

Exponentially Long Equilibrium Times in a One-Dimensional Collisional Model of Classical Gas

Giancarlo Benettin,¹ Poul Hjorth,² and Paolo Sempio³

Received August 6, 1998

Around 1900, J. H. Jeans suggested that the “abnormal” specific heats observed in diatomic gases, specifically the lack of contribution to the heat capacity from the internal vibrational degrees of freedom, in apparent violation of the equipartition theorem, might be caused by the large separation between the time scale for the vibration and the time scale associated with a typical binary collision in the gas. We consider here a simple 1D model and show how, when these time scales are well separated, the collisional dynamics is constrained by a many-particle adiabatic invariant. The effect is that the collisional energy exchanges between the translational and the vibrational degrees of freedom are slowed down by an exponential factor (as Jeans conjectured). A metastable situation thus occurs, in which the fast vibrational degrees of freedom effectively do not contribute to the specific heat. Hence, the observed “freezing out” of the vibrational degrees of freedom could in principle be explained in terms of classical mechanics. We discuss the phenomenon analytically, on the basis of an approximation introduced by Landau and Teller (1936) for a related phenomenon, and estimate the time scale for the evolution to statistical equilibrium. The theoretical analysis is supported by numerical examples.

KEY WORDS: Collisional equilibrium; kinetic theory; adiabatic invariants; specific heats; exponential estimates.

1. INTRODUCTION

We consider a classical mechanical model of a one-dimensional gas consisting of n identical diatomic molecules. See Fig. 1. Denoting by $x = (x_1, \dots, x_n)$

¹ Dipartimento di Matematica Pura e Applicata, Università di Padova, GNFM (CNR), and INFN, I-35131 Padova, Italy; e-mail: benettin@pdmatl.math.unipd.it.

² Department of Mathematics, Technical University of Denmark, DK-2800 Lyngby, Denmark.

³ ILGA Gomma, I-27029 Vigevano, Italy.

and $p = (p_1, \dots, p_n)$ the canonical variables of the centers of mass of the molecules, and by $\xi = (\xi_1, \dots, \xi_n)$, $\pi = (\pi_1, \dots, \pi_n)$ the (Cartesian) canonical variables describing the internal vibrations, the Hamiltonian has the overall form

$$H(x, p, \xi, \pi) = H_{\text{tr}}(p) + H_{\text{vib}}(\xi, \pi) + V_{\text{int}}(x, \xi) \quad (1)$$

with

$$H_{\text{tr}} = \sum_{i=1}^n \left(\frac{p_i^2}{2m} + U(r_i) \right), \quad H_{\text{vib}} = \sum_{i=1}^n \left(\frac{\pi_i^2}{2\mu} + \frac{\mu\omega^2 \xi_i^2}{2} \right)$$

and

$$V_{\text{int}} = \sum_{i=1}^{n-1} V(r_i, \xi_i, \xi_{i+1})$$

where m and μ denote respectively the total mass and the reduced mass of the molecules, while ω denotes the frequency of vibration for a single molecule, and $r_i = x_{i+1} - x_i - l$, with l the proper length of the molecule; the separation between U and V is established by requiring $V(r, 0, 0) = 0$. Both U and V are assumed to be smooth (in fact analytic, see later) functions and to vanish for $r \rightarrow \infty$. The Hamiltonian H_{tr} describes a gas of perfectly rigid molecules, with pairwise interaction described by the potential U ; as is natural, $U(r)$ will be assumed to diverge for $r \rightarrow 0$. The gas is assumed to be diluted, so that V_{int} is small compared to H_{tr} and H_{vib} .

A similar model was considered by Jeans⁽¹⁾ in 1903, in the investigation of the time scale of the approach to equilibrium between translational and vibrational degrees of freedom in classical gases. The basic idea of Jeans (after Boltzman, see refs. 3 and 4) is that the energy exchanges among the translational degrees of freedom, as well as among the vibrational degrees of freedom (exact resonance is here important), are easy, so that, practically, the two sub-systems described by H_{tr} and by H_{vib} reach separately their thermodynamical equilibrium, with temperatures T_{tr} and T_{vib} not necessarily equal; whereas collisional energy exchanges between H_{tr} and H_{vib} , in case of large ω , are exponentially small, so that an effective “freezing out” of the vibrational energy for quite large times (“billions of



Fig. 1. Illustrating the model.

years," in the words by Jeans!) is expected to occur, if ω is sufficiently large.⁴ The conclusion by Jeans is that, in principle, the experimentally observed "freezing" phenomena of various kind could be explained classically, without Planck's quantization. More precisely, Jeans focused the attention on the collision of two molecules, and introduced the drastic simplification of disregarding one of the internal degrees of freedom; the resulting Hamiltonian is

$$H'(p, r, \xi, \pi) = \frac{p^2}{2m} + U(r) + \frac{\pi^2}{2\mu} + \frac{\mu\omega^2\xi^2}{2} + V(r, \xi) \quad (2)$$

and represents the collision of a vibrating molecule with an unstructured particle (in the frame of the center of mass), or with a fixed wall. Denoting by ΔE the energy exchange between the two degrees of freedom due to a collision, and by E_0 the average of ΔE on the asymptotic phase of the oscillator, Jeans conjectured, and supported heuristically, an exponential law of the form

$$E_0 \approx \mathcal{E}_0 e^{-\tau_0 \omega}$$

where \mathcal{E}_0 is a typical microscopic energy, while the (crucial) constant τ_0 represents some time scale associated to the translational motion. Here, unfortunately, Jeans is not really precise, though he qualitatively identifies τ_0 with the typical duration of the collision process. The conclusion is that in typical conditions E_0 is negligibly small, and long-time freezing out occurs. However, a reasonable quantitative estimate of the time scale for equilibrium is lacking.

Essentially the same problem of determining ΔE in molecular collisions was independently considered by Landau and Teller⁽⁵⁾ in 1936.⁵ We follow here ref. 6, where the paper by Landau and Teller was revisited having in mind applications to Chemical Physics. The Hamiltonian is precisely the above one (2), with the special choice

$$U(r) = e^{-r}, \quad V(r, \xi) = \xi e^{-r}$$

⁴ This idea was stressed by Jeans in his book on gas theory,⁽²⁾ but only up to the second edition (1916), see Chapter XVI. In the next edition (1920) the chapter was removed.

⁵ The physical motivation by Landau and Teller is different from Jeans' one, namely it concerns the possible dispersion of sound waves in classical gases. But the two problems turn out to be intimately related. Jeans too, in Chapter XVI of the 1916 edition of his book on gas theory, applies the calculation to the dispersion of sound, in a manner similar to that of Landau and Teller.

which allows explicit computations; the method is the so-called “integration along unperturbed trajectories,” namely computation of ΔE along trajectories $(p_0(t), r_0(t))$ of the “zeroth-order” Hamiltonian

$$\mathcal{H}(p, r) = \frac{p^2}{2m} + U(r) \quad (3)$$

The result was of the form

$$\Delta E \simeq \mathcal{E}_0 e^{-\tau_0 \omega} + \mathcal{E}_1 e^{-\tau \omega} \cos \phi, \quad (4)$$

where ϕ is the asymptotic phase of the oscillator, that is, practically a random variable in the physical problem. A very important fact is that, in this approach, τ_0 and τ are precisely identified: indeed, τ coincides with the width of the analyticity strip of $r_0(t)$, thought of as a function of complex t . While $\tau_0 = 2\tau$. So, for individual collisions the latter term is much larger than the former one, but for many collisions it is averaged out statistically.⁶

The Landau–Teller (LT) approximation, for this and similar problems, has recently been revisited in the light of modern perturbation theory for Hamiltonian systems. In special examples⁽⁸⁾ it has been (rigorously) shown to provide the first and dominant contribution in a suitable convergent series expansion of ΔE ; in other cases^(7, 9, 10) very accurate numerical results indicated a complete agreement between the theoretical and the “experimental” values of ΔE (ΔE ranging over more than twenty orders of magnitude; more than ninety orders of magnitude in ref. 10). The LT approximation will be here assumed to be correct, and will be the basic tool of this paper.

Indeed, the purpose of this paper is to revisit Jeans’ program of deducing theoretically the law of the approach to equilibrium in the above model (1). To this end, we proceed as follows:

(i) We assume that, at any given moment, the translational and vibrational degrees of freedom are in equilibrium separately, with canonical

⁶ We cannot enter here the details of the LT procedure. But while there are good reasons to consider the latter term as reliable, the deduction of the former term is open to criticism, since terms of the same order of magnitude, coming from the next perturbative order, are disregarded; in particular, as is totally unrealistic, E_0 turns out to be always positive (it is a square). That term is in fact a second-order contribution, improperly taken into account in the first-order computation. In the quick revision of the LT approximation, that we shall report in the next section, the average of ΔE , correctly computed at the lowest order, will simply vanish.

distributions corresponding to temperatures T_{tr} and T_{vib} , not necessarily equal.

(ii) We assume that the dominant contribution to the energy exchanges between translational and vibrational degrees of freedom comes from well separated two-molecules collisions (however, see Section 5 for a critical discussion of this point);

(iii) We use the LT approximation, suitably adapted to the problem at hand, to determine ΔE in a single binary collision, as a function of the asymptotic data of velocity and phase of the colliding molecules;

(iv) We then combine together the mechanical model and the statistical assumptions, and deduce a law of the approach to equilibrium in the gas, of the form

$$\frac{d}{dt}(T_{\text{vib}} - T_{\text{tr}}) = -(T_{\text{vib}} - T_{\text{tr}}) f(\omega, T_{\text{tr}}) \quad (5)$$

The (positive) function f depends on the choice of the potentials, and with reasonable assumptions (including analyticity), it decreases with ω as a stretched exponential. In particular, if $U(r)$ behaves, for small r , as r^{-s} , one finds

$$f(\omega) \sim \exp - a\omega^\alpha, \quad \text{where } \alpha = \frac{2}{3 + 2/s} \quad (6)$$

This approach follows rather closely the study reported in refs. 12 and 13 on a related problem, namely the approach to equilibrium in a strongly magnetized pure electron plasma. In place of the internal vibration of molecules one has, in the plasma, the Larmor rotation of the electrons around the magnetic field lines. The essence of the problem, and its mathematical structure, are indeed quite similar. Some work of course is necessary to adapt the methods to the situation at hand.

In addition to the theoretical work, we also made some numerical studies, both as a general check of the theoretical results and as a test of some of the above assumptions. The agreement between theoretical and numerical results is, as we shall see, quite remarkable.

The next Section 2 is devoted to the mechanical part, that is, to the above point (iii); some numerical results concerning individual collisions are also included. The statistical analysis is reported in Section 3. Numerical results supporting (5) and (6) are reported in Section 4, while Section 5 discusses three body collisions.

2. REVISITING THE LT APPROXIMATION

In this section we adapt the LT method to our model. The Hamiltonian we shall start from is the complete Hamiltonian describing the two molecules collision: in the frame of the center of mass,

$$\begin{aligned} H^{(2)}(p, r, \pi_1, \pi_2, \xi_1, \xi_2) \\ = \mathcal{H}(p, r) + \frac{\pi_1^2 + \pi_2^2}{2\mu} + \frac{\mu\omega^2}{2} (\xi_1^2 + \xi_2^2) + V(r, \xi_1, \xi_2) \end{aligned} \quad (7)$$

with $\mathcal{H}(p, r)$ as in (3). Let us remark that the coupling term is small, namely as small as ω^{-1} : indeed, the term itself is $\mathcal{O}(|\xi_1| + |\xi_2|)$, and in turn, for fixed energy, ξ_1 and ξ_2 are of order ω^{-1} .

We now pass to the usual action-angle variables (I, ϕ) of the oscillators,

$$\pi_i = \sqrt{2I_i\omega} \cos \phi_i, \quad \xi_i = \omega^{-1} \sqrt{2I_i\omega} \sin \phi_i, \quad i = 1, 2 \quad (8)$$

which give the Hamiltonian the form

$$\hat{H}(r, p, I_1, I_2, \phi_1, \phi_2) = \omega(I_1 + I_2) + \mathcal{H}(r, p) + \hat{V}(r, I_1, I_2, \phi_1, \phi_2) \quad (9)$$

Because of the exact resonance, it is convenient to introduce the further canonical change of variables $(I_1, I_2, \phi_1, \phi_2) \mapsto (J, \Gamma, \psi, \gamma)$ defined by

$$J = I_1 + I_2, \quad \Gamma = I_2, \quad \psi = \phi_1, \quad \gamma = \phi_2 - \phi_1$$

Notice that the angles now appear as one fast angle, ψ , and one slow angle, γ . The coupling term now becomes of order $\omega^{-1} \sqrt{\omega J}$, and for given energy (given temperature) and large ω , it is as small as ω^{-1} . As a reminder of this smallness, we shall write a small parameter ε in front of it, and use ε as the small parameter of our perturbative study. The final Hamiltonian, on which we shall work, is thus of the form

$$K(r, p, J, \Gamma, \psi, \gamma) = \omega J + \mathcal{H}(r, p) + \varepsilon \sqrt{\omega J} W(r, J, \Gamma, \psi, \gamma) \quad (10)$$

with ε and ω independent parameters; only at the very end will ε be replaced with ω^{-1} . (The presence of the factor $\sqrt{\omega J}$ will be relevant, and for this reason it has been left in the expression.)

The approximation of “integrating along unperturbed trajectories,” applied to the above Hamiltonian, runs as follows:

(i) One makes a choice of the asymptotic data at $t = -\infty$, say

$$\begin{cases} p(t) \rightarrow p^o \\ r(t) - p^o t \rightarrow r^o \end{cases} \quad \begin{cases} J(t) \rightarrow J^o \\ \psi(t) - \omega t \rightarrow \psi^o \end{cases} \quad \begin{cases} \Gamma(t) \rightarrow \Gamma^o \\ \gamma(t) \rightarrow \gamma^o \end{cases}$$

and uses as the unperturbed trajectory the motion at zero ε , namely the solution $p_0(t), r_0(t)$ of the Hamiltonian problem \mathcal{H} , together with the trivial motion

$$J_0(t) = J^o, \quad \Gamma_0(t) = \Gamma^o, \quad \psi_0(t) = \psi^o + \omega t, \quad \gamma_0(t) = \gamma^o$$

for the internal degrees of freedom. r^o, ψ^o and γ^o are defined up to a constant, corresponding to the choice of the time origin; for definiteness, we shall take $r^o = 0$.

(ii) One assumes that $r_0(t)$ is analytic in a complex strip $|\Im t| < \tau = \tau(p^o)$. More precisely, one introduces the Fourier components \mathcal{W}_k of W ,

$$W(r, J, \Gamma, \psi, \gamma) = \sum_{k \in \mathbb{Z}} \mathcal{W}_k(r, J, \Gamma, \gamma) e^{ik\psi}$$

and assumes that all of them are individually analytic as functions of t in the strip $|\Im t| < \tau$, if computed along the above unperturbed motion. Indeed, typically there is a lack of analyticity in all of them, whenever $r_0(t)$ has a singularity.⁷

(iii) One computes

$$\Delta J = -\varepsilon \int_{-\infty}^{\infty} \sqrt{\omega J_0(t)} \frac{\partial W}{\partial \psi}(r_0(t), J_0(t), \Gamma_0(t), \psi_0(t), \gamma_0(t)) dt$$

As a result, one gets ΔJ in the form of a Fourier series in the asymptotic angle ψ^o :

$$\Delta J = \varepsilon \sum_{k > 0} \mathcal{J}_k \cos(k\psi^o + \theta_k)$$

with

$$\begin{aligned} \mathcal{J}_k &= \sqrt{\omega J^o} A_k(J^o, \Gamma^o, \gamma^o) e^{-k\omega\tau}, \\ A_k &= \left| k \int_{-\infty}^{\infty} \mathcal{W}_k(r_0(t + i\tau), J^o, \Gamma^o, \gamma^o) e^{ik\omega t} dt \right| \end{aligned}$$

⁷ It might happen that some Fourier components are not affected by the singularity of $r_0(t)$, and are analytic in a larger strip. Such a situation could be easily handled, at the price of opaque notations; the present assumption is made for simplicity.

One should remark that A_k is not really constant in ω , but it depends on ω only weakly, the precise form depending on the analytic properties of the potential. The dominant dependence of ΔJ on ω resides for each k in the factor $e^{-k\omega\tau}$.

For large ω , the dominant term is the one with $k=1$, and one has

$$\Delta J \simeq \varepsilon \sqrt{\omega J^o} A e^{-\omega\tau} \cos(\psi^o + \theta), \quad A \equiv A_1, \quad \theta \equiv \theta_1$$

At this lowest order in ε the average of ΔJ over the phase ψ_0 vanishes; the statistical average $\langle \Delta J \rangle$ over the initial data also vanishes, and this is in a sense disappointing, since the average energy exchange is the quantity we are mainly interested in. Nonvanishing contributions are expected from the next perturbative order. As already remarked, the original computation by Landau and Teller retains some of them, and these, see (4), are of order $e^{-2\omega\tau}$; from the analysis of ref. 8 (rigorous, although concerning a specific model), one understands that at any order in ε the contributions to the average are small (at least) as $e^{-2\omega\tau}$, so in particular they are much smaller than the first harmonic.⁸

Second order contributions, including the contributions to the average which we are interested in, could be produced in principle by iterating the procedure of integrating along the unperturbed trajectory, see ref. 8 for details. Such a procedure, however, is rather hard in practice. Fortunately, this annoying computation is not necessary: as we shall see in Section 3, it is enough to take for ΔJ the expression

$$\Delta J = \Delta' J + \Delta'' J \quad (11)$$

with

$$\Delta' J = \varepsilon \sqrt{\omega J^o} A e^{-\omega\tau} \cos(\psi^o + \theta), \quad \Delta'' J \ll \Delta' J \quad (12)$$

and take into account very general properties of the dynamics (conservation of volume and time reversal), to compute correctly the dominant contributions to the average $\langle \Delta J \rangle = \langle \Delta'' J \rangle$, and find in particular $\langle \Delta J \rangle = \mathcal{O}(e^{-2\omega\tau})$, even in lack of any detailed informations about $\Delta'' J$.

Before passing to the statistical part, let us show the results of a numerical test of the LT approximation. Test and results are similar to those of ref. 7, but differ from them by the presence of two oscillators (instead of one) in the Hamiltonian. The coordinates most appropriate for

⁸ In fact, in ref. 8 one proves (for a simple model) that at any order in ε the k th Fourier harmonic has in front an exponential factor $e^{-k\omega\tau}$, while the average has in front a factor $e^{-2\omega\tau}$. It is important that such exponentials are present at each perturbative order, otherwise higher order could dominate the lower ones, and completely destroy the result.

numerical integration are $r, p, \phi_1, \phi_2, I_1, I_2$: indeed (see ref. 11 for a rigorous proof, and ref. 10 for particularly accurate numerical results), one can reliably measure *extremely small* energy exchanges, as is necessary for a significant check the exponential laws, if: (i) one uses a symplectic integration scheme; (ii) the algorithm is asymptotically free of errors (save for round-off). To comply with the latter requirement, the use of action-angle variables for the oscillators is mandatory (although apparently annoying: symplectic algorithms become implicit, and apparently lot of time is wasted). The symplectic algorithm we used is the simplest possible one, namely the symplectic transformation generated by

$$S(r, p', \phi_1, \phi_2, I_1', I_2') = rp' + \phi_1 I_1' + \phi_2 I_2' + hH(r, p', \phi_1, \phi_2, I_1', I_2')$$

h denoting the time step. Concerning the potentials entering the model, we made a simple choice in (7), namely

$$U + V = \frac{e^{-\rho^2}}{\rho}, \quad \text{where } \rho = r - \frac{\xi_1 + \xi_2}{2} + l$$

(numerically, there is no need of distinguishing between U and V), and then we replaced ξ_1, ξ_2 by their expressions (8) in terms of the action-angle variables. The super-exponential decay of the interaction is quite useful to reduce computation time: practically, the interaction is completely negligible, even in quadruple precision (33 decimal digits), for $\rho \geq 10$. Similar potentials were used in refs. 7, 9 and 10. Our choice of the constants entering the Hamiltonian is $m = 1, \mu = 0.5, l = 1$. We shall not enter here the delicate question of the reliability of numerical results; for a wide discussion see the above quoted references, in particular ref. 10.

Practically, in our numerical study we proceed as follows:

(a) We fix initially $r = r^*$ with r^* large, typically $r^* = 10$; we make a choice of the initial data (essentially coinciding with the asymptotic data) $p^o, J^o, \Gamma^o, \gamma^o, \psi^o$, with $p^o < 0$; we then start the numerical integration, and stop it when r gets again larger than r^* . We measure ΔE at the end of the run as the difference between the final and the initial vibrational energy.

(b) In order to separate the Fourier components \mathcal{E}_k of ΔE , we repeat each collision with K different values of ψ^o *equally spaced in the circle*, namely

$$\psi^o + \frac{2\pi j}{K}, \quad 0 \leq j < K$$

The quantities we actually compute are (omitting in ΔE all arguments but ψ)

$$\tilde{\mathcal{E}}_k = \left| \frac{1}{S} \sum_{j=0}^{K-1} \Delta E \left(\psi^o + \frac{2\pi j}{K} \right) e^{-ik(\psi^o + j(2\pi/K))} \right|,$$

approximating the Fourier amplitudes, with discrete sums in place of integrals. One immediately recognizes^(7, 10) that in our conditions $\tilde{\mathcal{E}}_k$ practically coincides with \mathcal{E}_k , as far as $K \geq 2k + 1$ ($K \geq 3$ for the average). Indeed, one easily finds

$$\tilde{\mathcal{E}}_k = \left| \sum_{s=-\infty}^{\infty} \hat{\mathcal{E}}_{k+sK} \right|, \quad \text{with} \quad \hat{\mathcal{E}}_{k+sK} = \frac{1}{2\pi} \int_0^{2\pi} \Delta E(\psi) e^{-ik\psi} d\psi;$$

but precisely because $\tilde{\mathcal{E}}_k \sim e^{-|k|\tau\omega}$ ($\tilde{\mathcal{E}}_0 \sim e^{-2\tau\omega}$ for the average), the term $s=0$ dominates the sum, as fast as $K \geq 2k + 1$ ($K \geq 3$ for the average). So, in order to compute the harmonics up to $k=3$, we used in most cases $K=7$. Occasionally, as a check, we used higher values of K (with full agreement).

(c) Finally, we repeat the entire procedure for varying ω values, keeping $p^o, J^o, \Gamma^o, \gamma^o$ fixed, and plot \mathcal{E}_k vs. ω in semi-log scale.

According to the above theoretical analysis, we expect to observe (for large ω) straight lines with slope λ_k proportional to k for $k > 0$, and $\lambda_0 = \lambda_2$. A typical result is shown in Fig. 2. Four lines clearly appear,

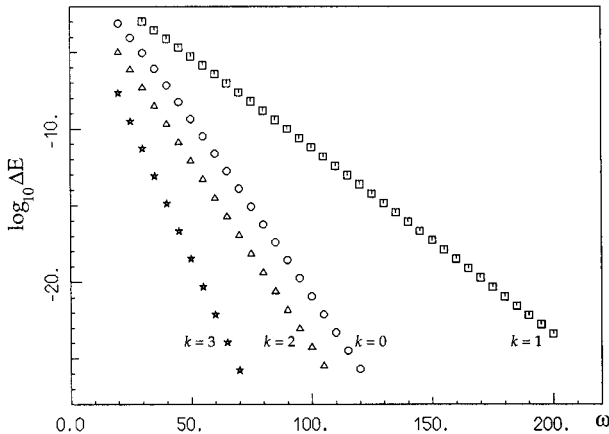


Fig. 2. The different exponential laws for the different Fourier components, in agreement with the Landau–Teller approximation. Initial data: $p^o = -2$, $J^o = 0.088$, $\Gamma = 0.01$, $\psi^o = 0.3$, $\gamma = 5.454$.

corresponding (right to left) to $k = 1, 0, 2, 3$. The slopes are in the correct ratio: one finds indeed (least squares fit, excluding a few data for small ω) λ_0/λ_1 and λ_2/λ_1 between 1.9 and 2, λ_3/λ_1 between 2.9 and 3. The experiment was repeated by varying the initial data $p^o, J^o, \Gamma^o, \gamma^o$ with no qualitative change; as is remarkable, the slopes depend in an essential way on p^o , but are practically independent of the other data, and are always in the correct ratio $\lambda_0 : \lambda_1 : \lambda_2 : \lambda_3 = 2 : 1 : 2 : 3$. These results make us confident that the LT approximation describes correctly the energy exchanges of binary collisions in our model, too.

3. THE STATISTICAL PART

Here we proceed essentially as in refs. 12 and 13; the only difference is that here we do not use explicitly the "law of detailed balance," as in the above references, but more elementary facts from dynamics, namely the time-reversal property and the conservation of volume in the phase space (which are also at the basis of the law of detailed balance).

It is convenient to eliminate one variable, namely r , by introducing a Poincaré section $r = r^*$; r^* is taken so large that the interaction W is negligible. To proceed statistically, we must count the number dn of pairs of molecules which cross the section $r = r^*$ (with $\dot{r} < 0$) in time dt ; assuming, as explained in the Introduction, that the translational and vibrational degrees of freedom are separately in equilibrium with temperatures T_{tr} and T_{vib} , this number is given by

$$dn = N\nu C^{-1} e^{-\beta_{\text{tr}} E_{\text{tr}}(p) - \beta_{\text{vib}} E_{\text{vib}}(J)} \left| \frac{p}{m} \right| dt dp dJ d\Gamma d\psi d\gamma \quad (13)$$

where $\beta_{\text{tr}} = 1/(k_B T_{\text{tr}})$, $\beta_{\text{vib}} = 1/(k_B T_{\text{vib}})$, while N is the total number of molecules, ν is the density (number of molecules per unit length), and

$$E_{\text{tr}}(p) = \frac{p^2}{2m}, \quad E_{\text{vib}}(J) = \omega J$$

the domain of the variables, denoted \mathcal{D} , is

$$p \in (-\infty, 0), \quad J \in (0, \infty), \quad \Gamma \in (-J, J), \quad \psi, \gamma \in (0, 2\pi)$$

finally, the normalization constant is $C = C_p C_{JJ} C_\psi C_\gamma$, with

$$C_p = \int_0^\infty e^{-\beta_{\text{tr}} p^2/(2m)} dp, \quad C_{JJ} = \int_0^\infty dJ e^{-\beta_{\text{vib}} \omega J} \int_{-J}^J d\Gamma, \quad C_\psi = C_\gamma = 2\pi$$

The quantity we aim to compute is the average energy exchange per unit time and per molecule, $\langle \dot{E}_{\text{vib}} \rangle = \omega \langle \dot{J} \rangle$; from the expression (13) for dn , one has clearly

$$\langle \dot{E}_{\text{vib}} \rangle = \frac{v}{mC} \int_{\mathcal{D}} \omega \Delta J e^{-\beta_{\text{tr}} E_{\text{tr}}(p) - \beta_{\text{vib}} E_{\text{vib}}(J)} |p| dp dJ d\Gamma d\psi d\gamma \quad (14)$$

with ΔJ as in (11). Let us introduce the compact notation

$$x = (p, J, \Gamma, \psi, \gamma), \quad dx = dp dJ d\Gamma d\psi d\gamma$$

Suppose that after the collision, when the distance r between the molecules reaches again the value r^* , the state x has evolved into the state $\tilde{x} = (\tilde{p}, \tilde{J}, \tilde{\Gamma}, \tilde{\psi}, \tilde{\gamma})$. The preservation of volume in the phase space implies that the map $\tilde{g}: x \mapsto \tilde{x}$ has Jacobian $|p|/|\tilde{p}|$. In turn, the time-reversal symmetry R applied to \tilde{x} gives the state $x' = (p', J', \Gamma', \psi', \gamma')$, with

$$p' = -\tilde{p} < 0, \quad J' = \tilde{J}, \quad \Gamma' = \tilde{\Gamma}, \quad \psi' = \pi - \tilde{\psi}, \quad \gamma' = -\tilde{\gamma}$$

the overall map $g = R \circ \tilde{g}: x \mapsto x'$ has obviously Jacobian $|p|/|p'|$, and leaves unchanged the integration domain \mathcal{D} . We now proceed as follows: we first rewrite (14) by trivially replacing the dummy integration variable x by x' ; we then make the substitution $x' = g(x)$. The result is

$$\langle \dot{E}_{\text{vib}} \rangle = \frac{v}{mC} \int_{\mathcal{D}} p \rho(g(x)) \omega \Delta J(g(x)) dx$$

where we introduced the short notation $\rho(x) = e^{-\beta_{\text{tr}} E_{\text{tr}}(p) - \beta_{\text{vib}} E_{\text{vib}}(J)}$. Using now the trivial relation $\Delta J(g(x)) = -\Delta J(x)$, and summing with (14), one gets

$$\langle \dot{E}_{\text{vib}} \rangle = \frac{v}{2mC} \int_{\mathcal{D}} p [\rho(x) - \rho(g(x))] \omega \Delta J(x) dx$$

We then use $E_{\text{tr}}(p') = E_{\text{tr}}(p) - \omega \Delta J$ and $E_{\text{vib}}(J') = E_{\text{vib}}(J) + \omega \Delta J$; for small ΔJ we have that

$$\rho(x) - \rho(g(x)) \simeq \omega \rho(x) (\beta_{\text{vib}} - \beta_{\text{tr}}) \Delta J(x)$$

and consequently

$$\begin{aligned} \langle \dot{E}_{\text{vib}} \rangle &= \frac{v}{2mC} (\beta_{\text{vib}} - \beta_{\text{tr}}) \int_{\mathcal{D}} |p| \rho(x) (\omega \Delta J(x))^2 dx \\ &= \frac{1}{2} (\beta_{\text{vib}} - \beta_{\text{tr}}) \langle (\omega \Delta J)^2 \rangle \end{aligned} \quad (15)$$

using (11) and (12), and neglecting $\Delta''J$ compared to $\Delta'J$, the result is

$$\begin{aligned} \langle \dot{E}_{\text{vib}} \rangle &= \frac{v}{2mC} (\beta_{\text{vib}} - \beta_{\text{tr}}) \int_{\mathcal{D}} p e^{-\beta_{\text{tr}} E_{\text{tr}}(p) - \beta_{\text{vib}} E_{\text{vib}}(J)} \\ &\quad \times (\varepsilon \omega \sqrt{\omega J} A(x))^2 e^{-2\tau(p)\omega} \cos^2(\psi^o + \theta) dx \end{aligned}$$

We now introduce the further approximation to retain the x -dependence only where it is really sensitive, that is in $E_{\text{tr}}(p)$ and $E_{\text{vib}}(J)$, as well as in $\tau = \tau(p)$ and in the factor $\sqrt{\omega J}$, and to treat instead as a constant. The integration in J , Γ , γ and ψ is then straightforward, and one finds (also replacing ε by ω^{-1})

$$\langle \dot{E}_{\text{vib}} \rangle = \frac{v^2}{2m} \frac{T_{\text{tr}} - T_{\text{vib}}}{T_{\text{tr}}} \frac{1}{C_p} \int_0^\infty p e^{-\beta_{\text{tr}}(p^2/2m)} e^{-2\tau(p)\omega} dp \quad (16)$$

From this expression, using that, in agreement with assumption (i) of Section 1,

$$\frac{d}{dt} T_{\text{vib}} = \frac{2}{k_B} \langle \dot{E}_{\text{vib}} \rangle, \quad \frac{d}{dt} T_{\text{tr}} = \frac{1}{k_B} \langle \dot{E}_{\text{tr}} \rangle = -\frac{1}{k_B} \langle \dot{E}_{\text{vib}} \rangle$$

one finally gets the differential equation describing the approach to thermal equilibrium, in the form

$$\begin{aligned} \frac{d}{dt} (T_{\text{vib}} - T_{\text{tr}}) &= -(T_{\text{vib}} - T_{\text{tr}}) f(T_{\text{tr}}, \omega) \\ f(T_{\text{tr}}, \omega) &= \frac{v}{k_B T_{\text{tr}}} \frac{A^2}{2m} \frac{1}{C_p} \int_0^\infty p e^{\beta_{\text{tr}}(p^2/2m)} e^{-2\tau(p)\omega} dp \end{aligned}$$

One could work out the same expression using, as in refs. 12 and 13, the law of detailed balance.

Let us stress that the above procedure is quite general, and holds for essentially any choice of the potentials U and V entering the initial Hamiltonian; concerning the unperturbed potential $U(r)$, which plays a very essential role providing, in particular, the crucial quantity $\tau(p)$ entering the exponential law, we only required it is analytic and it describes a scattering, say it diverges for $r - l \rightarrow 0$ and that it vanishes for $r \rightarrow \infty$.

Some remarkable features of the above expression are the following:

- It clearly describes an approach to equilibrium, with $(d/dt)(T_{\text{vib}} - T_{\text{tr}})$ proportional to the difference $T_{\text{tr}} - T_{\text{vib}}$.

• The expression is complete and explicit but for a multiplicative constant, if one is able to determine the coefficient $\tau(p)$. As remarked in the previous section, this is a zero-order quantity depending only on the properties of the unperturbed motion $r_0(t)$, which can be at least roughly estimated.

The characteristic time to reach equilibrium

$$\mathcal{T}(\beta_{\text{tr}}, \omega) \sim \frac{1}{f(T_{\text{tr}}, \omega)}$$

is certainly a rapidly increasing function of ω , as expected by Jeans. However, as noticed in refs. 12 and 13, $\mathcal{T}(\beta_{\text{tr}}, \omega)$ is not a pure exponential⁹ of ω . For instance, if for small r

$$U(r) \sim \frac{1}{r^s}, \quad s \geq 1$$

then a rough estimate based on dimensional considerations, see refs. 12 and 13 for details, gives

$$\tau(p) \sim p^{-(s+2)/s}$$

and correspondingly

$$\mathcal{T} \sim \exp \omega^{2/(3+2/s)} \quad (17)$$

Note how this less than exponential dependence on ω arises through the statistical averaging. The point is that, because of the factor $e^{-\tau(p)\omega}$ in the function to be integrated, the most significant contributions to energy equipartition come from collisions involving molecules with a large relative velocity (large values of p , corresponding to small values of $\tau(p)$). However, because of the Boltzmann distribution, there are very few collisions with large p . As a matter of fact, the compromise between these two scaling laws results in the above functional dependence on ω . Such a mechanism will be illustrated in detail in the next section, where we report the results of further numerical computations, and check, in particular, the exponential law (17).

⁹ By reading refs. 1 and 2 one gets the impression that on this point the intuition of Jeans failed.

4. FURTHER NUMERICAL RESULTS

A direct numerical simulation, like putting n molecules in a box and looking for the energy exchanges in a long time interval, meets (for large ω) with two essential difficulties:

(i) For large ω , only *very few* collisions with sufficiently large $\beta_{\text{tr}} E_{\text{tr}}$, and correspondingly small probability, do contribute to the energy exchange; most collisions, namely those with $\beta_{\text{tr}} E_{\text{tr}}$ of order one, do not produce any appreciable energy exchange, and simulating them is useless.

(ii) In addition, *many* similar collisions with different asymptotic phase ψ^o are necessary, if one wants to separate the average $\langle \Delta E \rangle$ from the much larger fluctuations. In particular, if the energy exchanges follow the Landau–Teller law

$$\Delta E \simeq \mathcal{E}_0 e^{-2\tau(p)\omega} + \mathcal{E}_1 e^{-\tau(p)\omega} \cos(\psi^o + \theta)$$

and ψ^o is random, then the number of collisions one needs to average out the second term (for given $p^o, J^o, \Gamma^o, \gamma^o$) is larger than $e^{\tau\omega}$.

Quite clearly, in such conditions a brute-force calculation, based on the numerical simulation of the dynamics of a gas with a realistic number of particles, is hopeless.

An alternative approach is a Monte-Carlo procedure, in which one simulates numerically a large number of binary collisions, with initial data chosen partially at random and partially in a systematic way. Let us rewrite (14) in the form

$$\langle \dot{E}_{\text{vib}} \rangle = \frac{\nu}{mC_p} \int_0^\infty e^{-\beta_{\text{tr}} E_{\text{tr}}} F(E_{\text{tr}}) dE_{\text{tr}}$$

where

$$F(E_{\text{tr}}) = (2\pi)^{-2} C_{JJ}^{-1} \int_{\mathcal{D}'} e^{-\beta_{\text{vib}} E_{\text{vib}}} \Delta E dJ d\Gamma d\psi d\gamma \quad (19)$$

\mathcal{D}' denoting the domain of J, Γ, ψ, γ . The idea is to compute $\langle \dot{E}_{\text{vib}} \rangle$ by regularly scanning the E_{tr} axis (for fixed $\beta_{\text{tr}}, \beta_{\text{vib}}$ and ω), and to compute $F(E_{\text{tr}})$ by a Monte-Carlo method. Specifically, we adopted the following procedure:

(i) For each E_{tr} , we supply a large number M of random initial data $J^o, \Gamma^o, \psi^o, \gamma^o$, with the appropriate distribution: namely¹⁰ J^o with exponential distribution $e^{-\beta_{\text{vib}} \omega J^o}$, Γ^o flat in $(0, J^o)$, and ψ^o, γ^o flat in $(0, 2\pi)$.

¹⁰ In practice, it is easier to chose I_1 and I_2 both exponentially distributed, and then defining $J = I_1 + I_2, \Gamma = I_2$.

(ii) Further, for each value ψ^o , we simultaneously consider (as in Section 2) K different values of the phase, regularly spaced in the circle, namely

$$\psi^o + \frac{2\pi j}{K}, \quad 0 \leq j < K$$

(iii) For each of these KM initial data we compute ΔE (as in Section 2), and average. As explained in Section 2, $K \geq 3$ is enough to eliminate the fluctuations (due to the harmonics $k=1$ and $k=2$), and correctly extract the average. Concerning M , experience shows that for a good statistics, that is for a reasonable precision, it is sufficient to take $M = 10^3$ or 2×10^3 .

The result, namely $F(E_{\text{tr}})$ as function of E_{tr} (in semi-log scale, with E_{tr} in units β_{tr}^{-1}), is shown in Fig. 3, curve (a). In the same figure, the Boltzmann factor $e^{-\beta_{\text{tr}} E_{\text{tr}}}$ is represented by the line (b). The product $F(E_{\text{tr}}) e^{-\beta_{\text{tr}} E_{\text{tr}}}$ is the curve (c). According to (18), the integral of this last curve gives $\langle \dot{E}_{\text{vib}} \rangle$.

The results exhibited in Fig. 3 refer to $\beta_{\text{tr}} = 4$, $\beta_{\text{vib}} = 0.6$, and a not too large value of ω , namely $\omega = 40$ (the Hamiltonian is the same as in Section 2). Curve (c), if represented in a linear vertical scale, gets the shape of a well defined peak, around the maximum at $\beta_{\text{tr}} E_{\text{tr}} \simeq 14$; this peak is represented in Fig. 4, left curve (left vertical scale). If one increases ω , the peak moves to the right and its value decreases: for example, for $\omega = 160$,

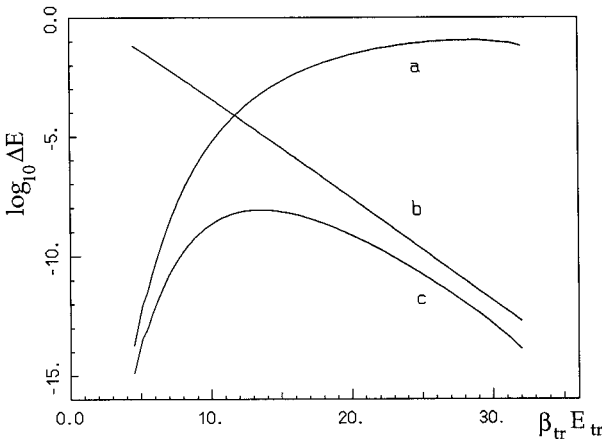


Fig. 3. Illustrating the numerical computation of $\langle \dot{E}_{\text{vib}} \rangle$. Curves (a)–(c) represent respectively $F(E_{\text{tr}})$, the Boltzmann factor $e^{-\beta_{\text{tr}} E_{\text{tr}}}$, and their product (semi-log scale), vs. $\beta_{\text{tr}} E_{\text{tr}}$. Data: $\beta_{\text{tr}} = 4$, $\beta_{\text{vib}} = 0.6$, $\omega = 40$.

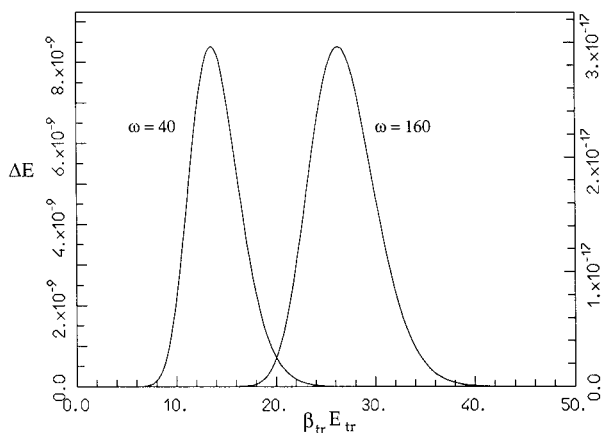


Fig. 4. The curve (c) of the previous Fig. 3, with vertical linear scale. Same temperatures. Left (and left scale): $\omega = 40$; right (and right scale): $\omega = 160$.

the peak is around $\beta_{tr} E_{tr} \simeq 26$, see the right curve of Fig. 4 (right vertical scale). As shown by the scales, the equal height of the peaks is a graphic artifact; their height, and area, are *very* different. It is perhaps worthwhile to remark that, already for $\omega = 40$, practically all contributions to the energy exchanges come from *very few* collisions with large E_{tr} ($e^{-14} < 10^{-6}$). For $\omega = 160$, the situation is even more dramatic ($e^{-26} < 10^{-11}$).

By varying ω at fixed temperatures, one expects to obtain the (stretched) exponential (6), the coefficient a depending on β_{tr} but not on β_{vib} . The result is represented in Fig. 5, where $\langle \dot{E}_{vib} \rangle$ is reported vs. $\omega^{2/5}$ (logarithmic vertical scale), for fixed $\beta_{tr} = 4$ and three different values of

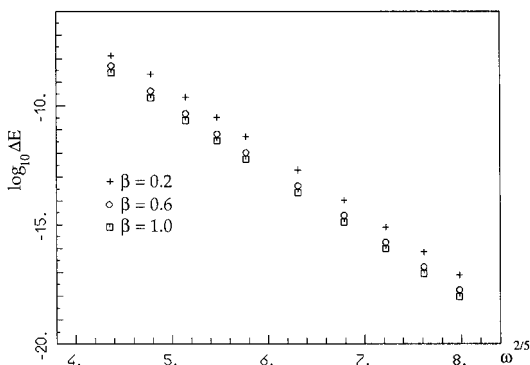


Fig. 5. The stretched exponential law (6), for $\beta_{tr} = 4$, $\beta_{vib} = 0.2, 0.6, 1$ (top to bottom).

β_{vib} . The straight lines are consistent with the exponential law (6). The nearly perfect parallelism indicates that the coefficient a is indeed, as theoretically expected, independent of β_{vib} .

As a final check of the theory, we considered the dependence of the rate of the energy exchange $\langle \dot{E}_{\text{vib}} \rangle$ on the temperature T_{vib} , in order to verify, see (16), the proportionality to $T_{\text{tr}} - T_{\text{vib}}$. As a matter of fact, working numerically at low T_{vib} is painful, since at low E_{vib} one encounters the singularities (with corresponding numerical instabilities) associated with the square roots of the small actions. We found a practical limit for accurate results at $T_{\text{vib}} = 0.5$ (units such that $k_B = 1$). Figure 6 reports $\langle \dot{E}_{\text{vib}} \rangle$ vs. $T_{\text{tr}} - T_{\text{vib}}$, at fixed $T_{\text{vib}} = 0.25$ (i.e., $\beta_{\text{vib}} = 4$, as before), for three different values of ω . Although the curves show a rough proportionality to $T_{\text{tr}} - T_{\text{vib}}$ for small $T_{\text{tr}} - T_{\text{vib}}$, for larger T_{vib} one finds significant deviations from linearity. We did not investigate this lack of linearity (but it is not really surprising that linearity is lost, if one is too far from equilibrium). In our opinion, the most remarkable feature of Fig. 6, and perhaps of this entire paper, is that all curves tend to zero when the temperature difference vanishes. Although physically not surprising, this is not at all trivial. Indeed we assumed separate equilibria for the two subsystems, but then we let the microscopic dynamics evolve, obeying Hamilton's equations: it is a fact that the energy exchanges produced by the microscopic laws of motion,

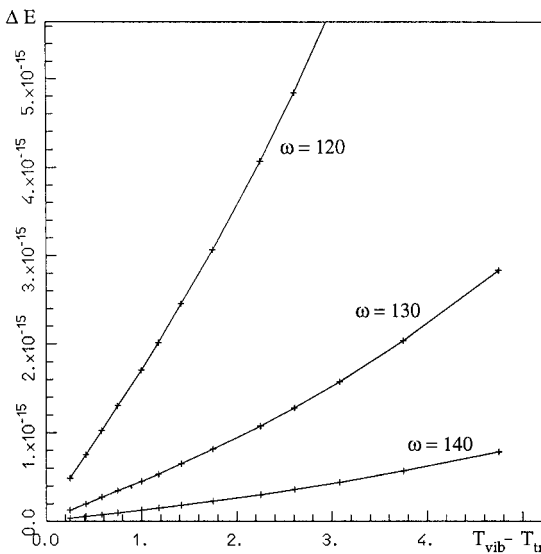


Fig. 6. The dependence of the rate of the energy exchange vs. $T_{\text{vib}} - T_{\text{tr}}$, at fixed T_{tr} , for three different values of ω .

weighted with the *equilibrium* statistics, do produce the correct *non equilibrium* behavior, namely relaxation towards thermal equilibrium. The theoretical mechanism, actually a very robust one, resides in Eq. (15), together with the fact that the average is much smaller than the fluctuations; all other details are irrelevant.

5. THREE-MOLECULE COLLISIONS

As mentioned in Section 1, the theoretical development is based among other things on the assumption that the dominant mechanism in the equilibration is well separated binary collisions between molecules. If the gas is sufficiently dilute, there are statistically more binary collisions than there are close collisions involving three or more particles. The average ratio of two-molecule collisions to three-molecule collisions depends on the density and on the longitudinal velocity distribution, but does not depend on any part of the vibrational dynamics, and in particular it does not depend on ω at all.

One might therefore worry, since we are collecting exponentially small quantities, that the contribution to equilibration from the few, but not exponentially few, three-molecule collisions could amount to the same order of magnitude, or even dominate, the contribution from the binary collisions.

A theoretical estimate of the energy resulting from a three-molecule collision is, even in our simplified model of the 1-D gas, a serious challenge. A numerical investigation is called for to throw some light on the issue.

As Hamiltonian, we took the Hamiltonian (1) with $N=3$. In terms of individual molecule action-angle coordinates (see Eq. (8)),

$$H(p, x, \pi, \xi, \phi) = \frac{p_2^2}{4m} + \frac{p_2^2}{4m} + \frac{p_3^2}{4m} + \omega(I_1 + I_2 + I_3) + V(y_{12}) + V(y_{13}) + (y_{23})$$

where $y_{ij} = x_j - x_i - \omega^{-1/2}(\sqrt{I_j} \sin \phi_j - \sqrt{I_i} \sin \phi_i) - \ell$ and $V(y) = e^{-y^2/y}$.

Choosing initial conditions, one can carefully arrange a close three-molecule collision. Figure 7 shows a typical evolution with time of both the individual vibrational actions, I_i , and the total vibrational action, $I_1 + I_2 + I_3$.

Because of the exact resonance, only the sum of the actions remains a true adiabatic invariant, returning to (exponentially near) its initial value when the molecules separate after the collision. Each individual vibrational action has changed notably from initial value, but they have “conspired” to keep the sum (near) constant. And it is whether the change in this sum is

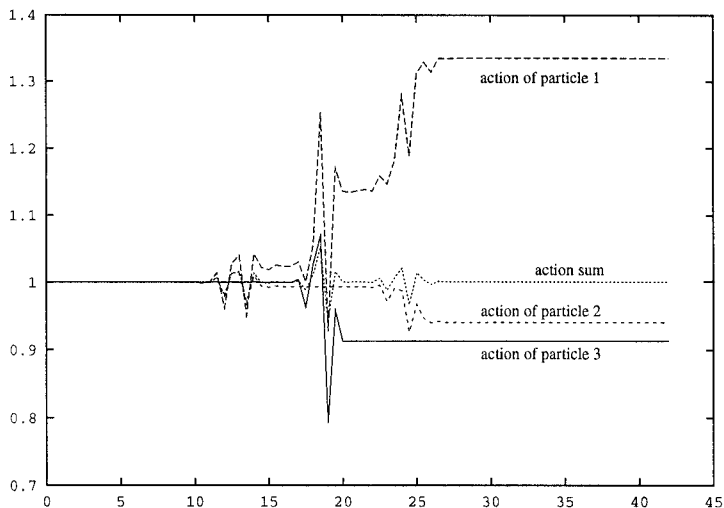


Fig. 7. The time evolution, normalised to pre-collision value, of the individual actions, and of the sum of the actions, for a close three-molecule collision.

of different magnitude when three molecules are involved, rather than two, that we wish to investigate.

We therefore arranged a family of initial conditions, depending on a parameter δ . The parameter δ being zero implies an evolution that has first molecule 1 collide with molecule 2, and then later molecule 2 collide with

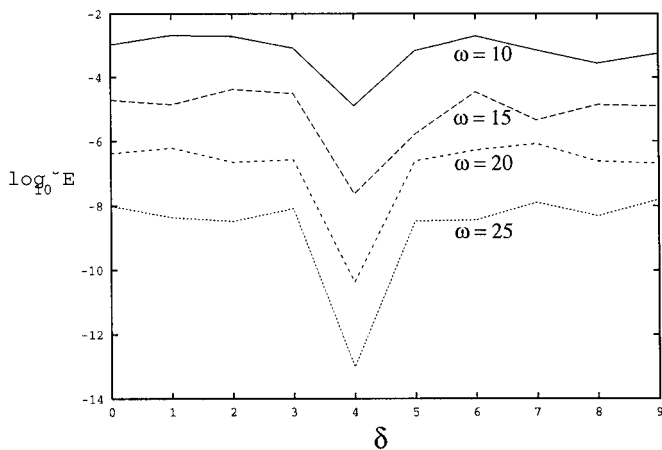


Fig. 8. Energy exchange over a range of initial conditions, resulting in pairs of well-separated binary collisions ($\delta \approx 0$ and 10), and collisions involving all three particles ($\delta \approx 5$).

molecule 3. In the middle range of $\delta \approx 5$, all three molecules are brought to interact simultaneously, and then scatter, as the experiment of Fig. 7.

A typical scan across “degree of three-molecule involvement” is illustrated in Fig. 8, for moderate ω values between 10 and 25.

The phase-averaged energy exchange, as a function of δ is plotted. One can see that, at least for the ω values examined, the close three-body collision ($\delta \approx 5$) results in no dramatic change in the order-of-magnitude for the energy exchange; in fact, a small decrease is observed. Other values of ω and other sets of initial conditions gave the same quantitative picture.

Although not a proof, we find this numerical evidence regarding three-molecule collisions reassuring, and consistent with the (independent) agreement between on one hand the Monte-Carlo simulation of the previous section, and on the other hand the theoretical prediction of Sections 2 and 3.

REFERENCES

1. J. H. Jeans, On the vibrations set up in molecules by collisions, *Phil. Mag.* **6**:279–286 (1903).
2. J. H. Jeans, *The Dynamical Theory of Gases*, 2nd Ed., Chapter XIV (Cambridge University Press, Cambridge, 1916).
3. L. Boltzmann, On certain questions of the theory of gases, *Nature* **51**:413–415 (1895).
4. L. Boltzmann, *Vorlesungen über Gastheorie* (Barth, Leipzig, 1896), Vol. I; (1898), Vol. II [English translation: *Lectures on Gas Theory* (University of Cal. Press, 1966)].
5. L. Landau and E. Teller, Zur Theorie der Schalldispersion, *Physik. Z. Sowjetunion* **10**:34–43 (1936). Engl. translation: On the theory of sound dispersion, in *Collected Papers of L. D. Landau*, D. Ter Haar, ed. (Pergamon Press, Oxford 1965), p. 147.
6. D. Rapp, Complete classical theory of vibrational energy exchange, *J. Chem. Phys.* **32**:735 (1960).
7. G. Benettin, A. Carati, and P. Sempio, On the Landau–Teller approximation for the energy exchanges with fast degrees of freedom, *J. Stat. Phys.* **73**:175 (1993).
8. G. Benettin, A. Carati, and G. Gallavotti, A rigorous implementation of the Jeans–Landau–Teller approximation for adiabatic invariants, *Nonlinearity* **10**:479–505 (1997).
9. G. Benettin, A. Carati, and F. Fassò, On the conservation of adiabatic invariants for a system of coupled rotators, *Physica D* **104**:253–268 (1997).
10. G. Benettin and F. Fassò, From Hamiltonian perturbation theory to symplectic integrators, and back, *Appl. Num. Math.* **29**:73–87 (1999).
11. G. Benettin and A. Giorgilli, On the Hamiltonian interpolation of near to the identity symplectic mappings, with application to symplectic integration algorithms, *J. Stat. Phys.* **73**:1117–1144 (1994).
12. T. M. O’Neil and P. G. Hjorth, *Phys. Fluids* **28**:3241 (1985); M. E. Glinsky, T. M. O’Neil, M. N. Rosenbluth, K. Tsuruta, and S. Ichimaru, *Phys. Fluids B* **4**:1156 (1992).
13. T. M. O’Neil, P. G. Hjorth, B. Beck, J. Fajans, and J. Malmberg, in *Strongly Coupled Plasma Physics* (North-Holland, Amsterdam, 1990), p. 313.