Analog of Planck's formula and effective temperature in classical statistical mechanics far from equilibrium

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We study the statistical mechanics very far from equilibrium for a classical system of harmonic oscillators colliding with point particles (mimicking a heat reservoir), for negligible initial energies of the oscillators. It is known that for high frequencies the times of relaxation to equilibrium are extremely long, so that one meets with situations of quasiequilibrium very far from equilibrium similar to those of glassy systems. Using recent results from the theory of dynamical systems, we deduce a functional relation between energy variance and mean energy that was introduced by Einstein phenomenologically in connection with Planck's formula. It is then discussed how this leads to an analog of Planck's formula. This requires using Einstein's relation between specific heat and energy variance to define an effective temperature in a context of quasiequilibrium far from equilibrium, as is familiar for glassy systems.

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I. INTRODUCTION

Classical statistical mechanics is confronted with a paradoxical situation concerning the mean energy U of a system of harmonic oscillators of angular frequency ω in contact with a heat reservoir at absolute temperature T_{res}. Indeed, while the equilibrium Maxwell-Boltzmann distribution predicts equipartition of energy, i.e., $U = T_{\mathrm{res}}$ (with Boltzmann's constant equal to 1), it turns out that the times of relaxation to equilibrium depend exponentially on frequency and inverse temperature, so that for sufficiently high frequencies or low temperatures equilibrium will never be reached within the available times; this is very well known since the times of Boltzmann [1] and Jeans [2] and of Landau and Teller [3] and was amply discussed in recent times in the frame of the theory of dynamical systems (see, for example, Refs. [4–8] and [9,10]). In a typical example one can have a frequency $\overline{\omega} \simeq 10^{14}$ Hz which relaxes to equilibrium in 1 s, while the relaxation time is 10^{-8} s and 10^{5} years for the frequencies $\overline{\omega}/2$ and $2\overline{\omega}$, respectively. Situations of such a type are actually met in plasma physics where the description is essentially classical [9,10]. Thus, systems of oscillators of sufficiently high frequencies are in general very far from equilibrium, and one is confronted with the problem of whether a thermodynamic description can be given for them, presenting some kind of universality. An analogy with the themes discussed in the physics of glasses was pointed out quite recently [11].

In the present paper we show that a quasithermodynamic formula for the mean energy U of a system of a large number N of oscillators of the same frequency ω very far from equilibrium indeed exists and has the analytical aspect of Planck's formula, namely,

$$U = N\left(\frac{\epsilon}{e^{\beta\epsilon}-1} + \frac{\epsilon}{2}\right), \tag{1}$$

with suitable parameters ϵ and β. The main difference is that while in Planck's law one has $\epsilon = \hbar\omega$ ($\hbar$ being Planck's constant) and β^{-1} is the temperature of the reservoir, here one instead has $\epsilon = a^*\omega$ with a suitable action a^* depending on the initial data, while β^{-1} is an "effective" temperature, which is different from that of the reservoir, and depends on time in a practically imperceptible way, as is familiar in the aging phenomena of glasses (see especially Refs. [12–15]). This result is obtained by combining two ingredients, which we call "Einstein's thermodynamic fluctuation formula" and "Einstein's dynamical fluctuation formula," respectively. The former is just the familiar formula relating specific heat to variance of energy [16], which is an identity in the canonical ensemble and is here used far from equilibrium as a tool for defining an effective temperature, in the sense familiar for glassy systems. The latter formula is instead a functional relation between energy variance and mean energy which was conjectured by Einstein [17] to be possibly true for some "mechanics." To such a formula we address our attention in the present paper, proving that it is a consequence of pure dynamics. The proof is obtained by considering the exchange of energy between an oscillator and a point particle under smooth collisions according to classical dynamics, and by exploiting a simple formula which was recently proven [6] to describe the essence of the phenomenon when the energy of the oscillator is negligible with respect to that of the particles mimicking the reservoir.

Einstein's formulas concerning Planck's law are recalled in the next section, while the proof of the functional relation between energy variance and mean energy is given in Sec. III. In this section the model is also described, and the relevant dynamical facts presently available are summarized. Some further considerations of a heuristic character concerning Einstein's thermodynamic formula and its use for the definition of an effective temperature are given in the conclusive Sec. IV.

II. ON PLANCK'S FORMULA, AND ITS INTERPRETATION BY EINSTEIN IN TERMS OF ENERGY FLUCTUATIONS

To explain the motivation of the present paper, it is convenient to recall how Planck's formula (1), without the zero-point energy term $N\epsilon/2$, was deduced by Planck in his origi-

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nal first memoir [18] and how it was interpreted by Einstein in terms of energy fluctuations in his paper [17]. In fact, Planck was working in terms of the entropy S as a function of the energy U, while Einstein was working in terms of the energy U as a function of temperature T; we equivalently work in terms of $U(\beta)$, the energy as a function of inverse temperature.

Planck's remark was that formula (1), without the zero-point energy term $N\epsilon/2$, is obtained by integrating the differential equation

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

with a suitable choice for the integration constant (such that in the limit $\epsilon \to 0$ the classical equipartition formula $U = N/\beta$ is recovered). As a matter of fact, Planck had remarked that the differential equations $dU/d\beta = -U^2/N$ and $dU/d\beta = -\epsilon U$ lead to the relations $U(\beta) = N/\beta$ and $U(\beta) = C\exp(-\beta\epsilon)$, $C=$const, namely, equipartition and Wien's law, which are valid for low frequencies and high frequencies, respectively, and this suggested to him the interpolation formula (2).

The contribution of Einstein, of interest for the aims of the present paper, consisted in an interpretation of formula (2) in terms of energy fluctuations. Indeed, having remarked [19] that the relation

$$\frac{dU}{d\beta} = -\sigma_E^2, \tag{3}$$

where σ_E^2 is the energy variance, holds as an identity in the canonical ensemble, and having given arguments to show that such a relation should have a broader range of validity [20] (see also Ref. [16]), he was led to split relation (2) into two relations, namely Eq. (3) and

$$\sigma_E^2 = \epsilon U + U^2/N, \tag{4}$$

the second of which might have, in his opinion, a dynamical basis. In his very words [17], formulas (3) and (4) ''exhaust the thermodynamic content of Planck's'' formula; and ''a mechanics compatible with the energy fluctuation (4) must then necessarily lead to Planck's'' formula.

The original contribution of the present paper consists in showing how the functional relation (4) between energy variance and mean energy with a suitable ϵ is deduced, with a quite natural procedure of averaging, from the most advanced results of the theory of dynamical systems concerning energy exchanges in atomic collisions (see Benettin's formula recalled below). This is shown in a simple model, describing a system of oscillators of the same frequency in interaction with a heat reservoir.

III. THE MODEL AND THE DEDUCTION OF EINSTEIN'S FLUCTUATION FORMULA FROM DYNAMICS

Our model is a minor variant of one already discussed by Poincaré [21] in connection with the dynamical foundations of statistical mechanics, which was subsequently studied by Jeans and Landau and then rather intensively discussed in recent times in the spirit of the theory of dynamical systems. To start, we consider a harmonic oscillator of frequency ω suffering a smooth collision with a point particle on a line through a given interatomic potential, and recall some relevant facts. The energy exchange δe in a single collision, for negligible initial energy of the oscillator and a significative class of potentials, was recently proven to be given to a very good approximation [6] (see also Refs. [22], [23] and [2]) by what we call Benettin's formula, namely,

$$\delta e = \eta^2 + 2\eta\sqrt{e_0}\cos\varphi_0 . \tag{5}$$

Here e_0 is the oscillator's initial energy and φ_0 the oscillator's initial phase, while η^2 is a quantity exponentially small in the frequency, namely,

$$\eta^2 = \mathcal{E}\exp(-\omega v^{-a}), \tag{6}$$

where v is the velocity of the incoming particle, while $\mathcal{E}$ and a are positive parameters depending on the interaction potential.

Obviously the first qualitative consequence of formulas (5) and (6) is that, for sufficiently high frequencies or low reservoir temperatures (i.e., for small v), the oscillators are almost frozen, i.e., essentially do not exchange energy at all; this is indeed the reason for the need of a nonequilibrium description in the present model. Notice that, while formula (6) exhibits a quite nonuniversal character, inasmuch as it contains parameters $\mathcal{E}$ and a which depend on the specific interaction potential, formula (5) presents instead in its analytic structure a great character of universality. To illustrate this point, we recall that a formula of the analytical structure of Eq. (5) holds exactly for a harmonic oscillator subject to any given forcing, i.e., governed by the equation

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

with any given function f. Indeed, in terms of $z = \dot{x} + i\omega x$ this is immediately solved by

$$z(t) = z_0 \exp[i\omega(t-t_0)] + g(t)$$

with a suitable complex valued function g. Formula (5) then immediately follows by remarking that the energy $E = (\dot{x}^2 + \omega^2 x^2)/2$ is given by $E = |z|^2$, if one obviously defines the exchanged energy δe by $\delta e = E(+\infty) - E(t_0)$ with $t_0 \to -\infty$, and η by $\eta = |g(+\infty)|$. The validity of a formula of the type $\delta e \simeq \eta$ [with η^2 of the form (6)] for the exchanged energy between an oscillator and a point particle, according to the exact solution of the corresponding coupled system of Newton equations, was proven by Jeans and by Landau and Teller. The relevance of the fluctuating term proportional to η was pointed out in Ref. [22], and a complete Fourier expansion in the phase φ_0 was discussed in Ref. [23] and proven in Ref. [6]. From the results of the latter paper it can be proven that Benettin's formula (5) is a good approximation for the energy exchanged in a collision between a harmonic oscillator and an atom interacting through a smooth potential if the initial oscillator's energy is sufficiently small.

To define our model, we consider the energy exchange δe in a single collision between a harmonic oscillator and a point particle on a line, and assume it to be given exactly by formula (5), which, as recalled above, is physically meaningful if e_0 is sufficiently small. We then study a sequence of k

such collisions. For simplicity's sake, we introduce in the present paper the further assumptions (which could rather easily be removed) (i) that the incoming particles have all the same initial velocity v, and (ii) that the time of flight between two successive collisions is a constant. Consequently, the quantity η in Eq. (6) appears as a constant, and the current time t is just proportional to the number k of collisions suffered by the oscillator. Finally, the complete model is defined by considering a global system of N independent oscillators of the same frequency ω, each suffering k independent collisions with point particles as described above. The energy exchanges of the global system of oscillators are thus trivially obtained from the energy exchanges of the single oscillators, simply by means of the central limit theorem.

We show now how Eq. (5) leads to Einstein's dynamical fluctuation formula (4). Consider first the case of a single oscillator suffering k successive collisions. Its energy e_k after k collisions is conveniently written as

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

Given the initial energy e_0, this is a function of the phases $\varphi_0,\ldots,\varphi_{k-1}$, which are assumed to be independent and uniformly distributed; thus, averaging over the phases in the familiar way of random walk theory, one gets for the mean energy $u_k := \langle e_k\rangle$ after k collisions the expression

$$u_k = e_0 + k\eta^2. \tag{7}$$

Analogously, with $\langle(\cos\varphi_j)^2\rangle = 1/2$ and Eq. (7), one finds $\langle e_k^2\rangle = u_k^2 + 2\eta^2\Sigma_{j=1}^{k} u_{j-1}$. Using again Eq. (7) with $j-1$ in place of k, the variance $\sigma_{e_k}^2 := \langle e_k^2\rangle - u_k^2$ then takes the form $\sigma_{e_k}^2 = 2e_0 k\eta^2 + k(k-1)\eta^4$ or also, in the approximation of large k so that we can identify $k(k-1)$ with k^2,

$$\sigma_{e_k}^2 = 2e_0 k\eta^2 + (k\eta^2)^2. \tag{8}$$

The relevant point is that in Eq. (8) the ''time'' k enters only in the combination $k\eta^2$, so that it can be eliminated through Eq. (7); this leads to an analog of relation (4), namely, $\sigma_{e_k}^2 = 2e_0(u_k - e_0) + (u_k - e_0)^2$. 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 $\sigma_{\tilde{e}_k}^2$ are then related by

$$\sigma_{\tilde{e}_k}^2 = 2e_0\tilde{u}_k + \tilde{u}_k^2. \tag{9}$$

A similar relation also holds for the global system of N independent identical oscillators. Indeed, the quantities of interest are the total energy $E_k = \Sigma_{i=1}^{N} e_k^{(i)}$ (where $e_k^{(i)}$ denotes the energy of the ith 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 $\sigma_{\tilde{E}_k}^2$ which are obtained by adding up the corresponding quantities for each oscillator, namely, are given by $\tilde{U}_k = N\tilde{u}_k$ and $\sigma_{\tilde{E}_k}^2 = N\sigma_{\tilde{e}_k}^2$. So, denoting by $\tilde{U}$ and $\sigma_{\tilde{E}}^2$ the expectation and variance at any ''time'' k, from Eq. (9) one gets between $\sigma_{\tilde{E}}^2$ and $\tilde{U}$ a functional relation which is independent of ''time'' k, namely,

$$\sigma_{\tilde{E}}^2 = 2a^*\omega\tilde{U} + \tilde{U}^2/N, \tag{10}$$

where a^* denotes the initial action per oscillator, $a^* := E_0(\omega N)$. Notice that the quantity η, which contains the molecular parameters $\mathcal{E}$ and a, has now completely disappeared. Formula (10) is our analog of Einstein's functional relation (4), and its proof constitutes the original contribution of the present paper. In connection with Einstein's sentence recalled above (''a mechanics compatible...''), one might thus say that the energy fluctuation formula (4) is indeed consistent with a mechanics which is nothing but the familiar classical mechanics.

IV. BACK TO PLANCK'S FORMULA, VIA THE DEFINITION OF AN EFFECTIVE TEMPERATURE: HEURISTIC CONSIDERATIONS

We finally add some considerations which are mostly of a heuristic character. If one uses Einstein's thermodynamic relation (3), then obviously one finds for the mean energy $U = \tilde{U} + E_0$ exactly Planck's formula (1) with $\epsilon = 2a^*\omega$. However, it is clear that in such a way one has $\beta^{-1} \neq T_{\mathrm{res}}$, because the mean energy U increases linearly with the number k of collisions (i.e., with time), and so β, which can be obtained by inverting the relation $U = U(\beta)$, depends on time too.

Actually, such a fact is consistent with the present frame, where one deals with a system in a state of quasiequilibrium very far from equilibrium. Indeed, first of all, we notice that the mean energy U depends linearly on time [see Eq. (7)], but with a proportionality factor η^2 which is exponentially small with the frequency, so that its increase with time can be said to be practically imperceptible. Thus Planck's formula (1) should be read, in the present context, in the following way: the second term at the right hand side is nothing but the initial energy $E_0 = Na^*\omega$, while the first term gives the additional energy that the system acquires from the reservoir, and is actually increasing, extremely slowly, with time (as β too does). The essence of our result is that such an additional energy does not depend on the details of the interatomic potentials [entering through η in Eq. (6)], but has instead a quasithermodynamic character.

The quantity β^{-1} so introduced can be said to present the character of an effective temperature, in the sense which is by now rather common in the theory of aging phenomena of glassy systems. To define it, one formally proceeds as follows. One considers Einstein's thermodynamic relation (3) with the variance σ_E^2 given explicitly in terms of the mean energy U through Einstein's functional relation (4). This leads to the differential equation (2) which by integration gives Eq. (1) and by inversion a corresponding effective temperature β^{-1}, depending extremely slowly on time. It can be easily proven that the inverse of such an effective temperature is an integrating factor for the expression of the heat exchanged with the reservoir, a fact supporting the above interpretation. But we leave this interesting problem for possible future work.

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