

Comments on Some Aspects of Boltzmann H Theorem Using Reversible Molecular Dynamics

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We calculate the Boltzmann H function for a repulsive Lennard-Jones fluid using Levesque and Verlet's reversible molecular dynamics algorithm. We find, as predicted by Jaynes, that for certain initial states, H increases as a function of time. We also discuss the Grad limit within such a simulation.

KEY WORDS: Numerical simulations; Boltzmann H theorem; Grad limit.

1. INTRODUCTION

In a recent article, Levesque and Verlet⁽¹⁾ introduced a time-symmetrical integer arithmetic algorithm for molecular dynamics (MD) simulations of classical fluids. This algorithm makes use of integer variables instead of real, floating point, variables, and it was shown that since there are no round-off errors, it preserves the time-reversal symmetry of Newton's equations. This remarkable feature of the simulations makes them ideal, not only to improve on previous MD calculations, but also to explore fundamental issues such as the origin of irreversible macroscopic behavior. Levesque and Verlet exemplified this behavior by studying a function similar to Boltzmann H function. Their calculation, in a very illuminating way, illustrates the typicality of time-asymmetric behavior for systems with many particles, despite the fact that their microscopic dynamics is time-reversible. The function calculated by Levesque and Verlet, however, hides the fact that in some cases the corresponding Boltzmann H function *increases* instead of *decreasing* as a function of time. This last result does

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not imply that the H Theorem⁽²⁾ is violated since Boltzmann equation is not obeyed within the conditions considered in those cases. That Boltzmann equation is not satisfied follows essentially from the fact that the potential interaction energy cannot be neglected. The result that in such cases H may increase was first indicated by Jaynes.⁽³⁾

In this article we briefly review Jaynes' argument and show that $H(t)$ indeed increases for a set of initial conditions commonly used in numerical simulations. We shall also show that for other type of initial states, very far from equilibrium, $H(t)$ decreases. Since it is known that Boltzmann equation, as well as the H Theorem, are strictly valid in the so-called Grad limit only,⁽⁴⁾ we also want to use this article to explore the feasibility of reaching this limit in a practical and useful way. We point out, as we shall show below, that since numerical simulations are usually performed very far from this limiting situation, it is not surprising that strong departures are observed.

Let us consider a monatomic classical fluid of N particles in a volume V and with total energy \mathcal{E} . For simplicity, we assume pairwise interactions through a potential $u(|\vec{r}_i - \vec{r}_j|)$. Let $f(\vec{v}, \vec{r}, t) d^3r d^3v$ be the number of particles, at time t , with velocities between \vec{v} and $\vec{v} + d^3v$, and with positions between \vec{r} and $\vec{r} + d^3r$. We shall use the normalization,

$$\int d^3r \int d^3v f(\vec{v}, \vec{r}, t) = N \quad (1)$$

Boltzmann H -function is given by

$$H(t) = \int d^3r \int d^3v f(\vec{v}, \vec{r}, t) \ln f(\vec{v}, \vec{r}, t) \quad (2)$$

and Boltzmann H Theorem states that

$$\frac{dH(t)}{dt} \leq 0 \quad (3)$$

if $f(\vec{v}, \vec{r}, t)$ obeys Boltzmann equation.⁽²⁾

Jaynes' result that the H Theorem can be "violated" in real gases is clearly summarized in the abstract of his article:⁽³⁾ ... (a) *Any monatomic system for which the equilibrium potential energy exceeds the minimum possible value possesses a continuum of initial states for which the approach to equilibrium takes place through an increase, rather than a decrease, in Boltzmann's H .* (b) *If the initial distribution of particles is spatially homogeneous and Maxwellian, the approach to equilibrium will take place through an increase (decrease) in Boltzmann H , according as the initial potential energy is less (greater) than the equilibrium value.* ... Of course, the

apparent violation only indicates that $f(\vec{v}, \vec{r}, t)$ does not obey Boltzmann equation since the potential energy is not negligible (in other words, H cannot be identified with the entropy in those systems). Nevertheless, from the practical point of view of applying Boltzmann equation to actual situations, Jaynes' argument is very important to take into account.

The situation we shall address is (b) of the above paragraph: Consider a system of N particles pairwise interacting through a positive repulsive potential. The system is in an initial non-equilibrium state, spatially homogeneous with density $\rho = N/V$, zero potential energy (i.e. none of the particles undergoing a collision) and with the velocities distributed with a Maxwellian distribution at "temperature" T_0 , namely,

$$f(\vec{v}, \vec{r}, 0) = \frac{N}{V} \left(\frac{m}{2\pi k T_0} \right)^{3/2} e^{-mv^2/2kT_0} \quad (4)$$

When the system equilibrates, the velocities will be distributed à la Maxwell, as in Eq. (4), but with an equilibrium temperature T different from T_0 . At the same time, the average potential will be different from zero and positive and, therefore, the equilibrium temperature T will be *smaller* than T_0 . For the initial state, Boltzmann H function, cf. Eq. (2), yields,

$$H(t=0) = -\frac{3}{2} N + N \ln \left(\frac{N}{V} \right) - \frac{3}{2} N \ln \left(\frac{2\pi k T_0}{m} \right) \quad (5)$$

and an analogous expression for the function in equilibrium $H(t \rightarrow \infty)$ with T_0 replaced by T . Thus, these H functions are related as

$$H(t=0) < H(t \rightarrow \infty) \quad (6)$$

That is, H must *increase* for this particular initial condition.⁽⁵⁾ This is the situation we shall discuss below through MD simulations.

2. NUMERICAL SIMULATIONS

In this section we shall exemplify the above results by means of a series of MD simulations⁽⁶⁾ of a fluid interacting through the repulsive part of a Lennard-Jones potential,⁽¹⁾

$$u(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon, & r_{ij} \leq 2^{1/6}\sigma \\ 0, & r_{ij} \geq 2^{1/6}\sigma \end{cases} \quad (7)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$. For this intermolecular potential, the average potential energy will always be positive. Accordingly, the total conserved energy is also positive being the sum of the (positive) average kinetic energy plus the (positive) average potential energy.

As mentioned in the previous section, the initial condition corresponds to a state with *zero* potential energy, *uniform* density, and with the velocities Maxwell distributed. Clearly, the most delicate aspect of this state, from the point of view of a numerical simulation of a finite system, is its homogeneity. However, from a coarse-grained point of view, a state with uniform density may be considered as one having (approximately) the same number of particles in all subvolumes of a given size. Thus, for an initial state of the latter type, we assume that

$$f(\vec{r}, \vec{v}, 0) d^3r d^3v \approx f(v, 0) d^3r d^3v \quad (8)$$

where we have already taken into account the isotropy in the velocities, $v = |\vec{v}|$. Clearly, if the initial state obeys these conditions, we expect them to hold for any subsequent time. Furthermore, we know that the equilibrium state of the system must be of the form of Eq. (8).

Regarding the actual calculations, we obtain H at any time, by sorting the number of particles with *magnitude* of their velocities lying between v_i and $v_i + \Delta v$. The interval Δv is obtained as $\Delta v = 4v_0/M$, with v_0 the rms-deviation of the initial Maxwell distribution, and M the number of intervals, typically $M = 40$. We used $v_i = (i - 0.5) \Delta v$. Now, by calling $g_i(t)$ the number of particles whose magnitude of velocities are in the i th interval, we have

$$\sum_{i=1}^M g_i(t) = N \quad (9)$$

Hence, using Eqs. (1), (8), and (9), it follows that

$$f(\vec{r}, \vec{v}, t) \approx \frac{g_i(t)}{4\pi V v_i^2 \Delta v} \quad (10)$$

so that, Boltzmann H function, cf. Eq. (2), is calculated as

$$H(t) \approx \sum_{i=1}^M g_i(t) \ln \left(\frac{g_i(t)}{4\pi V v_i^2 \Delta v} \right) \quad (11)$$

The initial state that we actually use is obtained by placing the particles on the sites of an *fcc* lattice with their velocities Maxwell distributed.⁽¹⁾ Although one may object that such an initial state is of uniform density, we

argue that in a coarse-grained sense it is. Moreover, it can be considered as just one member of an ensemble of states all with *zero* potential energy and with the same velocity distribution. The average of the latter ensemble will yield a state with uniform density. The following results address this point.

In Fig. 1 we plot H vs t for a system of $N = 4000$ particles interacting via the repulsive Lennard-Jones potential, Eq. (7), with density $\rho = 0.45$ and with a MD time-step per iteration $h = 0.0046188$, in reduced units.⁽⁷⁾ The different cases correspond to different initial states, all having the *same* Maxwell velocity distribution, zero potential energy, but with positions of the particles on an *fcc* lattice, or with the particles randomly being moved away from the *fcc* lattice. With the assumption of Eq. (8) all these states have exactly the same value of $H(t=0) = -23916$, as shown in Fig. 1, and *increasingly* reach the same equilibrium value of $H(t \rightarrow \infty) \approx -23096$, within fluctuations due to the finite number of particles. The equilibrium temperature in all cases is $T \approx 1.6175$ and the initial one is $T_0 = 1.8570$;

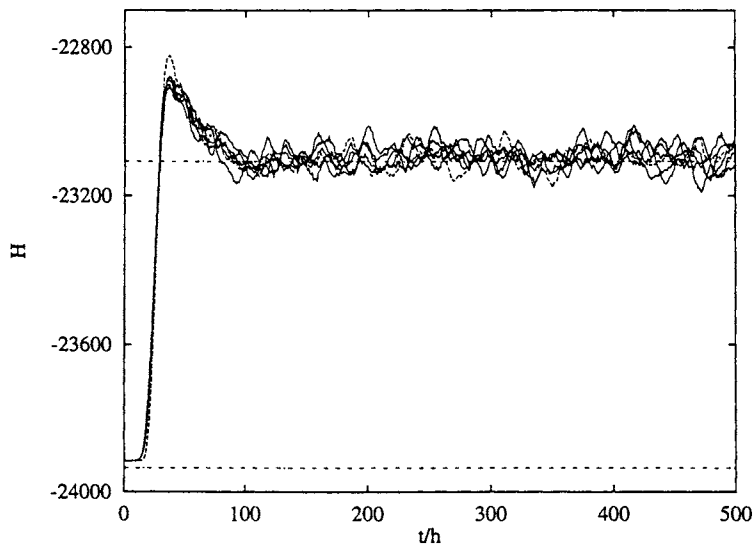


Fig. 1. Boltzmann H function vs. time t/h . The density is $\rho = 0.45$ and the number of particles is $N = 4000$. We used the definition of $H(t)$ given in Eq. (11). In all cases the initial velocities of the particles have the same values chosen from a Maxwellian distribution. The initial total potential energy is zero in all cases and the initial positions of the particles are on an *fcc* lattice (dashed line), and in the other five cases (continuous lines) the initial positions are randomly displaced from the *fcc* sites. The horizontal lines are the theoretical values $H_{teo}(t=0)$ and $H_{teo}(t \rightarrow \infty)$, see Eq. (5), using the corresponding temperatures $T_0 = 1.8570$ and $T = 1.6175$ obtained from the simulation.

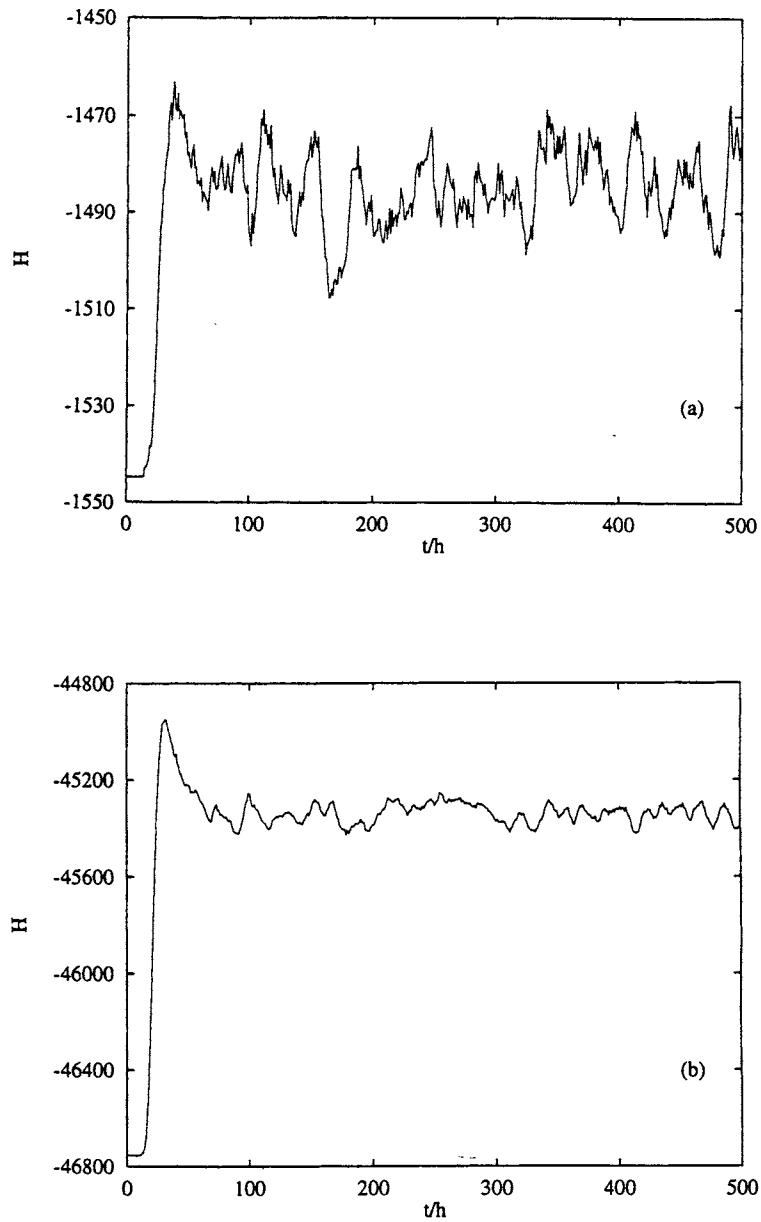


Fig. 2. Boltzmann H function vs. time t/h . The density is $\rho=0.45$ and the number of particles is (a) $N=256$ and (b) $N=6912$. We used the definition of $H(t)$ given in Eq. (11). In the two figures the initial state is an *fcc* lattice with zero potential energy and with the velocities of the particles chosen from a Maxwellian distribution.

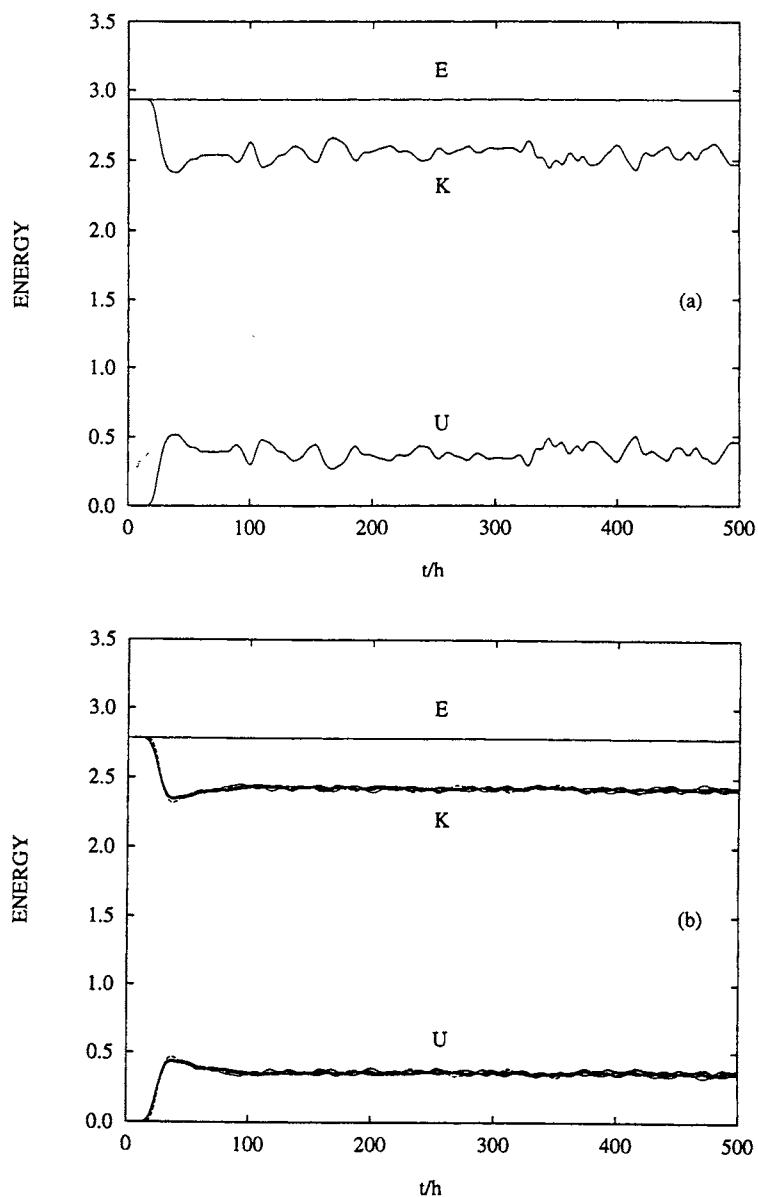


Fig. 3. Total energy per particle E , kinetic energy per particle K , and potential energy per particle U vs. time t/h . The density is $\rho=0.45$ and the number of particles is (a) $N=256$, (b) $N=4000$, and (c) $N=6912$, corresponding to the cases of Figs. 2a, 1, and 2b. The kinetic and the potential energies are directly calculated from the state of the system while the total energy is the sum of the former two.

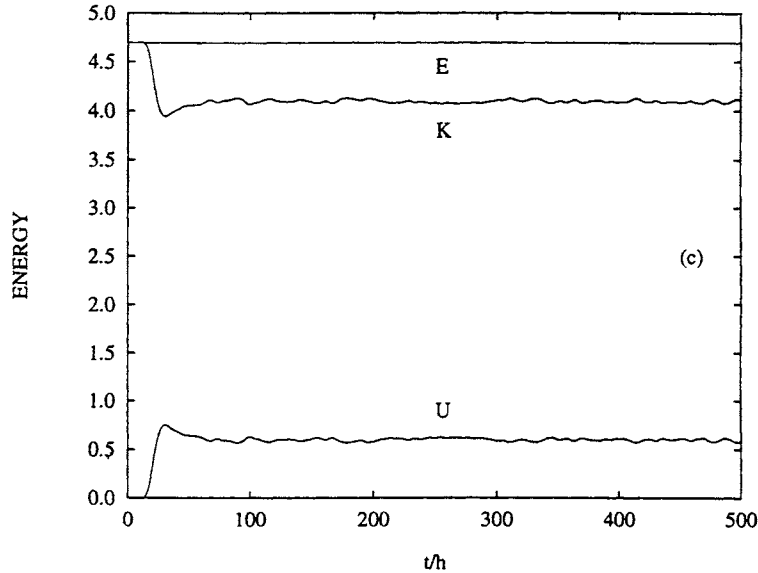


Fig. 3. (Continued)

with these values and the density $\rho = 0.45$, we can evaluate the theoretical expression of H given by Eq. (5), and we find $H_{teo}(t=0) = -23935$ and $H_{teo}(t \rightarrow \infty) \approx -23108$. The discrepancy between the theoretical difference $H_{teo}(t \rightarrow \infty) - H_{teo}(t=0)$ and that obtained from the simulation is only about 1.0%.

In Figs. 2a and 2b, the increase of $H(t)$ is also shown for a system of N particles with $N = 256$ and 6912, respectively. In both cases, the density is also $\rho = 0.45$. The initial state again corresponds to an *fcc* lattice with zero potential energy and with the velocities of the particles distributed à la Maxwell with temperatures $T_0(256) = 1.9544$ and $T_0(6912) = 3.1292$. The equilibrium temperatures are $T(256) \approx 1.7002$ and $T(6912) \approx 2.7273$. In Figs. 3a to 3c, it is shown the kinetic energy per particle, potential energy per particle and total energy per particle as a function of time, corresponding to the cases of Figs. 2a, 1 and 2b, respectively. One clearly sees how the potential energy is a considerable fraction of the total energy. Therefore, one should not expect Boltzmann equation to apply and the “violation” of the H Theorem should accordingly not be a surprise. On the other hand, as also pointed out by Jaynes,⁽³⁾ if the system starts from an arbitrary state far from equilibrium, H is expected to decrease. For instance, for an initial *fcc* lattice with the particle velocities uniformly distributed H decreases, as shown in Fig. 4.

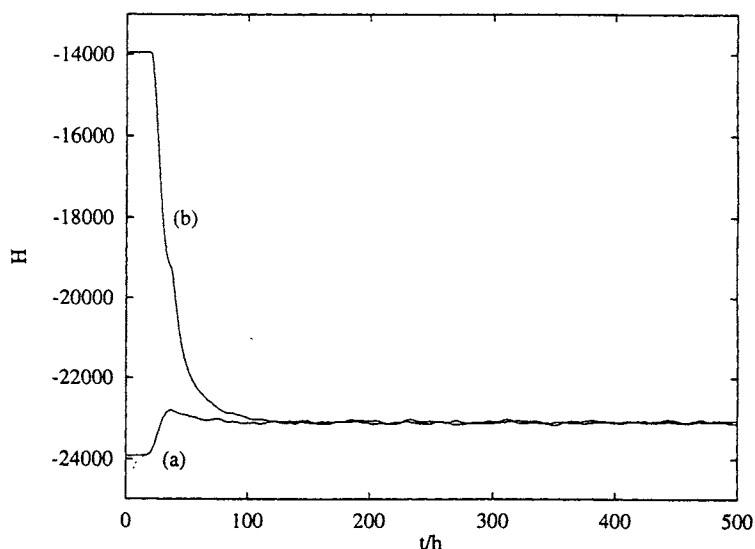


Fig. 4. Boltzmann H function vs. time t/h . In both cases the density is $\rho = 0.45$, the number of particles is $N = 4000$ and the total energy per particle is $E = 2.785$. The initial state is an *fcc* lattice with the velocities of the particles (a) Maxwell-distributed and (b) uniformly distributed with a given magnitude.

One important aspect must be realized from Figs. 1 and 2: It turns out that H is negative. As it is known, H is defined up to an additive constant that can be shifted by changing the units used. However, since $H(t=0)$ is negative, dividing the value of $H(t)$ by $H(0)$ would result in an inversion of the curves. Namely, $H(t)/H(0)$ would appear to be *decreasing* as a function of time, analogously to the behavior of the function calculated by Levesque and Verlet.⁽¹⁾

As a passing by comment, we stress one of the remarkable properties of the present reversible MD simulation: In Figs. 3a to 3c, the total energy was calculated as the sum of the kinetic plus the potential energies. In the scale of the figures the total energy appears as a constant; in fact, it does fluctuate, a consequence of the discretization of Newton's equations, but this fluctuation is at least an order of magnitude less than the actual fluctuations, $\sim N^{1/2}$, of the kinetic and potential energies. And more importantly, the total energy does not show any systematic drift.

Levesque and Verlet⁽¹⁾ explicitly showed that if all the velocities are reversed at a given time t_r , the system returns, *exactly*, to its initial state at a time $2t_r$.

3. GRAD LIMIT

Again, the apparent failure of the H Theorem only reflects the fact that Boltzmann equation should not be applicable. This is more evident for the high density ($\rho = 0.45$) used in the MD calculations of Figs. (1) to (4). As it is known, Boltzmann equation is rigorously valid in the so-called Grad limit, in which the *ratio of the mean-free-path to macroscopic dimensions is held fixed while the gas becomes more and more rarified*.⁽⁴⁾ This limit has the result that while the gas becomes ideal (i.e. $pV = NkT$), the effect of the collisions in the evolution remains finite. The latter is given by Boltzmann equation. As the ideal gas is approached the potential energy must become negligible. In the original argument given by Grad⁽⁴⁾, this limit is obtained by

$$N\sigma^2 = \text{constant while } N \rightarrow \infty \text{ and } \sigma \rightarrow 0 \quad (12)$$

with σ the size of the atoms. This procedure, however, is not easily amenable for calculational purposes since the “natural” value of σ is 1. One can use instead the equivalent limit of raryfing the gas by letting the *reduced* density vanish as,

$$N\rho^2 = \text{constant while } N \rightarrow \infty \text{ and } \rho \rightarrow 0 \quad (13)$$

Since the mean-free-path $\lambda \sim 1/\rho$, in reduced units, one can verify that the above limit leaves $\lambda/L = \text{constant}$, where L is the size of the system ($L = V^{1/3}$).

In order to explore this limit we performed a sequence of MD simulations, obeying Grad requirement $N\rho^2 = \text{constant}$, for $N = 864, 2048, 4000$ and 6912 . This is summarized in Table I. Since one of the main assumptions of Boltzmann equation is the condition of binary collisions only, we searched for small enough densities such that, on the one hand, triple collisions and higher were negligible but, on the other, the mean-free-path remained *smaller* than the size L of the box of the MD simulation. This is an important technical aspect since one can arbitrarily (though numerically costly!) lower the density for any given number of particles, leading to a situation where the mean-free-path is larger than the size of the system. The periodic boundary conditions of the MD simulation can then produce dangerous spurious effects.

In the sequence of simulations summarized in Table I, we found that the *duration* of the binary collisions, in equilibrium, were approximately 30 MD time-steps, while one can see from Table I that the time between collisions increases as the density is lowered. We also found in all the runs an

Table I. Grad Sequence of MD Simulations, Obeying $N\rho^2 = \text{constant}$ ^a

N	ρ	L	τ	T
864	0.028284	31.26	507	3.1134
2048	0.018371	48.13	778	3.1189
4000	0.013145	67.26	1083	3.1219
6912	0.010000	88.42	1424	3.1236

^a N , number of particles. ρ , density. L , size of the the system (i.e. $V=L^3$). τ , mean time between collisions, in MD steps. T , temperature. Note that the ratio τ/L and the temperature tend to their corresponding constant values in Grad limit.

approximate 1:25 ratio of triple to binary collisions per particle per MD time-step.

Figs. 5 and 6 help to visualize Grad limit. Fig. 5 shows the distributions of kinetic energy per particle. In the limit, the distribution approaches a delta function distribution that should coincide with the ideal-gas total energy per particle. The counterpart behavior can be observed in Fig. 6

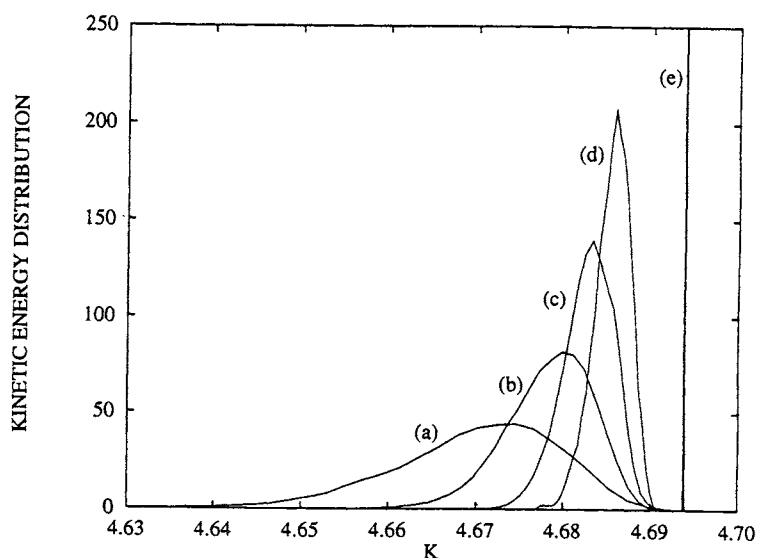


Fig. 5. Distributions of kinetic energy K per particle following Grad limit, $N \rightarrow \infty$, $\rho \rightarrow 0$ with $N\rho^2 = \text{constant}$. (a) $N = 864$, $\rho = 0.028284$; (b) $N = 2048$, $\rho = 0.018371$; (c) $N = 4000$, $\rho = 0.013145$; (d) $N = 6912$, $\rho = 0.010000$. In all cases the total energy per particle is the same and is plotted as (e).

where we show the distribution of number of binary collisions per time step per particle *scaled* with the size L of the system. That is, in Grad limit, the mean time between collisions τ divided by the length L of the system should tend to a constant value:

$$\frac{\tau}{L} = \frac{\lambda}{v(T) L} \sim \frac{1}{v(T)} \quad (14)$$

where $v(T)$ is the mean velocity of the particles, a function of the temperature. In Grad limit $v(T)$ is the ideal-gas mean velocity. In Fig. 6, we see that, indeed, the distributions of binary collisions are approaching a delta-function distribution centered in the limiting value of L/τ . In other words, Figs. 5 and 6 illustrate how, in Grad limit, while the gas becomes ideal the effect of the collisions remains. From an operational point of view and from the present results, we can say with certain confidence that for $N=6912$ and $\rho=0.01$ the system is close enough to Grad limit, so that some other issues of Boltzmann equation may be numerically studied.

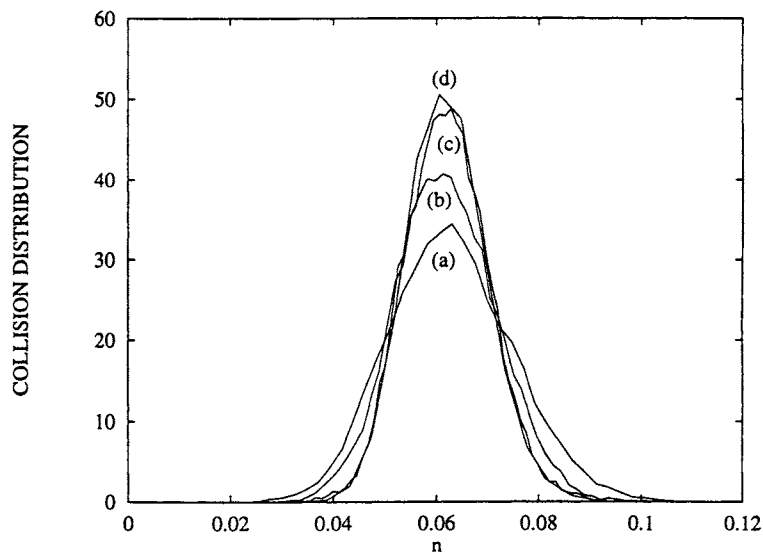


Fig. 6. Grad sequence of distributions of binary collisions n per particle per MD time step scaled with the size of the system. The variable n is the inverse of τ/L , the mean time between collisions divided by the size of the system. (a) $N=864$, $\rho=0.028284$; (b) $N=2048$, $\rho=0.018371$; (c) $N=4000$, $\rho=0.013145$; (d) $N=6912$, $\rho=0.01000$.

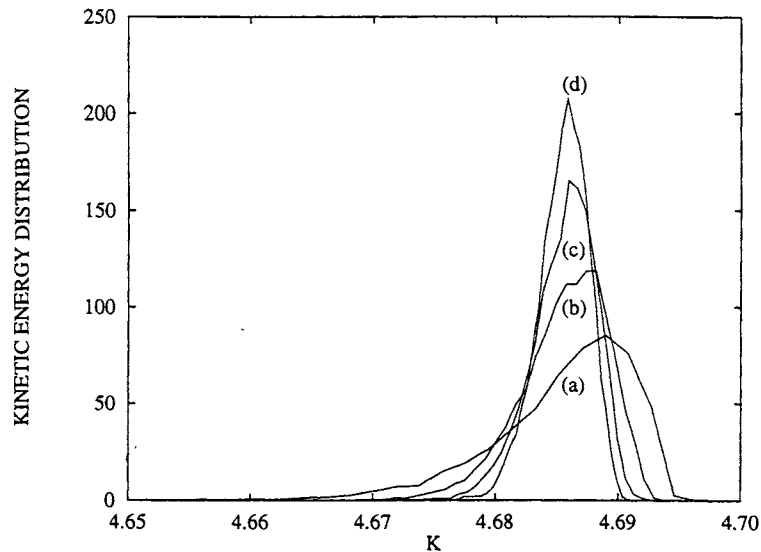


Fig. 7. Distributions of kinetic energy K per particle following the thermodynamic limit, $N \rightarrow \infty$, $V \rightarrow \infty$ with $\rho = 0.01$. (a) $N = 864$; (b) $N = 2048$; (c) $N = 4000$; (d) $N = 6912$.

For purposes of comparison we show in Fig. 7 a sequence of MD simulations following the *thermodynamic limit*, $N \rightarrow \infty$, $V \rightarrow \infty$ with $N/V \rightarrow$ constant, for $N/V = 0.01$. Besides illustrating the role of fluctuations in a finite system, Figs. 5 and 7 show the difference between the two limits.

4. FINAL REMARKS

As we have seen, the increase of Boltzmann H function is both due to the particular initial condition used and to the fact that the potential energy cannot be neglected. Both aspects are of considerable importance in actual numerical simulations. On the one hand, from a practical point of view, it is always much easier to initially place the particles on a lattice and then let them evolve, than to locate them in "random" sites but avoiding highly improbable states with particles very near to others. For studies of the properties of the equilibrium state, the initial condition is quite irrelevant, but certainly not so for analyzing states out of equilibrium. On the other hand, the potential energy is what makes the evolution possible. In this regard, it is interesting to point out that for a system of hard spheres, Jaynes' result should not be relevant since the potential energy is always zero and, therefore, for the initial state used throughout in this article, the corresponding H function should remain constant. We recall, however, that

the latter property does not imply that the system was initially in thermal equilibrium: H is not (minus) the entropy. For the hard-spheres case, H does not take into account the non-thermal excluded volume contribution. As we have stressed here, the apparent violation of the H Theorem is just an indication that Boltzmann equation is only valid in Grad limit and that in reality, and in numerical simulations, the systems considered are normally far from that extreme state.

As a matter of conclusion of this article, we present Fig. 8 where Boltzmann H function is plotted for a system of $N = 6912$ particles and for five different densities. In all cases, the system starts from exactly the same initial state, with zero potential energy and with the same values of the velocities Maxwell-distributed ($T_0 = 3.1292$). Two features we want to highlight. First, one clearly sees that the increase of H is more pronounced as the density is increased, as it should, according to Jaynes' argument. However, and secondly, one can also observe that a "shoulder" seems to be developing *before* the system finally relaxes to equilibrium. This hump appears earlier the higher the density. This effect should also be more noticeable as the number of particles increases (see also Figs. 1 and 2). This

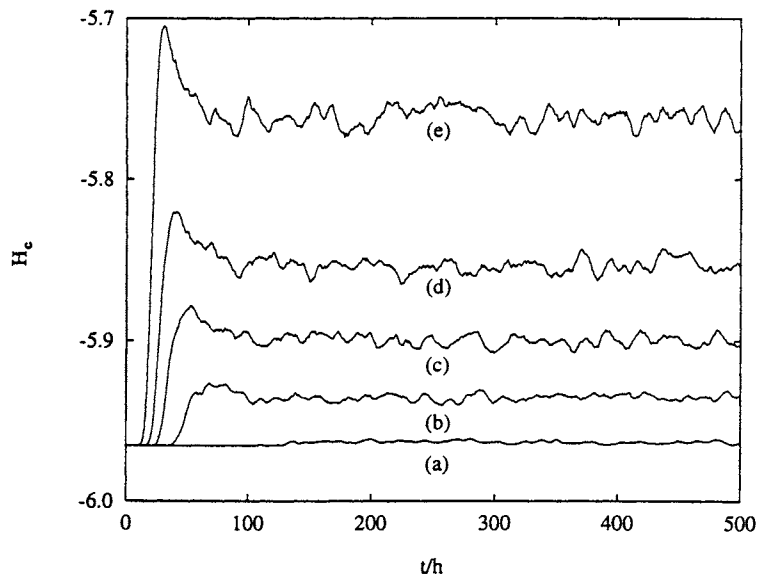


Fig. 8. Boltzmann H_c function vs. time t/h , for a system of $N = 6912$ particles and for different densities. All cases start with the same initial state. (a) $\rho = 0.01$; (b) $\rho = 0.15$; (c) $\rho = 0.20$; (d) $\rho = 0.30$; (e) $\rho = 0.45$. Since H depends on the density, we have here plotted $H_c = (H - N \ln \rho)/N$, so that the initial value of H_c is exactly the same for all cases.

phenomenon is reminiscent of a recent discussion of the “slippage” of initial conditions in reduced dynamics of systems coupled to heat-baths.⁽⁸⁾ That is, it appears that although, strictly speaking, $H(t)$ increases, it does so only for a very short period of time, during which, it “slips” towards an effective initial condition from which it actually decreases! The complete elucidation of this feature is certainly out of the scope of this article and will be discussed elsewhere,⁽⁹⁾ but we bring it here as a further example of the type of questions that can be addressed with reversible molecular dynamics.

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