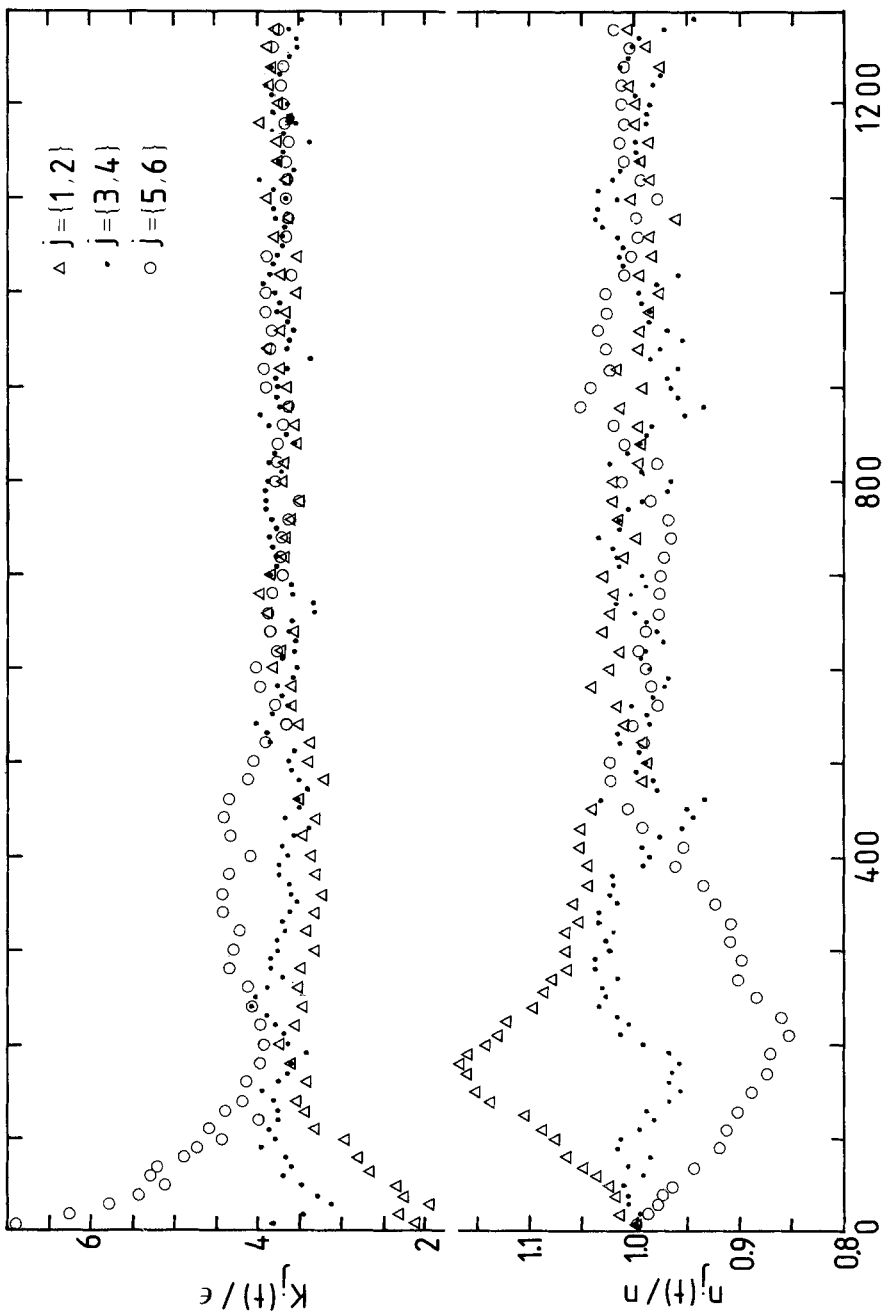


Figure 3. Time evolution of $K_J(t)$ and $n_J(t)/n$ for the case $(v_\alpha, v_\beta)=(1, 5)$.

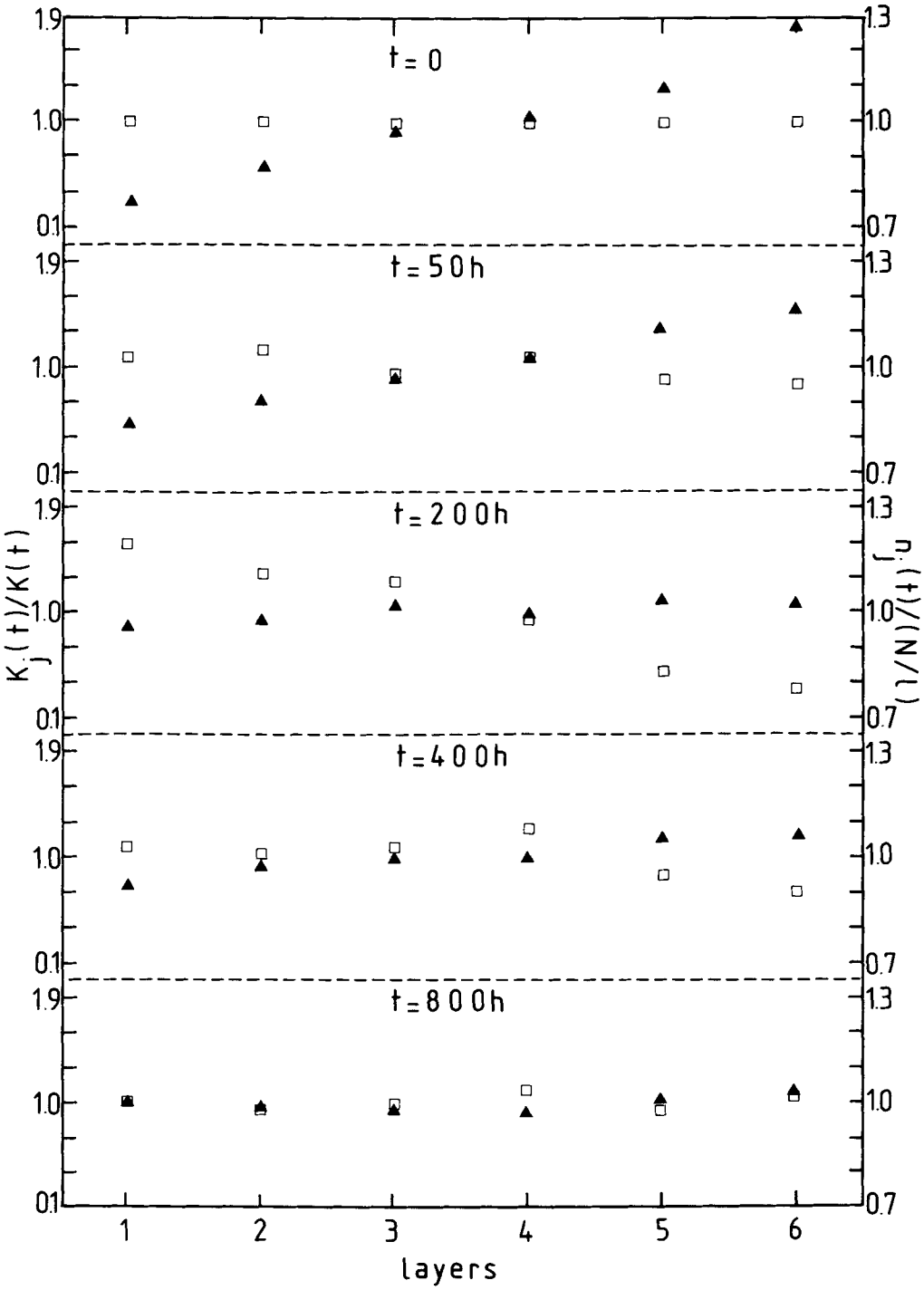


Figure 4. Ratios $K_j(t)/K(t)$ (triangles) and $n_j(t)/(N/l)$ (squares) for each layer $j$ in the case (1, 3) at different times. Notice that the scale is different for each quantity.

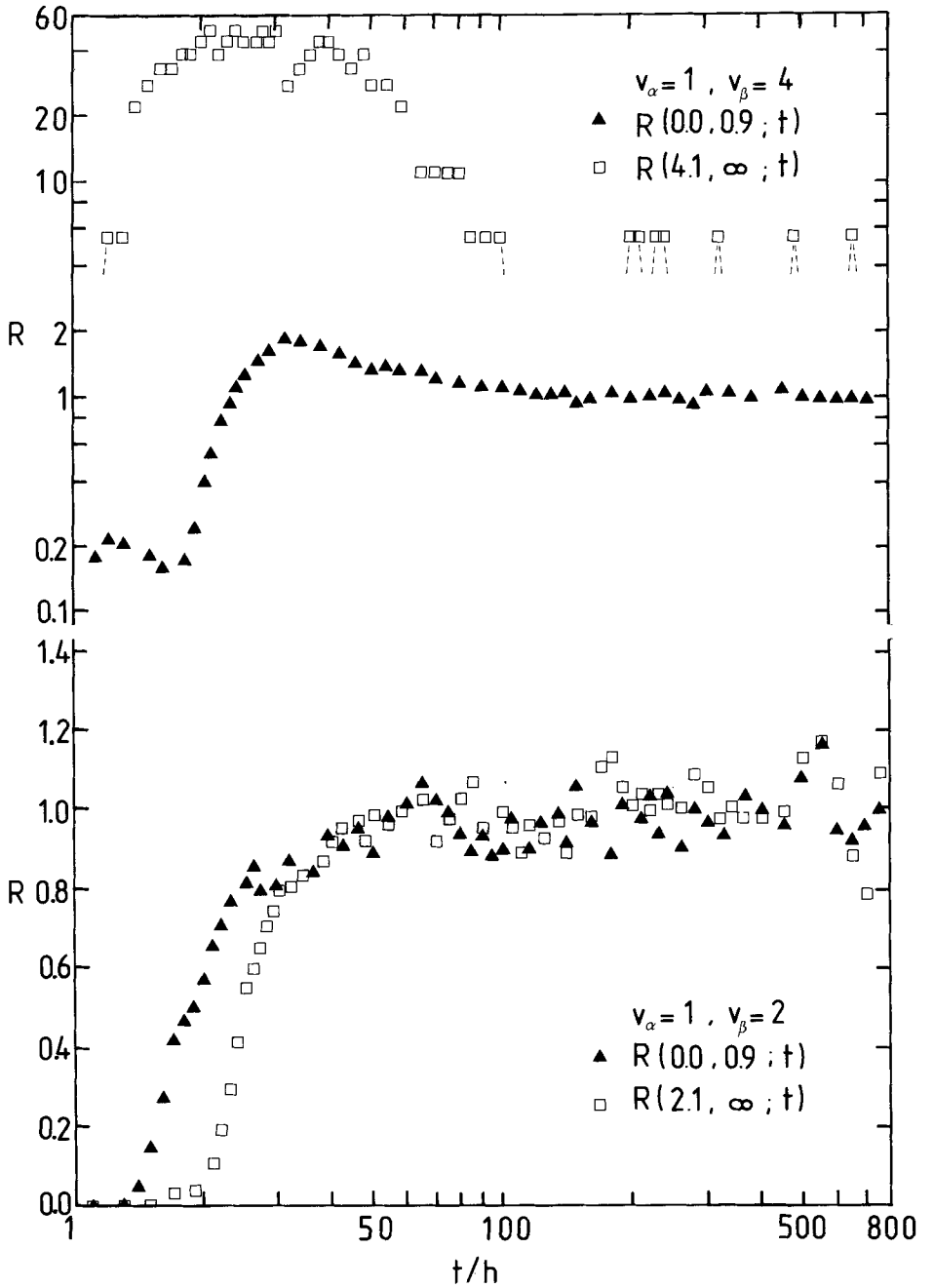


Figure 5. Time evolution of the relative population $R$ for speeds slower than $v_\alpha$ (triangles) and faster than $v_\beta$ (squares) in the cases (1, 4) and (1, 2). In the graph corresponding to the case (1, 4), the scale of $R$ is logarithmic. Thus, the points corresponding to a null population cannot be plotted. This is indicated by the broken lines.

figure 3. For the sake of clarity in the graph and trying to smooth the fluctuations we have grouped the layers in couples. Namely, we consider together the kinetic energy per particle and the number of particles of layers 1–2, 3–4 and 5–6.

In both figures, it is observed that $K_j(t)$ relaxes towards homogeneity in a first stage (up to $t \sim 200\ h$). But, during this stage, an increasing density gradient (in absolute value) is generated. That is, the temperatures of the different layers tend to equal at the expense of a depopulation of the initially hottest layers. At the next stage (up to $t \sim 400\ h$) the opposite effect takes place : the tendency towards homogeneity in the number of particles induces the presence of a new temperature gradient of the same sign as the initial one. We therefore observe a competition between the density and the temperature in the relaxation towards equilibrium, giving rise to successive inhomogeneities. There is a time lapse between the density and temperature inhomogeneities and both get smaller and smaller until a final equilibrium state is reached. Due to the reduced number of particles, the possible remaining inhomogeneities are blurred by the fluctuations for times $t \gtrsim 800\ h$. Comparing figures 2 and 3, we observe that the initial conditions have little influence on the amplitude of the inhomogeneities and its temporal evolution.

We find that the same essential aspects of figures 2 and 3 are present in the other cases considered. For instance, in figure 4 we graph $K_j(t)/K(t)$ and $n_j(t)/(N/l)$ for some characteristic times in the case (1, 3).

After analysing the relaxation to equilibrium of the density and the kinetic energy per particle, let us study some aspects of the relaxation of the velocity distribution function. We introduce the function [3]

$$R(v_1, v_2 ;\ t) = \frac{\phi(v_1, v_2 ;\ t)}{\phi^{eq}(v_1, v_2)}, \tag{2.8}$$

where $\phi(v_1, v_2 ;\ t)$ represents the number of particles in the system with speeds ranging from $v_1$ to $v_2$ at time $t$, and $\phi^{eq}(v_1, v_2)$ represents that number at equilibrium.

In figure 5, we represent the evolution of $R$ for speeds lower than $v_\alpha$ and for speeds higher than $v_\beta$ in the cases (1, 2) and (1, 4). Comparison with the results of [3], shows that the presence of the inhomogeneity does not appreciably alter the effect of overpopulation. Nevertheless, it seems that the effect is slightly more intense and lasting a longer time in the spatially inhomogeneous systems. Let us notice that the criterion of Hauge and Alexanian [2] seems still to be valid. Since the overpopulation effect was discussed with detail in [3], we shall not discuss this matter further.

It should be noted that the time scale on which the velocity distribution function varies is much smaller than the time scale characterizing the evolution of spatial inhomogeneities.

## References

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[5] In figure 2 of [3], $K$ and $E$ represent time averaged quantities. Thus, its evolution is smoother than in figure 1 presented in this paper.