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Mechanism of Blackbody Radiation

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The law of error for Bose statistics is not unique; the family of probability distributions differ insofar as zero-point energy is concerned. This is traced back to the spontaneous emission term in the Einstein mechanism of emission and absorption of radiation. It is argued that the spontaneous emission term is unimportant for blackbody radiation and an alternative mechanism is proposed in which thermal equilibrium is secured through a constraint on the number of quanta in any given mode of the radiation field. Both mechanisms predict a modification of the Maxwell velocity distribution at high frequencies and are compared in relation to Doppler broadening and their low-temperature behavior.

1. INTRODUCTION

Einstein's paper on the emission and absorption of radiation constitutes the first attempt to derive Planck's radiation law from a physical mechanism involving the rates of absorption and emission of radiation. The emission process, according to Einstein, consist of two terms. One term is independent of the radiation density present before emission. It describes spontaneous emission and is different from zero even in the case where the average number of photons in the given monochromatic standing wave is zero. This term Einstein attributes to Hertz, who assumed that an "oscillating Planck resonator radiates energy in a well-known way, regardless of whether or not it is excited by external radiation" (Einstein, 1917).

The other term is proportional to the intensity of radiation at the given frequency prior to the emission process. This induced emission process is credited to Einstein, who found it necessary in order to attain thermal equilibrium in a gas emitting and absorbing radiation (Heitler, 1954). The absorption process, like stimulated emission, is proportional to the intensity of radiation.

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Multiplying these rates by the probability of a molecule being in any one of a given number of discrete energy states, which he assumes is given by the classical Boltzmann statistics, Einstein goes on to suppose that in a state of thermal equilibrium, there exists a dynamical equilibrium between the rates of absorption and emission between any two states. In order to eliminate one of the three rate coefficients, Einstein takes the high-temperature limit, from which he concludes that if the statistical weights of the two states are equal, then the coefficients of absorption and induced emission are equal. Reintroducing this expression into the dynamical equilibrium condition, he obtains Planck's radiation law together with the Bohr frequency condition. The derivation can be criticized on the basis that the equivalence between the coefficients of absorption and stimulated emission is an asymptotic one, as the temperature increases without limit, and that it cannot be introduced into an expression which is supposed to be valid at *any* finite temperature (Lavenda, 1989).

Although Planck's radiation law can be derived from such a mechanism of absorption and emission of radiation by excited molecules, is the mechanism unique and is it the mechanism responsible for the blackbody radiation spectrum? Planck's radiation law concerns only the thermal part of the energy density of radiation at a given frequency. The total energy density of radiation consists of a thermal part and a contribution from an external source of electromagnetic radiation. The regions in which the thermal part will be dominant can be discerned from Planck's radiation law and interpreting the density of modes in terms of the ratio of the spontaneous to the stimulated coefficients of emission (e.g., Loudon, 1983). The boundary occurs where stimulated and spontaneous emission will be approximately equal; at room temperature, the radiation will have a wavelength of $\lambda \approx 50\ \mu\text{m}$, corresponding to a frequency of about 6×10^{12} Hz, which is in the far-infrared region. For frequencies small (large) compared to this frequency, the stimulated emission rate is much larger (smaller) than the spontaneous emission rate. As far as the thermally excited energy density is concerned, it will be nonnegligible through the infrared region of the spectrum at room temperature, where the spontaneous emission rate is much smaller than the rates of thermally-stimulated emission or of absorption of thermal radiation.

Therefore, spontaneous emission does not appear to be an important mechanism in the region of the spectrum where the thermally excited energy density is the dominant contribution to the total energy density of radiation. Yet according to Einstein's mechanism, spontaneous emission, which is different from zero even if the average number of photons in a given mode of the field is zero, appears to be necessary in order to achieve thermal equilibrium in a cavity filled with radiation. The question is whether spontaneous emission can or cannot be replaced by another term in the rate equation so that thermal equilibrium can be secured in that part of the spectrum where the thermal contribution to the energy density is nonnegligible.

Is the picture of an excited molecule or charged "resonators" in the walls of the cavity applicable to the study of blackbody radiation? Since atomic excited states in the optical frequency region have negligible thermal populations at room temperature, one must either increase the temperature or use an external source whose frequency satisfies the resonance condition for the transition. Excited molecules hardly seem to be adapted to describe the processes of absorption and emission of blackbody radiation.

In this paper we propose a different mechanism of blackbody radiation that does not involve spontaneous emission but rather involves the constraint that the absorption process leaves a finite number of quanta in the mode of the field at the given frequency. This constraint formally behaves as a spontaneous emission term in securing equilibrium while differing from Einstein's mechanism by a zero-point energy. We discovered such a mechanism from the fact that the law of error for Bose statistics is not uniquely given by the negative binomial distribution, as the binomial distribution is the unique law of error for Fermi statistics (Lavenda, 1988). Rather, there is a family of distributions, geometric, Pascal, and negative binomial, all of which are laws of error for Bose statistics, but differing in the presence or absence of a zero-point energy.

2. THE QUESTION OF THE ZERO-POINT ENERGY

The binomial distribution is the *unique* law of error for which the mean value and most probable value give the Fermi "distribution" (i.e., the average number as a function of the temperature and frequency). However, there is a family of probability distributions which are laws of error that give the Bose distribution as the most probable and average value of the distribution. We have previously derived Bose statistics from the negative binomial distribution and the second law but, if we set the number of states equal to one, then it becomes the geometric distribution. In fact, this constitutes the simplest derivation of Bose statistics in which one assumes that the probability of occupying the state is independent of the number of particles already in this state, so that the probability distribution $f_{\mathrm{G}}^{s}(n) \propto q^{n}$, where the unknown parameter $q \in [0, 1]$ (Landsberg, 1959). The normalizing factor is easily found to be $p = 1 - q$, so that the distribution

$$f_{\mathrm{G}}^{s}(n; q) = pq^{n} \tag{1}$$

is the geometric distribution, which depends upon the parameter q. The maximum likelihood estimate of this parameter is the solution to the likelihood equation

$$\frac{\partial}{\partial q}\log f_G^s = -\frac{1}{1-q}+\frac{n}{q}=0 \tag{2}$$

which gives $q=n/(1+n)$. However, the value of n is not arbitrary, but rather coincides with its average value $\bar{n}=q(1-q)\sum_{n=1}^{\infty} nq_{n-1}$, so that the geometric distribution (1) becomes

$$f_G^s(n;\bar{n})=\frac{\bar{n}^n}{(1+\bar{n})^{n+1}} \tag{3}$$

when the maximum likelihood value of the parameter q is introduced.

The quantity f_G^s is the probability of observing the value n, whose true value we know to be $\bar{n}$. The most general form of such a law of error for which the most probable value is equal to the mean of the distribution is (Lavenda, 1988)

$$\log f^s(n;\bar{n})=\varphi'(\bar{n})(n-\bar{n})+\varphi(\bar{n})+\psi(n) \tag{4}$$

The connection with statistical thermodynamics is made by setting the normalization condition

$$\sum_n \exp\{n\varphi'(\bar{n})+\psi(n)\}=\exp\{\bar{n}\varphi'(\bar{n})-\varphi(\bar{n})\} \tag{5}$$

equal to one of the moment generating functions of statistical mechanics. Since it is essential that the particle number vary, we must be working in a grand canonical ensemble for which

$$\varphi(\bar{n})-\varphi'(\bar{n})\bar{n}=-PV/kT \tag{6}$$

where PV is the grand canonical potential, k is Boltzmann's constant, and T is the absolute temperature. From the property of Massieu functions, the potential φ can be identified with the negative of the *statistical* entropy, since

$$\begin{aligned}\mathcal{S}\left[\frac{1}{T},\frac{\mu}{T},V\right]&=\mathcal{S}(\bar{n})-\left(\frac{\partial\mathcal{S}}{\partial\bar{n}}\right)_V\bar{n}\\&=\mathcal{S}(\bar{n})-\left(\frac{\partial\mathcal{S}}{\partial\bar{\mathscr{E}}}\right)_{\bar{n},V}\bar{\mathscr{E}}-\left(\frac{\partial\mathcal{S}}{\partial\bar{n}}\right)_{\bar{\mathscr{E}},V}\bar{n}\\&=\mathcal{S}(\bar{n})-\frac{1}{T}\bar{\mathscr{E}}+\frac{\mu}{T}\bar{n}=\frac{PV}{T}\end{aligned} \tag{7}$$

The form of the logarithm of the moment generating function in (6) could have been achieved by minimizing the "discrimination information" (Kullback, 1968)

$$\varphi(\bar{n}) = \sum_n f^s(n;\bar{n}) \log\left(\frac{f^s(n;\bar{n})}{e^{\psi(n)}}\right)$$

subject to the constraints that $\sum_n nf^s(n;\bar{n}) = \bar{n}$ and $f^s(n;\bar{n})$ is normalized. Although both the minimization of the discrimination information statistic subject to the imposed constraints and Gauss' principle lead to probability distributions which belong to exponential families, Gauss' principle does not make use of constraints and the identification of the system is made by specifying the moment generation function.

With the identification made in (7), Gauss' law of error (4) leading to the average value as the most probable value becomes

$$\begin{aligned} f^s(n;\bar{n}) &= \exp\left\{\frac{-1}{k}[\chi(n-\bar{n}) + \mathcal{S}(\bar{n}) - \mathfrak{S}(n)]\right\} \\ &= \frac{\exp\{-[\chi n - \mathfrak{S}(n)]/k\}}{\Xi(1/T, \mu/T, V)} \end{aligned} \tag{8}$$

where $\Xi = \exp(PV/kT)$ is the moment generating, or grand partition, function and

$$\chi = \left(\frac{\partial\mathcal{S}}{\partial\bar{n}}\right)_V = \left(\frac{\partial\mathcal{S}}{\partial\bar{n}}\right)_{\bar{\mathscr{E}},V} + \left(\frac{\partial\mathcal{S}}{\partial\bar{\mathscr{E}}}\right)_{\bar{n},V}\varepsilon = -\frac{\mu}{T} + \frac{\varepsilon}{T} \tag{9}$$

is the thermodynamic force, where μ is the chemical potential and the average energy $\bar{\mathscr{E}}$ is related to the average number of particles $\bar{n}$ according to $\bar{\mathscr{E}} = \bar{n}\varepsilon$, so that ε is the energy per particle.

In expression (8), we have set ψ equal to the *stochastic* entropy

$$\mathfrak{S}(n) = k \log \Omega(n) \tag{10}$$

where $\Omega(n)$ is known in statistical mechanics as the "structure" function (Khinchin, 1949). In probability theory, $\Omega(n)$ represents the *prior* distribution, which is converted into the *posterior* distribution $f^s(n;\bar{n})$ through observations made on the random quantity n. In this interpretation, $\bar{n}$ would be the arithmetic mean of the measurements, which we have assumed equal to the mean of the distribution (McBride, 1968). This is rigorously so when the number of observations increases without limit.

According to Greene and Callen (1951), there is a fundamental theorem in statistical mechanics, "rooted in the enormously high dimensionality of the phase spaces," to the effect that the statistical entropy $\mathcal{S}$ is the same function of $\bar{n}$ as the stochastic entropy $\mathfrak{S}$ is of n. Otherwise, they claim, there would be a separate thermodynamics for each of the ensembles in statistical mechanics.

Applying the foregoing results to the geometric distribution (3), the statistical entropy is found to be (Lavenda, 1988)

$$S_G(\bar{n}) = k\{(1+\bar{n})\log(1+\bar{n}) - \bar{n}\log\bar{n}\} \tag{11}$$

while the stochastic entropy vanishes. The thermodynamic force (9), equating the derivative of the statistical entropy with that of the thermodynamic entropy, then gives

$$k\log\left(\frac{1+\bar{n}}{\bar{n}}\right) = \frac{\varepsilon-\mu}{T}$$

which, when rearranged, is easily seen to be the Bose distribution

$$\bar{n} = 1/[e^{(\varepsilon-\mu)/kT} - 1] \tag{12}$$

Apparently, the Greene-Callen principle does not apply, since the stochastic entropy vanishes. Furthermore, the statistical entropy (11) has lost the property of extensivity, since the structure function (10) has shrunk to unity, which implies a uniform prior distribution.

In regard to blackbody theory, the resonator energy $\bar{\mathscr{E}}$ is obtained by multiplying (12), with $\mu \equiv 0$, by $\varepsilon = h\nu$. It is related to the equilibrium field energy $\rho = m\bar{\mathscr{E}}$, where $m\,d\nu = 8\pi\nu^2 V\,d\nu/c^3$ is the number of modes in a volume V in the frequency interval $d\nu$ (Planck, 1900). But if there were two separate entities, then the entropy of the resonators would approach zero for values of $\bar{n}$ large in comparison to unity, while the entropy of the field would remain finite. Einstein's (1917) argument applies to the entropy of radiation, where he concluded that for large values of ν/T it displays particle, rather than wave, characteristics.

The entropy per oscillator which is derived from the negative binomial distribution is

$$s_{\mathrm{NB}}(\bar{n}) = \left(1+\frac{\bar{n}}{m}\right)\log\left(1+\frac{\bar{n}}{m}\right) - \frac{\bar{n}}{m}\log\frac{\bar{n}}{m} \tag{13}$$

where $s_{\mathrm{NB}} = \mathscr{S}_{\mathrm{NB}}/m$. Working backward, we construct the corresponding distribution according to Gauss' law of error (4) as

$$f^s(n;\bar{n}) = \frac{(\bar{n}/m)^{n/m}}{(1+\bar{n}/m)^{1+n/m}}\,\frac{(1+n/m)^{1+n/m}}{(n/m)^{n/m}} \tag{14}$$

which is the negative binomial distribution per oscillator, $f^s_{\mathrm{NB}} = (f^s)^m$. For $m = 1$, it does not reduce, however, to the geometric distribution (3).

An immediate generalization of the geometric distribution pq^{n-1} is the Pascal distribution

$$f_{\mathrm{P}}^{s}(n;q)=\binom{n-1}{m-1}p^{m}q^{n-m}, \qquad n=m, m+1, \ldots \tag{15}$$

where m must be an integer, which need not be the case for the negative binomial distribution. In fact, the normalization of the Pascal distribution is guaranteed because (15) is p^m times the $(n-m+1)^{\text{th}}$ term in the series expansion of $(1-q)^{-m}$ in powers of q; namely,

$$\begin{aligned}(1-q)^{-m} &= \sum_{n=0}^{\infty}\binom{-m}{n}(-q)^{n}\\ &= \sum_{n=0}^{\infty}\binom{m+n-1}{n}q^{n}\\ &= \sum_{n=m}^{\infty}\binom{n-1}{m-1}q^{n-m}\end{aligned} \tag{16}$$

In fact, the Pascal distribution (15) is closely related to the negative binomial distribution

$$f_{\mathrm{NB}}^{s}(n;q)=\binom{m+n-1}{m-1}p^{m}q^{n} \tag{17}$$

The Pascal distribution (15) is usually interpreted in probability theory as giving the probability that n repetitions are needed in order that an event has occurred m times. The negative binomial distribution (17), on the other hand, gives the probability that there will be exactly n trials prior to the occurrence of the m^{th} event. The coefficient in the negative binomial distribution (17) has been interpreted by Ehrenfest and Kamerlingh Onnes (1914) to be the number of distinguishable distributions of n "energy grades" among m "oscillators". The number of distinguishable distributions in which no cell remains empty is given by the binomial coefficient appearing in the Pascal distribution (15). It will be seen that the requirement that each cell be occupied by at least one particle is reponsible for the so-called "zero-point" energy.

Both the negative binomial, (17), and Pascal, (15), distributions can be written in the form of Gauss' law of error (4), where

$$\mathscr{S}_{\mathrm{NB/P}}(\bar{n})=k\{\pm(\bar{n}\pm m)\log(\bar{n}\pm m)\mp\bar{n}\log\bar{n}-m\log m\} \tag{18}$$

and

$$\mathfrak{S}_{\mathrm{NB/P}}(n)=k\{\pm(n\pm m)\log(n\pm m)\mp n\log n-m\log m\} \tag{19}$$

are the statistical and stochastic entropies of the two distributions, respectively. The statistical entropies give rise to two thermal distributions which differ by a zero-point energy. Invoking the second law to the entropy of the negative binomial distribution gives

$$\left(\frac{\partial \mathcal{S}_{\mathrm{NB}}}{\partial \bar{n}}\right)_V = k \log\left(\frac{m+\bar{n}}{\bar{n}}\right) = \frac{\varepsilon-\mu}{T} \tag{20}$$

or

$$\bar{n} = m/[e^{(\varepsilon-\mu)/kT} - 1] \tag{21}$$

while the same law applied to the entropy of the Pascal distribution results in

$$\left(\frac{\partial \mathcal{S}_{\mathrm{P}}}{\partial \bar{n}}\right)_V = k \log\left(\frac{\bar{n}}{\bar{n}-m}\right) = \frac{\varepsilon-\mu}{T} \tag{22}$$

or

$$\bar{n} = m\{1/[e^{(\varepsilon-\mu)/kT} - 1] + 1\} \tag{23}$$

It is quite remarkable that whereas both the negative binomial and Pascal distributions describe boson statistics, the lack of uniqueness is directly related to the absence or presence of a zero-point energy. The distinction between the two distributions can be discussed in terms of the variances of the distribution. Differentiating (20) a second time, we find the dispersion to be given by

$$\sigma_\infty^2 = -k\left(\frac{\partial^2 \mathcal{S}_{\mathrm{NB}}}{\partial \bar{n}^2}\right)_V^{-1} = \frac{\bar{n}}{m}(m+\bar{n}) \tag{24}$$

while (22) yields

$$\sigma_\infty^2 = -k\left(\frac{\partial^2 \mathcal{S}_{\mathrm{P}}}{\partial \bar{n}^2}\right)_V^{-1} = \frac{\bar{n}}{m}(\bar{n}-m) \tag{25}$$

The variance of the negative binomial distribution (24) can be interpreted as a sum of two independent contributions, one arising from the particle nature of bosons and the other from the wave nature (Einstein, 1909). For photons with frequencies much greater than kT/h, $\bar{n}/m \ll 1$, so that the second term is negligible in (24) with respect to the first term. In this limit, the negative binomial distribution transforms into the Poisson distribution (Lavenda, 1988); the field contribution has vanished and what subsists is characteristic of the particle nature of light. In terms of Einstein's theory of radiation, the particle nature corresponds to spontaneous emission, while the wave or field contribution is represented by stimulated emission.

Although the variance of the Pascal distribution (25) is numerically equal to the negative binomial variance (24), the decomposition of the variance into particle and wave components is no longer possible. And, in fact, it indicates a variation of the Einstein radiation mechanism, as we shall now describe.

3. AN ALTERNATIVE RADIATION MECHANISM

Radiation is introduced into a cubical volume V with ideally reflecting walls. We impose the condition that each stationary mode must contain at least m quanta. Let n ($\geq m$) be the total number of quanta in a stationary wave of frequency ν. Photons are absorbed by minute blackbodies, such as a few particles of ideal coal dust placed in the cavity, at a rate $\alpha(n-m)$ and are reemitted at a rate βn. In comparison to Einstein's radiation mechanism (Einstein, 1917), the rate of absorption is αn, while the rate of (stimulated + spontaneous) emission is $\beta n + \gamma$.

Although both the negative binomial and Pascal distributions yield Bose statistics, there is a clear distinction in the interpretation of the parameter m. In the negative binomial distribution, m represents the number of standing waves or "cells" whose frequency lies in a given interval, while, in the Pascal distribution, m represents the minimum number of photons that must be in each monochromatic standing wave.

The master equation describing the process is

$$\dot{f}(n) = \{\alpha(\mathbb{E}-1)(n-m) + \beta(\mathbb{E}^{-1}-1)n\}f(n) \tag{26}$$

where the step operator $\mathbb{E}$ acts to give $\mathbb{E}f(n) = f(n+1)$ and $\mathbb{E}^{-1}f(n) = f(n-1)$. The step operator possesses the property that (e.g. van Kampen, 1981)

$$\sum_{n=m} g(n)\mathbb{E}f(n) = \sum_{n=m+1} f(n)\mathbb{E}^{-1}g(n)$$

The stationary probability distribution which satisfies $\alpha(n-m)f^s(n) = \beta\mathbb{E}^{-1}nf^s(n)$ is easily seen to be

$$f^s(n) = \binom{n-1}{m-1}\left(\frac{\alpha-\beta}{\alpha}\right)^m\left(\frac{\beta}{\alpha}\right)^{n-m} \tag{27}$$

which is the Pascal distribution (15) with $q = \beta/\alpha$. Furthermore, from the fact that

$$\left(\frac{\partial \mathcal{S}_{\mathrm{P}}}{\partial \bar{n}}\right)_V = k \log \frac{\alpha}{\beta} \tag{28}$$

and the second law, we obtain in the case of photons in the mode with frequency ν that

$$\frac{\beta}{\alpha} = e^{-h\nu/kT} \tag{29}$$

The average equation of motion,

$$\dot{\bar{n}} = \beta\bar{n} - \alpha(\bar{n} - m) \tag{30}$$

is obtained by multiplying the master equation (26) by n and summing over all $n \geq m$. The stationary solution to (30) is

$$\bar{n} = \frac{\alpha m}{\alpha - \beta} = \frac{m}{1 - e^{-h\nu/kT}} \tag{31}$$

where the consequence of the second law (29) ensures that the absorption coefficient is greater than the coefficient of stimulated emission. In the high-frequency limit, $\bar{n} \to m$, while in the low-frequency limit, $\bar{n} \to mkT/h\nu$.

The equation of motion for the variance $\sigma^2 = \overline{(n - \bar{n})^2}$ is

$$\tfrac{1}{2}\dot{\sigma}^2 = -(\alpha - \beta)\sigma^2 + \tfrac{1}{2}\alpha(\bar{n} - m) + \tfrac{1}{2}\beta\bar{n} \tag{32}$$

The asymptotic stationary value of the variance is found to be

$$\sigma_\infty^2 = \alpha\beta m/(\alpha - \beta)^2 \tag{33}$$

which is seen to coincide with expression (25) when (33) is evaluated with the aid of the asymptotic expression for the mean value, (31). In the diffusion approximation, the diffusion coefficient in the particle number is defined as

$$D_{\mathrm{P}} \equiv \tfrac{1}{2}\{\alpha(\bar{n} - m) + \beta\bar{n}\} = \alpha m/(e^{h\nu/kT} - 1) \tag{34}$$

which is precisely the last two terms in (32).

4. A MODIFIED MAXWELL DISTRIBUTION FOR BLACKBODIES

Einstein's (1917) derivation of the Planck radiation law was motivated in large part by Wien's (1896) original argument leading from the Maxwell velocity distribution

$$f^s(v)\,dv = \left(\frac{1}{2\pi\Theta}\right)^{1/2} e^{-v^2/2\Theta}\,dv \tag{35}$$

for the number of molecules in the velocity range dv, where v is the velocity in a single direction, to his "chromatic" distribution function. Parenthetically, we may add that Maxwell's (1860) original derivation of his velocity distribution was both stimulated and based upon the law of errors which is a function of the error only, and for which positive and negative errors are equally probable. Viewed in these terms, the derivation of the statistical distributions in Section 2 is a generalization of the law of errors to Bose statistics.

Wien set the constant Θ in (35) proportional to the absolute temperature on the strength of the equipartition law. Then he considered the wavelength of radiation λ emitted by any molecule to be a function of its velocity. Inverting this unknown dependence between λ and v and assuming that the energy density of the field is proportional to the number of molecules radiating in the range $d\lambda$, Wien obtained $\rho(\lambda, T) = g(\lambda)\exp[-h(\lambda)/T]$, where g and h are two unknown functions. But from his previous work, Wien knew that ρ had to be of the form $\lambda^{-5}\phi(\lambda T)$, where the function ϕ depends only on the product λT. Setting the two expressions equal to one another, he came out with $\rho(\lambda, T) = a\lambda^{-5}\exp(-b/\lambda T)$, where a and b are adjustable parameters. Wien actually employed the law of equipartition of energy for *translatory* motion, while his distribution law is in contradiction with the Rayleigh–Jeans result, which is a direct consequence of the law of equipartition of energy as applied to the *vibrational* modes of electromagnetic radiation.

We now consider the physical processes involved in establishing a type of Maxwell distribution without imposing the law of equipartition for translational motion. It was already clear from the work of Einstein and Hopf (1910) that the law of equipartition failed even in the case of the translatory motion in blackbody radiation. The fact that the law of equipartition of energy breaks down even for translational motion will be seen to be related to the fact that the average kinetic energy of the Brownian particle is related to the average oscillator energy [cf. equation (41) below].

The Einstein–Hopf analysis dealt with oscillators that are free to move and oscillate only in a single direction. Their argument was based on Brownian motion of a system with two degrees of freedom, although they considered only fluctuations in the momentum caused by the emission and absorption of radiation. Damping results from the process of emission, while the process of absorption of radiation creates a residual acceleration that is caused by fluctuations in the impinging radiation and give rise to a radiation pressure.

The velocity space diffusion coefficient is obtained by multiplying (34) by $h\nu$. We then obtain

$$\mathcal{D}_{\mathrm{P}} = \alpha m h\nu/(e^{h\nu/kT} - 1) \tag{36}$$

which is a prototype of a fluctuation-dissipation relation (Lavenda, 1985). The diffusion coefficient is proportional to the mean square displacement in the velocity over a short but finite time interval and the term αm is related to the dissipation. This formula applies even when there is only one Brownian particle.

In the low-frequency limit, it reduces to the Einstein formula

$$\mathscr{D}_{\mathrm{P}} = \eta kT/M \tag{37}$$

if we identify αm with η/M, where M is the mass of a Brownian particle and η has dimensions of a frequency which is proportional to the viscosity coefficient. The diffusion coefficient, in the case of gases, is directly proportional to the viscosity, which explains the fact that the viscosity of a gas increases when the temperature is raised (e.g., Frenkel, 1946).

The term αm has the same role here that the coefficient of spontaneous emission has in Einstein's theory of radiation (Lavenda, 1989). There, the coefficient of radiation damping is the linewidth at half-maximum, which is just equal to the total spontaneous transition probability per unit time (Heitler, 1954, p. 33). If αm plays the same role as the radiation damping coefficient, then in a state of dynamical equilibrium the "damping" force

$$\mathscr{F} = -(\alpha m)Mv \tag{38}$$

is balanced at each instant in time by an "osmotic" pressure force originating in the statistical fluctuations of the radiation pressure. The dynamical equilibrium condition is

$$\mathscr{F}_{\mathrm{P}} = \mathscr{D}_{\mathrm{P}} \frac{\partial \log f^{s}_{\mathrm{P}}}{\partial v} \tag{39}$$

With the diffusion coefficient given by (36) and the damping force by (38), the stationary probability density must be given by

$$f^{s}_{\mathrm{P}}(v)\, dv = \left\{\frac{M[\exp(h\nu/kT)-1]}{2\pi h\nu}\right\}^{1/2} \exp\left\{-\frac{Mv^2}{2h\nu}\left[\exp\left(\frac{h\nu}{kT}\right)-1\right]\right\} dv \tag{40}$$

The average kinetic energy of the Brownian particle is just one-half as great as the average oscillator energy at the same temperature,

$$M\overline{v^2} = h\nu/(e^{h\nu/kT}-1) \tag{41}$$

since the average motion is in one direction while the radiation is traveling in both directions.

In contrast to (36), the diffusion coefficient in the Einstein (1917) mechanism is

$$\mathscr{D}_{\mathrm{NB}} = \gamma h\nu/(1-e^{-h\nu/kT}) \tag{42}$$

where γ is the coefficient of spontaneous emission. With the damping force

$$\mathscr{F}_{\mathrm{NB}} = -\gamma Mv \tag{43}$$

the condition of dynamical equilibrium, $\mathscr{F}_{\mathrm{NB}} = \mathscr{D}_{\mathrm{NB}}\, \partial \log f^s_{\mathrm{NB}}/\partial v$, yields the stationary distribution

$$f^s_{\mathrm{NB}}(v)\, dv = \left\{\frac{M[1-\exp(-h\nu/kT)]}{2\pi h\nu}\right\} \exp\left\{-\frac{Mv^2}{2h\nu}\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right]\right\} dv \tag{44}$$

Consequently, according to Einstein's radiation mechanism, twice the average kinetic energy is given by the expression

$$M\overline{v^2} = h\nu/(1-e^{-h\nu/kT}) \tag{45}$$

instead of (41).

The difference between (41) and (45) lies in the presence of the zero-point energy $h\nu$ in the latter expression. In contraposition, the average energy of the field at frequency ν is

$$\bar{\mathscr{E}}_{\mathrm{P}} = \bar{n}h\nu = mh\nu\{1/(e^{h\nu/kT}-1)+1\} \tag{46}$$

for the Pascal distribution while

$$\bar{\mathscr{E}}_{\mathrm{NB}} = \bar{n}h\nu = mh\nu/(e^{h\nu/kT}-1) \tag{47}$$

for the negative binomial distribution. Therefore, if the zero-point energy is absent in the expression for twice the average kinetic energy of the particle, it is found in the field and vice versa. The effect of the zero-point energy can be discerned most easily in the case of Doppler broadening.

Atoms in a gas at temperature T have a spread in their velocities which through the Doppler effect produce a corresponding distribution in the frequencies at which they can absorb or emit light. If light is emitted, say in the x direction, then the line will be shifted by an amount

$$\Delta\nu = \nu_0 v/c$$

where ν_0 is the frequency that an atom would absorb if it were at rest before and after absorption. It usually assumed (Heitler, 1954, p. 187) that the vecloties are distributed according to the Maxwell distribution (35) with $\Theta = kT/M$, so that the probability distribution, proportional to the intensity, will be given by

$$f^s_{\mathrm{C}}(\nu)\, d\nu = (M/2\pi kT)^{1/2} \exp(-Mc^2\Delta\nu^2/2\nu_0^2 kT)\, d\nu \tag{48}$$

Thus, the full-width of the Doppler-broadened line at half-maximum is

$$\delta_{\mathrm{C}} = \nu_0\left(\frac{2kT}{Mc^2}\log 2\right)^{1/2} \tag{49}$$

according to classical theory. However, if we do not assume equipartition, we obtain

$$\delta_{\mathrm{P}} = \nu_0 \left\{ \left(\frac{2h\nu}{Mc^2} \right) \log 2 \cdot \frac{1}{e^{h\nu/kT} - 1} \right\}^{1/2} \tag{50}$$

or

$$\delta_{\mathrm{NB}} = \nu_0 \left\{ \left(\frac{2h\nu}{Mc^2} \right) \log 2 \cdot \frac{1}{1 - e^{-h\nu/kT}} \right\}^{1/2} \tag{51}$$

depending upon whether the Pascal, (40), or negative binomial, (44), velocity distribution were used, respectively, instead of the Maxwell distribution (48).

The breadths at half-maximum predicted by the three distributions are reported in Table I for the typical values $h\nu/2Mc^2 \approx 10^{-9}$ and $v/c \approx 10^{-5}$. For a rest mass of $Mc^2 \approx 1.5 \times 10^{-10}$ J, this corresponds to a wavelength of visible light between red and orange. It is apparent that the Pascal distribution cannot account for Doppler line broadening. If $\nu \ll kT/h$ could be reached, all three line breadths would coincide with the classical breadth based on the law of equipartition. In the opposite limit $\nu \gg kT/h$, the line breadth resulting from the negative binomial distribution becomes independent of the temperature, which, at room temperature, occurs in the lower part of the visible portion of the spectrum, as indicated in Table I. It predicts a square root dependence on the frequency of the external light source, independent of the temperature, whereas the classical line breadth predicts a square root of the temperature, independent of the frequency. At higher frequencies, the line shift predicted by the negative binomial distribution would be an order of magnitude greater than that predicted classically.

According to kinetic theory, the pressure of a gas is given by

$$p = \tfrac{1}{3} m M \overline{v^2} \tag{52}$$

where m is the number of modes in the interval $d\nu$ in the negative binomial distribution, or the minimum number of quanta in any mode of the electromagnetic field in the case of the Pascal distribution. In terms of the

Table I. Line Breadths at Half-Maximum Predicted by the Three Distributions

T(K)	λ(nm)	$h\nu_0/kT$	$\delta_{\mathrm{C}}/\nu_0$	$\delta_{\mathrm{P}}/\nu_0$	$\delta_{\mathrm{NB}}/\nu_0$
300	666	72	6.2×10^{-6}	10^{-20}	5.3×10^{-5}
1600	666	13.5	1.4×10^{-5}	6.2×10^{-8}	5.3×10^{-5}

average energy of the field per unit volume at a given frequency, expression (52) can be written as

$$p = \tfrac{1}{3}\bar{\mathscr{E}}_{\text{par}} \tag{53}$$

which is the expression for a photon gas or an extreme relativistic electron gas where the average particle energy $\bar{\mathscr{E}}_{\text{par}} = M\overline{v^2}$. It is usually attributed to the fact that there is a linear relation between energy and momentum as opposed to the classical, or quasiclassical, case, where the energy is proportional to the square of the momentum (Landau and Lifshitz, 1969). This can also be understood in terms of the difference of the number of degrees of freedom between a particle with one degree of freedom as opposed to a wave with two degrees of freedom. In the particle–wave duality, the average energy must be twice the average kinetic energy in order to account for the missing degree of freedom in the particle description.

If equipartition of energy were to apply, then the pressure would tend to zero with the temperature. In Bose statistics, the value of the gas pressure becomes less than the classical value as the temperature is lowered. This is interpreted as an effective "attraction" between the particles. Now, in the case of the Pascal distribution, the pressure is given by

$$p_{\mathrm{P}} = \tfrac{1}{3} h\nu m e^{-h\nu/kT} \tag{54}$$

at low temperatures, which corroborates this tendency of the particles to attract one another. At absolute zero, all the particles are in their lowest quantum state with no momentum and consequently make no contribution to the pressure. In contradistinction, the negative binomial distribution would predict that

$$p_{\mathrm{NB}} = \tfrac{1}{3} h\nu m \tag{55}$$

which resembles more a Fermi gas having a nonzero energy at absolute zero. This would give rise to a molecular agitation at absolute zero Kelvin, which would be foreign to the usual behavior of a Bose gas which undergoes condensation in momentum space, for it would predict that there would always be a finite number of molecules in higher energy states.

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