Lévy Flights in the Landau–Teller Model of Molecular Collisions

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We consider the Landau–Teller model, which is a prototype for the exchanges of energy, in molecular collisions, between internal degrees of freedom and those of the center of mass. We show that the statistics of the energy exchanges computed through the dynamics over a finite time is of the Lévy type for high enough frequencies of the internal motions, while it reduces to the familiar gaussian one in the limit of low frequencies. The relevance for the definition of the times of relaxation to equilibrium is also pointed out.

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The Landau-Teller model was introduced in the years thirties [1] (see also [2]) and is still commonly used [3] as the simplest significant model for the dynamics of the energy exchanges between the internal degrees of freedom and those of the centers of mass in molecular collisions. The aim was to estimate the rate of relaxation to equilibrium in polyatomic gases in order to explain the phenomenon of anomalous sound dispersion; however, in our opinion, one is here actually dealing with a problem of a much more general character first raised by Boltzmann [4], namely that of establishing how much does the specific heat depend on the observation time [5].

The model describes the collinear collision of an "external atom" with a diatomic molecule having one of its two atoms fixed; the intramolecular force (between the two atoms of the molecule) is taken linear, while the intermolecular potential (between the external atom and the free atom of the molecule) is chosen to be of exponential type, just for the sake of simplicity in the analytical estimates. Thus one has a system of two points on a line, namely the external atom and the free atom of the molecule; if x and y denote their respective coordinates, the origin coinciding with the fixed atom of the molecule, the Lagrangian is then

$$L(x,y,\dot{x},\dot{y}) = \frac{1}{2}m(\dot{x}^2+\dot{y}^2-\omega^2y^2) - A\exp\big(-\frac{x-y}{a}\big)\ ,$$

where m is the mass of the atoms, ω the angular frequency of the molecule, A the strength and a the range of the potential. In the very words of the authors, the aim was just to "*discover the qualitative behaviour*" of the system. This is spirit of the present work too.

In order to estimate the relaxation time to equilibrium, the dynamical quantity of interest is the exchange of energy δE between atom and molecule in a collision, and the main result of Landau and Teller was that it is exponentially small with the frequency of the molecule. Indeed, at least for a certain set of initial data (vanishing initial energy $E=\frac{1}{2}m(\dot{y}^2+\omega^2y^2)$ of the molecule), they found for the modulus of δE the estimate

$$|\delta E|\,(\omega,v) \simeq C\exp\left(-\omega a/v\right)\ ,$$

where v the is velocity of the atom before collision, while C is a slowly varying function of ω which in a first approximation can be thought of as a constant. Actually such a formula has an asymptotic character for $\omega a/v$ large [6], while for $\omega a/v$ small it just gives a lower bound, and the formula for $|\delta E|$ should be slightly modified.

The relevant point for the aims of the present paper is however the dependence of δE on the velocity v of the impinging atom. Indeed, thinking of the molecule as being in dynamical contact with a heat bath, the model is completed by assuming that the velocity v of the atom before each collision is extracted from a Maxwell–Boltzmann distribution at a certain temperature T. In the literature on sound dispersion the mean value $\overline{\delta E}$ of the energy exchange is computed by averaging over the Maxwell–Boltzmann distribution for the velocities, and the time τ of relaxation to equilibrium is then defined as proportional to the inverse of $\overline{\delta E}$. In such a way, analytical estimates are obtained, which were usually considered to fit rather well the experiments, although serious doubts were also raised. For example, in the words of Rapp and Kassal [3], "*It is impossible to determine whether the choice of the potential parameters is physically significant, because all errors in the theory are compensated by adjustable potential parameters*". Later, a more accurate analysis using arguments similar to those leading to the fluctuation dissipation theorem has shown (see for example the papers [7], which deal with an analogous problem occurring in plasma physics) that the definition of the relaxation time τ should involve not only the mean value of δE, but also its variance; however, the estimates

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for the relaxation times are not essentially changed.

On the other hand, the way in which the mean and the variance of δE are defined appears to be questionable. The problem rests on the distinction between averaging over the velocities through the equilibrium Maxwell–Boltzmann distribution, or through a finite number of extractions from such a distribution (i.e. by taking into account, in the spirit of Boltzmann, the finiteness of the observation time).

The point is that, for fixed values of ω and a, according to the Landau-Teller formula conspicuous energy exchanges can occur only for velocities which are high enough, say for $v > \omega a$, i.e. lie in the tail of the Maxwell–Boltzmann distribution. So, if the temperature is low enough or the frequency high enough, the occurrence of such a high velocity is a rare event, whose actual realization might require an extremely large number of extractions (i.e. an extremely long time), of the order of $\exp(m\omega^2 a^2/2kT)$, where k is the Boltzmann constant. Thus one expects that the statistics of δE obtained from a finite number of extractions of the velocity, inasmuch as it actually contains an intrinsic cut–off of the high velocities, might significantly differ from the equilibrium one, namely that obtained from a formula for δE of the type given above, making use of the whole Maxwell–Boltzmann distribution for the velocity.

So one is led to consider an experiment in which one observes over a certain fixed time an actual "history" of energy exchanges of a given molecule through collisions with a sequence of impinging atoms, whose velocities are extracted from a Maxwell–Boltzmann distribution at a given temperature T. In such a case, if the observation time is not long enough, one should expect that the statistics for the energy exchanges obtained from the dynamics, i.e. from a typical actual history, does not at all agree with the statistics obtained from the formula for δE of the type given above, using the Maxwell–Boltzmann distribution for the velocity. Equivalently, for a fixed temperature and a fixed observation time, the agreement between the two statistics should occur only if the frequency is low enough.

With such a motivation, we numerically computed actual histories (or "sample paths") E_n, $n = 0, 1, 2 \cdots$, where E_n is the energy of the molecule after the n–th collision with an atom, whose asymptotic velocity is extracted from a Maxwell–Boltzmann distribution at a given temperature T; from such data we then computed some relevant statistical distributions. The result we found is that, with a fixed observation time, the statistics induced from the dynamics over a finite time agrees indeed with that induced by the Maxwell–Boltzmann distribution in the case low frequencies, but not at all in the case of large frequencies. Correspondingly, it turned out that for high enough frequencies the statistics for the energy exchanges induced by the dynamics presents a nongaussian character, exhibiting features typical of the so-called Lévy processes. Perhaps, the most characteristic of such features is the presence of the so–called Lévy flights: namely, in the "sample paths" for the energy of the molecule versus the number n of collisions the energy remains practically constant (quiescent) for a long time, while presenting sudden perspicuous jumps from time to time (see the figure at page 294 of the book of Feller [8]). In fact, "intermittent" phenomena of the type just described had already been observed in numerical studies of molecular collisions [9], but the general connection with the frame of the Lévy processes had not been pointed out. Lévy flights were however observed in recent times in several domains of physics [10].

Here are some details concerning the computations. The sample paths were computed up to 10^5 collisions for two different values of the frequency of the molecule, namely $\omega = 3$ and $\omega = 15$, while the temperature T of the atoms and the initial energy E_0 of the molecule were fixed at $kT = 1$ and $E_0 = 1$ ("natural" units having being chosen, with $m = 1$, $a = 1$ and $A = 1$). The "initial" data before each collision and the "final" energy after each collision should in principle be identified with the corresponding asymptotic values for $t \to -\infty$ and $t \to +\infty$ respectively; in practice, with an exponential interaction as in our case, the energy of the molecule (and of the atom) turns out to remain sensibly constant when the atom is far enough from the origin. In our computations we thus fixed a convenient distance l from the origin, actually $l = 32$, and determined numerically the motions, with the atom starting at $x = l$, up to the time it came back to the same position. The initial phase of the molecule and the velocity of the atom were chosen at random before each collision, being extracted, respectively, from a uniform distribution in the interval $(0, 2\pi)$ and from a Maxwell–Boltzmann distribution at temperature T (adapted to the present one–dimensional case as in [9]). The choice of the particular value of the distance l was checked to be irrelevant for l large enough. The equations of motion were integrated through a suitable symplectic numerical scheme [11].

The main results are illustrated through three figures. All of them refer to two sample paths, one for the high frequency case $\omega = 15$ (left), and the other one for the low frequency case $\omega = 3$ (right). The presence of the Lévy flights in the high frequency case is well exhibited by Fig. 1 (left), where we report the sample path for the energy E_n of the molecule after the n–th collision as a function of $n = 0, \ldots, 10^5$. The similarity with the above mentioned illustration of Lévy flights given by Feller is striking. The difference with respect to the analogous sample path for the low value $\omega = 3$ of the frequency (right) is also impressive.

Concerning the statistical properties of the process of energy exchanges, the qualitative difference between the two cases is illustrated in the next two figures. In Fig. 2 we report the densities ρ of the probability distribution functions of the energy E of the molecule induced by the dynamics, i.e. calculated from the sample paths of Fig. 1. In the case of low frequency (right) the statistical distribution agrees very well with the one expected at equi-

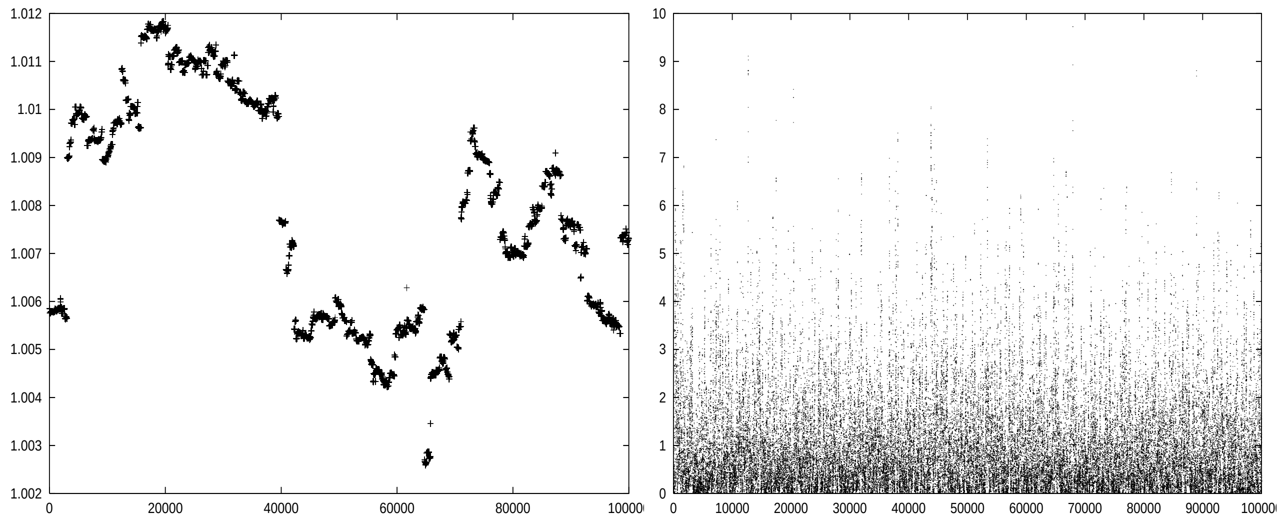

FIG. 1: Sample path of E_n versus n, $\omega = 15$ (left), $\omega = 3$ (right) .

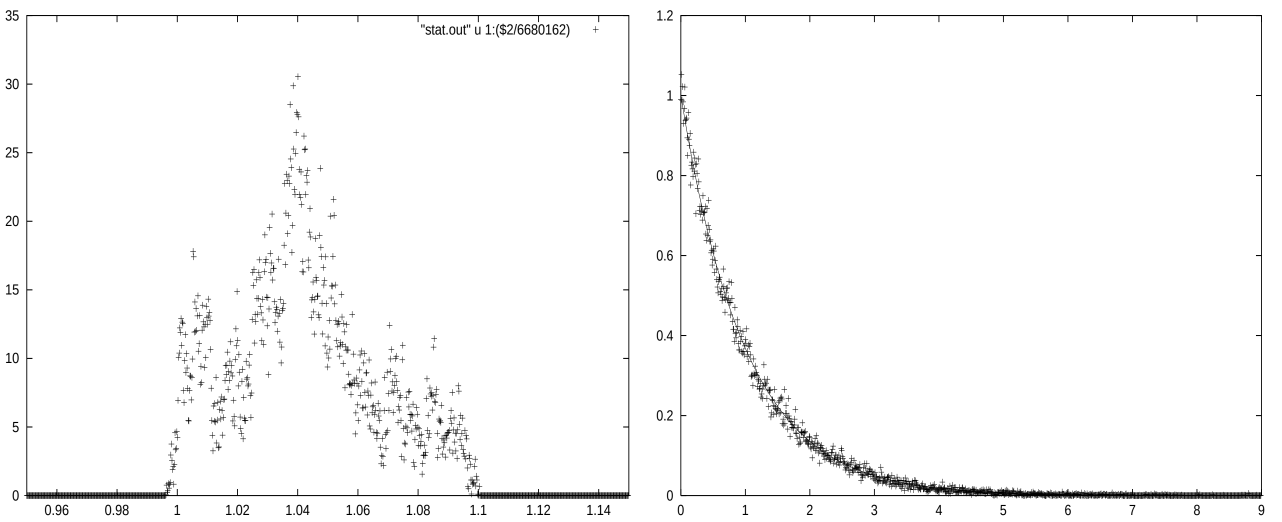

FIG. 2: Density of the p.d.f. of E , $\omega = 15$ (left). $\omega = 3$ (right) .

librium, i.e. obtained through the Maxwell–Boltzmann distribution; the latter is drawn as a continuous line, but is actually almost invisible in the figure, as it superposes to the histogram obtained from the dynamics. Instead, for the high value of ω (left) the distribution is completely different. Recall that the initial value E_0 of the energy was the same in both cases, namely the equipartition value $E_0 = 1$ expected at equilibrium. Notice moreover the difference in the scales in the two figures: if plotted at the same scale of the right histogram, the left one looks as a delta–like function, centered near $E = 1$ and rising up to a value of 30.

Finally, in Fig. 3 we report (in log–log scale) analogous densities of the probability distribution functions, still calculated from the sample paths of Fig. 1, but now for the quantity δE (with $\delta E > 0$), namely for the energy exchanged in each collision; analogous curves could have been drawn for the negative values of δE. Notice that a suitable normalization factor was a used. One sees that in the high frequency case (left) the curve is rather well fitted by the power law (continuous line) $\rho = C\,(\delta E)^{-\alpha}$ with $\alpha = 2.4$ and $C = 0.8 \times 10^{-8}$ (but no special meaning should be attributed to these particular values), while in the low frequency case (right) the curve seems to decay, for δE large, faster than any power. In connection with the result for the high frequency case, we recall that, at least for processes with independent increments, from the general theory it is known (see [8] and [12]) that for a Lévy process the density decays as a power with an exponent $\alpha < 3$.

In conclusion, it has been shown that the main qualitative difference between the statistics defined through

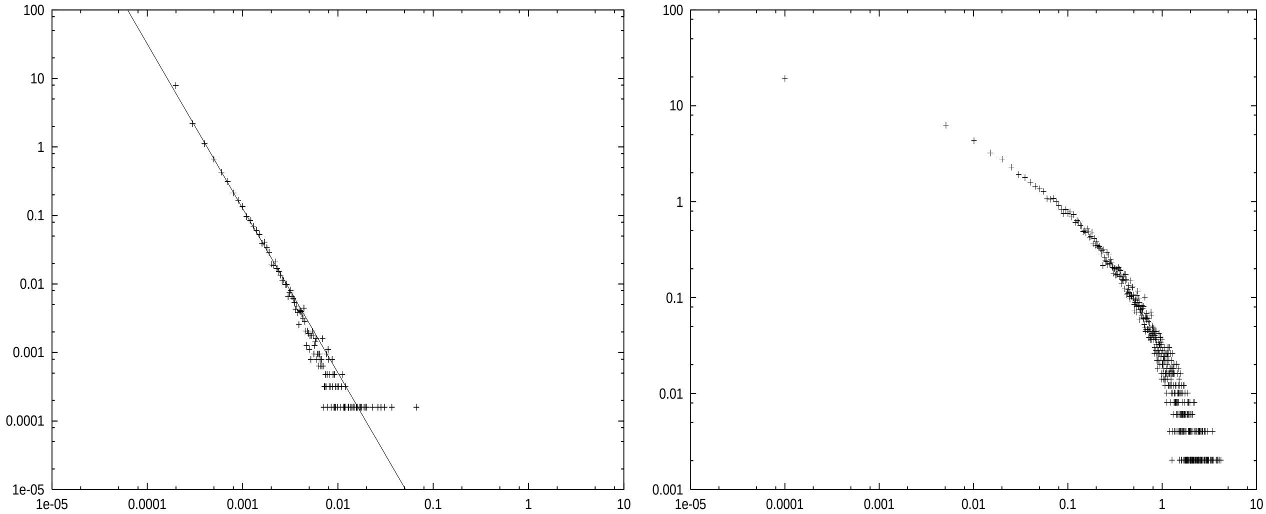

FIG. 3: Density of the p.d.f. of $\delta E > 0$ in log–log scale, $\omega = 15$ (left), $\omega = 3$ (right).

the equilibrium distribution and the one defined through the dynamics up to a finite time, in the case of high frequencies, is that the second moment of δE is finite in the former case and diverging in the latter one. This fact has a nontrivial physical impact in connection with the estimates for the times of relaxation to equilibrium of the internal degrees of freedom in polyatomic molecules. Indeed, the relaxation times are usually defined through formulas involving the mean and the variance of δE, while, as shown in the present work, for high enough frequencies the variance is divergent, if the statistics is defined through the dynamics up to finite times. In fact, the nongaussian statistics that is met in such a case seems to indicate the presence of an anomalous diffusion, for which the relaxation times should be defined through more complicated procedures [12]. Thus the present work appears to have shown that the problem of the theoretical quantitative estimates for the relaxation times to equilibrium in polyatomic molecule, which was considered to be settled since a long time, in instead reopened. We hope to come back to this problem in the future, even in connection with more realistic models of molecular collisions and more realistic values of the parameters.

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