Journal of Statistical Physics, Vol. 62, Nos. 1/2, 1991

Classical "Freezing" of Fast Rotations. A Numerical Test of the Boltzmann–Jeans Conjecture

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Received July 27, 1990

We study numerically a very simple model representing a classical planar molecule, with only translational and rotational degrees of freedom, which collides with a fixed wall. On this model we test numerically an old conjecture by Boltzmann and Jeans, according to which the rate of the energy exchanges between the translational and the rotational degrees of freedom, due to collisions, decreases exponentially with the angular velocity of the molecule, giving rise to a purely classical phenomenon of "freezing" of fast rotations. Our results are in full agreement with the Boltzmann–Jeans conjecture. More precisely, we find that for each collision the average on the initial phase of the energy exchange, and the fluctuation, follow two different exponential laws; this fact turns out to have a rather delicate role in the approach of statistical equilibrium. A discussion of the numerical accuracy—which is rather high, since we are able to measure energy exchanges of one part over 10^{16}—is also reported.

KEY WORDS: Numerical experiments; exponential estimates; equipartition times; Boltzmann–Jeans conjecture.

1. INTRODUCTION

At the turn of the century, before quantum mechanics, Boltzmann[1] and Jeans[2,3] proposed a completely classical mechanism to explain the failure of the principle of equipartition of energy for statistical systems containing high-frequency degrees of freedom. A typical model they refer to is a classical gas of diatomic molecules which can translate, rotate, and vibrate; on the basis of the principle of equipartition of energy, which is the heart of classical statistical mechanics at equilibrium, one would expect seven con-

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0022-4715/91/0100-0201$06.50/0

tributions to the specific heat (three from translations, two from rotations, one kinetic and one potential for vibrations), and thus a classical value $C_V = \frac{7}{2}R$. On the contrary, at not too high temperatures one has $C_V = \frac{5}{2}R$ (freezing of vibrations), while at low enough temperatures one finds $C_V = \frac{3}{2}R$ (freezing of both vibrations and rotations).

The basic idea by Boltzmann and Jeans (see, for comments, refs. 4–7) is that the above equilibrium description, although in principle correct, nevertheless could be not really significant if the equilibrium times are too large. More precisely, they conjectured that the energy exchanges due to collisions, leading ultimately to equipartition, could be so small that either the vibrational or both the vibrational and rotational degrees of freedom could appear as practically frozen for extremely long time scales ("days or years,"[1] "hundreds of centuries,"[2] in their own words).

Jeans, in particular, discussed the freezing of vibrations, and (on the basis of heuristic considerations) proposed an exponential law of the form[3]

$$\Delta E \simeq \mathscr{E} e^{-\tau\omega} \tag{1.1}$$

for the average energy exchange ΔE produced by a collision; τ is here a constant of the order of the collision time, while ω is the frequency of the internal vibration, and $\mathscr{E}$ is some natural microscopic unit. From (1.1) one then gets an exponential law of the form

$$T \simeq T_0 e^{\tau\omega} \tag{1.2}$$

for the equilibrium times, T_0 being a constant of the order of the average time between collisions. It is worthwhile to remark that such an exponential law could produce rather sharp freezing phenomena[11]: for example, assume (as is reasonable) $T_0 = 10^{-12}$ sec, $\tau = 10^{-13}$ sec, and denote by $\omega_1 \simeq 2.8 \times 10^{14}\,\text{sec}^{-1}$ the value of ω at which one has $e^{\tau\omega} = 10^{12}$; i.e., $T \simeq 1$ sec. Then for $\omega = \frac{1}{2}\omega_1$ one has $T = 10^{-6}$ sec, while for $\omega = 2\omega_1$ one has $T = 10^{12}\,\text{sec} \simeq 3 \times 10^4$ years.

Quite recently, the exponential law (1.2) has been successfully tested numerically,[11] although on a very simple and rough one-dimensional model of purely translating and vibrating molecules, and on a quite limited range of frequencies. The elementary law (1.1) was also proved rigorously,[12,13] under rather general assumptions, within classical perturbation theory (see also refs. 5 and 14), although, as is typical in this

[3] An exponential law of this form was later reconsidered by Landau and Teller[8] and by Rapp,[9] still on the basis of heuristic considerations, and apparently unaware of the Boltzmann–Jeans ideas. Similar heuristic procedures are also considered in plasma physics.[10]

framework, the estimates one gets for the most relevant constants (such as τ) are definitely too poor to be used in connection with physical applications.

The aim of the present paper is to test numerically the validity of the exponential law (1.1) with regard to the freezing of fast rotations. More precisely, working in the same spirit as ref. 11, we consider here a drastically simplified model, namely a planar model with purely rotating and translating molecules, and also restrict ourselves to the simpler case of collisions of molecules with a fixed wall (work is in progress, however, for the case of molecule–molecule collisions); indeed, as in ref. 11, our purpose is just to show that the Boltzmann–Jeans phenomenon, i.e., the long-time freezing of the high-frequency degrees of freedom, in principle does exist for the rotations, too.

Deeply connected to the present paper is ref. 15, where, in the same spirit as refs. 12 and 13, one makes use of perturbation theory to study theoretically the freezing of fast rotations. Some of the phenomena here observed are there rigorously proven, for a rather wide class of dynamical systems, including the model here considered. However, as we shall see, there still remains, both qualitatively and quantitatively, a rather wide gap between the theory and the numerical results; we shall come back to this point in the conclusions.

The paper is organized as follows: In Section 2 we describe the model we are dealing with, and present the basic results on the elementary collision process, while in Section 3 we discuss the approach to statistical equilibrium induced by a long sequence of collisions. Section 4 is devoted to a discussion of the numerical accuracy; a conclusion follows.

2. DESCRIPTION OF THE MODEL, AND STUDY OF THE ELEMENTARY COLLISION PROCESS

Let us consider a planar molecule which can translate and rotate on a given plane. The configuration of the molecule is conveniently described by three coordinates, say the Cartesian coordinates x, y of the center of mass, and an angle φ giving the orientation. Denoting by m and I the total mass and the inertia moment of the molecule, respectively, and by p_x, p_y, p_φ the conjugate momenta, we write the Hamiltonian

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{p_\varphi^2}{2I} + V(x, y, \varphi) \tag{2.1}$$

V is here the external potential, which in particular provides the interaction between the translational and the rotational degrees of freedom.

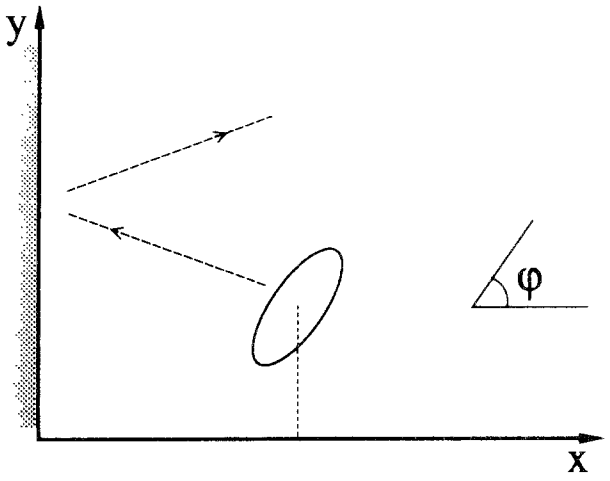


Fig. 1. The model.

The form of V is chosen in order to simulate, although in a very rough schematic way, a smooth[4] reflection by a wall. To this purpose, let us assume that the wall is flat, and parallel to the y axis (see Fig. 1); the potential V is chosen to be short range and independent of y, more precisely, of the form

$$V = U \frac{e^{-(r/d)^2}}{r/d}, \qquad r = |x + a \cos \varphi| \tag{2.2}$$

U and d are here suitable constants, which provide natural microscopic units of energy and length, while a, or better, the ratio a/d, gives the sensitivity of the interaction potential to the orientation of the molecule. There is no deep motivation for the above choice of V: however, the fast decay, due to the superexponential cutoff $e^{-(r/d)^2}$, turns out to be rather convenient in numerical computations, since it drastically reduces the effective interaction length, and consequently the computer time.

Since V is independent of y, the y coordinate plays no role at all in the dynamics of a collision, and can be omitted; one is then confronted with the two-degrees-of-freedom Hamiltonian

$$H(p_x, p_\varphi, x, \varphi) = \frac{p_x^2}{2m} + \frac{p_\varphi^2}{2I} + U \frac{e^{-(r/d)^2}}{r/d}, \qquad r = |x + a \cos \varphi| \tag{2.3}$$

[4] It is clear from classical perturbation theory that the smoothness of the Hamiltonian is a quite important assumption. As shown (by numerical computations) in ref. 16, if one considers hard-core collisions, then the exponential law disappears.

Throughout our computations we took U, d, and m, respectively, as units of energy, length, and mass; we also fixed $a/d = 0.1$. The only constant which remains to be specified is then the inertia moment I, or better, the dimensionless quantity $\mathscr{I} = I/ma^2$. We set, typically, $\mathscr{I} = 1$, and only occasionally changed this value, which, as we shall see below, turns out to be largely irrelevant.

Let us denote by $E_x = p_x^2/2m$, $E_\varphi = p_\varphi^2/2I$ the translational and the rotational energy, respectively, and by ΔE the energy exchange during a collision (positive, if E_φ decreases and E_x increases). To measure ΔE, one should consider, in principle, the whole dynamics from $t = -\infty$ to $t = +\infty$; practically, it is enough to fix a sufficiently large distance d_0 and say that the collision begins and ends when one has $x = d_0$. Because of the strong cutoff in the potential, it is fairly sufficient to take, for example, $d_0/d = 6$ (when using double precision, namely 16 significant digits), or $d_0/d = 8$ (with so-called quadruple precision, or the H-floating representation of real numbers, corresponding to 33 significant digits). Since x is initially fixed, ΔE can be thought to be a function of the initial velocity of the center of mass v, of the initial angular velocity ω, and of the initial phase ψ, $\Delta E = \Delta E(v, \omega, \psi)$.

In agreement with the idea that collisions lead eventually to statistical equilibrium, that is, to energy equipartition among all degrees of freedom, one expects that, for given E_x and sufficiently high E_φ, positive values of ΔE are statistically favorite (actually, if x is fixed, and E_x, E_φ are also given, the only quantity on which one can average is the initial phase ψ). It is not difficult to see that equipartition corresponds to having, at the beginning of a collision, $E_x = \frac{2}{3}E$, $E_\varphi = \frac{1}{3}E$ (and not, as one could naively expect, $E_x = E_\varphi = \frac{1}{2}E$). The reason is as follows: since x is fixed, we are not looking at the whole phase space, but at a surface of section. Now, the microcanonical measure, which is assumed to describe the statistical equilibrium in the phase space, induces a corresponding equilibrium measure on the section; while the former is uniform, the latter has a density proportional to the component of the velocity in the phase space perpendicular to the section: that is, in our case, proportional to $|v|$. Practically, if $\langle f \rangle$ denotes the microcanonical average of any dynamical variable f, and $\langle f \rangle'$ denotes the corresponding average on the surface of section, one has $\langle f \rangle' = \langle E_x^{1/2} f \rangle / \langle E_x^{1/2} \rangle$. Taking f equal to E_x or E_φ, and computing in the standard way the microcanonical averages, one finally finds

$$\langle E_\varphi \rangle' = \tfrac{1}{3}E, \qquad \langle E_x \rangle' = \tfrac{2}{3}E \tag{2.4}$$

Thus, as far as $E_\varphi > \frac{1}{2}E_x$, i.e., $\omega^2 > (m/2I)\, v^2$, one has an excess of rotational energy; in this condition ΔE is expected to be, on the average,

positive. At the same time, according to the Boltzmann–Jeans conjecture, ΔE is expected to be small, namely to decrease exponentially with ω, if ω is sufficiently large. This is precisely what we are going to test now.

Let us first fix v, and look at the dependence of ΔE on ω and ψ. Figure 2 represents ΔE versus ψ, for several values of ω, at $E_x = 1$, i.e., $v = \sqrt{2}$. One can observe that:

(i) For increasing ω, ΔE becomes a nicer and nicer function of ψ, in fact almost indistinguishable from a sinusoid already at $\omega \gtrsim 10$; however, each sinusoid does not oscillate around zero, but (consistently with the above analysis) around a positive average value $\mathscr{E}_0$ (dashed line). For sufficiently large ω one can then write

$$\Delta E \simeq \mathscr{E}_0(v, \omega) + \mathscr{E}_1(v, \omega) \cos(\psi + \psi_0) \tag{2.5}$$

with suitable ψ_0.

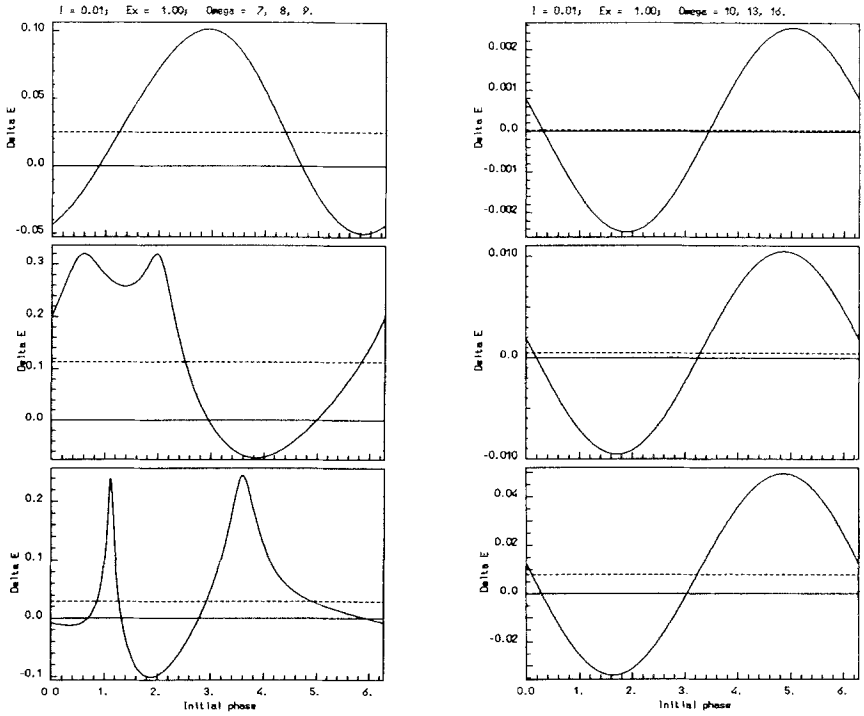


Fig. 2. Plot of ΔE vs. ψ, for fixed E_x and (a) $\omega = 7, 8, 9$, (b) $\omega = 10, 13, 16$, bottom to top. The dashed line corresponds to $\mathscr{E}_0$.

(ii) Both $\mathscr{E}_0$ and $\mathscr{E}_1$ are rapidly decreasing functions of ω (let us notice that the scale of each figure is adapted to the extreme values of ΔE). However, $\mathscr{E}_0$ decreases faster, so that one has soon $\mathscr{E}_0 \ll \mathscr{E}_1$.

The dependence of $\mathscr{E}_0$ and $\mathscr{E}_1$ on ω, at $v = \sqrt{2}$, is reported in Fig. 3, on a semilogarithmic scale. It is quite evident that, for sufficiently large ω, both $\mathscr{E}_0$ and $\mathscr{E}_1$ follow almost exactly exponential laws, namely

$$\mathscr{E}_0 = \mathscr{E}_0^* e^{-\tau_0 \omega}, \qquad \mathscr{E}_1 = \mathscr{E}_1^* e^{-\tau_1 \omega}, \qquad \tau_0 > \tau_1 \tag{2.6}$$

Actually, by interpolating the last data (last five points), one finds

$$\tau_0 \simeq 0.972, \qquad \tau_1 \simeq 0.494, \qquad \frac{\tau_0}{\tau_1} \simeq 1.97 \tag{2.7}$$

It is reasonable to conjecture $\tau_0/\tau_1 = 2$. Concerning $\mathscr{E}_0^*$, $\mathscr{E}_1^*$, one gets $\mathscr{E}_0^* \simeq 3.5 \times 10^2$, $\mathscr{E}_1^* \simeq 9.3$. As one can see, we could follow the exponential law for $\mathscr{E}_0$ from $\mathscr{E}_0 \simeq 10^{-3}$ to $\mathscr{E}_0 \simeq 10^{-16}$, that is, *for 13 orders of magnitude.* In fact, the possibility of reaching such an accuracy[5] did surprise us, and requires some discussion; a few comments on this point are deferred to a special section (Section 4).

[5] At low cost: Fig. 3 requires a few hours on a VAX 8600, using quadruple precision.

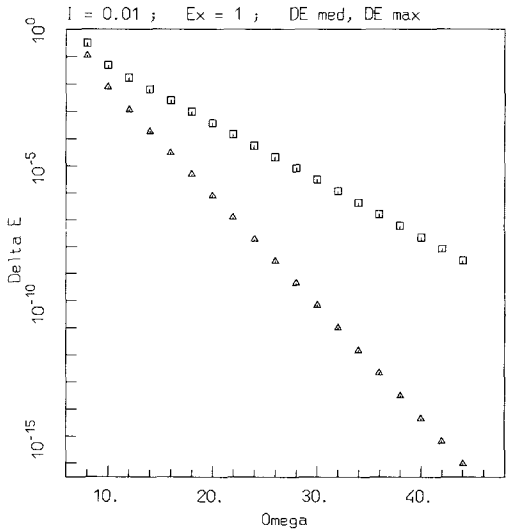
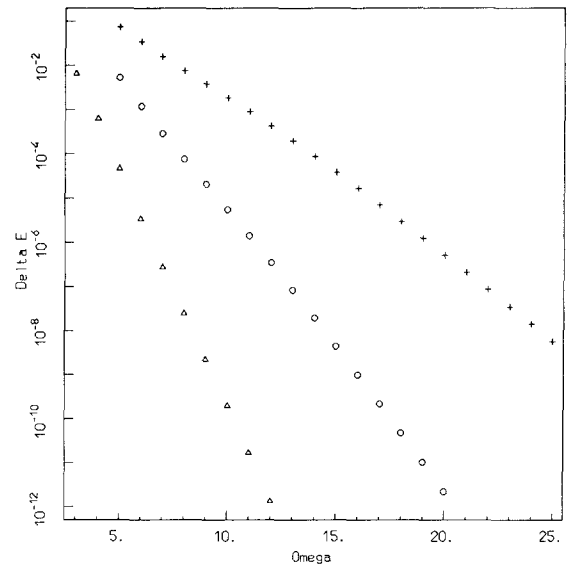
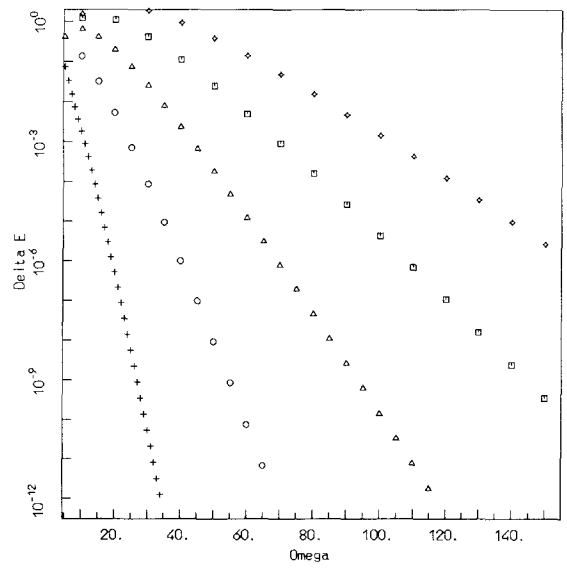


Fig. 3. Plot of $\mathscr{E}_0$ (triangles) and $\mathscr{E}_1$ (squares) as functions of ω, for $E_x = 1$ and $\mathscr{I} = 1$.



(a)



(b)

Fig. 4. Plot of $\mathscr{E}_0$ as a function of ω, for $\mathscr{I} = 1$ and different values of E_x: (a) $E_x = 0.2, 0.5, 1$, (b) $E_x = 1, 2, 3, 4, 5$.

The presence of two different exponential laws for the mean value $\mathscr{E}_0$ and for the fluctuating part $\mathscr{E}_1$ is, in our opinion, a remarkable fact. Since $\tau_0 > \tau_1$, the ratio $\mathscr{E}_0/\mathscr{E}_1$ decreases exponentially with ω, soon becoming negligible (for example, at $\omega = 44$ one has $\mathscr{E}_0 \simeq 10^{-8}\mathscr{E}_1$). Now, if one is interested in a single collision,[6] then, for large ω, the more relevant term is $\mathscr{E}_1$. On the other hand, for a statistical problem (imagine that a very large number of molecules simultaneously collide with a wall, with the same initial v and ω, and random initial phase), then the more significant quantity is the average $\mathscr{E}_0$ (although, as we shall see in the next section, the fluctuations, too, play a rather delicate role).

Let us now come to the dependence of ΔE on v; actually, we limited ourselves to study the v dependence of the most important quantities, namely τ_0 and τ_1. Our results can be summarized by saying that: (i) for each value of v, one finds exponential laws similar to those appearing in (2.6); (ii) both τ_0 and τ_1 are decreasing functions of v, and remarkably, one has $\tau_0/\tau_1 \simeq 2$ for all values of v. Figure 4 represents the exponential law for $\mathscr{E}_0$, at several different values of E_x, and thus of v, while Table I reports the precise results for τ_0 and τ_1. The fact that τ_0 and τ_1 decrease with v is not surprising, since these constants have the meaning of a "collision time," which must decrease, for increasing v, both because the molecule is faster and because, for higher translational energy, it does reach regions where the interaction potential is steeper; in fact, one could see from the data in Table I that τ_0 and τ_1 increase more than linearly with v^{-1}. As we shall see in the conclusions, the v dependence of τ_0 and τ_1 is a quite crucial point for the physical interpretation. Nevertheless, we did not further investigate this question, since at the moment we have not enough theoretical insight into it. Let us also remark that, while the qualitative features of the

[6] One can easily imagine a problem similar to the one considered here, but at a macroscopic scale (for example, the close encounter of an asteroid with a planet).

Table I

E_x	τ_0	τ_1	τ_0/τ_1
0.2	2.592	1.318	1.97
0.5	1.557	0.795	1.96
1.0	0.972	0.494	1.97
2.0	0.488	0.251	1.94
3.0	0.292	0.151	1.94
4.0	0.193	0.995	1.94
5.0	0.135	0.069	1.94

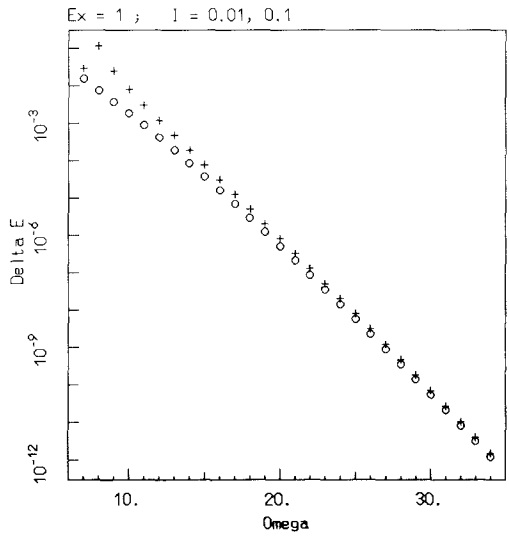


Fig. 5. Plot of $\mathscr{E}_0$ as function of ω, for $E_x = 1$ and different values of $\mathscr{I}$: $\mathscr{I} = 1$ (crosses), $\mathscr{I} = 10$ (circles).

phenomena here put in evidence are expected to be widely independent of the model at hand, instead the precise dependence of τ_0 and τ_1 on v certainly depends on the smoothness of the interaction potential, so that it might be better to reconsider this (not easy) problem in connection with a more realistic model.

Let us close this section by showing that one of the constants entering the model, namely the dimensionless inertia moment $\mathscr{I} = I/ma^2$, which was set equal to one in all of the above computations, is indeed widely irrelevant. Actually, Fig. 5 shows $\mathscr{E}_0$ as function of ω, at $v = \sqrt{2}$, for $\mathscr{I} = 1$ and $\mathscr{I} = 10$; one can see that not only the slope τ_0, but even the values of $\mathscr{E}_0$ are, for large ω, almost independent of $\mathscr{I}$. This shows in particular that ω —and not, say, the rotational energy $E_\omega = \frac{1}{2}I\omega^2$—is, so to speak, the correct independent variable to look at.

3. SEQUENCES OF COLLISIONS

Imagine now that a given molecule has a sequence of collisions with the walls of a container. From the analysis of the previous section, it follows that, if ω is initially sufficiently large, then a very large number of collisions are needed in order that an appreciable amount of energy is transferred from the rotational degree of freedom to the translational one.

Actually, after n collisions, if the energy exchange is so small that ω and v do not change appreciably (otherwise the exponents $\tau_i\omega$ in the exponential law get modified), and if we imagine that the initial phase ψ at the beginning of each collision is random, then, according to (2.5), (2.6), the overall energy exchange $\Delta E^{(n)}$ is a random variable, whose average $\langle \Delta E^{(n)} \rangle$ and variance $\sigma^{(n)}$ are given by

$$\langle \Delta E^{(n)} \rangle = n\mathscr{E}_0 \simeq ne^{-\tau_0\omega}\mathscr{E}_0^*, \qquad \sigma^{(n)} = \left(\frac{n}{2}\right)^{1/2} \mathscr{E}_1 \simeq (ne^{-\tau_0\omega})^{1/2} \frac{\mathscr{E}_1^*}{\sqrt{2}} \tag{3.1}$$

where one has used $\tau_0 = 2\tau_1$. For large initial ω, as far as $ne^{-\tau_0\omega} \ll 1$, one has $\langle \Delta E^{(n)} \rangle \ll \sigma^{(n)}$; one then expects a slow decreasing of E_φ with n, i.e., a slow tendency toward equilibrium, with, however, relatively large fluctuations. Later on, say for n of order $e^{\tau_0\omega}$, both $\langle \Delta E^{(n)} \rangle$ and $\sigma^{(n)}$ become of order one, and the energy transfer becomes significant. However, one should notice that, just because of the energy transfer, the exponent $\tau_0\omega$ decreases, and correspondingly the energy exchanges become much easier. Practically, one expects that, after a large time interval (growing exponentially as $e^{\tau_0\omega}$) during which E_φ and E_x are separately almost constant, one gets, more or less abruptly, a quite different regime, characterized by rather large energy fluctuations.

Such behavior is represented in Fig. 6, where E_φ, or more precisely, the ratio $E_\varphi/(E_x + E_\varphi)$, is plotted versus the number n of collisions; the

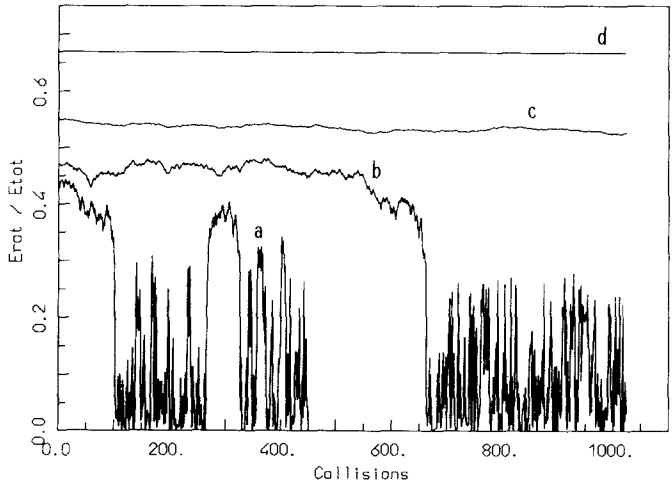


Fig. 6. Plot of $E_\varphi/(E_x + E_\varphi)$ for different sequences of collisions with initially $E_x = 1$, and (a–d) $\omega = 5.4, 6, 7, 8$.

four curves there represented correspond to the same initial v, and differ for the initial value of ω. Curves a and b exhibit quite clearly the behavior described above; curves c and d had not enough time to "jump down" (they would do it much later). The strict correlation between the value of E_φ (and thus of ω) and the amplitude of the fluctuations is quite evident.

Of course, the microscopic dynamics being reversible, the inverse process of the one exhibited in Fig. 6 should also be dynamically possible (although statistically less favorable, since the random fluctuations of order $\mathscr{E}_1$ are superimposed on a systematic energy transfer $\mathscr{E}_0 > 0$). An example of a sequence of collisions where the inverse process takes place on a reasonably short time scale (so that it is possible to see it numerically) is shown in Fig. 7. The behavior there exhibited is remarkably similar to intermittency. The basic idea is that, in principle, all regions of the phase space can be reached; however, it is quite unlikely to enter those regions where the rotational energy is high, and correspondingly, once one enters them, one is there trapped for a long time. Let us notice that, within the time scale of Fig. 7, a quite large part of the phase space, namely the one with $E_\varphi/(E_x + E_\varphi) \gtrsim 0.5$, is never visited; in particular, if one looks at the time average of any dynamical variable, this region does not contribute. Clearly, if one wants to "see" regions with higher E_φ, with the correct statistical weight, one needs much longer times, in fact times growing exponentially, as $e^{\tau_0 \omega}$. Thus, energy equipartition and statistical equilibrium are possibly reached, but, so to speak, only on a "really infinite" time scale. Practically, in any reasonable experiment, one expects that the regions of the phase space where E_φ exceeds some threshold value[7] do not contribute to the statistics, as if the rotational degree of freedom were, to some extent, frozen. The picture here discussed is certainly rough, and needs further

[7] The threshold depends, in principle, on the experimental time scale; however, according to the exponential law, the dependence is only logarithmic, and thus not appreciable over a rather wide range of times.

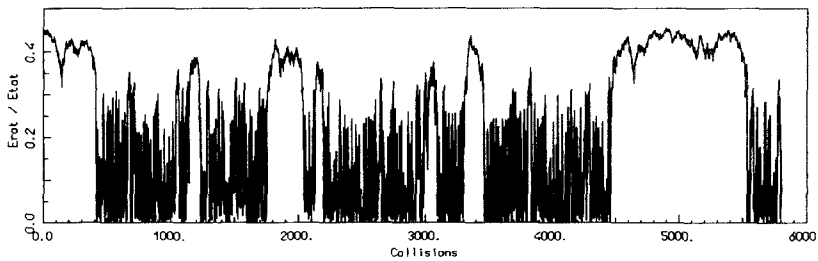


Fig. 7. The intermittency phenomenon. Initial data: $E_x = 0.5$, $\omega = 9$.

investigation (in particular, for a thermodynamic interpretation, one should pass from the microcanonical to the canonical description). Nevertheless, it provides, in our opinion, a possible starting point for a deeper dynamical understanding of the Boltzmann–Jeans phenomenon.

4. PROBLEMS OF NUMERICAL ACCURACY

A first question we would like to discuss here concerns the possibility of getting reliable values for the average $\mathscr{E}_0$ of ΔE in spite of the presence of large fluctuations of order $\mathscr{E}_1 \gg \mathscr{E}_0$. The problem in principle is serious: even assuming that ΔE is computed exactly (this point will be considered later), a huge number of data could be expected to be necessary, in order to compute reliably the integral

$$\mathscr{E}_0 = (2\pi)^{-1} \int_0^{2\pi} \Delta E(\omega, v, \psi)\, d\psi \tag{4.1}$$

For example, if one has $\mathscr{E}_0/\mathscr{E}_1 \simeq 10^{-8}$ (as happens for the last data of Fig. 3), and one wants to get, say, three significant digits of $\mathscr{E}_0$, then the precision one needs in the computation of the above integral is of the order of one part over 10^{11}. In general, a simple procedure, like the trapezoidal rule, allows one to replace the integral by a finite sum on N points, with an error decreasing as N^{-2}. More accurate procedures, like the Simpson rule, or the use of extrapolations, would lead to better results. Fortunately, however, none of these tricks is necessary here: indeed, for sufficiently large ω (i.e., when $\mathscr{E}_0/\mathscr{E}_1$ is small and the problem arises), as an immediate consequence of the decomposition (2.5), one gets

$$\mathscr{E}_0(v, \omega) = \sum_{j=1}^{N} \Delta E\left(v, \omega, \frac{2j\pi}{N}\right) \tag{4.2}$$

(exactly, if the decomposition is exact), in principle for any $N \geqslant 2$.

Practically, since we wanted to reproduce the whole curve representing ΔE as function of ψ, and in particular to measure accurately $\mathscr{E}_1$, too, we used a relatively large N, ranging (typically) from 128 to 512. It turns out that (at least) three significant digits of $\mathscr{E}_0$ are perfectly stable in this range. But in fact, we observed that (for large enough ω), even much lower values of N, for example, $N = 4$, give essentially identical results. By the way, this fact indirectly proves, far beyond the visual impression, that the shape of ΔE as function of ψ appearing in Fig. 2 really corresponds to the decomposition (2.5). In fact, occasionally we made a Fourier analysis of ΔE, and observed that the amplitude of the kth Fourier coefficient of ΔE decreases

very rapidly with k, namely as $e^{-|k|\tau_1\omega}$. It could be seen that, for large ω, this is enough to get good results for $\mathscr{E}_0$ with small N.

A second, more relevant question concerns the accuracy of the algorithm used to integrate numerically the equations of motion, and in particular to get, at the end of each collision, a reliable value of ΔE. The problem is quite delicate, because of the very high precision one needs for this quantity. We used a very elementary algorithm, sometimes called the "leap-frog algorithm" or "central differences method"; such an algorithm is adapted to differential equations of the second order of the form $\ddot{z} = f(z)$, $z \in \mathbb{R}^n$, and is based on the easy relation

$$z(t+\varepsilon) = 2z(t-\varepsilon) - z(t) + \varepsilon^2 f(z(t)) + \mathcal{O}(\varepsilon^4) \tag{4.3}$$

[in our case one has $z = (x, \varphi) \in \mathbb{R}^2$, $f = (-m^{-1}\,\partial V/\partial x, -I^{-1}\,\partial V/\partial\varphi)$]. The velocities do not appear explicitly in the algorithm; when needed, they are obtained by $\dot{z}(t) = (1/2\varepsilon)[z(t+\varepsilon) + z(t-\varepsilon)] + \mathcal{O}(\varepsilon^2)$: thus, the error on the velocities is relatively big, but does not propagate. This algorithm can be written in the form of a symplectic map in $\mathbb{R}^{2n}$: in fact, denoting $z_j = z(j\varepsilon)$, $w_j = z_j - z_{j-1}$ (and forgetting about the truncation error), one can give it the form of a symplectic mapping, namely

$$w_{j+1} = w_j + \varepsilon f(z_j), \qquad z_{j+1} = z_j + \varepsilon w_{j+1} \tag{4.4}$$

This integration scheme is well known to work efficiently[17] in connection with conservative systems; here, however, the precision one needs is so high that one should wonder whether the accuracy of the algorithm is, in principle, compatible with the results: in fact, elementary estimates would show that apparently, in order to keep the truncation error[8] within the limits of the required precision, one should take the time step ε so small that there would be no hope to perform, in a reasonable computer time, the thousands of numerical integrations which are necessary to produce the above reported results.

Practically, however, the situation is totally different. Indeed, we have the following *facts*:

(i) The computed energy exchange ΔE, in particular the relevant quantities $\mathscr{E}_0$, $\mathscr{E}_1$, turn out to be widely independent of the time step ε, as far as ε is of order, say, $10^{-2}(2\pi/\omega)$ or smaller. For example, at least three significant digits of $\mathscr{E}_0$ and $\mathscr{E}_1$ are stable if one changes ε from $10^{-2}(2\pi/\omega)$ to $10^{-4}(2\pi/\omega)$.

[8] Concerning the roundoff errors, there are no serious difficulties: using quadruple precision, these errors are of order 10^{-33}, so that (recalling that the integration time is short, and that there is no sensitive dependence on the initial conditions) one can confidently forget about them.

(ii) Still independently of ε in the above range, the energy conservation *at the end of each collision* is incredibly good: the relative error δ on the total energy is as small as 10^{-30}.

(iii) The energy conservation is, however, much worse, *for many orders of magnitude*, and also depends on ε, at the middle of collisions. Thus, there is some unexpected mechanism of compensation of errors to be understood.

These facts can be understood theoretically, by means of classical perturbation theory, using in an essential way the symplectic character of the integration algorithm. We cannot give here a full discussion, which will be reported elsewhere, in a paper devoted to the symplectic integration schemes. Here we limit ourselves to a simple sketch of the essential idea, with the only aim to show that the above reported results are not (as we did believe for some time) manifestly absurd. To this purpose, let us discuss in detail only one problem, namely the "exaggeratedly good" energy conservation, and illustrate, in particular, the mechanism of the error compensation.

As is well known,[18] a smooth symplectic map close to the identity, such as the above algorithm (4.4), can be interpolated formally by a convenient Hamiltonian flow; this means that there exists a convenient Hamiltonian H_ε such that its time-ε map coincides with the symplectic map (4.4), with an error decreasing faster than any power of ε. Actually, within suitable assumptions, one can prove that the error decreases exponentially with ε, say is of order $e^{-1/\varepsilon}$. On the other hand, it is quite evident that H itself interpolates the map (4.4), with an error of order ε^2; as a consequence, one immediately gets $H_\varepsilon = H + \mathcal{O}(\varepsilon^2)$. Moreover, it is quite clear that, if the interaction forces vanish, then H interpolates the map exactly; taking into account the form of the interaction potential, and recalling that $r = x + a\cos\varphi \simeq x$, one then easily obtains the more precise "local" relation

$$H_\varepsilon(p_x, p_\varphi, x, \varphi) - H(p_x, p_\varphi, x, \varphi) = \mathcal{O}(\varepsilon^2 e^{-(x/d)^2}) \tag{4.5}$$

Now, let $\xi_t = (p_x(t), p_\varphi(t), x(t), \varphi(t))$ be a computed orbit; the error in the energy conservation at time t is, by definition, $\delta(t) = H(\xi_t) - H(\xi_0)$. On the other hand, since H_ε interpolates the map, one has $H_\varepsilon(\xi_t) - H_\varepsilon(\xi_0) = \mathcal{O}(e^{-1/\varepsilon})$, and consequently

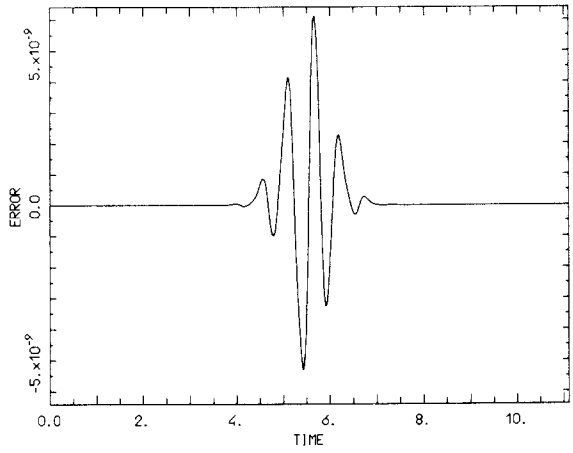
$$\begin{aligned}\delta(t) &= H(\xi_t) - H_\varepsilon(\xi_t) + H_\varepsilon(\xi_0) - H(\xi_0) + \mathcal{O}(e^{-1/\varepsilon}) \\ &= \mathcal{O}(\varepsilon^2 e^{-(x(t)/d)^2}) + \mathcal{O}(\varepsilon^2 e^{-(d_0/d)^2}) + \mathcal{O}(e^{-1/\varepsilon})\end{aligned} \tag{4.6}$$

where one also used $x(0) = d_0$. For generic t (in particular, at the middle

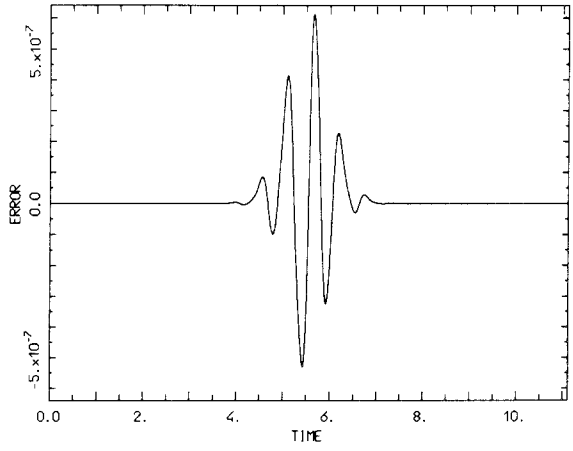
of a collision), one has $x/d = \mathcal{O}(1)$, and consequently $\delta = \mathcal{O}(\varepsilon^2)$. Instead, at the end of the collision, when one has again $x(t) = d_0$, one obtains

$$\delta = \mathcal{O}(\varepsilon^2 e^{-(d_0/d)^2}) + \mathcal{O}(e^{-1/\varepsilon}) \tag{4.7}$$

Because of the exponentials, the rhs of this expression is easily made negligible, by taking ε sufficiently small and d_0 sufficiently large; as a matter of fact, $\varepsilon = 10^{-2}(2\pi/\omega)$ and $d_0/d = 6$ or 8, depending on the number of digits one is working with, are sufficient.



(a)



(b)

Fig. 8. Error in the energy conservation as function of time, for $E_x = 1$, $\omega = 10$, and two different time steps: (a) $\varepsilon = 10^{-3}(2\pi/\omega)$, (b) $\varepsilon = 10^{-4}(2\pi/\omega)$. In both cases the error is, at the end, of order 10^{-30}.

Figure 8 reports δ as function of time for a collision process with $E_x = 1$, $\omega = 10$, and initial phase $\psi = 0$; the two curves refer to $\varepsilon = 10^{-3}(2\pi/\omega)$ and $\varepsilon = 10^{-4}(2\pi/\omega)$. Apart from the scale, they look identical; in fact, they are exactly scaled of a factor 100, consistent with the above illustrated dependence of δ on ε (exactly means that, for example, the ratio of the heights of the largest peaks is found to be 100.00007). At the end of the collision one finds, in both cases, $\delta \simeq 10^{-30}$.

5. CONCLUSIONS AND OPEN PROBLEMS

In this paper we studied numerically, on a very simple model, the rate of the energy exchanges between the translational and the rotational degrees of freedom of a molecule due to collisions with a wall. In full agreement with the Boltzmann–Jeans conjecture, the energy exchange ΔE is found to depend strongly, namely exponentially, on the angular velocity ω. More precisely, according to (2.5), (2.6), we found two different exponential laws for the average $\mathscr{E}_0$ of ΔE on the initial phase and for the fluctuation $\mathscr{E}_1$, with different coefficients τ_0 and τ_1, namely $\tau_0 = 2\tau_1$.

Since, for large ω, one has $\mathscr{E}_0 \ll \mathscr{E}_1$, it is quite important to distinguish between these quantities; in fact, as we have seen, the presence of two different exponential laws for $\mathscr{E}_0$ and $\mathscr{E}_1$, and in particular the relation $\tau_0 = 2\tau_1$, play a rather delicate role in the approach to statistical equilibrium, giving rise to a phenomenon similar to intermittency. Such a distinction between $\mathscr{E}_0$ and $\mathscr{E}_1$ does not appear in the heuristic approach of refs. 2, 3, 8 and 9, where only the average $\mathscr{E}_0$ is considered, nor in the rigorous approach of classical perturbation theory,[12–15] where only the maximal value of $|\Delta E|$, practically coinciding with $\mathscr{E}_1$, is taken into consideration. It is clear that, on both sides, one needs further investigation; our personal feeling is that a significant improvement could be achieved by combining in some way the two methods.

The accuracy of our numerical computation is rather high; in fact, we could (easily) measure average energy exchanges of the order of one part over 10^{16}. This corresponds to very large equilibrium times, since, as we have seen, one then needs a number of collisions of order 10^{16} to get energy exchanges of order one, and consequently to possibly reach the statistical equilibrium. Our model is too poor to allow any physical conclusion to be drawn; anyhow, let us recall that, for ordinary gases, 10^{16} collisions already represent a macroscopic time, namely a few hours, if one assumes, as is realistic, 10^{12} collisions per second.[9]

[9] The value $\mathscr{E}_0 \simeq 10^{-16}$ is taken from the last point of Fig. 3, and refers to $\omega = 44$ (in natural units). It is amusing to note that, according to the exponential law, by doubling ω, one would get an average energy exchange per collision of order 10^{-32}; the corresponding equilibrium time exceeds the lifetime of the universe.

Besides the very relevant limitation that the model is not realistic, there are other questions which make difficult a physical interpretation. First of all, in addition to the molecule–wall collisions, one should also consider the molecule–molecule collisions. A minimal familiarity with perturbation theory is enough to say that the exponential laws are not going to disappear: however, the phenomenon is certainly more complicated, and in particular the coefficients τ_0 and τ_1 could be significantly smaller; as a consequence, the contribution of these collisions could be, for high ω and not too dilute gases, the dominant one.

Another relevant question, perhaps the most crucial one, concerns the dependence of the coefficients τ_0, τ_1 on v. In fact, we have here described the Boltzmann–Jeans conjecture as a phenomenon of freezing of the fast rotations; however, by analogy with quantum physics, one should expect that the freezing occurs at low temperatures, i.e., when ω is small. The point is the following: according to (2.6), the basic quantities determining the rate of the energy exchanges are the products $\tau_i\omega$. Now, by lowering the temperature, v and ω decrease in the same way, namely as the square root of the temperature; the behavior of $\tau_i\omega$ depends then crucially on the dependence of τ_i on v: if, as mentioned in Section 2, the dependence is more than linear in v^{-1}, then for decreasing temperature the product $\tau_i\omega$ increases, and the freezing phenomenon does take place. For this reason we say that, in connection with a realistic model, it is particularly important to investigate this question, both theoretically and numerically.

In conclusion, we are aware that, for many different reasons, our results are still poor, and certainly not enough for a physical interpretation. Nevertheless, we think we have shown that, at least in principle, the Boltzmann–Jeans phenomenon exists, that it is worthwhile to further investigate it, and, moreover, that, although the Boltzmann–Jeans conjecture concerns the behavior of many-particle systems for macroscopic time scales, relatively simple numerical computation could give definite answers on it; this was indeed the main purpose of our work.

ACKNOWLEDGMENTS

We are indebted to A. Giorgilli (Milan) for many helpful comments and suggestions, and also for having kindly reviewed the manuscript. This work was completed during a stay by G.B. at the Physics Department, ETH, Zürich. The author is grateful to Prof. J. Fröhlich for his kind invitation.

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