THE DYNAMICAL FOUNDATIONS OF CLASSICAL STATISTICAL MECHANICS AND THE BOLTZMANN–JEANS CONJECTURE

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1. Overview

It is well known that the equipartition principle lies at the very basis of classical statistical mechanics. It is also known that the greatest difficulty with classical statistical mechanics is that some degrees of freedom seem to be frozen, and not to attain the energy expected from that principle. The problem we want to discuss here is whether such a phenomenon can be understood on a dynamical basis.

Usually, the difficulties related to the nonlinear character of the corresponding dynamical problem are just bypassed by making use of the so called ergodic *hypothesis*: essentially, one *assumes* that a typical dynamical system of the kind considered in statistical mechanics evolves towards some sort of equilibrium, well described by the canonical ensemble (see, for instance, the long and detailed discussion in the book of Khinchin[1]). The fact that other dynamical systems, like, e.g., the planetary one, do not present a statistical behaviour is tacitly attributed to the big difference either in the typical time scales or in the number of degrees of freedom between them and, say, a gas.

An old conjecture, going back to Boltzmann[2] and Jeans[3], is that in many cases of interest the equilibrium state, if any, is not reached in a reasonably short time; instead, each degree of freedom should have a characteristic relaxation time greatly increasing with the frequency. Boltzmann considered the model example of a gas of molecules with translational and rotational degrees of freedom. His remark was essentially that, if the molecules were perfectly symmetric, then there would be no energy exchange among the translational and the rotational degrees of freedom, so that the rotational energy would be constant; on the other hand, by the introduction of a small asymmetry one would expect to observe a relaxation to equilibrium after a characteristic relaxation time. In fact he spoke, even if without any definite justification, of relaxation times of the order of "days or years", so that the equilibrium would not occur in many ordinary experiments, and the rotational degrees of freedom would just

appear as "frozen". Jeans studied the similar problem of the exchange of energy between translations and internal vibrations during the collisions of molecules. His idea, supported by heuristic considerations, was that there should be general mechanism according to which the energy exchange ΔE per collision could be estimated as

$$\Delta E \sim E_0 e^{-\tau\omega} \ , \tag{1}$$

where E_0 is a natural energy unit for the system, τ is a typical collision time, and ω is the internal frequency of the molecule; it is assumed that $\tau\omega$ is large. Thus, in order to observe a significant exchange of energy (e.g., of the order of E_0) one would need a number $N \sim e^{\tau\omega}$ of collisions, and so a time $T \sim T_0 e^{\tau\omega}$, where T_0 is the average time between two collisions. He also remarked that, in realistic situations, such a time could be as large as "hundreds of centuries", or even "billions of years". For a detailed discussion including quotations of the original works, see ref. [4].

The point of view of Boltzmann and Jeans was in fact soon forgotten by the scientific community (essentially, after the 1911 Solvay conference): the interest of physicists was captured by the impressive and successful development of quantum mechanics. But more than 40 years later two works caused a renewal of interest around nonlinear problems connected with statistical mechanics. We refer here, on the one hand, to the numerical work of Fermi, Pasta and Ulam on their celebrated model of nonlinear chain[5], and, on the other hand, to the not less celebrated Kolmogorov's theorem on the persistence of conditionally periodic motions under perturbations of nonlinear integrable Hamiltonian systems[6]. Let us briefly recall these results.

The initial purpose of the research of Fermi, Pasta and Ulam was, as claimed by the authors, to observe the rate of thermalization of the system. But they write: "Let us say that the the results of our numerical computations show features which were, from the beginning, surprising to us. Instead of a gradual, continuous flow of energy from the first mode to the higher modes, all of the problems show an entirely different behaviour. (...) Instead of a gradual increase of all the higher modes, the energy is exchanged, essentially, among only a certain few." The relevance of the FPU work for the foundations of Statistical Mechanics was pointed out by Izrailev an Chirikov and their coworkers[7]. In general, it seems that all such authors were suggesting that the dynamics should be consistent with equipartition in the thermodynamic limit, i.e., the limit $n \to \infty$ with finite specific energy E/n. A first clear indication of a result going in the opposite direction was given by Bocchieri, Scotti, Bearzi and Loinger[8], who studied a chain of the FPU type, just replacing the cubic or quartic nonlinearity of the original model with the more realistic Lennard–Jones potential. They observed the existence of a kind of energy "threshold" above which a statistical behaviour (in the classical sense) sets up, the threshold in specific energy E/n being largely independent of n (in the range $10 < n < 100$). It is interesting here to remark that the existence of a threshold was also discovered (before Bocchieri et al.) by Hénon and Heiles[9] in a very simple model with two degrees of freedom, thus contradicting the idea that the statistical behaviour should be due just to the large number of degrees of freedom. Subsequent studies, most of them performed in Italy, confirmed these pioneering results, also adding a number of new informations of phenomenological

character[10]. But an analytical understanding of the problem was still completely lacking; the only exceptions were some rather awkward estimates provided by Izrailev and Chirikov, where reference was made for the first time to the mathematical works related to what is now called KAM theory.

The theorem of Kolmogorov, and the related theorems of Moser and Arnold, deal with small perturbations of integrable systems, like, e.g., the planetary system. As is known, they are concerned with an analytic Hamiltonian of the type

$$H(p,q) = H_0(p) + \varepsilon H_1(p,q,\varepsilon) \ , \tag{2}$$

where $p \in \mathbf{R}^n$ are the action variables, $q \in \mathbf{T}^n$ are angle variables and ε is a small parameter controlling the size of the perturbation due to H_1; this problem was referred to by Poincaré as "the fundamental problem of dynamics". For $\varepsilon = 0$ the phase space is foliated into invariant tori $p = \text{const}$, carrying either periodic or quasi periodic motions. The KAM theory states, in rough terms, that for ε small enough most (in the sense of the Lebesgue measure) of the invariant tori are not destroyed by the perturbation. The possible interest of such a result for statistical mechanics is due to the fact that the ergodic hypothesis is incompatible with the existence of a set of invariant tori of positive measure. However, there is a common objection, that we summarize in a few sentences. "The KAM theorem applies *if ε is small enough*. Although nothing is stated for large values of ε, this can be interpreted as a claim that if the perturbation is larger than some critical value, ε_* say, then the arguments of classical statistical mechanics should be applied (by the way, this agrees with the existence of a threshold, as observed by Hénon and by Bocchieri et al). But, according to the available analytical estimates, ε_* is a rapidly decreasing function of the number n of degrees of freedom. Thus, the KAM theorem is meaningless in the thermodynamic limit." Although some recent works have established the existence of invariant tori (but nothing is said about their measure) in infinite systems, the question should be considered, in the best case, as still open.

Even if we disregard the latter question, the KAM theory, despite its invaluable mathematical beauty and interest, seems not to be suited for application to physical systems. Indeed, the invariant tori form a nowhere dense set in the phase space. Moreover, their complement is connected for systems with more than two degrees of freedom. Thus, an orbit could in principle go anywhere in the complement of the invariant tori. This possible phenomenon has been named "Arnold diffusion" because Arnold illustrated it in a simple, although non "generic", example[11] (a proof of the existence of diffusion in typical Hamiltonian systems has been recently found by Chierchia and Gallavotti[12]). This state of affairs could be hardly compatible, e.g., with an approximate knowledge of the initial conditions. In this respect the less famous Nekhoroshev's theorem is more relevant, in our opinion[13]. In its original formulation the theorem can be stated, roughly, as follows: for the Hamiltonian system (2) the actions p satisfy

$$|p(t) - p(0)| < C\varepsilon^b \quad \text{for} \quad |t| < T_0 \exp\left(\frac{\varepsilon_*}{\varepsilon}\right)^a \ , \tag{3}$$

provided ε is small enough (say, less than ε_*) and the unperturbed Hamiltonian H_0

satisfies some steepness (or convexity) conditions. Here, C, T_0, b, a and ε_* are constants depending on the number n of degrees of freedom. The interesting point is the exponential dependence of the time on the perturbation parameter ε: in realistic situations, such a time could be as large as the estimated age of the universe (see also refs. [14]).

The similarity between Nekhoroshev's result and the conjecture of Boltzmann and Jeans is evident. However, making explicit the connection is not easy at all. The main difficulty is that in the formulation of the theorem there are constants which, according to the original estimates, vanish when the number n of degrees of freedom increases to infinity. Typical estimates are $a \sim 1/n$, and that ε_* and T_0 decrease as fast as some power of $1/n$. Thus, the theorem seems not to be applicable to the large systems of interest for statistical mechanics, its relevance being limited to systems with only few degrees of freedom (e.g., the planetary system).

Despite this difficulty, we maintain that the Nekhoroshev theory can be used to give the conjectures of Boltzmann and Jeans a strong support. In this spirit we started a long investigation, both from a numerical and an analytical viewpoint. Our aim here is to give a short but comprehensive report on the state of our research. For a discussion of the possible relevance for the foundations of quantum mechanics see [15]. The results we are presenting here are the fruit of a long collaboration among the authors, and more recently with younger coworkers, namely Dario Bambusi, Andrea Carati, Alessandra Celletti, Francesco Fassò, Alessandro Morbidelli, Andrea Martinoli, Paolo Sempio and Stefano Vanzini.

2. Models, and numerical results

We consider here two classes of models: molecular collisions, and FPU type models. The underlying idea in all these investigations is just the conjecture of Boltzmann and Jeans: we bring into evidence the fundamental role played by the frequencies of the system, and the existence of exponential laws of Nekhoroshev type.

2.1 One–dimensional model of a diatomic gas

We consider n identical molecules moving on a segment of length L with fixed end points; each molecule consists of two atoms connected by a linear spring; one of the atoms is neutral, the other one has a charge; the charged atoms interact through a smooth, short range potential, like

$$V(r) = V_0 \frac{\sigma}{r} \exp\left[-\left(\frac{r}{\sigma}\right)^2 \right] , \tag{4}$$

where r is the distance and V_0 and σ are constants. This model was proposed and studied in ref. [16]. Denoting by x_j the coordinate of the center of mass of a molecule, by ξ_j the length of the molecule, by p_j and π_j the corresponding momenta, by $m/2$ the mass of an atom and by ω the internal frequency of the molecule, the Hamiltonian

of the system can be written as

$$H = h_\omega(\pi, \xi) + \sum_{j=1}^{n} \frac{p_j^2}{m} + \sum_{j=0}^{n} V\big((x_{j+1} + \xi_{j+1}) - (x_j + \xi_j)\big) \ . \tag{5}$$

where

$$h_\omega(\pi, \xi) = \frac{1}{2} \sum_{j=1}^{n} \left(\frac{\pi_j^2}{m} + m\omega^2 \xi_j^2 \right) \ . \tag{6}$$

Our idea was to consider the system h_ω, describing the internal vibrations, as essentially decoupled from the translations. Indeed, the coupling term coming from V can be proven to decrease as $1/\omega$. We computed the auto–correlation function $\varrho(\tau)$, for $\tau \geq 0$ of the total vibrational energy h_ω. In case of a statistical behaviour, $\varrho(\tau)$ is expected to decay from the value 1 at $\tau = 0$ to zero. However, since we are interested in observing the relaxation time to equilibrium, we consider as a good indication the time τ_c at which $\varrho(\tau)$ attains the value $1/2$. The numerical experiment was performed for different values of the internal frequency ω and for $n = 16$ and $n = 64$. In both cases we found that τ_c as a function of ω is consistent with the law

$$\tau_c(\omega) = A e^{\alpha\omega} \ , \tag{7}$$

with suitable constants A and α. A comparison with the Nekhoroshev exponential law (3) shows immediately that the exponent a should have here the value 1, and not $1/n$ as in the best theoretical estimates. We shall come back to this point in discussing the analytical results.

Recently the same system was considered also by Erpenbeck and Cohen[17], with the aim of proving that the relaxation time is actually short, so that the conclusions of statistical mechanics do apply. They replaced the analytical potential (4) by a hard core interaction, and found relaxation to equilibrium in short times. In our opinion, this should be expected a priori. Indeed, the typical interaction time of the hard core potential is zero; on the other hand, as will be discussed below, the exponential bound has to be expected only for frequencies higher than the inverse of the typical interaction time.

2.2 Molecular collisions

A second set of numerical experiments is more strictly connected with the verification of the Jeans law (1). This can be heuristically justified as follows. The exchange of energy in a gas between the translational degrees of freedom and the rotational or the vibrational ones is due to the collisions between molecules. Now, one has to expect that the most efficient mechanism is the two body collision, while the contribution due to collisions of more than two molecules should be irrelevant. Thus, in order to show that the relaxation time to equilibrium for a gas can exceed any physically realistic time scale, it should be sufficient to prove that the exchange of energy in a single collision is actually exponentially small with the frequency.

The model studied is either a purely rotating or a purely vibrating molecule which collides with a wall. The system is described by the Hamiltonian

$$H(\pi, \varphi, p, x) = \frac{\pi^2}{2I} + \frac{p^2}{2m} + V(\varphi, x) \ , \tag{8}$$

in the case of the rotating molecule, and by

$$H(\pi, \xi, p, x) = \frac{1}{2}(\pi^2 + \omega^2 \xi^2) + \frac{p^2}{2m} + V(\xi, x) \ , \tag{9}$$

for the vibrating molecule. Here, p, x are canonical variables associated with the translation, π, φ and π, ξ are associated with the rotation and the vibration respectively, and V is the potential describing the interaction with the wall. The potentials used have the form

$$V(r) = U \frac{e^{-(r/d)^2}}{r/d}$$

with $r = x + a\cos\varphi$ and $r = \xi - x$ in the rotational and in the vibrational cases respectively; U, d and a are constants. These models have been proposed and studied in refs. [18] and [19].

Denoting by v and ω the initial velocity and angular velocity respectively of the molecule, and by Φ the initial value of the phase φ (either of the rotator or of the oscillator representing the internal vibration), one computes the energy exchange ΔE between the translational and the rotational energy after one collision. Clearly, ΔE depends on v, ω and Φ. The results can be summarized as follows.

i. For not too small ω the dependence of ΔE on Φ follows quite closely a sinusoidal law like

$$\Delta E = E_0(v, \omega) + E_1(v, \omega)\sin(\Phi - \Phi_0) \ .$$

ii. Both the average E_0 and the coefficient E_1 of the zero–average term follow an exponential law of Jeans type, precisely

$$E_0 = \mathcal{E}_0 e^{-\tau_0 \omega} \ , \quad E_1 = \mathcal{E}_1 e^{-\tau_1 \omega} \ , \quad \tau_0 = 2\tau_1 \ ;$$

moreover, the ratio $\mathcal{E}_0/\mathcal{E}_1$ is independent of v.

iii. Finally, τ_0 and τ_1 are decreasing functions of v, apparently faster than v^{-1}.

2.3 Systems of FPU type

As is well known, the FPU system is a chain of $n + 2$ identical mass point on a line connected by identical nonlinear springs; the ends of the chain are fixed, so that the system has n degrees of freedom. The system considered here is a modification of the FPU original system, in the sense that the chain is composed by an even number of alternating light and heavy masses. The Hamiltonian of the system can be written as

$$H(x, y) = \frac{1}{2}\sum_{j=0}^{n}\left[\frac{y_j^2}{m_j} + (x_{j+1} - x_j)^2\right] + \frac{\alpha}{3}\sum_{j=0}^{n}(x_{j+1} - x_j)^3 + \frac{\beta}{4}\sum_{j=0}^{n}(x_{j+1} - x_j)^4 \ , \tag{10}$$

where $m_j = 1$ for j odd and $m_j = m < 1$ for j even; for $m = 1$ one recovers the original FPU model. Here, x, y are canonically conjugate coordinates, and α, β are constants.

The interesting feature of this model is the frequency spectrum, which is given by

$$(\omega_l^{\pm})^2 = \frac{1 + m \pm \sqrt{1 + m^2 + 2m\cos 2k_l}}{m} \ , \quad k_l = \frac{l\pi}{n+1} \ , \quad 1 \le l \le \frac{n}{2} \ . \tag{11}$$

Here, the signs $\pm$ refer to the two possible choices of the sign in computing the square root. For $m \ll 1$ the spectrum splits into two well separated components: the set of frequencies ω^- constitute the so called acoustic modes, while the frequencies ω^+ characterize the so called optical modes. Thus, the system can be considered as composed of two well defined subsystems, namely the acoustic and the optical ones, with a small coupling between them; moreover, the frequencies of the optical modes are very close to each other, so that they can be considered essentially as equal. The results reported here were published in ref. [20].

The results for the FPU model ($m = 1$) can be summarized in a few words: the harmonic actions of the system behave as predicted by the Nekhoroshev estimate (3), but it seems quite evident that the freezing disappears with increasing n. Indeed, a fitting of the experimental data for values of n ranging from 6 to 120 shows that the constants T_0 and ε^* go to zero roughly as $1/n^2$, and a goes to zero roughly as $1/n$. These results agree with the best analytical estimates available.

Things are very different for the FPU model with alternating masses, namely with $m \ll 1$. The relevant parameter here is $\lambda = \omega/\omega^-_{\max}$, where ω is the average frequency of the optical modes, and $\omega^-_{\max}$ is the maximal frequency of the acoustic modes. The quantity of interest is the harmonic energy of the optical subsystem, that we shall denote by E^+, or, more precisely, the maximal absolute value of its time derivative $|\dot{E}^+|$. All the experiments refer to initial data with the whole energy initially concentrated on the subsystem of the acoustic modes, with *specific* energy E/n constant as n is varied. The value of n ranged form 6 to 200, and the value of λ from 10 to 400. The results can be summarized as follows.

i. The two subsystems go rapidly to separate equilibria.

ii. Only a very small amount of the energy flows toward the subsystem of the optical modes, according to the Nekhoroshev type law

$$\lambda |\dot{E}^+| < A e^{-B\lambda} \ , \tag{12}$$

with A and B constants.

iii. The constant B is apparently independent of n, while the behaviour of A is not well established; however, A appears to grow less than $\log n$.

3. Analytical results

As explained in section 1, the greatest problem in dealing with the analytical apparatus of perturbation theory, and in particular with Nekhoroshev like results, is the dependence of the estimates on the number n of degrees of freedom.

Looking at the exponential law (3), it is immediately seen that the most dangerous constant is the exponent a. Now, some recent analytical works[21] show that the behaviour $a \sim 1/n$ is essentially optimal, as is also indicated by the numerical experiment on the FPU model discussed in sect. 2.3. At first sight, this seem to confirm the idea that the exponential relaxation time of the Nekhoroshev theorem is not relevant for statistical mechanics. However, in our opinion, this means only that in the ordinary formulation of Nekhoroshev's theorem one is still referring to a too strong property: the separate conservation of *all* the actions. On the other hand, the numerical experiment illustrated in sect. 2.1 suggest the possibility that there are only a few conserved quantities. This is the basis of the analytical approach that we now illustrate.

The general idea is to consider a system with an Hamiltonian of the form

$$H(\pi, \xi, p, x) = h_\omega(\pi, \xi) + \hat{h}(p, x) + f(\xi, x) \ , \tag{13}$$

where

$$h_\omega(\pi, \xi) = \frac{1}{2} \sum_{j=1}^{\nu} \left(\pi_j^2 + \omega_j^2 \xi_j^2\right) \ . \tag{14}$$

Here, $h_\omega(\pi, \xi)$ describes a system of harmonic oscillators with an n-vector of frequencies $\omega = (\omega_1, \ldots, \omega_n)$; $\hat{h}(p, x)$ is the Hamiltonian of a generic system with n degrees of freedom, and $f(\pi, \xi, p, x)$ is a coupling term, which is assumed to vanish for $\xi = 0$. Remark that the hamiltonian $\hat{h}(p, x)$ is not assumed to be integrable; one just needs some hypothesis meaning essentially that the typical frequencies characterizing that system are small with respect to the frequencies ω. Thus, one can say that the system actually considered is composed of two subsystems characterized be well separated proper frequencies. The interesting fact is that all the models illustrated in sect. 2, with the only exception of the original FPU model (i.e., with $m = 1$) can be given this form. This system was investigated analytically, in the light of Nekhoroshev theorem, in refs. [22], which refer to the simper case $\nu = 1$ and in ref. [23] for arbitrary ν.

Under quite general hypotheses one proves the following: if there are s independent resonance relations between the frequencies (i.e., there are s independent vectors $k \in \mathbf{Z}^\nu$ such that $k \cdot \omega = 0$), then one can find $\nu - s$ quantities the time derivatives of which are exponentially small with the frequencies ω. More precisely, denoting by Φ any of these quantities, and introducing a parameter λ by $\omega = \lambda\Omega$ in such a way that Ω is of the same size as the proper frequencies of $\hat{h}(p, x)$, one has the estimate

$$|\dot{\Phi}| < A \exp\left[-\left(\frac{\lambda}{\lambda_*}\right)^{1/(\nu - s)}\right] \tag{15}$$

with suitable constants A and λ_*. This formula can be used to conclude that $\Delta\Phi = |\Phi(t) - \Phi(0)|$ is either exponentially small for a short time, or of the order, say, $1/\lambda$ for an exponentially large time.

Comparing (15) with the exponential law (3) one immediately sees that the constant a appearing there is $1/(\nu - s)$. This fact is particularly interesting when h_ω is a completely resonant system, which means $s = \nu - 1$, and so $a = 1$. This is exactly the

case for the one–dimensional model of gas illustrated in sect. 2.1, and also for the FPU model with alternating masses of sect. 2.3 (in the latter case the optical frequencies are not exactly equal, but the small difference can be considered as a perturbation). This removes the worst dependence on n in the exponential, and gives full theoretical support to the numerical result $a = 1$. Remark however that in this case there is *only one* conserved quantity, which is nothing but the harmonic energy h_ω. Thus, the system of oscillators behaves essentially as if it were isolated from $\hat{h}$, but nothing can be said about its internal dynamics, which could be expected to be chaotic, as was observed in the case of the optical frequencies in the modified FPU model.

A very recent analytical result for infinite systems was published in ref. [24]. The theorem is quite general, but let us discuss only its relations with the modified FPU model. In this case one proves that if the *total* energy of the system is small enough, then the harmonic energy satisfies the estimate (15), with *all* the constants independent of n This gives an almost complete support to the numerical results of sect. 2.3. The support is not complete, because the numerical experiment refers to the case of fixed *specific* energy, which is the interesting one for statistical mechanics. However, we think that such a result cannot be improved on a purely dynamical basis. The reason, roughly speaking, is the following: one can not exclude by dynamical considerations that the whole energy of the optical system gets concentrated for a long time on a single optical mode, while in working out the analytical estimates one has to take into account also such an unlikely situation. A full result useful for statistical mechanics could perhaps be obtained by adding statistical considerations on the initial data (see also [25]).

4. Conclusions

Let us now summarize the whole discussion about the problem of the dynamical foundations of Classical Statistical Mechanics. Usually one mentions the problem of proving ergodicity, or rather mixing, in order to justify the use of the traditional equilibrium ensembles. Now, the definition of ergodicity or mixing makes reference to infinite times. In the present paper we have made reference to a somehow complementary problem, namely that of the time necessary for each subsystem to reach equilibrium. Indeed, as first suggested by Boltzmann and Jeans and then supported by modern mathematical theorems it can occur that the relaxation times might be exponentially large with some parameter, typically a characteristic frequency, of a subsystem. Thus, the ergodicity or mixing of the whole system might be compatible with a freezing of a subsystem (i.e., essentially a nonequilibrium situation) over time scales which from a physical point of view are incommensurable (a considerable slice of eternity, in the words of Littlewood).

The problem of giving a rigorous proof of the existence of nonequilibrium situations of such a type for systems of interest for Statistical Mechanics should be considered, as we have tried to show here, still undecided. However, things seem to have changed a lot with respect to twenty years ago, when in the scientific commu-

nity it was considered as almost obvious that the freezing phenomena discussed above should not occur in Classical Statistical Mechanics; it seems to us that the opposite conjecture, supported especially by the Italian school, is today in rather good shape.

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