

FÍSICA ESTADÍSTICA I-PCF

TAREA 1

Fecha de entrega: viernes 16 de agosto de 2013

■ Problemas

1. Examine de manera concisa y rigurosa los resultados presentados en las siguientes referencias, las cuales abordan la termodinámica de la radiación electromagnética.

(i) Leff, Am. J. Phys. **70** (8), pág. 792 (2002)

(ii) Kelly, Am. J. Phys. **49** (8), pág. 714 (1981)

(iv) Lee, Am. J. Phys. **69** (8), pág. 874 (2001)

Se considerará de manera mínima una discusión unificada, clara y crítica de dichos resultados.

2. Considere un gas ideal clásico en tres dimensiones.

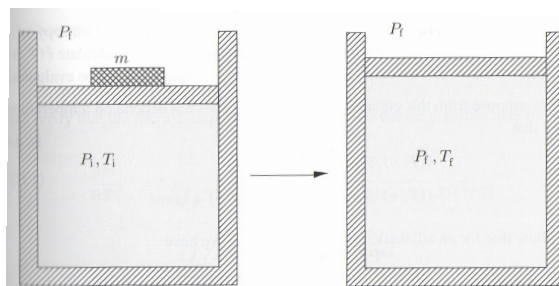
a) Suponga que un mol de dicho gas, que se encuentra inicialmente en el estado (P_i, T_i, V_i) , es sometido a una expansión adiabática reversible llevándolo al estado (P_f, T_f, V_f) , con $P_f < P_i$. Calcule T_f y demuestre que el trabajo realizado sobre el gas es $W = C_V(T_f - T_i)$

b) Suponga ahora que un mol de gas es comprimido por un pistón en el que se coloca una masa m de tal manera que la presión inicial es

$$P_i = P_f + \frac{mg}{A},$$

donde P_f es la presión atmosférica y A es el área del pistón (ver figura). La masa es removida instantáneamente y se asume que el gas está aislado térmicamente de manera perfecta y que el pistón resbala sin fricción. ¿Cuál es la temperatura final T'_f como función de T_i , P_f/P_i y $\gamma = C_P/C_V$? Dibuje curvas representativas de T_f/T_i y T'_f/T_i como función de P_f/P_i para $0 \leq P_f/P_i \leq 1$.

c) ¿Se pudo haber predicho, sin calcular, que $T'_f > T_f$? ¿En cuál de las expansiones anteriores se proporciona más trabajo a los “alrededores”? En el experimento del inciso anterior reincorporamos la masa sobre el pistón. Calcule la temperatura y volumen final, T''_f y V''_f . Compare con T_i y V_i .



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 suppressed 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 measurable 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 Lewis⁴ 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

Table I. Thermodynamic relations for blackbody radiation.

<i>F</i>	<i>S</i>	<i>H</i>	<i>U</i>	<i>P</i>	<i>N</i>	<i>G</i>	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 Zemansky⁶ 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 μdN 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

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

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, $b = 8\pi^5 k^4 / (15h^3 c^3)$. 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:

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

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:

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

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

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

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

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 $S \rightarrow 0$ as $T \rightarrow 0$, 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,

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

resulting in

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

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

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

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 Sychev¹⁵ and by Epstein.¹⁶ Since $S = S(V, T)$, one may write

$$\begin{aligned} \int_{S(0,0)}^{S(V,T)} dS &= S(V, T) - S(0, 0) \\ &= \int_0^T \left(\frac{\partial S}{\partial T} \right)_{V=0} dT + \int_0^V \left(\frac{\partial S}{\partial V} \right)_T dV, \end{aligned}$$

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

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

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,

$$W = \int P dV = P \Delta V = (1/3) b T^4 \Delta V. \quad (13)$$

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 $dQ = T dS$, 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 ($PV^{4/3} = \text{const.}$), which is of the form $PV^\gamma = \text{const.}$, 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 $PV^{4/3} = \text{const.}$ in order to calculate the work done by the system in expanding from P_i, V_i to P_f, V_f :

$$W = \int P dV = \dots 3(P_i V_i - P_f V_f). \quad (14)$$

Recall from elementary thermodynamics that the work done in an adiabatic process is $W = (P_i V_i - P_f V_f)/(\gamma - 1)$, 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 $VT^3 = \text{const.}$, resulting in $\lambda T = \text{const.}$, 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 invariants²⁴; 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 equation²⁷ $dP/dT = Q/(T\Delta V)$ 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 rule²⁸ 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 $P_4 = P_3$:

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

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

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

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

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 sys-

tem 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, $\lambda T = \text{const.}$, 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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Teaching the photon gas in introductory physics

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The ideal gas is often the only thermodynamic system for which equations of state are studied in introductory physics. The photon gas can be a rich supplement to the ideal gas, and a vehicle for introducing 20th century physics concepts. © 2002 American Association of Physics Teachers.
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I. INTRODUCTION

The monatomic classical ideal gas, which is called the ideal gas in this paper, is a staple of introductory physics. It is understandable in the context of a system of noninteracting point particles,¹ and its equations of state are tractable mathematically. These virtues of the ideal gas are summarized in Table I. With them come several less desirable characteristics. First, it is based on classical physics or the semiclassical limit of a quantum ideal gas, and hence does not provide insights on quantum or relativistic phenomena. Second, the internal energy is independent of volume, a property that holds only in the low density limit for real gases. Third, the ideal gas gives no insight into changes of state such as the vapor to liquid transition. Finally, because it is usually the only system for which equations of state are encountered, students tend to come away with a sense that every system behaves as an ideal gas.

In contrast, the photon gas is a quantum mechanical system of particles (quanta of the electromagnetic field) called photons.² The thermal behavior of photons in blackbody radiation has played a pivotal role in the development of quantum mechanics. In addition, because photons move with the speed of light, the photon gas is a relativistic system. Thus it reflects two major developments of 20th century physics: quantum mechanics and relativity. Over a decade ago, the Introductory University Physics Project called for more 20th century physics in introductory courses.³ Inclusion of the photon gas would work toward this goal.

The quantum mechanical probability amplitudes for photons can interfere constructively or destructively with one another, but photons do not ordinarily affect one another's energies, momenta, or polarizations, which simplifies their thermodynamic behavior. Unlike the ideal gas, the internal energy function for the photon gas is volume dependent. Remarkably, despite its nonatomic nature, the photon gas can provide insights into the liquid-vapor phase transition. Finally the very notion of the photon gas disabuses students of the thought that every thermodynamic system behaves as an ideal classical gas.

A key feature of the photon gas is that it has a variable particle number, N . Consider a container of volume V , whose walls are maintained at temperature T . Suppose it has been emptied of matter by a vacuum pump. It cannot be entirely "empty" because the walls radiate photons into the container. Some photons scatter off the walls, with some being absorbed and new ones being emitted continually. A dynamic equilibrium exists when the average absorption and

emission rates are equal. Thus, an apparently empty container actually is filled with a photon gas, a fact that can intrigue students.

Unlike the ideal gas, for which there are three independent variables, N , T , and V , the photon gas has just two independent, controllable variables, T and V . We can envisage building a photon gas from energy stored in the container walls. Consider the container in Fig. 1. Imagine purging it of all atoms with a vacuum pump, and then moving the piston to the left until it touches the left wall. The volume is then zero and the walls (including the piston) have temperature T . Now slowly move the piston to the right, keeping the wall temperature constant using a reservoir. Photons will pour out of the walls as the volume increases, until the dynamic equilibrium described above occurs. In this way, we mentally construct a photon gas of volume V and temperature T , with average photon number $N(T, V)$. Building the photon gas using this thought experiment can help develop an understanding of the nature of the variable particle photon gas.

The most straightforward approach for introducing the photon gas in introductory physics is to define it in a way similar to that in the preceding paragraphs, and to then display the relevant thermodynamic equations of state and examine their implications. The extent to which the equations of state are used can vary. At minimum, the equations can be presented and interpreted. If time allows and the interest level is sufficient, they also can be used to analyze isothermal and adiabatic processes for the photon gas, as is done in the body of this paper.

A more ambitious approach is to use kinetic theory to establish the connection between internal energy and pressure for the photon gas, and to use calculus to derive the equations of state. This procedure is presented in the Appendix as a resource for teachers.

A rich literature, mainly related to blackbody radiation, exists in books on modern physics,⁴ quantum physics,⁵ optics,⁶ and classical and statistical thermodynamics.⁷⁻¹³ Numerous citations to the literature are given in Ref. 14. Nevertheless, the photon gas has not found its way into introductory physics textbooks. The main purpose of this paper is to encourage teachers of introductory physics and textbook authors to adopt the photon gas as a supplement to the ideal gas. Some of the ideas here might also be useful to teachers of modern physics and junior-senior level thermal physics.

II. PHOTON GAS EQUATIONS OF STATE AND PROCESSES

The equations of state for the internal energy $U(T, V)$ and pressure $P(T)$ are

Table I. Summary of monatomic classical ideal gas properties.

Property type	Description
Independent variables	N, V, T
System	Collection of N noninteracting point particles, each with mass m , described by classical mechanics
Temperature-independent result from kinetic theory, relating the internal energy U and pressure P	$U = \frac{3}{2}PV$
Internal energy	$U = \frac{3}{2}NkT$
Pressure	$P = NkT/V$
Entropy ^a	$S = Nk[\ln(T^{3/2}V/N) + \ln(2\pi mk/h)^{3/2} + \frac{5}{2}]$
Work W on the gas for isothermal volume change by ΔV	$W = -NkT \ln(1 + \Delta V/V)$
Energy Q added to gas by heat process for isothermal volume change by ΔV	$Q = NkT \ln(1 + \Delta V/V)$
Entropy change of gas for isothermal volume change by ΔV	$\Delta S = Nk \ln(1 + \Delta V/V)$
Reversible adiabatic condition, where the heat capacity ratio $C_p/C_v = 5/3$	$PV^{5/3} = \text{constant}$

^aThe expression for the entropy is the Sackur–Tetrode equation, the classical limit for Bose–Einstein and Fermi–Dirac quantum ideal gases with atoms of mass m . Planck’s constant h connotes the Sackur–Tetrode equation’s quantum origin, and k reflects the thermodynamic nature of the gas.

$$U(T, V) = bVT^4 \tag{1}$$

and

$$P(T) = \frac{1}{3}bT^4. \tag{2}$$

The constant b cannot be determined from thermodynamics, but its value can be borrowed from statistical physics or experimental results. It is given by

$$b = \frac{8\pi^5 k^4}{15h^3 c^3} = 7.56 \times 10^{-16} \text{ J K}^{-4} \text{ m}^{-3}. \tag{3}$$

Note that b depends on Planck’s constant h , which reflects the quantum mechanical nature of the photon gas, the speed of light c , which reflects its relativistic nature, and Boltzmann’s constant k , which reflects its thermodynamic nature. At the introductory level, we can introduce Eqs. (1) and (2) and give the numerical value of b , without broaching the formula in Eq. (3).

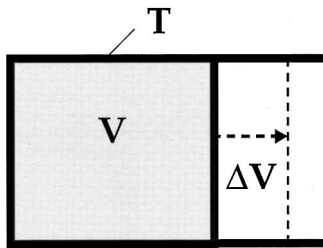


Fig. 1. Photon gas in a container with wall temperature T and volume V . The right wall is movable and its quasistatic movement can alter V reversibly by ΔV .

Given the foregoing, it is straightforward to analyze isothermal processes for the photon gas. Consider a quasistatic volume change from V to $V + \Delta V$. From Eq. (1), if T is constant,

$$\Delta U = bT^4 \Delta V. \tag{4}$$

From the first law of thermodynamics, $\Delta U = Q + W$, where $W = -\int P(T)dV$ is the work done on the photon gas. When T is constant, so is $P(T)$, and Eq. (2) implies that

$$W = -\frac{1}{3}bT^4 \Delta V. \tag{5}$$

Thus the energy gained by the photon gas from the concomitant increase or decrease in the number of photons, which constitutes a radiative heat process, is

$$Q = \frac{4}{3}bT^4 \Delta V. \tag{6}$$

The slow isothermal volume change under consideration is reversible, and the entropy change, Q/T , of the photon gas is

$$\Delta S = \frac{4}{3}bT^3 \Delta V. \tag{7}$$

This entropy change, which is linear in ΔV , is very different from the logarithmic volume dependence of the corresponding entropy change for an ideal gas, which is shown in Table I.

Now suppose we build the photon gas as described earlier by choosing the initial volume in Eq. (7) to be zero and the final volume to be V . We then allow the piston to move to the right slowly to volume V , creating the photon gas. Because at zero volume, the photon number $N=0$, evidently $S=0$; that is, there can be no entropy if there are no photons. Equation (7) then implies that at volume V ,

$$S = \frac{4}{3}bVT^3. \tag{8}$$

Notice that Eqs. (1) and (2) imply that the enthalpy¹⁵ $H = U + PV$ is

$$H = \frac{4}{3}bVT^4. \tag{9}$$

Clearly for an isothermal volume change, $\Delta H = Q$ and for an expansion from zero volume to volume V , $H = Q = TS$. This example makes clear that enthalpy is the energy needed to form the photon gas and to do the work needed to make available the volume V it occupies.¹⁶

Next, consider a slow adiabatic volume change. Adiabatic means that no photons are emitted or absorbed by the container walls. For a photon gas, the *only* possible type of heat process is via radiation; that is, energy can be exchanged with the container *only* by the emission and absorption of photons. An adiabatic volume change requires that the container walls be perfectly reflecting mirrors. Under such a process the photon number cannot change because a perfect reflector is also a nonemitter of photons. Because the number of photons cannot change, $N(T, V) = \text{constant}$. Furthermore, a slow, reversible adiabatic process leaves the entropy of the photon gas unchanged, so $S(T, V) = \text{constant}$. The constancy of both $N(T, V)$ and $S(T, V)$ implies that $N(T, V) = \text{constant} \times S(T, V)$, which along with Eq. (8), leads to the conclusion that

$$N(T, V) = rVT^3, \tag{10}$$

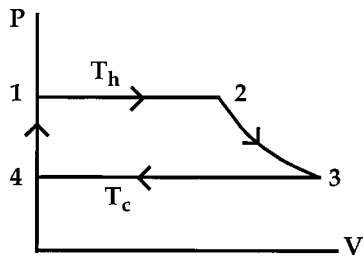


Fig. 2. A plot of pressure P versus volume V for a reversible Carnot cycle using a photon gas as the working fluid. The horizontal segments 1–2 and 3–4 are isothermals at temperatures T_h and T_c , respectively. Segment 2–3 is a reversible adiabatic expansion. Segment 4–1 occurs at zero volume and therefore entails only the container walls and not the photon gas.

where r is a constant. As was the case for b , r cannot be evaluated within the domain of thermodynamics, but its value can be borrowed from statistical physics,¹⁷

$$r = 60.4 \left(\frac{k}{hc} \right)^3 = 2.03 \times 10^7 \text{ m}^{-3} \text{ K}^{-3}. \quad (11)$$

As before, the constants h , c , and k illustrate the quantum mechanical, relativistic, and thermodynamic nature of the photon gas. Also as before, to keep the discussion elementary, the value of r can be stated without broaching the formula in Eq. (11).

From Eqs. (8) and (2), it is clear that the condition of constant entropy is

$$T^3 V = \text{constant} \quad \text{or} \quad P V^{4/3} = \text{constant}. \quad (12)$$

Interestingly, the second form in Eq. (12) is similar to the corresponding condition in Table I for an ideal gas, for which $P V^\gamma = \text{constant}$, where $\gamma = C_p/C_V = 5/3$. However, the similarity is only formal because for the photon gas, C_p does not even exist, because one cannot vary the temperature at constant pressure for a photon gas.

Having found Eqs. (2) and (12), we can sketch a reversible Carnot cycle on a pressure–volume diagram. We take advantage of the fact that the photon gas can be brought to zero volume, so that the Carnot cycle looks as shown in Fig. 2. The horizontal isotherms 1–2 and 3–4 come from the fact that $P = P(T)$. The adiabatic segment 2–3 is qualitatively similar to reversible adiabatic curves for the ideal gas. The vertical segment 4–1 corresponds to heating the container walls from T_c to T_h , with zero photons in the zero volume container. Along this segment, the walls undergo a heat process, but there is no photon gas present and thus $Q = 0$ for a photon gas working fluid.

Figure 2 makes it clear that the pressure–volume representation of a Carnot cycle does not necessarily appear as it does for an ideal gas. The purpose here is not to exhibit a *real* working fluid, but rather to illustrate that a Carnot cycle’s P – V plot can differ from that obtained for the ideal gas. It is a good exercise for students to use the photon gas equations to show that, as expected, the thermal efficiency is $\eta = 1 - T_c/T_h$, the reversible Carnot cycle efficiency for *any* working fluid.

III. COMPARISON: IDEAL AND PHOTON GASES

After introducing the photon gas and examining its behavior under isothermal and adiabatic processes, it is useful to

Table II. Comparison of equations for classical ideal and photon gases.

Classical ideal gas	Photon gas
N is specified and fixed	$N = r V T^3$
$U = \frac{3}{2} N k T$	$U = b V T^4 = 2.7 N k T$
$P = N k T / V$	$P = \frac{1}{3} b T^4 = 0.9 N k T / V$
$S = N k [\ln(T^{3/2} V / N) + \ln(2 \pi m k / h)^{3/2} + \frac{5}{2}]$	$S = \frac{4}{3} b V T^3 = 3.6 N k$

compare it with the ideal gas. One comparison examines corresponding equations of state of the two gases. Such a comparison is shown in Table II, using the fact that $N = 2.03 \times 10^7 V T^3$. In this view, the pressure and internal energy functions are remarkably similar if the dependent variable N is displayed explicitly for the photon gas. Thus for example, the average energy per photon in a photon gas is $2.7 kT$, compared with $1.5 kT$ for the ideal gas. Similarly, the pressure P of the photon gas is $0.9 N k T / V$ compared with $N k T / V$ for the ideal gas. Keep in mind, however, that N is *not* an independent variable for the photon gas, so the similarities are strictly formal. The entropy functions are very different looking for the photon and ideal gases. Notably, the entropy per photon is $3.6k$, independent of temperature.

A numerical comparison is shown in Table III. The ideal gas is taken to have the mass of monatomic argon and is at 300 K and normal atmospheric pressure. The numerical values of N , U , P , and S for the photon gas are all approximately 10 or more orders of magnitude smaller than for the ideal gas, which is why we can ignore the photon gas when discussing the thermodynamics of an ideal gas in the vicinity of room temperature and atmospheric pressure.

On the other hand, for sufficiently high temperatures, the number of photons can exceed the number of ideal gas atoms in an equal volume V . Indeed, it is straightforward to show that if 1.00 mol of argon ideal gas is at standard atmospheric pressure, 1.01×10^5 Pa, the corresponding average number of photons exceeds the number of atoms for any V if $T > 1.38 \times 10^5$ K. The equations in Table II imply that for $T \approx 1.41 \times 10^5$ K, the ideal and photon gases have nearly the same internal energies and pressures, while the ideal gas entropy is still significantly larger than the photon gas entropy. Of course, because of the T^3 behavior of N and S , and the T^4 behavior of P and U , the photon gas will dominate the ideal gas in *all* respects for sufficiently high T . In this discussion we have ignored the ionization of the ideal gas atoms that would occur at such high temperatures.

Other comparisons are possible. For example, the ideal gas entropy becomes negative for sufficiently small T and diverges to negative infinity in the limit $T \rightarrow 0$. This inad-

Table III. Numerical comparison of classical ideal and photon gas functions. Here the ideal gas is 1.00 mol of monatomic argon at $P = 1.01 \times 10^5$ Pa, $V = 2.47 \times 10^{-2}$ m³, and $T = 300$ K.

Function	Classical ideal gas	Photon gas
N	6.02×10^{23} atoms	1.35×10^{13} photons
U	3.74×10^3 J	1.51×10^{-7} J
P	1.01×10^5 Pa	2.04×10^{-6} Pa
S	155 J/K	6.71×10^{-10} J/K

equacy of the ideal gas model comes from its classical character. In contrast, the photon gas entropy approaches zero in the $T=0$ limit. Similarly, the ideal gas constant volume heat capacity is constant and remains so in the zero temperature limit, unlike real gases, whose heat capacities approach zero, consistent with the third law of thermodynamics. The photon gas heat capacity at constant volume, $C_V=4bVT^3$, approaches zero in this limit, as the number of photons approaches zero. The behavior of the photon gas reflects its quantum mechanical nature.

The ideal gas gives no indication of the condensation phenomenon that a real gas experiences at temperatures below its critical temperature. As a real gas is compressed isothermally at a temperature below its critical temperature, part of it begins to condense into the liquid state, keeping the pressure constant. Although it is a very different kind of system, with very different physics, the photon gas can shed light on this phenomenon because under isothermal compression, photons get absorbed, becoming part of the energy of the walls, providing an analogy to the vapor-to-liquid transition: the photons play the role of the vapor molecules, and the absorbed energy of the walls are the analog of the liquid molecules. The energy of compression to zero volume for the photon gas is the rough analog of the heat of condensation for the real gas.

For the photon gas, the pressure remains constant as the volume decreases at constant temperature because the number of photons decreases while the energy of the walls increases. For a real gas, the pressure remains constant during isothermal compression because the number of gas molecules decreases as gas molecules become liquid molecules. Condensation phenomena occur because of attractive forces between molecules, while photon absorption occurs because atoms and molecules continually absorb and emit radiation, as their electronic energies increase and decrease. Although the physics differs for the two phenomena, both are characterized by constant temperature, constant pressure, and a variable number of gas particles. Discussion of these matters can shed light not only on radiation, but on the phenomenon of condensation.

IV. TWO BRIEF EXAMPLES

Perhaps the most exciting example of a photon gas is the cosmic microwave background radiation.¹⁸ The latter is in essence a gas of “old” photons that was created in the early, hot Universe approximately 13 billion years ago, and which has cooled to 2.7 K. Inserting the latter temperature and the value of r in Eq. (11) into Eq. (10) gives $N/V=416$ photons/cm³. Such photons, which make even dinosaur bones seem rather young, are in our vicinity all the time. An awareness of the photon gas opens the door to an understanding of this remarkable phenomenon.

A second example uses a well-known result from kinetic theory¹⁹ together with Eq. (10). Suppose a photon gas exists in a cavity within a solid that is at temperature T , and that photons can leak out through a small opening in the walls. The kinetic theory result for the particle flux is $\frac{1}{4}(N/V)c=\frac{1}{4}rcT^3$, and the energy flux, measured in watts/m², is $\frac{1}{4}(N/V)(U/N)=\frac{1}{4}cbT^4$. This result is the well-known energy flux from a blackbody, where $cb/4=\sigma=5.67\times 10^8$

$W m^{-2} K^{-4}$, is the Stefan–Boltzmann constant. In appropriate contexts, one can move on to study Planck’s radiation law and, ultimately, quantum mechanics.

V. CONCLUSIONS

The photon gas can enrich the introduction to thermodynamics. Its basic equations lead students into new territory involving creation and annihilation of photons, which provides a thought provoking introduction to modern physics ideas.

An important related point is that photons are everywhere. That is, because all matter radiates, it is literally impossible to have a region of space that is free of photons. In this sense, the photon gas has the distinction of being ubiquitous, another point that can pique the intellectual curiosity of students.

Despite the evident richness of the photon gas, its equations of state are tractable and have straightforward interpretations. In addition to its potential for enriching the study of thermal physics, the photon gas serves as a good foundation for subsequent introduction to cavity radiation.

In summary, the photon gas has much to offer teachers and students. Its study can supplement the ideal gas or can be initiated in a course on modern physics. A more in-depth treatment is appropriate for junior or senior level thermal physics.

ACKNOWLEDGMENT

I thank John Mallinckrodt and Ron Brown for very helpful comments on a first draft of this paper.

APPENDIX

The objective of the Appendix is to derive Eqs. (1) and (2). Kinetic theory enables us to deduce a simple relationship between the internal energy U and pressure P of a photon gas,

$$P(T)=\frac{1}{3}\frac{U(T,V)}{V}=\frac{1}{3}u(T). \quad (A1)$$

The right-hand side defines the energy density $u(T)$.

To obtain Eq. (A1), we make several assumptions. First, we assume isotropy, namely, the average number of rightward moving photons within a specified range of velocity is the same as the corresponding average number of leftward moving photons. Denote the number of photons per unit volume with x components of velocity between c_x and c_x+dc_x by $n(c_x)dc_x$. The assumed isotropy implies $n(c_x)=n(-c_x)$. (Because photons all have speed c , c_x varies solely because of differing velocity directions.) Integration over c_x gives

$$\int_{-c}^c n(c_x)dc_x=2\int_0^c n(c_x)dc_x=\frac{N}{V}, \quad (A2)$$

where N is the (average) number of photons. The function $Vn(c_x)/N$ is a probability distribution function that can be used to calculate averages such as

$$\overline{c_x^2}=\int_{-c}^c \frac{Vn(c_x)}{N}c_x^2 dc_x=2\int_0^c \frac{Vn(c_x)}{N}c_x^2 dc_x. \quad (A3)$$

The last step follows because $n(c_x)c_x^2$ is an even function of c_x . Equation (A3) will be used in our derivation of Eq. (A1).

Our second assumption is that there is a well-defined average photon energy $\langle e \rangle$, which depends solely on the wall temperature and not on the system volume V . This assumption is motivated by the expectation that the energy distribution of the emitted photons depends on the wall temperature. In contrast, the average number of photons N must depend on both temperature T and volume V because in equilibrium, the absorption and emission rates can be equal only if N achieves a sufficiently large value, which increases with V . Our last assumption is that N is proportional to the system volume; that is, $N(T, V) = n(T)V$. We now proceed with the kinetic theory derivation.

Fix the right wall in Fig. 1 and denote the container's horizontal length by L and its cross sectional area by A . Choose a small time interval $\Delta t \ll L/c$, and consider rightward moving photons with x -components of velocity between c_x and $c_x + dc_x$, located within distance $c_x \Delta t$ from the right wall. The latter region has spatial volume $Ac_x \Delta t$, and an average number of photons, $(Ac_x \Delta t)n(c_x)dc_x$, within it will collide with the right wall in time interval Δt . The momentum magnitude for a photon with energy e is e/c and the x component of its momentum is $(e/c)(c_x/c)$. In an elastic collision with the right wall a photon's momentum change is $2(e/c)(c_x/c)$, and the average force it exerts on the wall during time Δt is $2ec_x/(c^2 \Delta t)$.²⁰ The average force for all such collisions by photons with average energy $\langle e \rangle$ and x component of velocity between c_x and $c_x + dc_x$ is $(2\langle e \rangle c_x / c^2)(Ac_x)n(c_x)dc_x$.

If we integrate over c_x from 0 to c and divide by area A , the average pressure on the wall from photons impinging at all angles is

$$P = \frac{2\langle e \rangle}{c^2} \int_0^c n(c_x)c_x^2 dc_x = \frac{\langle e \rangle N}{Vc^2} = \frac{1}{3} \frac{\langle e \rangle N}{V}. \quad (\text{A4})$$

The penultimate step follows from Eq. (A3) and the last step follows from the isotropy condition, $c_x^2 = c^2/3$. In Eq. (A4), $N\langle e \rangle = U$, the internal energy of the photon gas. With our assumptions that $\langle e \rangle$ is solely a function of T and $N = n(T)V$, Eq. (A4) reduces to Eq. (A1), $P(T) = \frac{1}{3}u(T)$, where $u(T) = U/V$. It is clear from Eq. (A1) that pressure is solely a function of temperature and thus, the pressure-volume isotherms for a photon gas form a family of constant-pressure curves. We now use the forms $P = P(T)$ and $U = u(T)V$, along with the Carnot cycle in Fig. 2 to derive Eq. (1). Along segments 1-2, 2-3, 3-4, and 4-1, the internal energy changes of the photon gas are $\Delta U_{12} = u(T_h)V$, $\Delta U_{23} = -\frac{1}{3} \int_V^{V+\Delta V} u(T)dV$, $\Delta U_{34} = -u(T_c)(V + \Delta V)$, and $\Delta U_{41} = 0$, respectively. Because U is a state function, these changes must add to zero along the cycle. Simplification occurs when $T_h - T_c \ll T_c$ and $\Delta V \ll V$, in which case we replace ΔV by dV . Then the addition of the four internal energy changes gives $u(T_h)V - \frac{1}{3}u(T)dV - u(T_c)(V + dV) = 0$, where $T_c \leq T \leq T_h$. Replacement of $u(T)$ with $u(T_c)$ induces an additive error $\leq du \equiv u(T_h) - u(T_c)$. Thus to first order in du and dV the sum of the internal energy changes around the cycle reduces to

$$V du - \frac{4}{3} u dV = 0. \quad (\text{A5})$$

The individual entropy changes of the photon gas along the Carnot cycle are $\Delta S_{12} = \frac{4}{3}u(T_h)V/T_h$, $\Delta S_{23} = 0$, $\Delta S_{34} = -\frac{4}{3}u(T_c)(V + dV)/T_c$, and $\Delta S_{41} = 0$, respectively. Because S is a state function, these changes also must add to zero along the cycle. Using $dV \ll V$ and $dT \equiv T_h - T_c \ll T_c$, we have $1/T_h \approx (1 - dT/T_c)/T_c$, and the condition for zero entropy change along the cyclic path becomes

$$\frac{4}{3} \left[\frac{(u(T_h) - u(T_c))V}{T_c} - \frac{u(T_c)dV}{T_c} - \frac{u(T_h)V dT}{T_c^2} \right] = 0. \quad (\text{A6})$$

Replacing T_c with T and T_h with $T + dT$, and retaining only first order terms, Eq. (A6) becomes

$$V du - u dV - \frac{uV dT}{T} = 0. \quad (\text{A7})$$

We can eliminate dV by combining Eqs. (A5) and (A7) to obtain

$$\frac{1}{4} du = \frac{u}{T} dT. \quad (\text{A8})$$

Finally, integration of Eq. (A8) gives $u(T) = bT^4$, which is equivalent to Eq. (1). As mentioned, the numerical value of b is obtained from statistical mechanics. The combination of Eqs. (1) and (A1) gives Eq. (2).

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¹Weak interactions must exist in order for the gas to achieve thermodynamic equilibrium. It is assumed that these interactions have negligible effects on the equations of state.

²The term "photon" was coined by Gilbert N. Lewis, "The conservation of photons," *Nature (London)* **118**, 874-875 (1926).

³See Lawrence A. Coleman, Donald F. Holcomb, and John S. Rigden, "The introductory university physics project 1987-1995: What has it accomplished?" *Am. J. Phys.* **66**, 124-137 (1998), and references therein.

⁴Stephen T. Thornton and Andrew F. Rex, *Modern Physics*, 2nd ed. (Saunders College Publishing, New York, 2000), pp. 91-96, 296-298.

⁵David J. Griffiths, *Introduction to Quantum Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1995), pp. 216-218, 311-312.

⁶Eugene Hecht, *Optics* (Addison-Wesley Longman, Reading, MA, 1998), pp. 50-57, 575-583.

⁷C. J. Adkins, *Equilibrium Thermodynamics* (McGraw-Hill, New York, 1968), pp. 146-159.

⁸Ralph Baierlein, *Thermal Physics* (Cambridge University Press, Cambridge, 1999), pp. 116-130.

⁹Ashley H. Carter, *Classical and Statistical Thermodynamics* (Prentice-Hall, Upper Saddle River, NJ, 2001), pp. 186-190.

¹⁰Daniel V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, New York, 2000), pp. 288-307.

¹¹Keith Stowe, *Introduction to Statistical Mechanics and Thermodynamics* (Wiley, New York, 1984), Chap. 26.

¹²Raj K. Pathria, *Statistical Mechanics*, 2nd ed. (Butterworth-Heinemann, Oxford, 1996), Appendixes B, D, E.

¹³Daniel J. Amit and Yosef Verbin, *Statistical Physics: An Introductory Course* (World Scientific, Singapore, 1995). Relevant kinetic theory is discussed in Part I, Chap. 1, and the photon gas is discussed in Part IV, Chap. 4.

¹⁴Harvey S. Leff (in preparation).

¹⁵Students of introductory physics do not typically encounter enthalpy in their courses, and the discussion in the text can be skipped. On the other hand, students are introduced to enthalpy in their chemistry courses, and the discussion in the text might help them appreciate, if not fully understand, enthalpy in a wider context.

¹⁶See Ref. 10, p. 33.

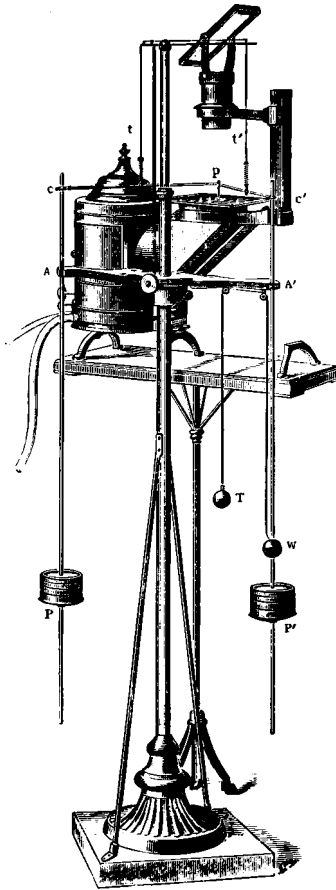
¹⁷In Eq. (11), the prefactor 60.4 in r arises from an integral, which gives $8\pi\zeta(3)\Gamma(3) = 60.4$. Here $\zeta(3)$ and $\Gamma(3)$ are zeta and gamma functions, respectively.

¹⁸Edward Harrison, *Cosmology: The Science of the Universe*, 2nd ed. (Cambridge University Press, Cambridge, 2000), Chap. 17.

¹⁹E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938), Sec. 37.

²⁰The assumption of elastic collisions does not hold for walls that can absorb and emit photons. In that case, however, isotropy guarantees that Eq. (A1)

still holds because the average number of photons coming from a wall section in any time interval must equal the number approaching the wall, and the average momentum approaching must equal the average momentum leaving. The mathematical treatment used for elastic collisions thus holds in an average sense when inelastic collisions occur, and isotropy holds.



Lissajous Figure Drawing Device. Lissajous figures are the resultant of two simple harmonic motions at right angles to each other. In this dedicated device, the SHMs are provided by two pendula swinging at right angles to each other. Horizontal rods coupled to the tops of the pendula drive a stylus P that scrapes the soot from a smoked glass plate held on the stage of the overhead projector. The audience thus sees a black screen with the figure being traced out in white. The illustration is from J. A. Zahm, *Sound and Music*, second edition (A. C. McClurg & Co., Chicago, 1900), p. 409 (Notes by Thomas B. Greenslade, Jr., Kenyon College)

Carnot cycle for photon gas?

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The Carnot cycle for a photon gas provides a useful means to illustrate the thermodynamic laws. It is particularly useful in showing the path dependence of thermodynamic functions. Thermodynamic relationships to a neutrino gas are also drawn. © 2001 American Association of Physics Teachers. [DOI: 10.1119/1.1371917]

I. INTRODUCTION

Almost all standard texts on thermodynamics present the Carnot cycle based on the thermodynamic behavior of the ideal gas.¹ This is certainly well justified. The ideal gas approximately represents the vapor phases of fluids at high temperatures for which the heat engine is constructed. For the ideal gas we also know the P vs V relationship on adiabatic and isothermal paths exactly.

Although not as practical perhaps, the thermodynamic behavior of a photon gas is simpler and in some ways richer than that of the ideal gas. Why not therefore construct the Carnot cycle for a photon gas? For a photon gas we know all the thermodynamic functions such as U , F , S , P , valid at all temperatures. It is easy to construct the Carnot cycle not just in the PV plane but also in other planes, especially because the entropy is given very simply (not logarithmic in T as it is for the ideal gas).

For a photon gas the chemical potential μ vanishes.^{2,3} This fact permits us to regard a photon gas as being placed in a state of coexistence. For this gas, then, there is an added richness provided by the physics of a first-order transition, out of reach for the conventional ideal gas. Perhaps most helpful pedagogically, the thermodynamic laws are lucidly illustrated through the Carnot cycle of a photon gas. There is no need to bring in statistical mechanics to achieve it. We can arrive at all the thermodynamic consequences starting from just one experimental fact, the one on the energy density.

II. THERMODYNAMIC FUNCTIONS OF A PHOTON GAS

Long ago it was already established that the energy density of a photon gas depends very simply on the temperature only.² If u is the energy density and T the temperature,

$$u \equiv \frac{U}{V} = \sigma T^4, \quad (1)$$

where σ is the Stefan-Boltzmann constant, V the volume, and U the total energy. From (1) it follows at once that the specific heat at constant volume C_V is

$$C_V = 4\sigma VT^3. \quad (2)$$

The entropy S can be obtained from C_V by the simple integral

$$S = \int_0^T C_V \frac{dT}{T} = \frac{4}{3} \sigma VT^3. \quad (3)$$

Hence the Helmholtz free energy F follows from the definition

$$F \equiv U - TS = -\frac{1}{3} \sigma VT^4. \quad (4)$$

Finally the pressure P follows from

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

The pressure depends only on one variable, in this case T , which is indicative of being at a phase boundary. Note also that (1) and (5) give the standard result $PV = (1/3)U$. We now have the knowledge of all the thermodynamic functions needed to construct the Carnot cycle for a photon gas. See Kelly⁴ for another way of obtaining these thermodynamic functions. Also see Pearson⁵ and Massa⁶ for the applicability of thermodynamics to blackbody radiation.

III. CARNOT CYCLE

The Carnot cycle expresses thermodynamic relationships in the P and V planes. The cycle or circuit is composed of four connected paths, alternatingly of constant T and constant S . For a photon gas the path of constant T is trivial since P does not depend on V . The path of constant S is determined if we combine P and S to eliminate T , see (3) and (5), giving

$$PV^\beta = f(S), \quad (6)$$

where $\beta = 4/3$ and $f(S)$ is a function of the entropy only, hence a constant on an adiabatic path.

Using (5) and (6) we can readily construct the Carnot cycle as shown in Fig. 1. The paths are indicated, 1–2 and 3–4 the isothermal and 2–3 and 4–1 the adiabatic. The isothermal paths are set at T' and T'' ($T' < T''$) and the adiabatic paths at S' and S'' ($S' < S''$).

Let $X(ij) = X(j) - X(i)$, where $X(i)$ is a thermodynamic function at the i th position of the cycle, and ij the adjacent positions. Observe that on the *isothermal* paths $U(ij) \neq 0$. Hence, $Q(ij) > W(ij)$, where Q and W are, respectively, the heat and work done. This behavior is different from that of the ideal gas. But on the *adiabatic* paths $U(ij) = -W(ij)$. For one cycle $Q = W$ still.

We can also calculate the heat exchanged. Since $Q = T\Delta S$, on the isothermal paths $Q(12) = T''(S'' - S')$ and $Q(34) = T'(S'' - S')$. On the two adiabatic paths $Q = 0$, of course. We can write down the efficiency η at once

$$\eta \equiv \frac{Q(12) - Q(34)}{Q(12)} = \frac{T'' - T'}{T''} < 1. \quad (7)$$

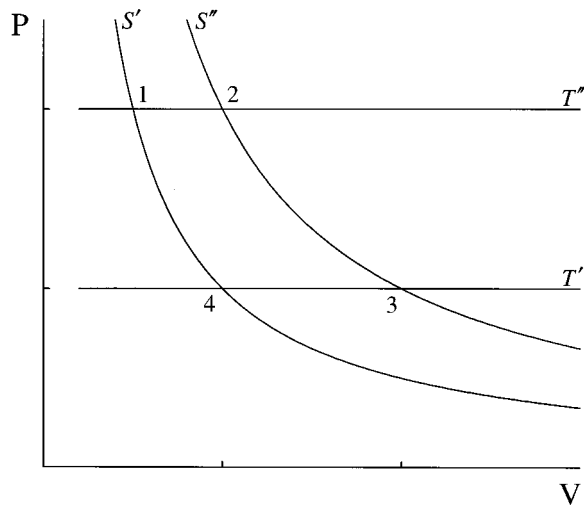


Fig. 1. P vs V . Isothermal and adiabatic paths are indicated by T and S , respectively. The two values of T are T' and T'' with $T' < T''$. Similarly the two values of S are S' and S'' with $S' < S''$. The paths following 12341 constitute one cycle.

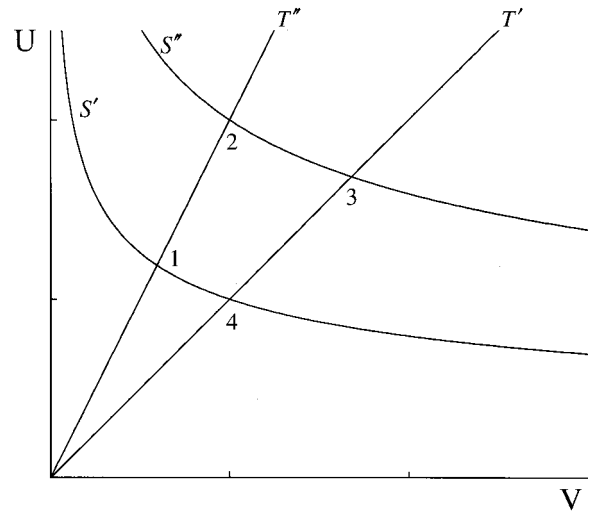


Fig. 2. U vs V . The cycle shown in Fig. 1 is redrawn in the UV plane. The slope of U along an adiabatic path is the (negative) pressure while the slope along an isothermal path is the energy density.

The photon engine yields the same efficiency as the conventional ideal gas.^{1,4} The inequality exists since T' can never be zero by the third law.

Since $\Delta U = 0$ for one cycle. $W = Q(12) - Q(34)$ by the first law. The work done is also represented by the area enclosed by the cycle. This is even simpler to demonstrate, since on the isothermal paths P is independent of V , so that $PdV = P\Delta V$. It is also elementary to transform the Carnot cycle to other sets of thermodynamic variables, e.g., UV as shown below.

IV. CARNOT CYCLE AND PHYSICAL PROPERTIES

The Carnot cycle is particularly useful for illustrating certain physical properties defined on an isothermal or adiabatic path. They are given by the slope of a path of the Carnot cycle (sometimes with a negative sign or by its inverse.)

As shown in Fig. 1, the isothermal paths (12 and 34) are flat, implying that the isothermal compressibility κ_T is ∞ . That is, a photon gas is infinitely compressible on an isothermal path since the radiation pressure is independent of the volume. The adiabatic paths (23 and 41) are not flat and their slope (actually the negative inverse) corresponds to the adiabatic compressibility $\kappa_S = 3/(4P)$. Curiously a photon gas is not infinitely compressible on an adiabatic path. On such a path the radiation pressure does in fact depend on the volume.

The inequality $\kappa_T > \kappa_S$ is trivially satisfied. Also $\kappa_T = \infty$ implies that $C_P = \infty$ from the well-known relation $\kappa_T/\kappa_S = C_P/C_V$. The slope of an adiabatic path is thus a measure of P . Observe that there is a decrease in the magnitude of the slope with V (compare, e.g., P_2 and P_3).

The above Carnot cycle can be transformed to the UV plane as shown in Fig. 2. The slope of a path here is also meaningful. By the second law, the slope of an adiabatic path is negative of the pressure. The slope of an isothermal path is the energy density.

We can also determine the angle formed by two paths at an intersection which amounts to a difference in the slope at that point. Let

$$\Delta \text{ slope} \equiv \left. \frac{\partial U}{\partial V} \right|_S - \left. \frac{\partial U}{\partial V} \right|_T. \quad (8)$$

The first term on the right-hand side may be replaced by $-P$ by the second law. Also, since

$$P = - \left. \frac{\partial F}{\partial V} \right|_T$$

and $F = U - TS$ quite generally

$$\Delta \text{ slope} = -T \left. \frac{\partial S}{\partial V} \right|_T \quad (8a)$$

$$= -T \left. \frac{\partial P}{\partial T} \right|_V. \quad (8b)$$

For the photon gas, (3) may be used in (8a) or (5) in (8b). If Eq. (5) is used,

$$\left. \frac{\partial P}{\partial T} \right|_V = \frac{dP}{dT} = S/V, \quad (9)$$

noting that P does not depend on V . Hence,

$$\Delta \text{ slope} = -TS/V. \quad (10)$$

At an intersection, say at point 2, the difference in slope is determined by V_2 , the position of the volume, and S'' and T'' , the values of the two intersecting paths. Hence at any given point on the UV plane $\partial U/\partial V$ remains highly path-sensitive.

We can also look at the differences at two different points on a path. Take, for example, points 1 and 2. The differences are, respectively, $-T''S'/V_1$ and $-T''S''/V_2$. But they are identically the same since on this isothermal path $S'/S'' = V_1/V_2$. Now take points 2 and 3. The differences remain, increasing with the volume as may be seen from Fig. 2.

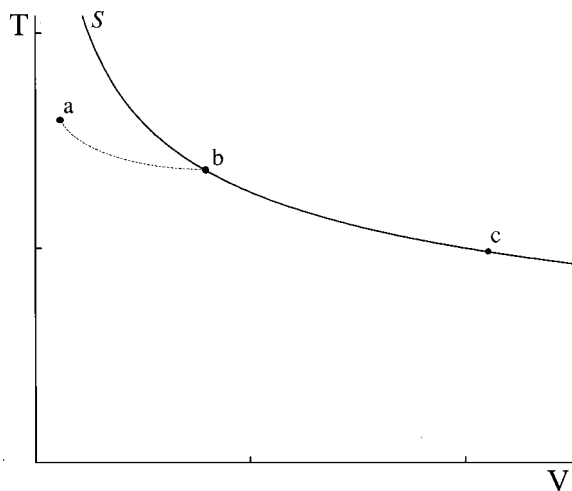


Fig. 3. T vs V . The adiabatic path (solid line) indicates the cooling of the universe starting at point b and continuing through the present day at point c . The early universe is assumed to have expanded ‘freely’ at some starting point a (dotted line) until the adiabatic cooling began at point b . Point a must lie left of the adiabatic line since the entropy must have increased with expansion until it attained the present day value.

We cannot end this section without looking, if only briefly, at what we might call grandiosely the adiabatic passage of the universe. Shown in Fig. 3 is an adiabatic path in the TV plane, which the expansion of the universe is said to follow.

From point a to point b (the dotted line of Fig. 3) the universe has undergone a ‘free’ expansion. At point b , at a temperature of about 3000 K, matter and radiation have become decoupled.⁷ As the entropy of the universe is contributed almost entirely by photons, the expansion of the universe falls on an adiabatic path, the solid line from point b to point c , the latter point representing the present day at a temperature of about 2.73 K. Observe that the slope of the temperature line on the adiabatic path is steeper than that on a free expansion path. Evidently the universe has cooled rapidly following an adiabatic expansion path, which, if it could be imagined, is one leg of a Carnot cycle for the universe.

V. PHOTON GAS AND STATE OF COEXISTENCE

It was asserted that the thermodynamics of a photon gas is simpler but richer than that of the ideal gas. In this section we will briefly illustrate an extra feature that makes a photon gas richer.

The form of P —depending only on T , not both T and V [see Eq. (5)]—is suggestive of the behavior at a phase boundary. One might thus think that dP/dT given by (9) is just the slope at this phase boundary in the PT plane, hence the latent heat L . The slope along a phase boundary between two coexisting phases (say 1 and 2) is described by the Clausius–Clapeyron equation¹

$$\left. \frac{dP}{dT} \right|_{1,2} = \frac{S_2 - S_1}{V_2 - V_1}. \quad (11)$$

If one were to set $S_1 = 0$ and $V_1 = 0$ in (11), the right-hand side of (11) corresponds exactly to (9).

Now the vanishing of entropy and volume for one of the coexisting phases is not unfamiliar. It occurs in an ideal ordinary Bose gas at a transition temperature, where two

phases coexist, the condensed and uncondensed. The entropy of the condensed phase is zero and this phase occupies zero volume.⁸ The other phase, made up of particles out of the condensate, has finite entropy and occupies finite space.

A signature of *BEC* is the vanishing of the chemical potential μ . When it vanishes, P does not depend on V [cf. (5)]. Also $dP/dT = S/V$ just as in (9). Since the latent heat $L = TS$ never vanishes, the transition is first order.⁸ The phase boundary is given by the condition $\rho T^{-2/3} = \text{const}$.⁸ This condition also implies that when $\mu = 0$ the entropy per excited particle is constant. Thus the *BEC* phase boundary is also an isentropic line. Let us see whether the above physics can be made to explain the behavior of a photon gas.

Now $G = F + PV = \mu N$, where G is the Gibbs free energy. For a photon gas (4) and (5) give $G = 0$, hence $\mu = 0$ provided that $N < \infty$. This result is also supported by $\mu = \partial F / \partial N_{V,T} = 0$ by (4). Alternatively if we set $\mu = 0$ in the Bose–Einstein function and use the photon energy spectrum, all the thermodynamic functions (1)–(5) are exactly recovered from it.^{8–10} Hence a photon gas is fundamentally no different from other Bose gases except for the special property that its chemical potential is zero at all T .

From (3), $\rho T^{-1/3} = (3/4\sigma)/(S/N)$. It is known that $S/k_B N = 2\pi^4/(45\zeta(3)) \approx 3.602$,^{8,9} where k_B is the Boltzmann constant and $\zeta(3)$ Riemann’s zeta function of order 3. Hence $\rho T^{-1/3} = \text{const}$, also delineating an isentrope (a linear-dispersion analog of the quadratic-dispersion result mentioned above). The analogy to *BEC* in an ordinary Bose gas thus leads us to say that the photon gas pressure, see (5), and its slope, see (9), are together describing a phase boundary. This slope also gives us the latent heat $L = TS = (4\sigma/3)VT^4$ by (3), which is finite for $0 < T < \infty$, implying a first-order transition.

The vanishing of its chemical potential at any T implies that a photon gas, unlike an ordinary Bose gas, is in a state of *BEC* always. These photons carry finite fixed entropy and occupy finite space just as the ordinary Bose particles out of the condensate do when at zero chemical potential. *BEC* further implies that this photon uncondensed phase coexists in the momentum space with another phase. The photon condensed phase is the state of zero point motion, a state not coupled to temperature. Since this ground state has infinite energy, it could simply refer to a photon reservoir (e.g., walls of a cavity in blackbody radiation), hence a vacuum state,¹¹ much like the ground state of phonons. It is strikingly similar to the condensate state of an ordinary Bose gas, also a particle reservoir for the uncondensed phase. Such a state has zero entropy and volume and is not coupled to T .

Being at zero chemical potential also means that photons may carry only fixed entropy. It is this fact that gives rise to the constancy of the entropy of the universe. When the universe expands and cools, the physical process is thus constrained to take place on an adiabatic path. See Fig. 3. The adiabatic paths in the photon Carnot cycle are really the phase boundaries of a photon gas.

VI. ADIABATIC EQUATION OF STATE

When thermodynamic functions are confined to an adiabatic path, their behavior becomes constrained. The particular relationship among PVT on an adiabatic path may be generally termed an *adiabatic* equation of state.

On an adiabatic path, we may take $U = U(T, V)$, with T replacing S . Then with the second law $dU = -PdV$, we deduce (see the Appendix)

$$\frac{dT}{T} + \frac{\partial PV}{\partial U} \frac{dV}{V} = 0. \quad (12)$$

Hence the relationship between T and V on an adiabatic path is determined solely by the relationship between the pressure and energy density, a fundamental relationship. For a photon gas we obtain

$$TV^\alpha = f(S), \quad (13)$$

where $\alpha = 1/3$ and f , a function of the entropy, is a constant on an adiabatic path. If the pressure energy–density relationship is applied to the second law, we obtain a second form of the adiabatic equation of state,

$$PV^\beta = g(S), \quad (14)$$

where $\beta = 1 + \alpha = 4/3$ and g is another constant on an adiabatic path. The values of these exponents can be readily verified from (3) and (5).^{12(a)}

The adiabat equation of state has but one independent variable. In several earlier texts^{12(a),12(b)} the exponent β (often denoted by γ) was incorrectly attributed (as pointed out by Pathria⁸) to the ratio of the specific heats C_p/C_v . For the ideal gas in $3d$ this ratio fortuitously is equal to $5/3$. But the origin is in the pressure energy–density relationship of the ideal gas $P = 2u/d$.

VII. NEUTRINO GAS

In the early universe, the neutrinos are thought to have played an important role in its evolution.^{13,14} As the universe cooled and freely expanded, the neutrinos presumably became decoupled from matter and thermalized in much the same way as the photons.

Neutrinos are Fermi particles. One might thus expect to find here thermodynamic functions which are very different from those of a photon gas.¹¹ But according to a recent unification work on ideal gases, this is not the case.⁹ Because the photon and neutrino gases both have zero chemical potential, their thermodynamic functions are simply related. There is a sort of reflection symmetry between the two gases of zero chemical potential. For example, for equal V and T , their energies are related by⁹

$$U(\nu) = \kappa U(\gamma), \quad (15)$$

where $\kappa = 1/2 \times 7/8$. Of this number κ , $1/2$ is the polarization degeneracy ratio between the two massless particles and $7/8$ is a measure of this reflection symmetry. (This number κ would go into the Stefan–Boltzmann constant for a neutrino gas.)

As C_v follows from U , S from C_v , and F therefrom, and finally P from F (see Sec. II), the neutrino thermodynamic functions are those given for a photon gas adjusted by the constant κ . Consequently all the thermodynamic conclusions drawn for a photon gas such as the adiabatic expansion, adiabatic equation of state apply equally as well. For example, each neutrino carries a fixed amount of entropy, independent of T . The neutrinos of the universe are thus on an adiabatic path of expansion and have a background temperature just as the photons do.^{14,15}

Since the neutrino pressure also depends on T only, one is also led to say that a neutrino gas is at a phase boundary. (Recall that condensation or coexistence is not a statistical property.) These neutrinos are distributed over excited states, collectively forming an *uncondensed* phase. It coexists with another phase, composed of those in zero point motion, the neutrino reservoir, the same as the condensed photon phase.

VIII. CONCLUDING REMARKS

It may perhaps come as a surprise that the thermodynamic functions of the two massless gases are so simply related in spite of their different statistics. A brief review of the recent work unifying the statistical thermodynamics of ideal gases may help shed some light. As is well known, ideal gases come in two species, Fermi and Bose. If their energy spectrum is either linear or quadratic, their thermodynamic functions are all expressible by a function called polylogs $\text{Li}_s(\zeta)$, where s and ζ are two parameters. [It is a transcendental function much like the Bessel function $J_\nu(t)$.] In any case, $s = d/2 + 1$ if a quadratic spectrum and $d + 1$ if a linear spectrum, where d is the dimensionality; and $\zeta = +z$ if Bose and $-z$ if Fermi, where $z = \exp(\mu/k_B T)$ the fugacity. For the ideal gases, $-\infty < \zeta < 1$.⁹

If, for example, $d = 2$ with a quadratic spectrum (e.g., ordinary Bose and Fermi gases), $-\text{Li}_2(-\infty < \zeta < 0)$ can be mapped onto $\text{Li}_2(0 < \zeta < 1)$ exactly, implying that the $2d$ Fermi and Bose gases are thermodynamically equivalent in spite of their different statistics. This explains an old result of May on the specific heats of the two gases.^{16,17}

If $d = 3$ with a linear spectrum (e.g., massless gases), there is no such mapping property for this function. But for photons and neutrinos, $\zeta = \pm 1$, respectively, and $-\text{Li}_4(-1) = 2\kappa \text{Li}_4(1)$, where $2\kappa = 7/8$, a reflection property of this function mentioned previously. What is being shown here is that insofar as thermodynamics goes, the difference in statistics is far outweighed by zero chemical potential.

Indeed the vanishing of the chemical potential implies that the entropy is free of log terms.⁹ It implies that the entropy per particle is a universal constant.⁸ It implies that these gases are confined to a point on a phase boundary and constrained to move along the boundary as T changes. This boundary is a line of first-order transition, also of constant entropy. Any expansion or cooling is thus adiabatic.

As regards the photons and neutrinos of the early universe, they must have followed the adiabatic cooling paths as the universe has expanded. The neutrino path is the same as the photon path shown in Fig. 3, merely shifted accordingly by the reflection property κ . If we were to assume that these primeval gases had reached their adiabatic paths at approximately the same time in the early universe, their present day background temperatures would also be approximately the same. The neutrino background temperature, estimated to be 1.95 K, is somewhat lower than the photon.¹⁵ That is, the initial temperature of the photons is somewhat higher, attributed to the reaction $e + \bar{e} \rightarrow \gamma$ before the photons attained final thermalization.

ACKNOWLEDGMENTS

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APPENDIX: ADIABATIC EQUATION OF STATE

The equation of state for a neutral, homogeneous fluid has two independent variables, say $P = P(V, T)$ if N is fixed. On adiabatic paths one of them may be reduced so that only one remains independent. The equation of state thus should generally be simpler on these paths, which might be termed the *adiabatic* equation of state. We will show that it has a universal structure, determined solely by the relationship between U and PV .

Let N be fixed henceforth. In general $U = U(S, V)$. But when on adiabatic paths, S therein may be replaced by T or P . We can consider both possibilities separately.

(1) Let $U = U(T, V)$ with $S = \text{constant}$. Then,

$$dU = \left. \frac{\partial U}{\partial T} \right|_{V,S} dT + \left. \frac{\partial U}{\partial V} \right|_{T,S} dV. \quad (\text{A1})$$

On adiabatic paths the second law gives

$$dU = -P dV. \quad (\text{A2})$$

Combining the two equations, and henceforth suppressing the subscript S (since our consideration is on adiabatic paths only) we have

$$\left. \frac{\partial U}{\partial T} \right|_V dT + \left\{ \left. \frac{\partial U}{\partial V} \right|_T + P \right\} dV = 0. \quad (\text{A3})$$

Using the well-known general relation

$$\left. \frac{\partial U}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P, \quad (\text{A4})$$

and rearranging a little we can put (A3) in the final form

$$\frac{dT}{T} + x_V \frac{dV}{V} = 0, \quad (\text{A5})$$

where

$$x_V = \left. \frac{\partial PV}{\partial U} \right|_V. \quad (\text{A6})$$

Note that if we had taken $\partial U / \partial V|_{T,S} = 0$ in (A1), it would not have affected (A5) since the same term is also present in (A4).

(2) Now let $U = U(P, V)$. Then,

$$dU = \left. \frac{\partial U}{\partial P} \right|_V dP + \left. \frac{\partial U}{\partial V} \right|_P dV. \quad (\text{A7})$$

Hence together with the second law (A2),

$$\left. \frac{\partial U}{\partial P} \right|_V dP + \left\{ \left. \frac{\partial U}{\partial V} \right|_P + P \right\} dV = 0. \quad (\text{A8})$$

We can rewrite (A8) in parallel to (A5) as

$$\frac{dP}{P} + (x_V + x_V/x_P) \frac{dV}{V} = 0, \quad (\text{A9})$$

where

$$x_P = \left. \frac{\partial PV}{\partial U} \right|_P. \quad (\text{A10})$$

Both (A5) and (A9) represent general relationships between V and T , and V and P , respectively, valid on any adiabatic path. Their solutions depend only on the relationship between U and PV , expressed through x_V and x_P .

If $x_V = x_P = \alpha$, i.e., $PV = \alpha U$, where α is a pure number, (A5) and (A9) give, respectively,

$$TV^\alpha = f(S), \quad (\text{A11})$$

and

$$PV^\beta = g(S), \quad (\text{A12})$$

where $\beta = \alpha + 1$, and f and g are functions of S only, hence constant on a given adiabatic path.

If $\alpha = 1/3$ and $2/3$, hence $\beta = 4/3$ and $5/3$, respectively, (A11) and (A12) yield the familiar results for the photon gas and the classical ideal gas in $3d$, respectively.

For systems whose PV is related to U by a simple number, (A11) and (A12) are two forms of the adiabatic equation of state. There is just one independent thermodynamic variable and also only one independent exponent α on adiabatic paths.

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