



Generalizing Planck's distribution by using the Carati–Galgani model of molecular collisions

Rubens D.B. Carvalho^a, Andre M.C. Souza^{b,c,*}

^a Instituto de Física, Universidade Federal do Rio Grande do Sul, 91501-970, Porto Alegre-RS, Brazil

^b Departamento de Física, Universidade Federal de Sergipe, 49100-000 Sao Cristovao-SE, Brazil

^c National Institute of Science and Technology for Complex Systems, Rua Xavier Sigaud 150, 22290-180 Rio de Janeiro-RJ, Brazil

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ABSTRACT

Classical systems of coupled harmonic oscillators are studied using the Carati–Galgani model. We investigate the consequences for Einstein's conjecture by considering that the exchange of energy in molecular collisions follows the Lévy type statistics. We develop a generalization of Planck's distribution admitting that there are analogous relations in the equilibrium quantum statistical mechanics of the relations found using the nonequilibrium classical statistical mechanics approach. The generalization of Planck's law based on the nonextensive statistical mechanics formalism is compatible with our analysis.

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1. Introduction

It has been observed that for blackbody radiation [1], the mean energy U of stationary electromagnetic waves is a function of frequency ν of these waves.

At temperature T , we can write

$$U(\nu \rightarrow 0) \rightarrow k_B T \quad \text{and} \quad U(\nu \rightarrow \infty) \rightarrow 0, \quad (1)$$

where k_B is the Boltzmann constant. This contradicts the energy equipartition law of classical statistical mechanics as U is frequency independent. The important contribution of Planck came when he discovered that one could obtain the experimental result of Eq. (1) by treating the energy of the stationary electromagnetic waves as a discrete spectrum. Planck's law opened the way to quantum mechanics.

In such a way, Einstein [2] gave an important contribution by noting that in the canonical ensemble, the fluctuation of energy of the blackbody radiation is compatible with Planck's law when, in terms of its variance σ_E , expressed in terms of the mean energy U through the relations

$$\frac{dU}{d\beta} = -(\sigma_E)^2 \quad (2)$$

and

$$(\sigma_E)^2 = \epsilon U + \frac{U^2}{N} \quad (3)$$

where $\beta = 1/(k_B T)$, $\epsilon = h\nu$ (h is Planck's constant) and N is the number of quantum particles. Einstein imagined the first relation as being exactly a type of general thermodynamic relation, while the second must have a dynamical character, being, in principle, deducible from a microscopic dynamics.

* Corresponding author at: Departamento de Física, Universidade Federal de Sergipe, 49100-000 Sao Cristovao-SE, Brazil.
E-mail address: amcsouza@ufs.br (A.M.C. Souza).

Recently, Carati and Galgani [3,4] have investigated classical systems of coupled harmonic oscillators with the procedure of the Jeans–Landau–Teller dynamics of molecular collisions [5,6]. The principal results of Carati and Galgani are that: (i) relaxation times to equilibrium are nonuniform and depend on the internal degrees of freedom of the considered system; (ii) Situations of nonequilibrium statistical mechanics very far from equilibrium are described in a first order approximation by the analogous relations found in quantum equilibrium statistical mechanics; (iii) as conjectured by Einstein, Eq. (3) is a consequence of the dynamics.

It is important to remark that Planck's law considers a real equilibrium state of the quantum statistical mechanics, while within the framework of Carati and Galgani, a similar relation to Planck's law was obtained using nonequilibrium classical statistical mechanics.

The purpose of the present work is to study classical systems of coupled harmonic oscillators along the line of Carati and Galgani. We studied three different aspects of this framework. First, we analyzed the consequence for Einstein's conjecture by assuming that the exchanges of energy, in molecular collisions, follow the Lévy type statistics for high enough frequencies. The Lévy statistics for the energy exchanges was recently obtained by Carati et al. [7], considering the dynamics over a finite time in the Jeans–Landau–Teller model. Secondly, admitting that there are analogous relations in the equilibrium quantum statistical mechanics of the relations found here using the nonequilibrium classical statistical mechanics approach, we will explore some possible consequences in quantum radiation theory. Third, we show that the generalization of Planck's law [8] within the framework of the recently introduced superstatistics formalism [9,10] is compatible with our analysis of Einstein's conjecture.

The organization of this paper is as follows. The Carati–Galgani model is briefly explained in Section 2. Our generalization is presented in Section 3. Discussions about the consequences of our results are presented in Section 4. Concluding remarks are given in Section 5.

2. The Carati–Galgani model

A good level of interest has been focused on the problem of estimating energy exchanges between vibrational and translational degrees of freedom in the dynamics of molecular collisions. One of the simplest and main model used to study this problem was published by Carati and Galgani [3,4]. It is based on the Jeans–Landau–Teller approach [5]. A possible example of a physical system that reproduces this formalism is presented below.

Let us imagine a one-dimensional system involving two particles P and Q in a line. P is attracted by a linear spring to the fixed origin through a harmonic oscillator potential. Q interacts with P through an analytical potential. In a first approximation, the variation of energy δe in a simple collision between P and Q for the oscillator P of frequency ν is given by the addition of a drift term and others terms which depend on the fluctuation of the oscillator's initial phase. It is easy to show [3] that after t collisions an oscillator has energy

$$\epsilon_t = \epsilon_0 + t\eta^2 + 2\eta \sum_{j=1}^t \sqrt{e_{j-1}} \cos(\varphi_{j-1}) \quad (4)$$

where ϵ_0 is the oscillator's initial energy which is considered to be very small in order that the motion of P and Q be decoupled. φ_j is the phase of the oscillator in the j th collision and η is evaluated as a function of ν , which is known to be decreasing exponentially with ν (for an analysis of η see Ref. [6]).

Let us consider an assembly of oscillators, averaging over the phases φ_j , so that

$$\langle \epsilon_t \rangle = \langle \epsilon_0 \rangle + t\eta^2 + 2\eta \sum_{j=1}^t \langle \sqrt{e_{j-1}} \cos(\varphi_{j-1}) \rangle. \quad (5)$$

where $\langle \dots \rangle$ is the phase average. Considering the phases to be independent and uniformly distributed, for large t , the average of energy and the variance are, respectively, given by

$$\langle \epsilon_t \rangle = \langle \epsilon_0 \rangle + t\eta^2 \quad (6)$$

and

$$\sigma_{\epsilon_t}^2 = 2\epsilon_0 \langle \mu_t \rangle + \langle \mu_t^2 \rangle. \quad (7)$$

Here $\sigma_{\epsilon_t}^2$ and $\langle \mu_t \rangle$ correspond, respectively, to the variance and mean of the exchanged energy ($\epsilon_t - \epsilon_0$). Observe that the functional form of the variance is independent of t and η .

Assuming N independent identical oscillators and considering the total energy $\langle E_t \rangle = \sum_j \langle \mu_t^j \rangle$, we immediately obtain for the variance $\sigma_E^2 = N\sigma_{\epsilon_t}^2$ and mean $U = N\langle \mu \rangle$ of the exchanged energy

$$(\sigma_E)^2 = 2\zeta \nu U + \frac{U^2}{N} \quad (8)$$

where ζ is the initial action per oscillator [3]. This result essentially represents the application of the central limit theorem, which arises from a large number of independent contributions of the oscillators [11].

Eq. (8) is analogous to Einstein's relation obtained in the Bose–Einstein statistical quantum mechanics theory. Despite the fact that this relation has been obtained considering the classical statistical mechanics very far from equilibrium, the approach recovers Einstein's conjecture, i.e., proving it to be a consequence of the dynamics.

3. The generalization of Einstein's conjecture

Recently, Carati et al. [7] showed that there are systems which present qualitative differences between the statistics obtained using the equilibrium distribution and that obtained through the dynamics over a finite time. Considering the dynamics over a finite time of the Jeans–Landau–Teller model, they obtained that the exchanges of energy follow the Lévy type statistics for high enough frequencies. An immediate consequence of this result, based on the Lévy flight random walk [12], is that $\langle \mu_t^2 \rangle$ is infinite.

We notice that in the Carati–Galgani model it is assumed that the oscillators have low energies and the collisions are separated from each other so that the oscillator phases are completely independent. Here, we must be able to answer what happens if the $\langle \mu_t^2 \rangle$ is not finite. In this way, we can no longer write Eq. (7) and, as consequence, Eq. (8) is not valid either.

It is well known that for $\langle \mu_t^2 \rangle \rightarrow \infty$ the theoretical basis is the Lindeberg–Lévy central limit theorem [13]. Since we are considering the case of low energies for the oscillators, using the same steps as that used to obtain Eq. (7), it is straightforwardly verified that

$$\sigma_\epsilon^2 = 2\epsilon_0 \langle \mu \rangle + \epsilon^{(2-\alpha)} \langle \mu^\alpha \rangle \quad 1 \leq \alpha < 2, \quad (9)$$

where ϵ is a constant that has dimension of energy and is suitably chosen by dimensional requirements.

Finally, for N independent identical oscillators, we find

$$\sigma_E^2 = 2\zeta \nu U + \epsilon^{(2-\alpha)} \frac{U^\alpha}{N^{\alpha-1}} \quad (10)$$

which generalizes the dynamics proposal of Einstein and will be our hypothesis to get the generalizations of Einstein's conjecture and Planck's law.

4. Possible relations in equilibrium statistical mechanics

Let us now explore the possibility of existing analogous relations in the equilibrium quantum statistical mechanics of the relations found here using the nonequilibrium classical statistical mechanics approach.

We start the process using Eq. (2) in conformity to Einstein's vision. In this case, using Eq. (10) in Eq. (2) we have

$$-\frac{dU}{d\beta} = 2\zeta \nu U + \epsilon^{(2-\alpha)} \frac{U^\alpha}{N^{\alpha-1}}. \quad (11)$$

It is straightforward to find the energy distribution

$$U = N \left\{ \frac{2\zeta \nu}{\epsilon^{(2-\alpha)} [e^{(\alpha-1)2\zeta \nu \beta} - 1]} \right\}^{\frac{1}{\alpha-1}}, \quad (12)$$

in order that we can consistently rewrite Eq. (12) as

$$\tilde{U} = \frac{H\nu}{(e^{\beta H\nu/d} - 1)^d}. \quad (13)$$

We have introduced $\tilde{U} \equiv \frac{Uz^{d-1}}{N}$, $H \equiv 2\zeta$ and $d \equiv \frac{1}{\alpha-1}$ with $1 \leq d < \infty$. We assumed $\epsilon \propto H\nu$ that leads to the expression $\epsilon = zH\nu$ with z being a pure dimensionless number. For $d = 1$, H coincides with Planck's constant h , and the U associated with the Bose–Einstein quantum statistic is reobtained.

In the same way as the Planck blackbody radiation has its origin in the Bose–Einstein statistics, here obtained using $d = 1$, we can take other values of d so that we can obtain new physical systems in which Eq. (13) may be applied. By following along standard lines, after straightforward calculations, the density of energy per unit volume is obtained as

$$\Omega_d(\nu) = g(\nu)U = \frac{8\pi H\nu^3}{z^{d-1}c^3 [e^{\beta H\nu/d} - 1]^d} \quad (14)$$

where we use the standard density of states of the photons ($g(\nu) = 8\pi\nu^2/c^3$). Fig. 1 presents $\Omega_d(\nu)$ versus energy $H\nu$ for typical values of d and $\beta = 1$. Note that if d increases then $\Omega_d(\nu)$ increases. Although $\Omega_3(0)$ has a finite value for $\nu \rightarrow 0$, it is null for $d < 3$ while it is infinity for $d > 3$ (see inset). Ω_d is significantly modified when d varies. Ω_d are illustrated in Figs. 2 and 3 for, respectively, $d = 2$ and $d = 4$ and various values of β . For d fixed, we note small changes for Ω_d when β varies.

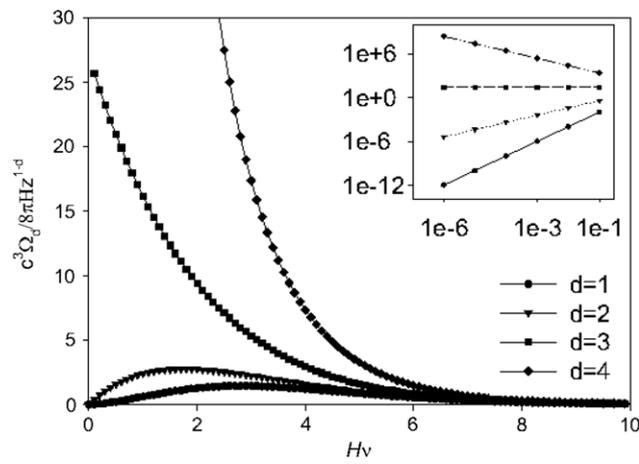


Fig. 1. The density of energy per unit volume versus energy for $d = 1, 2, 3, 4$ and $\beta = 1$. (Inset shows a closeup of part of the graph for $\nu \rightarrow 0$).

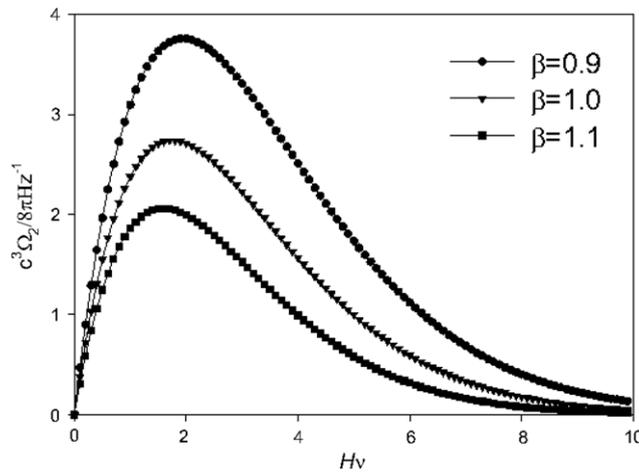


Fig. 2. The density of energy per unit volume versus energy for $\beta = 0.9, 1.0, 1.1$ and $d = 2$.

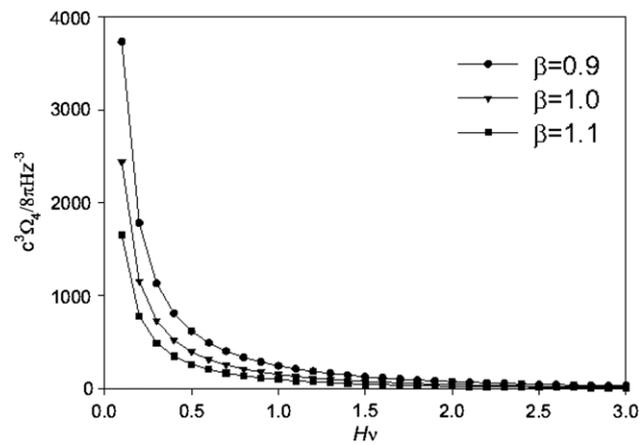


Fig. 3. The density of energy per unit volume versus energy for $\beta = 0.9, 1.0, 1.1$ and $d = 4$.

In the $H\nu\beta \ll 1$ regime

$$\Omega_d(\nu) \sim \frac{8\pi\nu^{3-d}}{(zH)^{d-1}c^3} (dK_B T)^d \tag{15}$$

which generalizes the Rayleigh–Jeans law. The generalization of Wien’s law is obtained in the $H\nu\beta \gg 1$ region

$$\Omega_d(\nu) \sim \frac{8\pi H\nu^3}{z^{d-1}c^3} e^{-\frac{H\nu}{k_B T}}, \quad (16)$$

and the Stefan–Boltzmann law for the total emitted power per unit surface is attained from the usual one, given by $j = \sigma_d T^4$, where the d -dependence is only present in the prefactor σ_d .

5. The Souza–Tsallis generalization from Einstein’s conjecture

Actually, one of the characteristics of Eq. (13) is that it reproduces the results of Souza and Tsallis results [8]. Observe that for $\tilde{U} = H\nu\bar{n}$ we can obtain the particle-number distribution

$$\bar{n} = \frac{1}{(e^{\beta H\nu/d} - 1)^d}. \quad (17)$$

Adopting the formal theory of statistical mechanics, it is straightforward to find the variance of an ensemble of n particles as being

$$\sigma_n^2 = \bar{n} + \bar{n}^\alpha \quad (18)$$

which generalizes the Landau’s relation for bosons [14].

Ref. [8] obtained Eqs. (17) and (18) heuristically based on the nonextensive statistical mechanics [15] and the Beck–Cohen superstatistics [9,10]. They were based on the discussion of the differential equation $dy/dx = -a_1 y - (a_q - a_1) y^\alpha$ (with $y(0) = 1$), whose particular case $\alpha = 2$ corresponds to the Bose–Einstein statistics. Our formalism describes the Souza–Tsallis generalization from Einstein’s dynamical fluctuation viewpoint.

Finally, we see that Eq. (17) can be written as

$$\bar{n} = \sum_{i=0}^{\infty} g(i, d) e^{-\beta E_i}, \quad (19)$$

where we obtain the energy spectrum

$$E_i(d) \equiv \frac{H\nu}{d}(i + d), \quad (20)$$

and its degeneracy

$$g(i, d) \equiv \frac{\Gamma(i + d)}{\Gamma(d) \Gamma(i + 1)}, \quad (21)$$

$\Gamma(x)$ being the gamma function. The spectrum is made of equidistant levels, like that of the quantum harmonic oscillator, with a constant energy difference between successive levels equal to $H\nu/d$.

6. Conclusions

Summarizing, we introduced a generalization of Einstein’s conjecture considering an approach along the line of the Carati–Galgani model of molecular collisions. We obtained Planck’s distribution compatible with Beck–Cohen superstatistics. Furthermore, establishing a metaequilibrium very far from equilibrium for the system studied, and admitting that there are analogous relations in the equilibrium quantum mechanics, we generalized Planck’s law.

For instance, the effects in the quantum radiation theory were theoretically obtained, as a first order approximation, of a classical system very far from equilibrium [4]. We emphasize that we are working with classical models of molecular collisions and not quantum models for blackbody radiation. Understanding the relationship between these two points of view is an open problem.

Finally, note that we do not write anything about the physical conditions that could apply to both the Carati–Galgani model and our generalization. The work of Carati and Galgani [3] leaves some doubt about this issue, making this problem the central discussion of two other works [16,17]. In summary, after the debate, the final conclusion about the validity regime of the theory was essentially based on two assumptions. The first one is that physical systems must be characterized by two well separated time scales. The second one is the appearance of a metaequilibrium state in a time scale. The metaequilibrium state emerges in the short time scale and evolves until it reaches the thermodynamic equilibrium in the larger time scale. Both the Carati–Galgani model and our generalization should be applied in the regime of metaequilibrium [18].

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