PLANCK'S FORMULA AND GLASSY BEHAVIOR IN CLASSICAL NONEQUILIBRIUM STATISTICAL MECHANICS

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Abstract

In statistical mechanics it is well known that one has to take into account the role of the relaxation times to equilibrium. We discuss the relevance of this fact for systems of weakly coupled harmonic oscillators in a classical framework, showing how one has a behavior similar to that of glassy systems and how one finds an analogue of Planck's formula. From this point of view, quantum equilibrium statistical mechanics thus appears as a first order approximation in classical nonequilibrium statistical mechanics very far from equilibrium.

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1 Introduction

In thermodynamics one always makes reference to some relaxation time to equilibrium; for example, for a gas inside a cilinder one commonly considers the displacement of a piston, and requires that a sufficiently long time be elapsed for the gas to have reached a new equilibrium state, and in such a way one considers a sequence of equilibrium states. The main thesis we want to discuss here is that, according to classical mechanics, there exists a high nonuniformity in the relaxation times for the different "internal" degrees of freedom, such times increasing exponentially fast with the frequencies of

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the internal motions, so that one is somehow compelled to take such a high nonuniformity into account. The zero-th order approximation turns out to be just the one in which such differences are altogether neglected (i.e. one considers extremely long times), and is well known to lead to energy equipartition, namely to predict the same mean energy for each degree of freedom (or rather for any quadratic term in the hamiltonian) irrespective of its frequency. We present here some recent results (obtained in the paper[1]), which show that in the next order of approximation a classical analogue of Planck's formula is recovered, so that quantum equilibrium statistical mechanics appears as a first order approximation within the framework of classical nonequilibriium statistical mechanics. In such a way we are bringing to its extreme consequences a point of view first proposed by Boltzmann and Jeans (for the references, see [2]), by actually implementing an idea which was proposed by Einstein, as we will try to illustrate below. We finally will point out that there should exist a kind of experimentum crucis showing whether the present point of view is correct. Indeed from the present point of view one expects that, as time goes on, equipartition is actually achieved for all frequencies, with a kind of equipartition front advancing very slowly with time from the low frequencies towards the high frequencies, while according to quantum statistical mechanics Planck's law corresponds to a real equilibrium state.

Preliminarly we address here, however, another point, namely the question of how can one obtain in classical mechanics something quantitatively comparable with quantum mechanics, as the latter involves a quantity, namely Planck's constant $\hbar$, which is completely extraneous to classical mechanics. A first answer, to which we limit oureselves in the present paper, is that Planck's constant can be introduced in classical mechanics simply through the molecular parameters. Indeed, consider for example a system of equal particles of the same mass m interacting through a typical interatomic potential, such as the familiar one of Lennard-Jones. Now, this potential contains two parameters, say V_0 and σ, with the dimensions of an energy and a length respectively, and from them and m one constructs an action A, namely $A = \sigma\sqrt{mV_0}$, which a priori can take any value. But if one takes for the parameters entering a model just the ones corresponding to actual atoms, as reported in the standard textbooks, one finds that the relation $A \simeq 2Z\hbar$ holds, where Z is the atomic number of the considered atoms. This is one way in which Planck's constant can be made to enter classical physics at the level of pure mechanics (see [3]). A more fundamental way would require considering the role of the electromagnetic field, but this interesting point will not be discussed here.

2 The analytical argument for the nonuniformity of the relaxation times

To go to the heart of the problem, we consider the simplest example describing the essence of the dynamics of a diatomic gas, which is the prototype physical system presenting "internal" degrees of freedom (see [4]). This is a one–dimensional model involving two points P and Q on a line; P is attracted by a linear spring to a fixed origin O, while Q collides with P through an analytic potential. Denote By x and y the abscissas of the spring P and of the impinging point Q respectively. Then one has a system of two coupled equations for the unknowns $x(t)$, $y(t)$, namely Newton's equations with the mutual opposite forces due to the given potential. In a first approximation a decoupling is obtained by considering the case in which the initial energy of the spring is very small. Indeed, in such a case, for a high frequency it turns out that the spring remains very close to the origin, i.e. one has $|x(t)| \ll 1$ in suitable units. Thus, in the mutual force, which depends on the relative distance $|x-y|$, one can simply replace $|x-y|$ by $|y|$, and so Newton's equation for the impinging particle decouples from the other one, becoming a closed equation for y, and this is in principle solved by a certain function $y = y(t)$ depending on the initial data. The equation of motion for the spring P then becomes

$$\ddot{x} + \omega^2 x = f(t)$$

with a given function $f(t)$, and it is well known that such an equation is solved by

$$z(t) = e^{i\omega t}[z_0 + \int_{t_0}^{t} e^{-i\omega s} f(s) ds]$$

in terms of the complex variable $z = \dot{x} + i\omega x$. On the other hand the energy $E = (1/2)(\dot{x}^2 + \omega^2 x^2)$ of the spring is immediately written down in terms of $z(t)$, by $2E = |z|^2$. Thus the energy $\delta E = E(+\infty) - E(-\infty)$ exchanged in a single collision turns out to be given by the simple formula (which we call Benettin's formula – see [5] and [6] –, although it was well known for example to Jeans)

$$\delta E = \eta^2 + 2\eta\sqrt{E_0}\cos\varphi_0 \ ,$$

involving the quantity

$$\eta = |\int_{-\infty}^{+\infty} e^{-i\omega s} f(s) ds \,|$$

and the initial phase φ_0 of the oscillator. Consequently in a first approximation the energy δE exchanged in a single collision between a particle and a spring of frequency ω is the sum of a drift term η^2 and of a fluctuating one depending on the initial phase φ_0 of the spring; but in any case the exchanged energy is estimated essentially by η, namely by the Fourier transform (evaluated at ω) of an analytic function, which is very well known to decrease exponentially fast with ω. It can be shown that the qualitative results of such a first order (or Landau–Teller, see [7]) approximation hold rigorously for the exact equations (see [8] and [9]).

The simplicity of the argument is so impressive that one could hardly imagine it has no physical consequences: we have indeed shown that, through collisions, the energy exchanges between the low frequencies (the point particle) and the high frequencies is exponentally small, and this just because the Fourier transform of an analytical function decreases exponentially fast with the frequency. So the establishment of equipartition between the internal degrees of freedom and the translational ones requires an exponentially large number of collisions, namely an exponentially long time. One can find meaningful examples (see [4]) in which there exists a frequency $\bar{\omega}$ having a relaxation time of the order of 1 second, while the frequency $\bar{\omega}/2$ relaxes in 10^{-8} seconds, and the frequency $2\bar{\omega}$ in 10^5 years, which indeed constitutes a case of high nonuniformity.

3 Planck's law as an approximate thermodynamic formula in a metastable regime, similar to that of glasses

Let us consider a model of a large number N of springs of the same frequency ω, each of which suffers collisions with a point particle of velocity v as discussed above. One should think of the point particles as mimicking a heat reservoir at a temperature T with $mv^2/2 = kT$, where k is Boltzmann's constant; the frequency ω of the springs is a parameter that can take any positive value. We address the problem of the statistical behavior of the internal degrees of freedom (the springs) initially at rest, trying to take into account the high nonuniformity of the exchange of energy at each collision as a function of frequency. Indeed for springs of low enough frequency one can expect that after a rather short time they go to equipartition with the reservoir, acquiring an energy kT. Thus, for any fixed observation time t there will exist a maximal equipartition frequency $\omega^* = \omega^*(t)$, such that one will have equipartition for the lower frequencies, while the larger frequencies will have an average energy exponentially decreasing with frequency. Clearly the "equipartition front" $\omega^*(t)$ will advance towards the high frequencies as time goes on, and this is indeed the main point where the present classical theory qualitatively differs from the quantum theory.

Indeed the latter predicts that the energy distribution at equilibrium will be Planck's law, which attributes equipartition only to the zero frequency, while all other strictly positive frequencies should have a lower energy. Let us recall that Planck's law for the average energy U of system of N oscillators of frequency ω at temperature $T = 1/k\beta$ is

$$U(\omega, T) = N\,(\frac{\epsilon}{e^{\beta\epsilon} - 1})\ ,$$

with $\epsilon = \hbar\omega$; so U tends to NkT for $\omega \to 0$, and decreases exponentially fast to zero as frequency increases (in fact one might also take into account a contribution $N\hbar\omega/2$ coming from the so called zero–point energy, but this is a quite delicate point we will briefly discuss below). Thus quantum mechanics predicts that at equilibrium only the zero frequencies will be at equipartition, while the higher frequencies will have lower and lower energies, decreasing exponentially fast as frequency increases. Classical mechanics predicts instead that at any fixed time there will be a plateau of equipartition for the low frequencies, with the equipartition front advancing towards the high frequencies at an extremely low rate. The higher frequencies will indeed have an average energy decreasing exponentially with frequency; but this should be a kind of metastable situation, because for any frequency the average energy should increase with time towards equipartition at an extremely low rate, as is by now very familiar in the so called aging phenomena of glasses or spin glasses. Such an analogy was pointed out quite recently (see [10]).

The problem then remains of understanding whether in classical mechanics one can go a little further, in the direction of finding a thermodynamic universal description for such a metastable situation. We will now describe how it was found that this is indeed the case, and that one thus obtains a classical analogue of Planck's formula. This was obtained in [1] by showing how the Benettin–Jeans formula recalled above for the energy exchange δE in a single collision is transformed, through statistics (i.e. through suitable averages), into what we call Einsten's dynamical fluctuation formula, which in turn is essentially equivalent to Planck's formula. But this requires recalling first the original interpretation of Planck's formula given by Einstein in the years 1909, 1912 (see [11] and [12]), which apparently is not familiar in the scientific community.

What Einstein did, was to provide a physical substantiation for the original deduction Planck gave of his law on October 19, 1900 (see [13]). Indeed it was only in his second communication (december 1900) that Planck gave his familiar deduction involving the standard statistical arguments and the revolutionary discretization of energy. In his first communication he was instead proceeding at a phenomenological heuristic and formal level, without invoking any discretization at all. In fact he had remarked (we are using here a contamination of the notations of Einstein and of Planck, using furthemore the inverse temperature $\beta = 1/kT$ instead of temperature T) that the differential equation

$$\frac{\mathrm{d}U}{\mathrm{d}\beta} = -\frac{U^2}{N}$$

leads by integration (with a suitable choice of the integration constant) to the equipartition law $U = NkT$, which is valid for low frequencies, while the differential equation

$$\frac{\mathrm{d}U}{\mathrm{d}\beta} = -\epsilon U$$

leads analogously to a law which was known to be valid for high frequencies, namely Wien's law $U = C\exp(-\beta\epsilon)$, with a suitable constant C. Just by virtue of imagination, through an interpolation he was then led to the differential equation

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

which by integration gives exactly Planck's formula. Such a firmula was found to fit very well the experimental data, with an appropriate choice for ϵ; in fact it was already known, by a general argument of Wien, that ϵ had to be taken proportional to frequency (namely one should put $\epsilon = \hbar\omega$) with a suitable constant action $\hbar$, so that the constant to be fitted to the data was the action $\hbar$, namely Planck's constant.

So much for what concerns Planck's first communication. The contribution of Einstein was the following one. Already in the year 1903 (see [14]) he had remarked that in the canonical ensemble the fluctuations of energy, described by the corresponding variance

$$\sigma_E^2 =< E^2 > -U^2$$

where $< \cdots >$ denotes the canonical expectation and $U :=< E >$, are expressed in terms of the mean energy U through a relation having a kind of universal thermodynamic character, namely $\frac{\mathrm{d}U}{\mathrm{d}\beta} = -\sigma_E^2$. Thus Einstein was led to split Planck's differential equation into two relations, namely

$$\frac{\mathrm{d}U}{\mathrm{d}\beta} = -\sigma_E^2$$

and

$$\sigma_E^2 = \epsilon U + U^2/N \, ,$$

the first of which was conceived to be just a kind of general thermodynamic relation, while the second one should rather have a dynamical character, being in principle deducible from a microscopic dynamics. In his very words (see [12]): 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. It was pointed out in [1] that the second of the above equations has indeed a mechanical character, coinciding essentially with the Benettin–Jeans formula. So we might say that the "mechanics" conceived by Einstein as leading to Planck's formula is nothing but the dear old classical mechanics of Newton.

This is seen as follows. The energy e_k that a single oscillator possesses after k collisions according to the Benettin–Jeans formula (we denote now by e the energy of a single oscillator, reserving the symbol E for the energy of the system of N oscillators, to be considered below) can be conveniently written in the form

$$e_k = e_0 + k\eta^2 + 2\eta \sum_{j=1}^{k} \sqrt{e_{j-1}}\ \cos\varphi_{j-1}\ ,$$

which depends parametrically on the phases $\varphi_0, \ldots, \varphi_{k-1}$ and on the initial energy e_0. The phases can be assumed to be independent and uniformly distributed; thus, averaging over them in the familiar way of random walk theory, one gets for the mean energy $u_k := < e_k >$ after k collisions ($< \cdots >$ denoting now average over the phases) the expression

$$u_k = e_0 + k\eta^2\ .$$

Analogously, with $< (\cos\varphi_j)^2 >= 1/2$, one finds $< e_k^2 >= u_k^2 + 2\eta^2 \sum_{j=1}^{k} u_{j-1}$. The variance $\sigma^2_{e_k} :=< e_k^2 > -u_k^2$ then takes the form $\sigma^2_{e_k} = 2e_0k\eta^2 + k(k-1)\eta^4$ or also, in the approximation of large k so that we can identify $k(k-1)$ with k^2,

$$\sigma^2_{e_k} = 2e_0k\eta^2 + (k\eta^2)^2\ .$$

The relevant point is that in the latter formula the "time" k (we are assuming here for simplicity's sake that the "time of flight" between two collisions is a constant) enters only in the combination $k\eta^2$, so that it can be eliminated through the expression of u_k; this leads to an analogue of Einstein's dynamical fluctuation formula, namely $\sigma^2_{e_k} = 2e_0(u_k - e_o) + (u_k - e_0)^2$. The analogy becomes even stronger if one introduces the "exchanged energy" after k collisions, $\tilde{e}_k = e_k - e_0$, because the corresponding expectation $\tilde{u}_k$ and variance $\sigma^2_{\tilde{e}_k}$ are then related by

$$\sigma^2_{\tilde{e}_k} = 2e_0\tilde{u}_k + \tilde{u}_k^2\ .$$

A similar relation also holds for the global system of N independent identical oscillators. Indeed, the quantities of interest are the total energy $E_k = \sum_{i=1}^{N} e_k^{(i)}$ (where $e_k^{(i)}$ denotes the energy of the i–th oscillator after k collisions) and the corresponding exchanged energy $\tilde{E}_k = E_k - E_0$, where E_0 is the initial energy. By the central limit theorem, $\tilde{E}_k$ is normally distributed with a mean $\tilde{U}_k$ and a variance $\sigma^2_{\tilde{E}_k}$ which are obtained by adding up the corresponding quantities for each oscillator, namely are given by $\tilde{U}_k = N\tilde{u}_k$ and $\sigma^2_{\tilde{E}_k} = N\sigma^2_{\tilde{e}_k}$. So, denoting by $\tilde{U}$ and $\sigma^2_{\tilde{E}}$ expectation and variance of the exchanged energy at any "time" k, one gets between $\sigma^2_{\tilde{E}}$ and $\tilde{U}$ a functional relation which is independent of "time" k, namely

$$\sigma^2_{\tilde{E}} = 2a_0\omega\tilde{U} + \tilde{U}^2/N\ ,$$

where a_0 denotes the initial action per oscillator, $a_0 := E_0/(\omega N)$. Notice that the quantity η, which contains the molecular parameters characterizing the considered system, has now completely disappeared, and the formula just found has a kind of thermodynamic universality. This is our analogue of Einstein's functional relation between variance and expectation of energy, which we call Einstein's dynamical fluctuation formula.

An important point to be stressed is that in our formula there appears as a parameter the quantity $2a_0$, twice the initial action per oscillator, which takes the place of Planck's constant $\hbar$. At the moment we are unable to say anything rigorous concerning this very relevant point. We only present here some heuristic considerations, on which we hope to come back in the future. The point is that, as was recalled above, the Benettin–Jeans dynamical formula was established for small initial energies of the oscillators; think for example of the fact that if the oscillator had an initial energy greater than that of the particle, then in order to go towards equipartition one should have a formula for the exchanged energy with a drift term of opposite sign with respect to the one given above. So the formula used above should hold only for low enough energy or action per oscillator, say for $a_0 < a_*$, with a certain critical or threshold action a_*. This naturally leads to think of a situation with the N oscillators having random initial actions all smaller than a_*, so that, on averaging over the initial actions, uniformly distributed over the interval $(0, a_*)$, one would get a formula as above with $2a_*/2$, namely a_*. in place of Planck's constant. The actual mean energy would correspondingly be given by Planck's formula with the addition of an analogue of the zero–point energy, namely $a_*\omega/2$, playing here the role of the initial energy. Naturally, in situations of metaequilibrium of a glassy type as the one described here, the energy distribution would depend on the initial distribution, as was particularly stressed in the paper [10].

Notice that it is exactly through the critical action a_* that the molecular parameters (namely m, V_0 and σ), and thus Planck's constant, are introduced into our classical problems. Indeed by any analytical or numerical estimate one would find

$$a_* = \alpha\,\sigma\sqrt{mV_0}\ ,$$

i.e.

$$a_* \simeq \alpha\, 2Z\hbar$$

with a suitable pure number α, possibly of order of magnitude 1. In fact it is just in a way analogous to this that Planck's constant was first introduced in a problem of this type in the paper [3], where the pure number α was estimated to be something as 0.01 (see also [15] [16]).

4 Conclusions

So we have illustrated how it can be conceived that in classical statistical mechanics one gets a formula of Planck's type as a kind of universal thermodynamic formula describing, in a first approximation, a situation of metaequilibrium very far from equilibrium for a system of harmonic oscillators interacting with a reservoir. We also stressed how the present point of view leads to a qualitative difference with respect to quantum mechanics, because Planck's formula should hold only for limited times, and one should observe, as time goes on, an advancing of the equipartition front towards the high frequencies. However this advancing should occur at an extremely slow rate, as is familiar in the aging phenomenology of glasses and spin glasses. An important point would be to establish whether such an advancement of the equipartition front is really observed or not. This is indeed the experimentum crucis mentioned in the introduction.

Finally, we would like to conclude by recalling some sentences by Einstein which seem to be appropriate in the present context. It is very well known that Einstein was critical towards the "orthodox" interpretation of quantum mechanics: although having greatly contributed to creating the new mechanics, he did not like the interpretation most physicists attributed to it. But much less known is the fact that this general attitude was explicitly expounded by Einstein in connection with the photon, namely in the framework of the statistical mechanics of a system of harmonic oscillators discussed here. Indeed, in his scientific autibiography (see [17]), when recalling the way he had invented the photon by substantiating Planck's formal approach, he said: "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 a few lines below he also added: "This interpretation, that almost all contemporary physicists consider as essentially definitive, to me appears instead as a simple provisional way out".

Now, what did he have in mind when writing down such words? In our opinion he had exactly in mind his "mechanical" interpretation of Planck's formula, recalled above, that he had illustrated in his contribution to the Solvay conference (see [12]), when he was speaking of a mechanics consistent with his dynamical fluctuation formula. Indeed, if such a formula could be proven in some mechanics, then everything would go "as if" energy were discretized, while a "real" discretization would not be necessary ("the statistical properties of the phenomenon are the same as if energy were transfered through integer numbers of quanta $\hbar\omega$"). And in fact there is even one passage where he explains how the energy level corresponding to the ground state should be understood in terms of the energy fluctuations equivalent to Planck's law. Indeed, having pointed out that the formula for the relative energy fluctuations σ_E^2/U^2 equivalent to Planck's formula has the form

$$\frac{\sigma_E^2}{U^2} = \frac{\epsilon}{U} + \frac{1}{N} \ ,$$

which for a large nunber N of oscillators and small energies becomes

$$\frac{\sigma_E^2}{U^2} \simeq \frac{\epsilon}{U}\,,$$

he adds: "If U becomes of the order of $\hbar\omega$ (namely of ϵ), the relative fluctuation becomes of the order of unity; in other terms, the fluctuation of energy is of the order of magnitude of energy itself, i.e. the total energy is alternatively present or absent, and consequently behaves as if it were not indefinitely divisible. It is not necessary to make the hypothesis that distinct energy elements of a definite magnitude exist".

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