Thermodynamics of blackbody radiation

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The thermodynamics of homogeneous, isotropic, unpolarized electromagnetic radiation in a cavity with volume and temperature controllable as the independent variables is analyzed. Internal energy, pressure, chemical potential, enthalpy, Gibbs free energy, heat capacities, expansivity, and compressibility are all derived from the Helmholtz free energy. Topics treated are the third law, isothermal, adiabatic, and free expansion, throttling process, phase equilibrium, stability, and the Carnot cycle.

INTRODUCTION

The basic problem of this paper is to examine the thermodynamics of blackbody radiation. The usual emphasis on the Planck distribution is almost completely surpressed in favor of the overall integrated results treated as a thermodynamic system. A prime purpose of this study is to form a detailed link between thermodynamics and cavity radiation in such a way so as to stimulate the interest and perhaps enhance the knowledge of the professional scientist, and to present the material in a fashion suitable for a course in thermodynamics.

There are probably many reasons why such a topic is important. The historical and both the theoretical and applied aspect of blackbody radiation are well known and need not be repeated here. Yet, the present emphasis is different in that the interest is on the macroscopic theory rather than the distribution law. One finds that it's possible to simultaneously think in terms of electromagnetic theory and thermodynamics, so that the problem tends to force a unity of thought between seemingly two unrelated subjects in physics. From a pedagogical viewpoint, the student learns (sometimes with considerable surprise) that thermodynamics can be applied to other systems besides the usual solids, liquids, and (ordinary) gases.

Many texts contain specialized treatments of blackbody thermodynamics. Rather than review the literature at this point, those that I've found most useful will be referenced in the body of the paper. Some of the topics treated here, as specifically applied to radiation, such as the third law, free expansion, phase change, Carnot cycle, couldn't be found in any of the source material, so that only general references to these phenomena are made. The historical aspect of the problem is well treated by Kangro.[1]

The paper begins with a presentation of the Helmholtz free energy as a function of temperature and volume, from which all of the other thermodynamic parameters follow. In particular, the various relations are summarized in Table I. By the usual definitions, the heat capacities, volume expansivity, and isothermal compressibility are derived. A short section is devoted to the Gibbs free energy and the chemical potential because of their unique (yet trivial) roles in cavity radiation. Likewise, a separate section is reserved for the third law of thermodynamics for similar reasons. This section includes also a brief discussion of zero-point entropy and energy. The emphasis then changes from theoretical to the more engineering type processes such as isothermal, adiabatic, and free expansions, a throttling process, phase equilibrium, stability, and the Carnot cycle. The paper concludes with some comments and discussion of the treated topics.

FUNDAMENTAL RELATIONS

The system to which the thermodynamics is being applied is certainly a strange one when compared to typical problems encountered in, say, engineering thermodynamics. This system consists of electromagnetic radiation in thermodynamic equilibrium inside a closed, completely evacuated cavity of arbitrary shape with volume V and temperature T. Volume and temperature represent the two independent and measureable parameters in terms of which all thermodynamic variables may be expressed. Since equilibrium is assumed, one may define the radiation temperature as that of the walls. The system is an isothermal enclosure, and every point has the property that the intensity is independent of position. Furthermore, the radiation is isotropic and unpolarized.

A typical approach taken by most modern physics texts[2,3] is to treat the radiation as a series of standing waves. The normal-mode density and energy per mode are calculated, and this leads to the Planck law. An alternate viewpoint is taken in most statistical mechanics texts where one considers the system to consist of a photon gas that obeys Einstein–Bose statistics. In a way, the latter school of thought may be more appealing in that gases are so familiar, especially when it is realized that the photon gas is very much an ideal gas, since there is no interaction between the particles (other than negligibly small quantum-mechanical effects). The fact that photons do not interact prevents a relaxation mechanism for energy transfer between photon states (corresponding to different frequencies) necessary to establish thermodynamic equilibrium. A small, black dust particle with very small heat capacity may be introduced into the cavity to serve as a coupling mechanism between states. The reader interested in the history of blackbody radiation would do well to read the article by Lewis[4] on Einstein's derivation of the Planck law.

The theme of this paper is to treat blackbody radiation as a thermodynamic system, although statistical concepts will sometimes be used, mainly in a qualitative fashion. In order to arrive at the various thermodynamic parameters as a function of T and V, many texts, such as Crawford,[5] use nonthermodynamic information to derive the fact that the radiation pressure is one third the energy density and then proceed to calculate other quantities of interest, such

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Table I. Thermodynamic relations for blackbody radiation.

F	S	H	U	P	N	G	μ
$-(1/3)\,bVT^4$	$(4/3)\,bVT^3$	$(4/3)\,bVT^4$	bVT^4	$(1/3)\,bT^4$	$[30\zeta(3)/\pi^4 k]\,bVT^3$	0	0
$-PV$	$(4/3)\,U/T$	$(4/3)\,U$	$3PV$	$(1/3)\,U/V$			
$-(1/4)\,TS$	$4(b/3)^{1/4}VP^{3/4}$	TS	$(3S/4)^{4/3}(bV)^{-1/3}$				
$-(1/3)\,U$	$(4/3)\,(bV)^{1/4}U^{3/4}$	$4PV$					
		$S(3P/b)^{1/4}$					

as the equation of state, as is done in Zemansky[6] and in Desloge.[7] One could take the pressure–energy density relationship or the equation of state as an experimental fact and then continue. The point here is, that because of the tremendous generality of thermodynamics, the latter is incapable of generating an equation of state on first principles; external information is required, whether theoretical or experimental.

An alternate approach is perhaps more appealing to students. A clue is contained in the natural choice of T and V as the independent (and controllable) variables. This immediately suggests the Helmholtz free energy F as the potential from which all thermodynamic information may be derived. Recall that

$$dF = -S\,dT - P\,dV, \tag{1}$$

where S is entropy and P is pressure. Usually, Eq. (1) includes a $\mu\,dN$ term where μ is the chemical potential and N is the number of particles in the system. This would imply that N is an independent variable, which it is not for blackbody radiation. Thus if we have F as a function of T and V, then S and P are both known from

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{2}$$

All other thermodynamic quantities may then be calculated. But how do we get $F = F(T,V)$? A successful solution at this point in a junior-level course is to take perhaps a half period to qualitatively explain the concept of a partition function, how it's calculated (in words), and its relationship with the Helmholtz function in general. Students seem to appreciate this. Then, without explicit derivation, the F function is written down for the problem, namely,

$$F = -(1/3)bVT^4, \tag{3}$$

where b is a known constant, $b = 8\pi^5k^4/(15h^3c^3)$. I've found this method, after many years of trial, to be accepted and better understood by undergraduates, especially because complete thermodynamic information for blackbody radiation is contained in Eq. (3).

Other parameters follow immediately:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4}{3}bVT^3, \tag{4}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3}bT^4. \tag{5}$$

Notice that Eq. (5) is the equation of state for the system, and it is very important to note the independence of volume. By definition, $F = U - TS$ (where U is internal energy), therefore

$$U = F + TS = bVT^4. \tag{6}$$

By combining Eqs. (5) and (6), one derives simply and routinely the relationship between energy density $u = U/V$ and pressure $P = u/3$. The enthalpy H follows immediately from its definition, $H = U + PV$, giving

$$H = (4/3)bVT^4. \tag{7}$$

Likewise, the Gibbs free energy G, by definition, is $H - TS$, thus

$$G = (4/3)bVT^4 - T[(4/3)bVT^3)] = 0. \tag{8}$$

The fact that G is identically zero presents a simplification in a formal calculation of physical results, but also marks a possible complication in interpretation. This null result may be traced to the fact that pressure is uniquely determined by temperature; thus G is not really definable for the present case where P and T are not independent.

The fact that G is zero also causes the chemical potential μ to be zero. Assume there are N particles (photons) in the single-component system, then $G = \mu N = 0$, which forces

$$\mu = 0, \tag{9}$$

where $N \neq 0$; otherwise no system exists! A more fundamental viewpoint for the zero value of μ is that the chemical potential is defined only with respect to a conserved particle number N, which is not the case for the blackbody system. Thus in a formal sense, G and μ are both zero; actually neither are defined for the present thermodynamic system.

Although N (which depends upon the Planck distribution) will be examined in more detail later, the equation for it will be quoted without derivation,[8,9] since it doesn't follow from the treatment in this paper:

$$N = [30\zeta(3)/\pi^4k]bVT^3, \tag{10}$$

where $\zeta(3)$ is the zeta function of argument three, equal to 1.202. Notice that N is strictly a function of T and V and must not be considered an independent parameter; that is, we're dealing with an open system where the number of particles is not conserved.

So far, P, U, F, S, H, and N have been expressed as functions of T and V (with G and μ both zero). However, it's often desirable for theoretical interpretation to present these parameters in terms of other combinations. Furthermore, while complete thermodynamic information is contained in Eq. (3) with $F = F(T,V)$, one may exhibit exactly the same information in terms of $U = U(S,V)$, $S = S(U,V)$, $H = H(S,P)$. Table I presents the various useful combinations of the thermodynamic variables.

HEAT CAPACITIES, COMPRESSIBILITY, EXPANSION COEFFICIENT

A simple calculation leads to C_v, the heat capacity at constant volume:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = 4bVT^3. \tag{11}$$

On the other hand, the heat capacity at constant pressure C_p, the volume expansivity β, and the isothermal compressibility κ are undefined for this system, because P and T are not independent variables, which is a requirement for the derivatives in their definitions, although one might make a heuristic case for assigning infinite values to all three. For a physical interpretation, consider C_p as an example. By virtue of its definition, we're essentially asking how much energy must be added to the system to change the temperature by ΔT at constant pressure. But at fixed P, $\Delta T = 0$, so that no finite amount of energy can increase the temperature.

In the case of C_v [Eq. (11)], notice that the temperature dependence is identical to that of a crystal at low temperature, as derived from the Debye theory. The reason for this is that the frequency distribution of the normal modes has the same mathematical form in both theories, and the mean energy of each mode is that of a harmonic oscillator. Thus just as photons are a result of the quantization of electromagnetic waves, phonons correspond to the quantization of elastic waves. Incidentally, a numerical evaluation of Eq. (11) shows that C_v is extremely small, being about 10^{-12} that of an equal volume of water at room temperature.

THIRD LAW OF THERMODYNAMICS

Consider two forms of the third law of thermodynamics,[10]

$$\text{weak form: } \lim_{T\to 0} \Delta S_T = 0,$$

$$\text{strong form: } \lim_{T\to 0} S = 0.$$

The weak form says that the change in entropy for an isothermal, reversible process approaches zero as temperature approaches zero, whereas the strong form decrees that entropy itself is zero at $T = 0$. Notice that the strong form contains the weak form as a special case. Historically, Nernst had considered the original statement of the third law to be restricted to condensed media, but he later modified it to apply to gases.[11]

If Eq. (3) is correct for blackbody radiation, then the entropy follows from Eq. (4), which shows that $S \to 0$ as $T \to 0$, corresponding to the strong form.[12] This also follows from the fact that at $T = 0$, $N = 0$, so there are no particles in the system.

From Eq. (1), it follows that $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ (a Maxwell equation) hence, from the third law,

$$\lim_{T\to 0} \left(\frac{\partial S}{\partial V}\right)_T = 0,$$

resulting in

$$\lim_{T\to 0} \left(\frac{\partial P}{\partial T}\right)_V = 0,$$

which should be true in general. The latter is correct for blackbody radiation because $(\partial P/\partial T)_V = 4bT^3/3$ [from Eq. (5)], and this goes to zero as T approaches zero.

Consider the behavior of C_v as absolute zero is approached. Assume $S = S(T,V)$, then

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV.$$

Then for constant volume, $dS = (\partial S/\partial T)_V dT$ and

$$\Delta S = \int_0^T \left(\frac{\partial S}{\partial T}\right)_V dT = \int_0^T \frac{C_v}{T} dT.$$

This is an improper integral at the lower limit, so in order for the change in entropy to be finite at $T = 0$, one concludes that

$$\lim_{T\to 0} C_v = 0,$$

as can clearly be seen for blackbody radiation from Eq. (11). On the other hand, one cannot repeat the argument with pressure substituted for volume, because P and T are dependent variables. Thus no conclusion for C_p similar to C_v can be made at absolute zero.

There is a subtlety so far overlooked in applying the third law to this exotic system. Equation (10) shows that the number of particles is a function of V and T alone, in fact, proportional to VT^3. As temperature approaches zero, N also approaches zero. Since thermodynamics is an average over the microscopic states, it becomes questionable to apply statistics to such small numbers at low temperature. In particular, at $T = 0$, $N = 0$, it may appear that there is no system to which any statistics or thermodynamics may be applied, whereas this is really just a particular state of a still well-defined system. In this respect, the interested reader may want to consult two related papers pertaining to blackbody radiation in small cavities at low temperature.[13,14]

The question of a zero-point entropy S_0 has been addressed by Sychev[15] and by Epstein.[16] Since $S = S(V,T)$, one may write

$$\int_{S(0,0)}^{S(V,T)} dS = S(V,T) - S(0,0)$$

$$= \int_0^T \left(\frac{\partial S}{\partial T}\right)_{v=0} dT + \int_0^V \left(\frac{\partial S}{\partial V}\right)_T dV,$$

where $S(0,0)$ is the entropy evaluated at both zero temperature and volume. Consider a process at constant temperature, then $dT = 0$. In particular, evaluate the expression as volume goes to zero, which results in $S(0,T) = S(0,0)$. Unless $S(0,0)$ is zero, then the result is a nonzero entropy for a system void of particles, hence the zero-point entropy may be taken as zero, as in the strong form of the third law.

If one adopts the modified Planck view of the system as an assembly of harmonic oscillators with energies given by $\epsilon = [n + 1/2]\hbar\omega$, then the energy density per unit frequency interval contains a temperature-independent term that becomes infinite upon integration.[17,18] Thus one is confronted with an infinite zero-point energy. The usual argument is that the infinite term may be omitted because radiated energy corresponds to energy differences, and the infinities "subtract out." Clearly this is a very unsatisfactory situation from a theoretical viewpoint.[19] Actually, the zero-point energy is infinite only for an idealized cavity whose walls reflect radiation of all frequencies; such a cavity would have an infinite inertial mass. An upper limit would exist for the frequency of radiation contained in a real cavity and result in a finite contribution to the inertial mass.[20-22]

ISOTHERMAL EXPANSION

Suppose the system is expanded (or compressed) isothermally and reversibly. The amount of heat absorbed from an external source (in order to keep the temperature constant) may be quickly found from

$$Q = \int T dS = T\Delta S = (4/3)bT^4\Delta V, \qquad (12)$$

where Eq. (4) has been used for S. Note that this result is also immediate from the enthalpy [Eq. (7)] $\Delta H = 4bT^4\Delta V/3$, since constant temperature also corresponds to constant pressure, in which case $Q = \Delta H$. The change in internal energy is $\Delta U = bT^4\Delta V$, as seen from Eq. (6).

By the first law of thermodynamics, the difference between Q and ΔU should be the amount of work involved in reversibly changing the volume, namely, $bT^4\Delta V/3$. This may be verified by computing the work directly,

$$W = \int P dV = P\Delta V = (1/3)bT^4\Delta V. \qquad (13)$$

Note that just as Q may be found from ΔH for a process at constant pressure (hence, temperature in this case), W may be computed from ΔF at constant temperature (hence, pressure).

ADIABATIC EXPANSION

An adiabatic expansion is especially interesting because of its statistical and quantum-mechanical implications. Assuming the process is performed reversibly, then from $dQ = TdS$, entropy is conserved. Since $S = 4bVT^3/3$, this implies that the product VT^3 is constant. Or by solving this for T, one gets,

$$T = \left(\frac{3S}{4b}\right)^{1/3} V^{-1/3};$$

and by combining this expression with $P = bT^4/3$, a familiar equation is derived ($PV^{4/3}$ = const.), which is of the form PV^γ = const., as is well known for an ideal gas for an adiabatic process. Yet, note that "γ" for the blackbody radiation is not C_p/C_V.

It's then a simple matter to use $PV^{4/3}$ = const. in order to calculate the work done by the system in expanding from P_i, V_i to P_f, V_f:

$$W = \int P dV = \cdots 3(P_iV_i - P_fV_f). \qquad (14)$$

Recall from elementary thermodynamics that the work done in an adiabatic process is $W = (P_iV_i - P_fV_f)/(\gamma - 1)$, which checks the above result since γ here is 4/3. Note also that from Table I, $U = 3PV$, so that the work done by the system is simply $U_i - U_f$; that is, the energy necessary to produce the expansion is extracted from the internal energy of the radiation. Likewise, since N is also proportional to VT^3, the number of photons is conserved for an adiabatic change.

Up to this point in the whole paper, no use of the spectral distribution of energy in frequency has been made, but the present topic is ideal for the illustration of an adiabatic invariant. Suppose the volume is expanded uniformly in all directions, then the mode wavelengths increase directly as the linear dimensions in such a way that the wavelength λ is proportional to the cube root of the volume.[23] Thus, λ is proportional to $V^{1/3}$ and VT^3 = const., resulting in λT = const., which will be recognized as the Wien displacement law. Furthermore, since λ goes as $V^{1/3}$ and $\lambda = c/\nu$, one arrives at the fact that $\nu^3 V$ is an adiabatic invariant.

The occupation numbers are also adiabatic invariants[24]; that is, the work done by the blackbody system in an adiabatic expansion causes a lowering of the energy levels without any transfer of particles between the levels. In other words, the particles ride up or down with the energy levels for an adiabatic compression or expansion, respectively.

FREE EXPANSION AND THROTTLING PROCESS

To achieve a free-expansion experiment with the photon gas, assume the cavity is thermally insulated with rigid, perfectly reflecting walls and divided by an opaque, insulated partition. One side of the partition is assumed to be at $T = 0$, hence, $P = 0$. A free expansion results when the partition is removed. Because of the nature of the walls as described, there is no heat transferred outside the cavity, and no work is done; hence, the internal energy remains constant. Since $U = bVT^4$, it is easy to see that the temperature decreases in a free expansion, because volume increases while U remains the same. This is in contrast to the ordinary ideal gas where T doesn't change. The reason for the different behavior may be traced to the fact that the blackbody internal energy is volume dependent, whereas the internal energy of an ideal gas is independent of volume, provided that the number of molecules is held fixed, as is usually assumed. The blackbody pressure decreases as may be seen from $P = bT^4/3$, and the entropy increases, as noted from $S = 4U/(3T)$.

Suppose a system, described by the relations in Table I, undergoes a throttling process from high to low pressure. As is well known,[25] the enthalpy remains unchanged. Since $H = 4U/3$, this means that the internal energy is constant. Also because $P = bT^4/3$, and the fact that pressure drops, this implies that the final temperature is less than the original. This can be seen by directly computing the Joule–Thomson coefficient μ from $P = bT^4/3$:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{(4/3)bT^3} > 0.$$

Thus μ is positive for all T, meaning that the photon gas always cools in a throttling process.

PHASE EQUILIBRIUM

Can we carry the thermodynamics of blackbody radiation so far as to consider different phases? The answer is yes, provided that the interpretation is that of a single system in a two-phase equilibrium state.[26] This possibility is strongly hinted via the fact that the equation of state, $P = bT^4/3$, is independent of volume, so that $P = P(T)$ only, which is characteristic of first-order phase equilibria. As a matter of fact, the system may be considered to be a gas that is in equilibrium with the cavity walls, a solid. The latter serves as a particle reservoir for photons such that a continual exchange of particles between the gas and solid is maintained with all thermodynamic parameters remaining constant.

Suppose now the system volume is expanded isothermally by an amount ΔV. Photons are then removed from the walls, since the number of particles depends upon VT^3, Eq. (1). The analogy here is sublimation. The amount of heat required to maintain the temperature constant has already been calculated in Eq. (12), $Q = 4bT^4\Delta V/3$, which is analogous to the heat of sublimation. The entropy clearly changes.

If the radiation is truly like a single system in two phases, then the Clapeyron equation[27] $dP/dT = Q/(T\Delta V)$ should apply. Thus

$$Q = T\Delta V \frac{dP}{dT},$$

but $P = bT^4/3$, so

$$Q = T\Delta V(4/3)bT^3 = (4/3)bT^4\Delta V,$$

as before.

An application of the phase rule[28] illustrates the simplicity of the system and verifies the interpretation as a situation involving phase equilibrium. Let f be the number of intensive parameters capable of independent variation, r be the number of components in the system, and M be the number of phases, then the phase rule is $f = r - M + 2$. As applied to blackbody radiation, $r = 1$ and $M = 2$ [gas plus condensed media (walls)], therefore $f = 1$, saying that only one intensive variable may be independently varied. This checks, since $\mu = 0$ and $P = P(T)$ only. On the other hand, one may reverse the argument to verify that there are actually two phases in the system; that is, knowing that f and r are both unity, this tells us that $M = 2$. The fact that the system is stable is reasonably apparent from physical considerations, but recall that to be so, both $(\partial T/\partial S)_V$ and $-(\partial P/\partial V)_T$ must be positive.[29] Both are satisfied for blackbody radiation.

CARNOT CYCLE

Consider the typical Carnot cycle consisting of an isothermal expansion from A to B (points on, say a P–V or T–S diagram), an adiabatic expansion from B to C, an isothermal compression from C to D, and finally, an adiabatic compression from D back to A. Let the working substance be a photon gas, or in general, a gas whose equation of state is $P = bT^4/3$. The amount of heat transferred and the work done may be easily calculated for each of the four steps; in fact, this has already been done in Eqs. (12), (13), and (14). Let pressure, volume, and temperature at points A, B, C, D be denoted by $P_1, V_1, T_h; P_2, V_2, T_h; P_3, V_3, T_c; P_4, V_4, T_c$, respectively. Note that $P_2 = P_1$ and $P_4 = P_3$:

$$A \to B: Q_h = (4/3)bT_h^4(V_2 - V_1), \quad W = P_1(V_2 - V_1);$$

$$B \to C: Q = 0, \quad W = 3(P_3V_3 - P_2V_2);$$

$$C \to D: Q_c = (4/3)bT_c^4(V_4 - V_3), \quad W = (1/3)bT_c^4(V_4 - V_3);$$

$$D \to A: Q = 0, \quad W = 3(P_1V_1 - P_4V_4);$$

The efficiency ϵ of the engine is found from its definition,

$$\epsilon = \frac{\text{net } W}{Q_h} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

$$= 1 - \frac{(4/3)bT_c^4(V_3 - V_4)}{(4/3)bT_h^4(V_2 - V_1)} = 1 - \frac{T_c(S_3 - S_4)}{T_h(S_2 - S_1)}.$$

But, $S_3 = S_2$ and $S_4 = S_1$ so that $(S_3 - S_4)/(S_2 - S_1) = 1$, giving

$$\epsilon = 1 - T_c/T_h,$$

which is the familiar result for Carnot efficiency. This example may be considered as a special case of the general result that the same expression will always occur for a reversible process when all heat is taken in at a constant temperature and all heat rejected at a constant lower temperature.[30] The above calculation makes a good homework or test problem in an undergraduate course as a contrast to using the ideal gas as a working substance.

COMMENTS AND DISCUSSION

One of the more common mistakes made in thermodynamics is the failure to define the system (and its boundaries) to which the theory is to be applied. In the present case, one might say loosely that thermodynamics has been applied to "nothing" (or vacuum), whereas in fact, the system has been chosen as the electromagnetic field within a cavity of volume V and temperature T. Or, perhaps more descriptively, the system consists of N photons within the cavity, with N not conserved. The thermodynamics has been shown to be simple, mainly because volume is absent in the equation of state; that is, pressure and temperature are uniquely related in a simple way.

There are two somewhat different historical approaches to blackbody radiation. The first, due to Planck in 1900, considered the system as an assembly of harmonic oscillators with quantized energies of $(n + 1/2)\hbar\omega$ (although Planck did not include the zero-point energy). The second viewpoint originated with Bose in 1924 and then Einstein in 1925, which considered the photon distribution over the energy levels. The two interpretations are actually the same; for example, in Planck's method, an oscillator of energy $(n + 1/2)\hbar\omega$ in the eigenstate n is equivalent to n photons in the energy level $\hbar\omega$.[31]

A microscopic observer would find experiments to be rather dull at any point immersed in the blackbody radiation field. Since the field is isotropic and homogeneous, the luminosity would be independent of direction and he would be unaware of the cavity size in any direction. Furthermore, no polarization effects would be detected. If the temperature were varied, then he would measure changes in intensity and energy distribution (corresponding to a color change).

From a pedagogical point of view, I've found that the most satisfactory method of solution and presentation to a class is by simply stating the Helmholtz equation (3) without any derivation, although students seem to appreciate a word description of the partition function. Keep in mind that complete thermodynamic information is contained in $F = -bVT^4/3$; the whole theory unfolds from it. The form of the Helmholtz function, together with that of the parameter b, is completely determined, apart from a numerical factor, by dimensional requirements, given that the photon is massless. This argument alone requires the presence of both h and c, showing that both quantum theory and relativity are necessarily involved in a complete understanding of the system.

One finds that the thermodynamics of this peculiar system is similar to those usually considered but with some exceptions. For example, the system obeys both the strong and weak forms of the third law, but in contrast to some conclusions normally associated with the third law, neither the limiting values of the expansivity or the heat capacity at constant pressure have meaning as temperature approaches zero. Both results can be traced back to the fact that the equation of state contains only pressure and temperature. In this respect, another unique feature is that, as T decreases, the number of particles also decreases.

The present problem can serve as a simple example of adiabatic invariants. As has been seen, VT^3 and PV^γ ($\gamma = 4/3$) are both constant for an adiabatic change. Since the number of photons is proportional to VT^3, N is also a constant. By a geometrical argument, we were able to derive the Wien law, λT = const., and also show that V/λ^3 is an adiabatic invariant.

The analogy with an ideal gas is especially evident when the system is considered to be composed of photons, but the analogy continues, since the equation of state may be written as $PV \simeq 0.9NkT$. Yet there are some subtle differences in, for example, a free expansion and a throttling process. Recall that an ideal gas experiences no temperature change after a free expansion, but, in contrast, the temperature of the radiation always falls.

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PROBLEM

Given a large supply of identical uniform bricks each of length l, determine the maximum possible overhang that can be obtained by stacking them in a cantilever structure. Make numerical estimates for the cases (a) $N = 10^6$ bricks and (b) a 10^6-m overhang of 20-cm bricks. (Solution on page 775.)

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