On the Law of Equipartition for Translational Motion of Excited Molecules in Equilibrium with Thermal Radiation

B. H. Lavenda and W. Figueiredo *
Università di Camerino, Camerino (MC), 62032 Italy

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Einstein's radiation theory consists of two parts: the derivation of Planck's radiation law from a physical mechanism of absorption and emission of radiation by excited molecules that are in thermal equilibrium with the radiation field and a demonstration of the validity of the law of equipartition of energy for the translational motion of the molecules. Several incongruities are observed: Einstein could not have legitimately substituted back into his dynamical equilibrium condition, valid at any finite temperature, a limiting condition between the coefficients of absorption and stimulated emission that he obtained in the high temperature limit. His justification of the law of equipartition involves, on the one hand, treating the motion of the excited molecule as brownian motion while, on the other hand, employing special relativity to obtain an expression for the diffusion coefficient. In the former the velocity of the molecule is a stochastic variable while in the latter it is a uniform velocity. Hence equipartition does not hold for the translational motion.

In his fundamental paper on the theory of radiation, Einstein [1] eloquently argued that the velocity distribution acquired through the interaction of molecules with a thermal radiation field, in which they are at equilibrium at a temperature T, must be the same as that distribution of the velocities which arises from their mutual collisions. Hence, since the latter distribution is Maxwellian, the average kinetic energy of a molecule (per degree of freedom) will be $\frac{1}{2}kT$. The law of equipartition of energy, he claimed, would be independent of the nature of the molecules and valid no matter what frequency of light is absorbed or emitted by the molecules.

Seven years earlier, in a paper [2] co-authored with Hopf, Einstein expressed his perplexity when he calculated on the basis of the usual electromagnetic theory the momentum fluctuations which are "*by far too small* compared with the *real* momentum fluctuations, if very high frequencies are involved". Although equipartition of energy will certainly not apply to the radiation field, why shouldn't it hold for translatory motion where it was "always brillantly corroborated?", Einstein queried. It seems that in the seven intervening years, he convinced himself that it did.

Basing his model on brownian motion, which served so well in the past to make explicit calculations, Einstein divides the momentum change in a small but finite time interval Δt into two parts: a systematic part $-RMv\Delta t$ representing radiative damping, where R is a constant having units of frequency which he will later evaluate, and a fluctuating momentum $\Delta W(t)$ which represents fluctuations in momtum that are caused by the erratic motion of electric charges in the radiation field. He attributes to this statistically defined term the properties of brownian motion. Consequently, the change in momentum during a short time interval Δt will be [1]

$$M\Delta v = -RMv\Delta t + \Delta W(t). \tag{1}$$

The term $\Delta W(t)$ physically represents the integral of the fluctuating force F over a small time interval Δt,

$$\Delta W(t) = \int_t^{t+\Delta t} F(s)\,\mathrm{d}s. \tag{2}$$

The fluctuating force does not influence the motion, *on the average*, since displacements to the left or right are equally as likely,

$$\bar{F} = 0, \tag{3}$$

while the interval Δt must be sufficiently long to guarantee the statistical independence of the fluctuat-

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* Departamento de Física, Universidade Federal de Santa Catarina, Florianópolis, Brazil.

Reprint requests to Prof. Dr. B. H. Lavenda, Università di Camerino, Via S. Agostino 1, I-62032 Camerino, Italy.

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ing force at the beginning and end of the interval,

$$\overline{F(t)\,F(t+\Delta t)} = 2D\,\delta(\Delta t), \tag{4}$$

where D is a fixed diffusion coefficient. The characteristic feature of brownian motion is therefore

$$\overline{\Delta W^2(t)} = 2D\,\Delta t\,. \tag{5}$$

The limit $\Delta t \to 0$ entails $\sqrt{\overline{\Delta W^2}}/\Delta T \to \infty$, which from a physical point of view is not relevant since when Δt becomes smaller than the elementary radiation processes, the successive momentum transfer become correlated. This correlation is a simple consequence of the law of inertia, and it prevents us from considering the dynamics of the individual processes themselves.

Although this formulation was known to Einstein as far back as 1905, being based on his fundamental investigations on brownian motion [3], he was willing in 1917 in infringe on it to salvage the law of equipartition of energy for translational motion. There are two parts to Einstein's argument. The first part consists in deriving Planck's radiation law from a physical mechanism of absorption and emission of radiation. Transitions between two energy levels, $\varepsilon_j > \varepsilon_i$, will occur through the process of emission. Classically, only spontaneous emission was known, having a rate parameter γ, and Einstein assumed that the probability of finding a molecule in the energy state ε_j was given by classical Boltzmann statistics. But knowing that he had to come out with the Planck radiation law in the end, he had to postulate the presence of an induced or stimulated emission which is proportional to the radiation energy density ϱ with a proportionality constant β representing the coefficient of induced emission. (Classically, it could be argued that induced emission comes from the interaction of charged oscillator and light wave which for certain phases, energy can be transferred from the oscillator to the light wave [4].) Multiplying the rates of spontaneous and induced emission by the probability $\omega_j\,e^{-\varepsilon_j/kT}$ that a molecule will be found in the state ε_j, where ω_j is the statistical weight of the state, Einstein found

$$\text{rate of emission} = \omega_j\,e^{-\varepsilon_j/kT}(\beta\varrho + \gamma)\,. \tag{6}$$

The rate of absorption of energy will be proportional to the radiation energy density with the coefficient of absorption α being the proportionality constant. Then multiplying it by the probability $\omega_i\,e^{-\varepsilon_i/kT}$ that a molecule will be found in the state ε_i, Einstein obtained

$$\text{rate of absorption} = \omega_i\,e^{-\varepsilon_i/kT}\,\alpha\,\varrho \tag{7}$$

In a state of dynamical equilibrium, these transition rates must balance one another,

$$\omega_i\,e^{-\varepsilon_i/kT}\,\alpha\,\varrho = \omega_j\,e^{-\varepsilon_j/kT}(\beta\varrho + \gamma)\,. \tag{8}$$

This dynamical equilibrium condition contains three unknowns, and in order to eliminate one of them so that the other two appeared only in a ratio which could subsequently be compared with Planck's radiation law, Einstein took the high temperature limit in which $\varrho \to \infty$ with temperature. He then concluded that

$$\omega_i\,\alpha = \omega_j\,\beta\,. \tag{9}$$

Quantum mechanics expresses the coefficient of absorption in terms of the matrix element of the square of the oscillator displacement for the transition $i \to j$. Likewise, the coefficients of stimulated and spontaneous emission are expressed in terms of the matrix element of the square of the displacement for the transition $j \to i$. This is dictated by the correspondence principle since classically these quantities are given in terms of the time average of the square of the displacement. Therefore, both in classical and quantum theory the coefficients are independent of the individual states of transition and depend only on the frequency of transition; this necessitates considering equal statistical weights for the endpoints of transition.

Even if (9) were to hold in the limit as $T \to \infty$, it is not permissible to substitute back into an expression, such as (8), which is valid for finite temperatures [5]. But this is precisely what Einstein did, and solving for ϱ he obtained

$$\varrho = \frac{\gamma/\alpha}{e^{(\varepsilon_j - \varepsilon_i)/kT} - 1}\,. \tag{10}$$

Then comparing it to Planck's radiation formula

$$\varrho(\nu, T) = \frac{8\pi\nu^2 V}{c^3}\,\frac{h\nu}{e^{h\nu/kT} - 1}\,, \tag{11}$$

where $8\pi\nu^2 V/c^3$ is the number of oscillators in the frequency range $d\nu$ in a volume V, he obtained

$$\gamma/\alpha = \frac{8\pi\nu^2 V}{c^3}\,h\nu \tag{12}$$

and the Bohr frequency condition

$$h\nu = \varepsilon_j - \varepsilon_i\,. \tag{13}$$

Actually, Planck obtained the relation

$$\varrho(\nu, T) = \frac{8\pi\nu^2 V}{c^3}\,\bar{E}_\nu(T) \tag{14}$$

between the energy density and the average oscillator energy $\bar{E}_\nu$ by considering only the processes of absorption and spontaneous emission, so that (14) is essentially a classical result. Furthermore, the volume of phase space occupied by a classical monatomic gas with momentum in the range dp is $4\pi p^2 \,\mathrm{d}p\, V/h^3$, which gives the correct coefficient in (14) when one sets $p = h\nu/c$ and multiplies by two. The latter is attributed to the two directions of polarization of light. But since Planck considered material oscillators, supposedly in the walls of the cavity, there is really no justification for multiplying by 2. The rate balance law (14) shows that the "particles" possess only kinetic energy although what is being counted are oscillators.

In fact, when we consider the high temperature limit of Einstein's expression of Planck's radiation law (10) and compare it with the Rayleigh-Jeans law, which is obtained by setting the average oscillator energy $\bar{E}_\nu = kT$, we can show that the ratio of the spontaneous emission to absorption coefficient *does* depend on the temperature. The high temperature limit of Planck's radiation law

$$\varrho(\nu, T) = \frac{\gamma}{\alpha}\left(kT - \tfrac{1}{2}h\nu\right), \quad kT \gg h\nu \tag{15}$$

was considered by Einstein and Stern [6] in conjunction with the problem of having to decide between Planck's origin expression

$$\bar{E}_\nu(T) = \frac{h\nu}{e^{h\nu/kT} - 1} \tag{16}$$

and another expression

$$\bar{E}_\nu(T) = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{1}{2}h\nu \tag{17}$$

proposed by Planck [7] in his "second radiation theory". The zero-point energy term in (17) comes from the averaging the mean energy of the oscillators in adjacent ellipses in the phase plane. Unlike (16), expression (17) does give the equipartition result in the high temperature limit, but if it were used in place of expression (16) it would lead anew to the "ultraviolet catastrophy". Hence, we must set (15) equal to the Rayleigh-Jeans law, and when this is done, we get

$$\frac{\gamma}{\alpha} = \frac{8\pi\nu^2 V}{c^3}\,\frac{kT}{kT - \frac{1}{2}h\nu} \tag{18}$$

which is *not* temperature independent.

In the second part of Einstein's theory, he attempts to prove that equipartition of energy is valid for the translational motion of the excited molecules. Writing "d" for "Δ" in (1), which means a "physical infinitesimal" (1) can be formally integrated to give

$$v(t) = v_0\, e^{-Rt} + e^{-Rt}\int_0^t e^{Rs} A(s)\, \mathrm{d}s\,, \tag{19}$$

where $A = F/M$, when it is known that the particle started with the velocity v_0 at time $t = 0$. Averaging (19) with respect to the Wiener transition probability density for the transition from v_0 to v in times t gives

$$\bar{v} = v_0\, e^{-Rt}. \tag{20}$$

Then squaring both sides of (19) and averaging gives

$$\overline{\Delta v^2} \equiv \overline{v^2} - \bar{v}^2 = \frac{kT}{M}\left(1 - e^{-2Rt}\right), \tag{21}$$

where the fact that the average of the random force is zero (3), and the law of equipartition of energy [8]

$$\lim_{t\to\infty} \overline{v^2} = \frac{kT}{M}$$

have been used. For small time intervals, the variance of the velocity distribution (21) becomes

$$\overline{(M\Delta v)^2} = 2RM\, kT\, \Delta t\,. \tag{22}$$

Expression (22) for the mean square fluctuations in the momentum of the brownian particle was arrived at by Einstein in a different way. He considered that the momentum of the particle in a small time interval Δt was given by

$$M\, v(t) - RM\, v(t)\, \Delta t + \Delta\,,$$

where Δ represents the irregularity of the radiation acting on the particle in the small time interval. The change in the momentum during the time interval is given by the second and third terms. He then squares this quantity and requires that, since the velocity distribution must remain invariant in time,

$$\overline{(M\, v(T) - RM\, v(t)\, \Delta t + \Delta)^2} = \overline{(M\, v(t + \Delta t))^2}\,. \tag{23}$$

Then, using the fact that $\overline{v(t)\,\Delta} = 0$ and neglecting terms higher than first order in the time interval he comes out with

$$\overline{\Delta^2} = 2R\,\overline{(M\, v)^2}\, \Delta t \tag{24}$$

provided $\overline{v^2(t)} = v^2(t + \Delta t)$, which he supposes follows from the invariancy of the Maxwell velocity distribution. Evaluating the right side of (24) by invoking the law of equipartition of energy, he arrives at (22). Rather, his condition (23) is equivalent to the small time approximation where the irreversibility of the radiation damping force is still not manifest; the motion of the particle appears as that of a "free" brownian particle.

The next step in his calculation is to calculate the damping coefficient R. If (22) is to coincide with the quantum mechanical result

$$\overline{\Delta^2} = \begin{pmatrix}\text{momentum change in}\\ \text{each elementary process}\end{pmatrix}^2 \times \begin{pmatrix}\text{number of elementary}\\ \text{processes in time } \Delta t\end{pmatrix} = \frac{1}{3}\left(\frac{h\,\nu}{c}\right)^2 \times l,$$

where the factor $\frac{1}{3}$ is due to the fact that a single spatial direction is being considered. It is apparent that the expression for the damping coefficient must contain the factor $(kT)^{-1}$ if equipartition of energy is to hold since l, the number of elementary processes occurring in time Δt, contains $(kT)^{-1}$ only in the form of a Boltzmann factor. With this end in mind, Einstein now considers a transformation of coordinates from a coordinate system K in which the molecule is moving with a *uniform* velocity v to K' in which the molecule is at rest. His aim is to calculate the damping force

$$F = -RM\,v \tag{25}$$

and in so doing identify R. Two points should be borne in mind. First, according to his theory of brownian motion, R is given phenomenologically and cannot be determined from first principles as he is trying to do here. Second, the velocity appearing in (25) cannot be identified with the velocity of the brownian particle which is not a *uniform* velocity but rather a stochastic variable.

For in order to attempt a calculation of the radiative damping coefficient he must transcend the limits of brownian motion and consider the elementary processes of radiation which occur on a time scale much shorter than the time interval Δt which is the smallest time interval that is open to observation in the theory of brownian motion. In the coordinate system K, the radiation energy density $\varrho(\nu)$ is isotropic and can only depend on the frequency of radiation and the temperature. However, Einstein points out that in K', the radiation density $\varrho'(\nu', \phi')$ will, in addition, depend upon the direction in which the molecule radiates. The frame of reference K' moves with the velocity v along a direction making an angle ϕ' with the direction of propagation of the emitted light. The angle ϕ' is, however, completely arbitrary and will vary from one instant to another. Put differently, as far as brownian motion is concerned, the angle ϕ' is as a "hidden" variable which is not open to direct observation and hence does not constitute part of the theory.

Since spontaneous emission takes place without the presence of the radiation field, it has no preferential direction and Einstein does not take it into consideration. Rather, he considers that radiation corresponding to the solid angle $\mathrm{d}\varkappa'$ will, according to the process of absorption, lead *per second* to $\alpha\,\varrho'(\nu', \phi')\,\frac{\mathrm{d}\varkappa'}{4\pi}$ elementary processes of absorption. Arguing that the "time" spent per second in the state i is $(1/Q)\,\omega_i\,e^{-\varepsilon_i/kT}$, where Q is the partition function for the two states, Einstein finds that the number of absorption processes *per second* is

$$\frac{1}{Q}\,\omega_i\,e^{-\varepsilon_i/kT}\,\alpha\,\varrho'(\nu', \phi')\,\frac{\mathrm{d}\varkappa'}{4\pi}\,. \tag{26}$$

Likewise he finds for the number of processes per second due to stimulated emission

$$\frac{1}{Q}\,\omega_j\,e^{-\varepsilon_j/kT}\,\beta\,\varrho'(\nu', \phi')\,\frac{\mathrm{d}\varkappa'}{4\pi}\,. \tag{27}$$

The net momentum transfer to the molecule per second will be the difference between (26) and (27) multiplied by the momentum transferred to the molecule

$$\frac{h\,\nu'}{c}\cos\phi' = \frac{\varepsilon_j - \varepsilon_i}{c}\cos\phi'$$

by the field and averaged over a sphere,

$$\frac{h\,\nu'}{c\,Q}\,\alpha\,\omega_i\,e^{-\varepsilon_i/kT}\,(1 - e^{-h\nu'/kT})\int \varrho'(\nu', \phi')\cos\phi'\,\frac{\mathrm{d}\varkappa'}{4\pi},$$

where Einstein has used his relation between the coefficients of absorption and stimulated emission (9) and the Bohr frequency condition (13).

Employing formulae which are valid to first order in v/c, for the Doppler effect and astronomical abberation from the theory of special relativity [9] together with the formula for the radiation energy in the range $\mathrm{d}\nu'$, measured in a moving system at a uniform velocity v with the radiation energy in the range $\mathrm{d}\nu$, measured in the system at rest, he comes out with the result

$$F = -\frac{(h\,\nu)^2}{c^2\,Q}\,\frac{\varrho}{3kT}\,\alpha\,\omega_i\,e^{-\varepsilon_i/kT}\,v\,, \tag{28}$$

where the frequency ν' has been replaced by ν. Comparing (25) with (28) leads him to the identification of the resistance coefficient R. But the velocity in expression (25) is a stochastic variable while in (28) it is a *uniform* velocity. Hence, the statistical considerations upon which the theory of brownian motion is based are incongruous with the kinematic considerations of special relativity.

Moreover, (26) and (27) cannot be the number of radiative processes per second due to the radiation field since the angle is a random quantity. We have no way of observing the individual radiative processes, and this is precisely the spirit of having introduced the fluctuating momentum term Δ, which in the words of Einstein is due to the irregularity of the action of the radiation field on the molecule. Therefore, since we have no information about the individual, directional, momentum transfers, we must average over all angles in (26) and (27), and then taking their difference gives

$$\frac{\gamma}{1+e^{h\nu/kT}}, \qquad (29)$$

where we have made use of Einstein's dynamic equilibrium condition (8). This is precisely what should be expected since the difference between the rates of absorption and stimulated emission is spontaneous emission. Now expression (29) cannot be multiplied by the elementary momentum transfers, for again they are unknown. All that can be done is to multiply by the stochastic momentum $M\,v$ so that force expression (25) becomes

$$F = -\frac{\gamma}{1+e^{h\nu/kT}}\, M\, v\,, \qquad (30)$$

from which the coefficient of radiative damping can be read off. Introducing it into the expression for the mean square fluctuation in the momentum (24) gives

$$D = \frac{\gamma}{1+e^{h\nu/kT}}\, M\, kT \qquad (31)$$

for the diffusion constant. This is entirely in agreement with the fluctuation-dissipation theorem [10]. Hence, the mean square fluctuation in the momentum which is calculated on the basis of brownian motion and the law of equipartition will not give the same result as the quantum mechanical one. Thus the law of equipartition of energy must be waived for the translational motion of excited molecules which are in thermal equilibrium with the radiation field [11]. Consequently, the equipartition result can not be used in the definition of the diffusion coefficient, and this necessarily implies a modification of the Maxwell velocity distribution for excited molecules which are in thermal equilibrium with a radiation field.

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