The Fermi–Pasta–Ulam Problem and the Question of the Rates of Thermalization

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Abstract. – *A critical and historical review is given of the problem of the distribution of energy in a system of weakly coupled harmonic oscillators at equilibrium, when the relevance of the rate of thermalization is taken into account. It is well known that the final equilibrium distribution should be equipartition according to classical mechanics, and Planck's law according to quantum mechanics. It is illustrated how the modern theory of dynamical systems, after Fermi Pasta and Ulam, has revived an idea pursued by Jeans who, following Boltzmann, was trying to explain the observed lack of equipartition as due a lack of thermalization. The idea is that according to classical mechanics the final approach to equipartition would take an extremely long time, as is familiar today for glassy systems, while on a much shorter time–scale one would have a metaequilibrium situation, described by a Planck–like distribution.*

1. – Introduction

The problem of the rate of thermalization consists in determining how long it takes for a system to reach thermal equilibrium. Thus enunciated, the problem appears to have no special relevance, because it is clear that every system will have some characteristic relaxation time, which should be estimated and suitably taken into account. The situation is however more delicate when relaxation times are met which are enormously large, as for example in the case of glasses. Indeed, these are fluids with the special property that the viscosity increases by even 18 orders of magnitude when the absolute temperature is reduced by only a factor of two, for example from 600 K to 300 K; thus the relaxation time to equilibrium can be extraordinarily large, and one meets with situations of a kind of metaequilibrium or metastability, for which a description by the ordinary methods of equilibrium statistical mechanics is not feasible.

The main motivation of the present paper consists in illustrating how such a situation of metaequilibrium is not confined to "strange" systems such as glasses, but is met in all common situations involving harmonic oscillators, when they present deviations from a classical behaviour by manifesting a quantum behaviour. Thus, the property of presenting enormously long relaxation times to equilibrium somehow seems to correspond to the manifestation of a quantum behaviour, and as such deserves to be investigated as a property of a general relevant interest.

It will be recalled below how the problem of the thermalization rate was actually introduced by Boltzmann just within such a foundational perspective, then pursued by Jeans and Rayleygh, and finally abandoned with a public retractation by Jeans, struck as he had been by a fundamental paper of Poincaré on the necessity of quantization. It will then be recalled how the problem of the thermalization rate reemerged, but only within a sectorial perspective, in the problem of the sound dispersion in gases, and how finally the problem was reconsidered in the original foundational spirit of Boltzmann, after the work of Fermi Pasta Ulam (1954) and the impact of the modern theory of dynamical systems. Finally, some perspectives will be given concerning the relations between classical and quantum mechanics in connection with the problem of the rates of relaxation.

2. – The first phase: from Boltzmann to the retractation of Jeans

Boltzmann was confronted with an essential qualiltative difficulty of classical statistical mechanics in connection with the equipartition principle. Indeed, according to classical statistical mechanics, equilibrium should be governed by the Maxwell–Boltzmann probability distribution, the main prediction of which is the equipartition of energy: every degree of freedom contributes to energy (in the harmonic approximation) with a term $1/2\ kT$ (or kT in the case of harmonic oscillators), where k is the Boltzmann constant and T the absolute temperature. So, at equilibrium the total energy of a system should be proportional to temperature, and thus the specific heat be constant, independent of temperature (and of frequency, for systems of harmonic oscillators). Instead, it was found experimentally that the specific heat of polyatomic molecules (whose internal motions could be assimilated to harmonic oscillators or rotators) was decreasing with decreasing temperature. An analogous qualitative discrepancy was also found to occur in the black–body spectrum, because the black–body can be assimilated to a system of harmonic oscillators with frequencies ranging from 0 to ∞, and the energy of the high frequency oscillators appeared to go to zero exponentially fast as frequency increases.

This is known to everybody, because it is exactly in this connection that quantum mechanics originated, on october 19, 1900, when Planck found empirically, by means of a skillfull interpolation, that the mean energy $U(\omega, T)$ of a system of N harmonic oscillator of angular frequency ω at absolute temperature T is well fitted by Planck's law

$$U(\omega, T) = N\,\frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = NkT\,\frac{x}{e^{x}-1} \qquad (x=\beta\hbar\omega,\ \beta = 1/kT)\,,$$

where $\hbar$ is the (rationalized) Planck's constant. The correspondence principle is saved because, from the second expression above, Planck's formula is seen to reduce to the "classical" formula kT for $x \ll 1$, i.e. for high temperatures or low frequencies, while decreasing exponentially fast to zero for $x \gg 1$, i.e. for low temperatures or high frequencies. Two months later Planck introduced quantization, i.e. understood that his law could be obtained by the "simple" prescription that the energy of an oscillator be quantized, in the sense that only discrete values of energy, actually $E_n = n\hbar\omega$, $n = 1, 2, \cdots$, should be allowed (later on, in his "second theory" of the year 1912, he added the controversial "zero–point energy" $1/2\ \hbar\omega$, which gives the "energy levels" $E_n = (n + 1/2)\,\hbar\omega$). Planck was originally concerned with the black–body problem, but his argument was extended by Einstein in the year 1906 to "material" harmonic oscillators. In the meantime, with the celebrated paper on the photon (1905) Einstein had also shown that quantization was a "real" fact, and not just a formal one (to this we will however come back below). At the first Solvay conference (1911, see [1]) the existence of quanta was finally sanctioned by the scientific community.

This is well known. Less familiar is instead the fact that Boltzmann had previously looked for a possible escape from the difficulties of the equipartition problem in a fully classical context. Indeed, he was just suggesting that the lack of equipartition could very simply be due to the fact that the system had not reached equilibrium within the measurement time; a hint in this direction was even given by Maxwell in the last page of his third memoir on kinetic theory, where he speaks of a relaxation time of 675 years [2]. The main idea was that the relaxation rates to equilibrium should be highly nonuniform with respect to frequency and temperature: for example, in the case of polyatomic molecules equilibration should be quite rapid for the "external" degrees of freedom such as those of the center of mass, but very slow for the "internal" motions, i.e. rotations and especially vibrations. This is well witnessed by a famous letter of Boltzmann to Nature (1895) [3], where he speaks of times of the order of years. Here is the quotation: "*But how can the molecules of a gas behave as rigid bodies? Are they not composed of smaller atoms? Probably they are; but the* vis viva *of their internal vibrations is transformed into progressive and rotatory motion so slowly that when a gas is brought to a lower temperature the moleecules may retain for days, or even for years, the higher* vis viva *of their internal vibrations corresponding to the original temperature.*" Even more interesting are the sections 43, 44, 45 of his Lectures on Gas Theory, Vol II, where one finds [4]: "*The constituents of the molecule are by no means connected together as absolutely undeformable bodies, but rather this connection is so intimate that during the time of observation these constituents do not move noticeably with respect to each other, and later on their thermal equilibrium with the progressive motion is established so slowly that this process is not accessible to observation*"; and finally, the most significant statement: " *The hypothesis proposed here would be confirmed experimentally if it were to be shown that, for any gas for which κ* (the ratio C_p/C_V of specific heats) *varies with temperature, observations extended over a larger period of time give a smaller value than for those of shorter duration*".

To this last remark we will come back below. For what concerns quantitative estimates for the phenomenon predicted by Boltzmann, we could find no trace in his works. However, estimates were soon provided by Jeans [5], who was able to prove that the times needed to reach equilibrium were exponentially long with frequency and (essentially) inverse temperature. This was obtained by showing that the energy δe exchanged between external and internal degrees of freedom through collisions is exponentially small. As a prototype example consider the head–on collision of a particle with a spring of frequency ω; by extremely elementary considerations Jeans shows that, in a first approximation, the exchanged energy δe is nothing but the square of the Fourier transform (evaluated at ω) of the function $F(t)$ expressing, as a function of time, the force acting on the free end of the spring by interaction with the impinging particle. Thus the exchanged energy δe turns out to be exponentially small with ω, namely of the form $\delta e = A \exp(-\tau\omega)$, just in virtue of a general property of the Fourier transform of an analytic function (the intermolecular potential having been assumed to be analytic). Here τ is a characteristic time of interaction, of the order l/v, where l is the range of the potential and v the velocity of the impinging particle. To have an idea of the relevance attributed by Jeans to such considerations, here is a quotation from the *incipit* of his paper: " *A steel ball dropped on a rigid steel plate will rebound perhaps half a dozen times before its energy is appreciably lessened; this is because of the great elasticity of steel. If the kinetic theory of gases is true, a system of molecules must rebound from one another and from rigid walls many billions of times before the total energy is appreciably lessened. The aim of the present paper is to show that, in so far as the data available enable us to judge, molecules will possess sufficient elasticity for this to occur.*"

The point of view of Boltzmann and Jeans was amply discussed at the first Solvay conference (1911), after the report of Jeans ([1], page 74) and after the reading of a letter that Rayleigh had sent in support of the nonequilibrium point of view ([1], page 51). Especially relevant was the opinion expressed by Nernst, who remarked: "*up to now it has never been observed that the measured values of the specific heat increase*" (with the time of measurement); in particular, he added, this was true for gases not obeying the equipartition principle, for which there were available experimental methods involving measurement times ranging from a millionth of a second to several minutes. An even stronger argument was given by Nernst in connection with the fusion temperature and the vapor tension. Indeed, as such quantities are well known from thermodynamics to depend on the specific heat, he pointed out that, if the specific heat were changing with time, a difference between the fusion temperature of natural minerals and that of synthetic compounds should have been observed, which was not the case. So the phenomenology appeared to require that the equilibration times should be longer than millions of years for some components of energy, while other components should equilibrate "immediately", and this, Nernst concluded, "*is very little probable*". By the way, this seems not to be so clear today, with the present popularity of the studies on glasses.

A very skeptical comment on the nonequilibrium interpretation was also made by Poincaré after the report of Jeans. Actually, just under the influence of the discussions at the Solvay conference, Poincaré himself was very soon led to perform a deep investigation which, in his opinion, constituted a proof of the necessity of quantization; not only quantization produces Planck's law, but conversely, Poincaré claims, quantization necessarily follows if Planck's law is assumed to hold at a phenomenological level [6] (see also [7]). A similar argument had previously been given by Ehrenfest [8]. This was the end of the story, because Poincaré's paper made so strong an impression on Jeans that he felt the need of making a public retractation. This occurred on the occasion of the meeting of the British Association of Physics of the year 1913, a report of which, published in Nature [9] (see also [10]), goes as follows: "*On Friday morning the most important discussion of Section A, if not of the whole meeting, took place. The subject was radiation and it was opened by Mr. J.H. Jeans in a masterly and concise manner. The discussion turned on the question of the validity of the laws which have hitherto been believed to be the ultimate laws of nature. The problem at its simplest occurs in the case of black body radiation. Mr.* Jeans regarded the work of Poincaré as conclusive: *when starting with the mean energy of each vibration of specified wave-length he deduces the quite definite result that* the exchange of energy must take place by finite jumps.*This leads directly to the quantum hypothesis which the opener assumed in its entirety.*" Moreover a few years later, in publishing the third edition of his Dynamical Theory of Gases, he introduced a very drastic change by completely eliminating the chapter 16 of the first two editions, by the title "*The transfer of energy and the propagation of sound*" [11], where the problem of the dependence of the specific heat on the time of measurement was discussed in connection with the dispersion of sound. See also [12].

3. – The second phase: from physics to chemistry; relaxation times in sound dispersion

After the retractation of Jeans, the problem of the times of relaxation to equilibrium in polyatomic molecules disappeared from the domain of fundamental physics, people being convinced that equilibrium was reached "immediately". Typically, in the case of gases such as air at ordinary conditions of pressure and temperature, by "immediately" one meant just "after a time of the order of 10^{-10} seconds", namely the mean time between two collisions, which gives the order of magnitude of the equilibration time for the center–of–mass energy.

The problem then reappeared twelve years later, in the year 1925, but only as a sectorial one within a particular subject, namely dispersion and absorption of ultrasound waves (see [13][14] [15], or the very concise review in sect. 4 of [16]). Indeed, by using ultrasounds with frequencies of the order of the megahertz, which had just become available, Pierce [17] discovered an anomalous absorption which could not be explained in terms of the "classical" mechanisms of viscosity and thermal conduction, already familiar from the times of Kirchhoff and Stokes. After a long discussion of about five years, people finally became convinced that such an anomalous absorption, which was intimately related with a corresponding phenomenon of dispersion, should be explained as due to the existence of a retardation in the equilibration of the internal degrees of freedom of polyatomic molecules with the external (or translational) ones, more or less in the way conceived by Boltzmann, Rayleigh and Jeans, although such authors and their foundational perspective essentially were never mentioned. The corresponding relaxation times were found, quite unexpectedly, to be of the order of 10^{-5} or 10^{-3} seconds, namely about 5 or 7 orders of magnitude larger than "immediately" [18].

Such a phenomenon of a slow relaxation to equilibrium for the internal motions was then investigated from a macroscopic point of view, in the frame of continuum mechanics. A good survey containing a detailed historical part can be found in Kneser [14] (see also [19]). Quite relevant are the work of Mandelstam and Leontovich, a summary of which is reported by Landau and Lifshitz in connection with the "second viscosity" [20], and the standard reference book of Herzfeld and Litovitz [21] (see also [22] and [23]).

Many works were also performed from a microscopic point of view, namely with the aim of determining the relaxation rate by estimating the exchange of energy between external and internal degrees of freedom through molecular collisions. The fundamental reference here is the paper of Landau and Teller of the year 1936 [24]. They consider the problem of the exchange of energy, according to quantum mechanics, in a collision between a harmonic oscillator and an impinging particle, interacting through a smooth potential; they claim that the result can be estimated classically, and give a classical estimate which is essentially equivalent to the one given 33 years before by Jeans, though apparently unaware of it. The only difference is that they take into account the Maxwell–Boltzmann distribution of the velocities of the impinging particle, which entails that only the collisions with particles of extremely high energy are relevant; this by the way is the reason why the calculation can be performed classically. In such a way Landau and Teller find that the exchanged energy is exponentially small with ω/kT (actually, a suitable power of it), but refrain from giving any quantitative estimates.

Quantitative theoretical estimates for the relaxation times, to be confronted with the experimental ones for several kinds of diatomic molecules, were later given by many people. An almost complete review up to the year 1969 can be found in Rapp and Kassal [25]. The essential conclusion of all such works is that everything is apparently in order, because the theoretical estimates are found to be in a more or less good agreement with the experimental data. Things are however more complicated, as we will try to illustrate below; a hint can be found in a standard book such as that of Lambert [15], where one finds the sentence: "*Even if a completely satisfactory theory were available, its quantitative application would be severely limited by the lack of accurate and realistic interatomic potentials.*"

4. – The third phase: back to physics; Fermi Pasta Ulam and the theory of dynamical systems; Einstein's interpretation of Planck's law

In the meantime, the problem of the relaxation times to equilibrium had emerged again, as a problem of a general interest, with the work of Fermi–Pasta–Ulam (FPU, 1954) [26]. Such authors were making a numerical investigation of the relaxation to equilibrium in a one-dimensional model of a nonlinear crystal, namely a chain of a certain number N of equal mass points on a line, with a coupling due to nonlinear springs: taking initial data with the energy concentrated on the low–frequency modes, they found by numerical integration of the equations of motion that energy did not flow to the high–frequency modes within the times they could attain. As Ulam reports in his preface to the work of FPU, reprinted in Vol. 2 of Fermi's collected papers (N. 266): "*The results of the calculations ... were interesting and quite surprising to Fermi. He expressed to us the opinion that they really constitute a little discovery, in providing intimations that the prevalent beliefs in the universality of mixing and thermalization in nonlinear systems may not be always satisfied.*"

We don't have time to enter here a discussion of the many works written on the FPU problem (see for example [27][28][29][30]), mostly with the intent of understanding whether classical mechanics really predicts extremely long relaxation times or not. It is just in this connection that many studies in the mathematical theory of dynamical systems were performed, in the spirit of modern perturbation theory, with reference to KAM theory and to the notion of weak stability in Nekhoroshev's sense [31][32]. Thus the works of Boltzmann and Jeans were rediscovered (see [33][34][35]), and the analogy with glasses was first mentioned [36].

There still remained a fundamental problem, namely how could one give a thermodynamic description for systems being in a state of metaequilibrium, such as glasses. Indeed, on the one hand it is found that, due to te exponentially small exchanges of energy, the high–frequency oscillators give an exponentially small contribution to the specific heat, which seems to be in a qualitative agreement with the description given by Planck's law; on the other hand, the dynamical laws describing the exponentially small exchanges of energy turn out to contain a dependence on the molecular parameters, which is not the case for the laws of themodynamics. A first step towards the solution of this fundamental problem was accomplished quite recently in the work [37](see also [38][39][40]), where it was shown that the elementary mechanical laws governing molecular collisions entail a functional relation between mean exchanged energy and energy flluctuations, which has exactly the analytic from corresponding to Planck's formula, in a way pointed out by Einstein in his contribution to the Solvay conference.

Let us briefly illustrate this point. It is known since its original derivation that Planck's law can be regarded as a solution of the differential equation

$$\frac{\mathrm{d}U}{\mathrm{d}\beta} = -(\epsilon U + U^2/N)\,,$$

with $\epsilon = \hbar\omega$. On the other hand it was pointed out by Einstein (see [1]) that such an equation should be better read as split up into the two relations

$$\frac{\mathrm{d}U}{\mathrm{d}\beta} = -\sigma_E^2\,,\ \ \sigma_E^2 = \epsilon U + U^2/N\,,$$

where σ_E^2 is the variance of energy; indeed the first one should be considered as a relation of a general thermodynamic character, while the second one should be looked at as having a dynamical character and might in principle be deducible from a microscopic dynamics. In his very words: these two relations "*exhaust the thermodynamic content of Planck's*" formula; and: "*a mechanics compatible with the energy fluctuation* $\sigma_E^2 = \epsilon U + U^2/N$ *must then necessasily lead to Planck's*" formula.

Now, in the paper [37] it was shown that the mechanics that leads to such a functional relation is nothing but the ordinary Newtonian mechanics. Indeed, considering for example the prototype model mentioned above, of a particle impinging on a spring, one easily shows (at least in a first approximation) that the equations of motion produce for the energy exchanged during a collision a certain expression, which in turn, by averaging over the collisions, leads exactly to the Einstein's functional relation between the mean exchanged energy and the corresponding variance. In such a way, one obtains for the mean exchanged energy an expression having the analytical form of Planck's law; the way in which Planck's constant should enter is not yet clear, although it might be worth mentioning that Planck's constant is known to be contained in the values of the actual molecular potentials.

5. – Perspectives: analogy with glasses and with stellar dynamics, Einstein versus Poincaré

Which conclusions can then be drawn from a complicated situation as the one described above? The first one seems to be that one of the main effects predicted by Boltzmann really exists. We refer to the prediction that "*observations extended over a larger period of time* (for the specific heat should) *give a smaller value than for those of shorter duration*". Indeed it is just this phenomenon that constitutes sound dispersion. Moreover, it is also commonly observed in polymers, where it is described under the name of "*time–dependent specific heat*" [41][23]; by the way, we are ourselves trying to observe the analogous phenomenon in crystals, in collaboration with G. Carini and F. Ragusa. There remains however the problem that the observed relaxation times are still somehow microscopic, being of the order of 10^{-3} or 10^{-5} seconds instead of the ones that would be needed to account for the actual lack of equipartition; for example, times of the order of billions of years as mentioned by Jeans would make the job.

This is the main problem with which we are presently confronted. In this connection, we are now trying to produce analytical and numerical estimates for the energy exchanges, in correspondence with realistic interatomic potential, and we are meeting with an apparently paradoxical situation. Indeed, in agreement with the sentence of Lambert quoted above [15], we find that the estimates turn out to depend in an incredibly strong way on the values of the parameters used, extremely small variations of the parameters leading to sharp changes in the order of magnitude of the exhanged energy. We might perhaps describe such a situation by saying that a *principle of unpredictability of the thermalization rate* seems to hold. The minimum we can say at present is that the agreement between theory and experimental data which is allegedly found in the literature might just be due to the fact that the relevant parameters are actually fitted to the data rather than taken as given in advance.

What we hope is that the relaxation times of classical mechanics, accurately calculated using realistic interatomic potentials without free parameters, can be proven to be extremely long, entailing extremely large time–scales as those occurring in glassy systems. But in such a case one would be confronted with the further problem of explaining the much shorter times which are actually observed, namely, as mentioned above, of the order of 10^{-3} or 10^{-5} seconds. Our conjecture is that according to classical mechanics one meets with two time–scales. The first is a short one, which leads to the reaching a state of metaequilibrium described by a quasi–thermodynamics in qualitative agreement with Planck's law, through a dynamical mechanism as the one conceived by Einstein and illustrated above. The second time–scale, which might be extremely large as in glassy systems, would instead lead to equipartition. An analogous situation seems to occur in stellar dynamics, where one meets with a rapid, violent, relaxation to a Fermi–like distribution, i.e. the Lynden–Bell distribution (see [42] and the review [43]); this is obtained in the approximation in which the collisions are neglected, while an extremely slow relaxation to a classical equilibrium occurs later, under the action of the interstellar collisions.

Of the two time–scales mentioned above as possibly predicted by classical mechanics, only the first, rapid one, would be predicted by quantun mechanics, according to which Planck's law is the final equilibrium distribution. If the scenario illustrated above as possibly predicted by classical mechanics is correct, namely if Planck's law describes a metaequilibrium situation evolving at an extremely slow pace towards equipartition, one would then meet with an observable effect, which we like to call the Jeans effect (see [44], quoted in [45]; see also [46]): in the low frequency region of the energy spectrum there would exist a *plateau* of equipartition, which advances, at an extremeley slow pace, towards the high frequency region. Indeed, the exponentially long relaxation times causing the exponential smallness of the thermodynamic energy are expected to occur only for frequencies above a certain threshold, below which equipartition should hold; on the other hand such an "equipartition front" has to advance at all, if a global equipartition has eventually to occur. Actually it seems to us that such an effect might already be visible in certain experimental data available for plasmas [47]. In conclusion, classical and quantum mechanics would agree in predicting the first rapid relaxation to a Planck distribution; whether the possible later slow relaxation to equipartition really occurs is a problem which was never seriously considered, and in our opinion is an interesting one.

In closing the present review, we would like to mention two quotations from Einstein and Poincaré, concerning the possibility of obtaining Planck's law without introducing quantization, i.e. a discretization of energy. For what concerns Einstein, we have already recalled how, since his contribution to the Solvay conference, he was striving to obtain a classical understanding. We show now that his attitude did not change up to his last years. This is witnessed by the following quotations from his scientific autobiography, which was written a few years before his death [48]. Indeed, he first recalls how, by inventing the photon, he had given some concreteness to the discretization of energy, previously introduced by Planck at a purely formal level. In his very words (see [48]): "*This way of considering the problem showed in a definitive and direct way that it is necessary to attribute a certain immediate concreteness to Planck's quanta and that, under the energetic aspect, radiation possesses a sort of molecular structure*". But after a few lines he adds: "*This interpretation, that almost all contemporary physicists consider as essentially definitive, to me appears instead as a simple provisional way out*". A further very impressive quotation concerning a classical understanding of the photon, still taken from his contribution to the Solvay conference, is reported in [39].

For what concerns Poincaré, we have already recalled how in his fundamental paper [6] he claimed that quantization should be necessary if Planck's law is assumed to hold. Actually, it is well known that he had a general negative attitude towards the metastability scenario of Boltzmann and Jeans, as is witnessed by the following quotation from a paper of a less technical type [49], written just after the one mentioned above: "*Jeans tried to reconcile things, by supposing that what we observe is not a statistical equilibrium, but a kind of provisional equilibrium. It is difficult to take this point of view; his theory, being unable to foresee anything, is* *not contradicted by experience, but leaves without explanation all known laws ...* ". However, curiously enough, the final words of the same paper have the following tone: "*Will discontinuity reign over the physical universe and will its triumph be definitive? Or rather will it be recognised that such a discontinuity is only an appearence and that it dissimulates a series of continuous processes? The first person that saw a collision believed to be observing a discontinuous phenomenon, although we know today that the person was actually seeing the effect of very rapid changes of velocity, yet continuous ones*", with the conclusion: "*To try to express today an opinion about these problems would mean to be wasting one's ink.*"

Now, our admiration for Poincaré is unlimited, but our personal feeling, or rather hope, is that perhaps on this point Einstein was seeing farther than him.

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