STATIC AND DYNAMIC DERIVATION OF RADIATIVE EQUILIBRIUM

E. C. G. SUDARSHAN

Centre for Theoretical Studies, Indian Institute of Science, Bangalore 560012

Abstract : There are two methods for deriving the equilibrium thermodynamics of a system. One of them is static and involves the computation of the partition function and used by Gibbs for classical systems and later on used by Planck, by Bose, and followed by Einstein and Fermi. The other method is dynamic and involves the use of transition processes and a dynamic equilibrium that is achieved as a result of this. The Classical approach is due to Boltzmann and it was extended to the treatment of radiation by Einstein for the special case of a Bohr atom. function

In his "second paper" Bose treated the general case of radiative equilibrium. A treatment of this kind enables us to learn of the relationship of radiative transition rates to the rates for the inverse reaction. We shall briefly discuss the "phase" model implicit in Bose's paper and its relation to quantum mechanics.

We will also briefly discuss certain radiative equilibrium models to show the role of conservation laws and the full quantum treatment of the dynamic method.

INTRODUCTION :

LIGHT appears in a heated cavity : higher the temperature, more is the light. To the extent that the cavity is such that radiation neither leaves the cavity nor enters it, the equilibrium radiation density and its spectral distribution is dependent only on the temperature, it is independent of both the materials inside or lining the cavity as well as of the mechanism of interaction of radiation and matter. Because of this universability we are able to compute the equilibrium radiation distribution in terms of any postulated mechanism : and it must be verified that it yields the same result for any other mechanism. It is universal : universality

Yadāditya gatam tejo
jagat bhāsayatekhilam
Yacchandramasi Yacchagno
tattejo viddhi māmakam (XV, 12)[1]

There are two classes of derivation : One makes use of static properties and seeks the statistical state with the maximum entropy consistent with total energy being kept fixed. This is the method pioneered by Wien, Rayleigh, Jeans and completed by Planck[2] and Bose[3]. The other makes use of the existence of transitions and seeks a dynamical balance. The roots of this method could be sought in Boltzmann's collision equation[4] and was developed in the context of black body radiation by Einstein and Einstein and Ehrenfest[5] and completed by Bose[6].

It is curious the Ācharya Satyendranāth Bose contributed to both these approaches and recognized that the equivalence of the distributions gained in this manner implied, in turn, definite relations between emission and adsorption rates of many-photon states.

It is also curious that while Albert Einstein generalized and completed Satyen Bose's work on the photon gas[3] to apply to any boson gas with nonvanising chemical potential[7], Satyen Bose[8] generalized and completed Albert Einstein's work[4] on radiative equilibrium of a Bohr atom to deal with a general system with transitions between arbitrary levels.

The 'First' Bose Paper[3]

Bose's first contribution to radiative equilibrium can now be reworded in contemporary terminology as follows : Each mode of the radiation field is associated with an assembly of photons each with energy $h\nu$. Each n-photon state is a level of the field mode with energy $E=nh\nu$. Each such level is a single complexion of the photon gas, and the photons are to be counted as being strictly identical. If there are r modes amongst which N photons are to be subdivided the statistical weight to be assigned to any partition

$$N=N_1+N_2+ \dots + Nr.$$

is simply given by the number of ways of arranging N particles and $(r-1)$ walls of partition and is given by

$$W=[\ (N+r-1)\ !\ /\ N!\ (r-1)\ !\ ].$$

Each of these states has energy $Nh\nu$. When there are a number of discrete modes with frequencies ν_j we get the total energy and total statistical probability :

$$E=\sum_j N_j\ h\nu_j$$

$$W=\frac{\pi\ (N_j+r_j-1)\ !}{j\ \ N_j!\ (r_j-1)\ !}$$

Maximizing the entropy $S=K\log W$ keeping the energy E constant and varying the numbers N_j we obtain the conditions (in the approximation of $N_j \gg 1$, $r_j \gg 1$)

$$\sum_j \delta N_j\ .\ \log\left[\frac{N_j+r_j}{N_j}\right]=0$$

$$\sum_j \delta N_j\ .\ \nu_j=0\ .$$

Introducing the Lagrange multiplier β to be identified with the inverse temperature $(kT)^{-1}$ we get the solutions :

$$N_j=\frac{r_j}{e^{\beta h\nu_{j-1}}}$$

so that per mode we get the Planck distribution

$$\rho(\nu)=(e^{\beta h\nu}-1)^{-1}\ .$$

It is to be noted that this result is entirely general and does not depend crucially on the spectrum of frequencies of the system. It is therefore equally applicable to any energy spectrum. So, for example, we understand it in the context of phonons of a Debye solid. Nor is it difficult to build in the conservation of bosons yielding to a further constraint

$$\sum_j \delta N_j = 0.$$

and a new Lagrange multiplir μ, this being eventually identified with the chemical potential. This observation together with the identification

$$\epsilon_j = h \nu_j = p_j^2/2m$$

appropriate for a non-relativistic free particle mode was the generalization made by Einstein[7] to complete Bose's work to Bose-Einstein statistics.

An Alternate Static Derivation

With the benefit of hindsight we see that we could make shortcuts in Bose's derivation (and in Einstein's as well !) by recognizing that the problem is the computation of the probabilities p_N for N-photon states which maximizes the entropy $S = \sum_N p_N \lg_e (p_N)$ keeping the *average* energy $E = \sum_N N h \nu p_N$ fixed and guaranteeing that the probablities sum to unity. This yields

$$\sum N \delta p_N = 0$$

$$\sum \delta p_N = 0$$

$$\sum (\log p_N + 1) \delta p_N = 0$$

with the general solution

$$p_N = \exp(-\alpha - \beta N h \nu)$$

where α and β are two suitable Lagrange multipliers. If we write

$$x = e^{-\beta h \nu}$$

we have

$$p_N = e^{-\alpha} x^N$$

Remembering that $\sum p_N = 1$ we evaluated e^{α} to be $\sum x^N = (1-x)^{-1}$. This yields the Bose distribution

$$p_N = (1-x)\, x^N$$

The average energy is given by

$$E = \sum_N p_N N h \nu$$

$$= \sum (1-x)\, x^N N h \nu = h\nu \frac{x}{1-x}$$

$$= h\nu \frac{1}{e^{h\nu/kT} - 1}$$

If we now remember that per unit volume we have $8\pi\nu^2/c^3$ modes per unit frequency interval we get the Planck formula for the spectral density of black body radiation

$$\rho(\nu) = \frac{8\pi h \nu^3}{c^3} (e^{h\nu/kT} - 1)^{-1}$$

In passing we note that the probabilities

$$p_N = (1 - e^{-h\nu/kT}) e^{-Nh\nu/kT}$$

are exactly the (normalized) Boltzmann weight factors for the field states with energies $Nh\nu$.

Bose Process as an Innovation on a Poisson Process

Satyen Bose's work pointed out that the strict identity of the photons (and therefore of other bosons) makes it necessary to note that the particles are not independent (even when there is no interaction between them). For a collection of independently occuring evants the probabilities define a 'Poisson process' :

$$\pi(n,\mu) = e^{-\mu} \frac{\mu^n}{n!}$$

In this case the mean number of particles and the mean square number of particles are given by

$$\bar{n} = \Sigma\, n\, \pi(n,\mu) = \mu$$

$$\overline{n^2} \longleftarrow \bar{n}^2 = \Sigma\, n^2\, \pi(n,\mu) = \mu^2 + \mu$$

The fluctuation in the particle counts is measured by the variance $\bar{n}^2 - \bar{n}^2 = \mu$. For the Bose process

$$\overline{n^2} - \bar{n}^2 = \mu$$

$$p(n,x) = (1-x)\, x^n$$

we get

$$\bar{n} = \sum n\, p(n,x) = \frac{x}{1-x}$$

$$\overline{n^2} \longleftarrow \bar{n}^2 = \sum n^2\, p(n,x) = \frac{x^2 + x}{(1-x)^2}$$

The fluctuation in the counts is now

$$\overline{n^2} - \bar{n}^2 \longleftarrow \bar{n}^2 - \bar{n}^2 = \bar{n}(1+\bar{n}).$$

This is larger than for the Poisson process and is sometimes referred to as 'photon bunching'. It suggests that the photons are *noninteracting but not independent* particles. Incidentally the Bose process may be thought of as an 'innovation' on the Poisson process :

$$p(n,x) = \int_0^\infty \pi(n,\mu)\, e^{-\mu/x}\, d\mu$$

Photon bunching is thus the particle version of the intensity fluctuation in the field version[3]. The thermal radiation field has a bivariate Gaussian distribution

$$P(A_1, A_2) = \frac{1}{\pi I} \exp\left(\frac{-(A_1^2 + A_2^2)}{I}\right)$$

So that the intensity $\mathcal{I}$ is Rayleigh distributed :

$$P(\mathcal{I}) = \frac{1}{I} \exp(\mathcal{I}/I)$$

Einstein's Dynamic Derivation for Bohr Atoms[5]

The dynamic method of determining radiative equilibrium consists of balancing the probabilities of direct and reverse transitions. For colliding material systems in which the energy alone is the conserved quantity the Boltzmann weight factor $\exp(-\beta E)$ incorporates this balance since the multiplication of the Boltzmann factors yields the exponential of the total energy which is therefore constant before and after the collision.

Albert Einstein showed that this dynamic balance between emission and absorption of radiation by a Bohr atom with two identified levels could lead to a different derivation of the Planck spectral distribution law. Let the two identified levels have energies E_1 and E_2 with the emitted or absorbed photon with frequency ν satisfying Bohr's condition

$$E_2 - E_1 = h\nu .$$

Einstein *assumed* that the relative populations of the levels E_1 and E_2 were given by the Boltzmann factors $e^{-\beta E_1}$ and $e^{-\beta E_2}$. Einstein also introduced the rates of induced and spontaneous transition rates A and B which depended on the internal dynamics and the details of the interaction of the atom with the radiation. The upward transition rate is all induced and given by

$$\rho(\nu) \cdot A \cdot e^{-\beta E_1} = R_1$$

The downward transitions contain an induced term

$$\rho(\nu) \cdot A \cdot e^{-\beta E_2} = R_2$$

and a spontaneous transition rate

$$\frac{8\pi\nu^2}{c^3} \cdot B \cdot e^{-\beta E_2} = R_3$$

Here the factor $8\pi\nu^2/c^3$ is the density of modes per unit volume. If we now look for radiative equilibrium we must start by equating rates of upward and downward transitions :

$$R_1 = R_2 + R_3 .$$

This gives

$$\rho(\nu) A e^{-\beta E_1} = \rho(\nu) A e^{-\beta E_2} + \frac{8\pi\nu^2}{c^3} B e^{-\beta E_2}$$

Using the Bohr relation we can rewrite this in the form

$$\rho(\nu) A e^{h\nu\beta} = \rho(\nu) A + \frac{8\pi\nu^2}{c^3} B$$

We reproduce Planck's spectral distribution formula

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3} \frac{B}{A} \frac{1}{e^{h\nu\beta} - 1}$$

provided we choose

$$B = h\nu \, . \, A$$

This shows that in addition to induced emission we must consider spontaneous emission also. The spontaneous rate cannot be zero.

The limitation to a two level system was removed in a subsequent paper by Einstein and Ehrenfest.

Bose's Generalized Dynamic Derivation[6]

Satyen Bose generalized this work to its full generality and considered an assembly of photons of various frequencies in interaction with arbitrary levels for the atomic system. He also took into account the Compton effect suffered by photons in interaction with moving electrons, an effect that was already pointed out by Pauli to be necessary for the steadiness of the Planck distribution. He showed that if the ratio of direct to reverse intrinsic transition rates is $e^{\beta h\nu}$ then the Planck distribution would be obtained : this meant that we must get the ratio of the intrinsic transition rates to be not equal to one but $(1+n)/n$ where n is the photon number density per mode. Einstein got it by assuming an additional spontaneous transition rate.

Bose proposed to get this by another means. He kept the total transition rate for the downward transition independent of the number of photons present. Neither did he have the proportionality of the induced downward (emission) transition rate to the number of photons present per mode ; nor have the upward (absorption) transition rate proportional to the number of photons present per mode. Instead he gave a combinatorial argument why the upward transition rate was less than the downward transition rate by the factor $n/(n+1)$. In terms of our present understanding of the quantum mechanical mechanism[9] this is incorrect nor was it even satisfactory in terms of the classical limit of electromagnetic radiation incident on an absorber. But Bose felt that his was a more satisfactory scheme since it did not introduce the motion of spontaneous emission.

The emphasis on this question (and the negative endorsement of Einstein[10] of these ideas !) obscured the essential contribution contained in Bose's 'second paper'. The paper contained a full dynamical theory of radiative equilibrium and showed the invariance of the final distribution on the particular states considerd or the number and kinds of transitions envisaged. It was as much a generalization of Einstein's paper on the A and B coefficients as was Einstein's paper on Bose gases a generalization of Bose's derivation of Planck's spectral distribution law from the photon picture. Yet all these years and in all literature including the writings of Satyen Bose's contemporaries and students this great contribution has been systematically ignored[11]. The notable exception is the publication of the collection of his papers on his 70th birthday[12].

Coming back to the dynamical derivation of blackbody radiation there is one unsatisfactory feature : the matter levels have relative weights given by the Boltzmann weight factors exp $(-BE_j)$. This introduces a certain amount of semi-classical restriction into the theory ; this is clumsy and unnecessary. Following the same path as used by Bose it is possible to give a more satisfactory derivation in which the entire interacting system is treated more symmetrically.

A Dynamical Theory of Radiative Equilibrium

Let us start from the notion of 'collisions'. The dynamically stable configuration should be one which is unaltered by any interaction between components. Let there be n_j particles (photons, electrons or anything else) of type j. Then we *assume* that the transition rate for the transition $n_j \to n_j - 1$ is proportional to n_j while the rate for the transition $n_j \to n_j + 1$ is some other function $\psi_j(n_j)$.

From a classical point of view we would say $\varphi_j(n_j)$ is independent of n_j since what is already present should have no relevance to whether a new particle of the jth species is created. This corresponds to all transitions being 'spontaneous'. This would lead to the Boltzmann distribution as we can see explicitly below. On the other hand on a classical wave picture one would expect that both downward and upward transitions are proportional to the intensity of the wave inducing the transitions and so $\varphi(n)$ is proportional to n. All the transitions are now 'induced'. This choice would not lead to a consistant distribution.

Let there be a 'collision' i.e. a reaction of the form

$$j + k + \ldots \to a + b + \ldots$$

and its inverse reaction. The intrinsic rate for the direct reaction is

$$n_j n_k \ldots \varphi(n_a)\varphi_b(n_b)\ldots$$

This must equal the rate for the reverse transition

$$n_a n_b \ldots \varphi_j(n_j)\varphi_k(n_k)\ldots;$$

we thus obtain

$$\frac{\varphi_a(n_a)}{n_a}\cdot\frac{\varphi_b(n_b)}{n_b}\ldots = \frac{\varphi_j(n_j)}{n_j}\cdot\frac{\varphi_k(n_k)}{n_k}\ldots$$

This balance must be there whatever be the reaction provided the conservation laws of energy and any other additive conservation laws are satisfied :

$$n_a\epsilon_a + n_b\epsilon_b + \ldots = n_j\epsilon_j + n_k\epsilon_k + \ldots$$

$$q_{\alpha a} n_a + q_{\alpha b} n_b + \ldots = q_{\alpha j} n_j + q_{\alpha k} n_k + \ldots$$

The first one is the energy conservation law and there is only one such law. The second one is the conservation law of particle species, the $q_{\alpha j}$ being the 'charge' labels of type α. In the usual case of interactions involving only photons and electrons there is only the conservation of electrons.

The general solution to the equation is expressed in parametric form[13] :

$$\frac{\varphi_j(n_j)}{n_j} = \exp\left[\beta\epsilon_j + \sum_\alpha q_{\alpha j}\,\mu_\alpha\right]$$

With the assumption of only spontaneous transitions, $\varphi_j(n_\epsilon)=1$, we get the Boltzmann weight factor

$$n_j = \exp\left[-\beta\epsilon_j - \sum_\alpha q_{\alpha j}\,\mu_\alpha\right]$$

so that β is the inverse temperature $(kT)^{-1}$, μ_α are chemical potentials. With the classical wave picture and only induced transitions the equations cease to yield any information and degenerate into identities. For the case of induced plus spontaneous transitions we get

$$\frac{n+1}{n_j} = \exp\left[\beta\epsilon_j + \sum_\alpha q_{\alpha j}\,\mu_\alpha\right]$$

or

$$n_j = \left[1 - \exp\left(-\beta_j - \sum_\alpha q_{\alpha j}\mu_\alpha\right)\right]^{-1}$$

which is the Bose-Einstein distribution law[7]. For the special case of photons we put $\epsilon_j = h\nu_j$ and $q_{\alpha j} = 0$ so that

$$n = [1 - \exp(-\beta h\nu)]^{-1}.$$

Finally for a Fermi-Dirac system there is an inhibition of the downward transition so that

$$\varphi_n = 1 - n.$$

This leads to the Fermi-Dirac distribution law[14] :

$$n_j = \left[1 + \exp\left(-\beta\epsilon_j - \sum_\alpha q_{\alpha j} n_j\right)\right]^{-1}$$

We have thus demonstrated that the approach of the Boltzmann collision ansatz automatically leads to a unified dynamic derivation of the Bose-Einstein and Fermi-Dirac distribution laws. This derivation is to be contrasted with the usual static derivation using notions of maximum entropy. The method used here to arrive at the equilibrium distribution can be extended to cover non-equilibrium cases also but a discussion of the detailed theory is beyond the scope of the present paper.

Some remarks are in order. The derivation that we have given here is a completion of the work of Satyen Bose's second paper. It shows the great universality of this method. It differs from Bose's own work essentially in the choice of the rates to be proportional to n and $n+1$ respectively rather than to $n/(n+1)$ and 1. Both the choices would give identical results regrading the equilibrium since it depends only on the ratio. For nonequilibrium processes they will differ.

A Critical Appreciation of Bose's Contribution[15]

I have studied Bose's arguments about the curious choice he made. I do not find them convincing. Einstein had pointed out that his choice conflicted with the correspondence principle but Bose seems to have not taken this comment too seriously. I am sorry that time has taken Satyen Bose from amongst us and we cannot find out why he felt so sure about his choice. The only hypothesis that I can offer is that Bose recognized what we saw above that the Boltzmann weight factor implies only spontaneous emission. He may have decided that this was both reasonable and desirable not only for the 'classical' atomic systems but also the photon assembly. And it may have appeared reasonable to postulate an altered absorption rate from a many-photon state. He may have dismissed the modification of the transition rate from 1 to $n+1$ as a case of precognition of of the emitted photon about the other photons it will find as its companions. I find a similar

reluctance on the part of Arjuna to accept the cosmology implicit in Krisna's statements, Krisna says (Gita)

imam vivasvate yogam
proktavanahamavyayam (IV,1)

and Arjuna asks :

aparam bhavato janma
param janma vivasvatah
kathametat vijāniyam
tmādau proktavāniti (IV,4)

I guess that if we had pressed him for such a choice for Fermi particles he would have again said that the absorption rate was to be chosen as $n/(1-n)$. Bose's choice may thus be due to his recognition of the many paradoxes of casuality with which quantum mechanics has made us acquainted. Again it is curious that Einstein in his later years fought a heroic battle against accepting the world picture suggested by quantum mechanics[16].

The essence of Bose's first paper was to tell us that particles were quanta of the field and as such were manifestations of the field. That the field was the primary entity and its knowledge conferred on us knowledge about the behaviour of the quanta ; thus echoing the sentiments of the Gita ;

kṣetrajnam capi mām viddhi
sarva kṣetreṣu Bhārata
kṣetra kṣetrajnayor jnānam
yattad jnānam matam mama (XIII,2)
jyotiṣamapi tat jyotis
tamasah param ucyate (XIII,17)

The static method of arriving at equilibrium is to look for a state unchanged by variations ;

dukheṣu anudvigna manah
sukheṣu vigatasprhiah
vita rāga bhaya krodhah
stitadhir munir ucyate (II,56)

The dynamic method on the other hand looks for the balance between upward transitions and seeks a state which is unaffected by the continuing changes :

yasmānno dvijate loko
lokānno dvijate ca yah
harṣāmarṣa bhayodvegaih
muktoyah sa ca me priyah (XII,15)

But these two methods are equivalent.

yat sānkhyaih prāpyate sthānam
tat yogairapi gamyate
ekam sānkhyam ca yogam ca
ya paśayati sa paśyati (V.5)

In fact when you see the equivalence of the two methods properly then the dynamic and static are seen as two aspects of the same dynamical system which is seen in its timeless aspect :

karmanyakarma yah paśyed
akarmani ca karma yah
sa budhimān manuṣyeṣu
sa yuktah krsna karmakrt (IV,18).

The contributions of Satyendranath Bose thus touched all aspects of dynamic equilibrium and was of such fundamental nature that it set the pattern for future developments in nonequilibrium statistical mechanics. The likes of him are seldom seen amongst us but then who could discern what future has in store for us ?

References

1. All the Ślokās are from the Bhagavat Gita. Those who do not find it enjoyable or enlightening to see parallels and listen to echoes may safely skip all these quotations. They are not essential to an understanding of the scientific discussion.
2. M. Planck, Verh. Deutsch. Phys. Ges. **2**, 237 (1900).
3. S. N. Bose, Z. Phys. **26**, 178 (1924).
4. L. Boltzmann, Wien. Ber. **66**, 275 (1872).
5. A. Einstein, Phys. Z **18**, 121 (1917).
   A. Einstein and P. Ehrenfest, Z Phys. 19, 301, (1923),
6. S. N. Bose, Z, Phys. **27**, 384 (1924).
7. A. Einstein, S. B. preuss. Akad. Wiss. **261**, (1924) **3**, (1925).
8. F. Zernike, Physica **5**, 785 (1938) ; E. Wolf, Nuovo Cimento **13**, 1165 (1959) ; L. Mandel, Proc. Phys. Soc. (London), **74**, 233 (1959) ; E.C.G. Sudarshan, Phys. Rev. Lett. **10**, 277 (1963). For a systematic exposition, see J. R. Klauder and E.C.G. Sudarshan, 'Quantum Optics' (Benjamin, New York 1968).
9. P.A.M. Dirac, Proc. Roy. Soc. **A114**, 661 (1926) ; 'Principles of Quantum Mechanics' (Oxford University Press, London 1935).
10. A. Einstein, note at the end of Bose's paper, reference 6.
11. See, for example, M.N. Srivastava, 'A Treatise on Heat', The Indian Press (Pubs.) Private Ltd., Allahabad, India, 5th Edition (1964).
12. 'S.N. Bose : 70th Birth day Commemoration Volume", (1964). See also : Physics Teacher, Vol. 16, No.2, April 1974, published by Indian Physical Society Calcutta-32 ; Physics News, Vol. 5, No. 2, June 1974, published by Indian Physics Association, Bombay-76.
13. E.C.G. Sudarshan and J. Mehra, Int. J. Theoret. Phys. **3**, 245 (1970).
14. E. Fermi, Z. Phys. **36**, 902 (1926),
15. Reference may be made to two papers : W.A. Blanpied, Am. J. Phys. **40**, 1212 (1272) ; E.C.G. Sudarshan, Am. J. Phys. **43**, 69 (1975).
16. P.A. Schilpp, 'Albert Einstein, Philosopher-Scientist' Cambridge Univ. Press, 1950.