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Citation: *American Journal of Physics* **83**, 362 (2015); doi: 10.1119/1.4904322

View online: <http://dx.doi.org/10.1119/1.4904322>

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Fluctuations in particle number for a photon gas

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(Received 6 May 2014; accepted 3 December 2014)

The fluctuation-compressibility theorem of statistical mechanics states that fluctuations in particle number are proportional to the isothermal compressibility. Given that the compressibility of a photon gas does not exist, this seems to suggest that fluctuations in photon number similarly do not exist. However, it is shown here that the fluctuation-compressibility theorem does *not* hold for photons and, in fact, that fluctuations *do* exist. © 2015 American Association of Physics Teachers.
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I. INTRODUCTION

The goal of this paper is to investigate fluctuations in a photon gas that is contained in a box of interior volume V and wall temperature T . The emission of photons by the walls generates the photon gas, and in thermodynamic equilibrium, fluctuations in the number of photons occur because of ongoing photon emission and absorption. The *average* number $\langle N \rangle$ of photons adjusts in accord with V and T , and the resulting pressure is solely a function of T ; i.e., $P = P(T)$.

The relevant equations of state for a photon gas of volume V and temperature T have been examined extensively.¹ The average number of photons $\langle N \rangle$, pressure $P(T)$, entropy $S(T, V)$, and internal energy (average total energy) $U(T, V)$ are:

$$\langle N \rangle = \alpha VT^3, \quad (1)$$

$$P(T) = \frac{1}{3} b T^4, \quad (2)$$

$$S(T, V) = \frac{4}{3} b VT^3, \quad (3)$$

$$U(T, V) = b VT^4, \quad (4)$$

with

$$\alpha = \frac{16\pi k^3 \zeta(3)}{h^3 c^3} = 2.03 \times 10^7 \text{ m}^{-3} \text{ K}^{-3} \quad (5)$$

and

$$b = \frac{8\pi^5 k^4}{15 h^3 c^3} = 7.56 \times 10^{-16} \text{ m}^{-3} \text{ J K}^{-4}. \quad (6)$$

In Eqs. (5) and (6), h , c , and k are Planck's constant, the speed of light, and Boltzmann's constant, respectively, and $\zeta(s) = \sum_n n^{-s}$ is the Riemann zeta function.

Because the pressure depends only on temperature, any slow, isothermal change of volume will leave the pressure unchanged, so the isothermal compressibility,

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad (7)$$

does not exist.² Meanwhile, the fluctuation-compressibility theorem states that³⁻⁵

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} = \frac{kT}{V} \kappa_T. \quad (8)$$

It is therefore tempting to combine the non-existence of κ_T , deduced from Eq. (7), with Eq. (8) to conclude that the variance of N does not exist.^{6,7}

Two specific objectives here are to show that the fluctuation-compressibility theorem does *not* hold for the photon gas, and that in fact, the fluctuations in photon number are well defined. It is difficult to find a discussion of either of these points in the existing literature.⁸

In the subsequent sections, I first review ways to obtain average occupation numbers and corresponding variances and then calculate relevant averages and show why the fluctuation-compressibility theorem fails to apply to the photon gas. Following this, I discuss a Gedanken experiment that illustrates how an attempt to measure κ_T fails, consistent with the known non-existence of κ_T . Brief concluding remarks are in Sec. VI.

II. CANONICAL AND GRAND CANONICAL AVERAGES

As preparation for the calculation of fluctuations in the number of photons in Sec. III, here I review relevant averages and variances and emphasize that the canonical and grand canonical ensembles give the same results.

Suppose that a photon gas has allowable single-photon energies $\{\epsilon_s\}$; i.e., ϵ_s is the (single-particle) energy of a photon in state s . Denote the corresponding occupation numbers by $\{n_s\}$. Then the possible energies for the gas are $E(n_1, n_2, \dots) = \sum_s n_s \epsilon_s$, where the sum is over the set $\{s\}$ of all single-particle states.

The canonical partition function for the photon gas is

$$Z(T, V) = \sum_{\{n_s\}} e^{-\sum_s n_s \epsilon_s / kT} = \prod_{s=1}^{\infty} \sum_{n_s=0}^{\infty} e^{-n_s \epsilon_s / kT}. \quad (9)$$

The last step in Eq. (9)—replacement of a sum of products by a product of sums—is understandable for a *finite* number M of states, i.e., when $s = 1, 2, \dots, M$, in which case,

$$\begin{aligned} Z(T, V) &= \sum_{n_M=0}^{\infty} e^{-n_M \epsilon_M / kT} \dots \sum_{n_2=0}^{\infty} e^{-n_2 \epsilon_2 / kT} \sum_{n_1=0}^{\infty} e^{-n_1 \epsilon_1 / kT} \\ &= \prod_{s=1}^M \sum_{n_s=0}^{\infty} e^{-n_s \epsilon_s / kT}. \end{aligned} \quad (10)$$

Assuming that the interchange of sum and product in the last step holds in the limit $M \rightarrow \infty$, Eq. (9) results.

For *material* particles, whose number is conserved, the sum over the set $\{n_s\}$ would carry the constraint $\sum_s n_s = N = \text{constant}$. Thus, the canonical partition function is sometimes written as $Z_N(T, V)$. However, for the photon gas, no such constraint applies, and each occupation number n_s can run from 0 to ∞ without constraint, so the partition function is denoted simply by $Z(T, V)$.

Notably, $Z(T, V)$ in Eq. (9) is identical to the corresponding grand canonical partition function \mathcal{Z} for a photon gas with zero chemical potential.^{9,10} To see this, group together all terms in Eq. (9) with $\sum_i n_i = N$, and then sum over all possible N , namely from $N=0$ to ∞ . I insert a (cosmetic) factor z^N in the summation expression—with the specification that $z = 1$. Here, z plays the role of fugacity in the grand canonical ensemble, defined by $z \equiv e^{\mu/kT} = 1$; this is consistent with $\mu = 0$, the known chemical potential for the photon gas. For each positive integer value of N with $\sum_i n_i = N$, the sum over $\{n_i\}$ is then *formally* Z_N , the canonical partition function for a *fictitious* system of N particles with the photon energy spectrum, but with N fixed. The result is that

$$Z(T, V) = \sum_{N=0}^{\infty} z^N Z_N = \mathcal{Z} = \text{the grand partition function.} \quad (11)$$

Equation (11) is the standard form of the grand canonical partition function. The appearance of the canonical fixed- N partition function Z_N arises solely from *mathematical* considerations and does not contradict the fact that actual photon gases have fluctuating numbers of photons.

Retaining the condition $z = 1$ in the remainder of this section, it is convenient to use the following notation and approach. As implied by Eq. (9) and used explicitly in Ref. 11, the average numbers of photons in the canonical and grand canonical ensembles, respectively, are

$$\bar{n}_s = -kT \left(\frac{\partial \ln Z}{\partial \epsilon_s} \right)_{T,V} \quad \text{and} \quad \langle n_s \rangle = -kT \left(\frac{\partial \ln \mathcal{Z}}{\partial \epsilon_s} \right)_{T,V}. \quad (12)$$

Because $Z(T, V) = \mathcal{Z}$ from Eq. (11), this implies¹²

$$\bar{n}_s = \langle n_s \rangle = \frac{e^{-\epsilon_s/kT}}{1 - e^{-\epsilon_s/kT}}. \quad (13)$$

Given that $\bar{n}_s = \langle n_s \rangle$, it follows that the variances of n_s in the canonical and grand canonical ensembles are equal; i.e.,

$$\begin{aligned} \langle n_s^2 \rangle - \langle n_s \rangle^2 &= -kT \left(\frac{\partial \langle n_s \rangle}{\partial \epsilon_s} \right)_{T,V} \\ &= -kT \left(\frac{\partial \bar{n}_s}{\partial \epsilon_s} \right)_{T,V} = \bar{n}_s^2 - \bar{n}_s^2. \end{aligned} \quad (14)$$

These equalities of average occupation numbers and their variances for a single-particle state in the two ensembles mean that I need use only one notation. In what follows I choose to retain only the grand ensemble notation $\langle \rangle$ for averages.

The average total number of photons can be written as

$$\langle N \rangle = \sum_s \langle n_s \rangle = \sum_s \frac{e^{-\epsilon_s/kT}}{1 - e^{-\epsilon_s/kT}}. \quad (15)$$

Meanwhile, inserting Eq. (13) into the derivative in Eq. (14) gives for the variance

$$\langle n_s^2 \rangle - \langle n_s \rangle^2 = \langle n_s \rangle (1 + \langle n_s \rangle). \quad (16)$$

Notably, the variance of n_s is expressible solely in terms of the average, $\langle n_s \rangle$. This is curious because one expects a variance to entail $\langle n_s^2 \rangle$. A similar property can be corroborated directly for the variance of N using the ensemble-independent variance expression

$$\begin{aligned} \langle N^2 \rangle - \langle N \rangle^2 &= \left\langle \left(\sum_s n_s \right)^2 \right\rangle - \left(\sum_s \langle n_s \rangle \right)^2 \\ &= \sum_r \sum_s [\langle n_r n_s \rangle - \langle n_r \rangle \langle n_s \rangle] \\ &= \sum_s [\langle n_s^2 \rangle - \langle n_s \rangle^2] \\ &= \sum_s \langle n_s \rangle [1 + \langle n_s \rangle]. \end{aligned} \quad (17)$$

In Eq. (17), n_s is an occupation number for single-particle state s and should not be confused with the *average* occupation number $\langle n_s \rangle$. The second line arises by writing each summation squared as a sum over s followed by a sum over r . The third line follows because of the statistical independence of n_r and n_s , namely $\langle n_r n_s \rangle - \langle n_r \rangle \langle n_s \rangle = 0$ for $r \neq s$, leaving only those terms with $r = s$. The last line comes about using Eq. (16). Evidently, it is the latter statistical independence that leads to the variance in N being dependent only on the set $\{\langle n_r \rangle\}$ and not on $\{\langle n_r^2 \rangle\}$.

In view of the third line in Eq. (17), the variance in the total number of photons is the sum of the variances of the occupation numbers for all the single-particle states. It is useful to define the relative root-mean-square (rms) fluctuation f_s for state s , and the corresponding rms fluctuation f for the total number of photons. These are, respectively,

$$f_s \equiv \frac{\sqrt{\langle n_s^2 \rangle - \langle n_s \rangle^2}}{\langle n_s \rangle} = \sqrt{\frac{1 + \langle n_s \rangle}{\langle n_s \rangle}} > 1, \quad (18)$$

and

$$f \equiv \frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{\langle N \rangle}. \quad (19)$$

Although $f_s > 1$, no such property emerges for f , and in fact—as we shall see—typically, $f \ll 1$.

III. FLUCTUATIONS IN THE NUMBER OF PHOTONS

To calculate the average number of photons and its variance, I first use the grand canonical ensemble with $z = 1$ (i.e., $\mu = 0$). I combine Eqs. (13), (15), and (17) and convert the sums over microstates to integrals following a standard technique³ for an assumed three-dimensional container of volume V . Note that there is no Bose condensation for a photon gas,¹³ so it is not necessary to split off a term from the integral, which is necessary for a *material* ideal gas of bosons in a three-dimensional box. Using the abbreviations

$$x \equiv \frac{\epsilon}{kT} \quad \text{and} \quad A \equiv \frac{8\pi V (kT)^3}{(hc)^3}, \quad (20)$$

the average number of photons is

$$\begin{aligned}\langle N \rangle &= \sum_s \frac{e^{-\epsilon_s/kT}}{1 - e^{-\epsilon_s/kT}} \rightarrow A \int_0^\infty \frac{x^2 e^{-x}}{1 - e^{-x}} dx \\ &= A[2\zeta(3)] = (2.028 \times 10^7 \text{ m}^{-3} \text{ K}^{-3}) VT^3.\end{aligned}\quad (21)$$

Similarly, converting the sum to an integral in Eq. (17) and using Eq. (21) leads to

$$\begin{aligned}\langle N^2 \rangle - \langle N \rangle^2 &= \sum_s \frac{e^{-\epsilon_s/kT}}{1 - e^{-\epsilon_s/kT}} + \frac{e^{-2\epsilon_s/kT}}{(1 - e^{-\epsilon_s/kT})^2} \\ &\rightarrow A \int_0^\infty \frac{x^2 e^{-x}}{(1 - e^{-x})^2} dx \\ &= \frac{1}{3} A \pi^2 = (2.776 \times 10^7 \text{ m}^{-3} \text{ K}^{-3}) VT^3 \\ &= 1.369 \langle N \rangle.\end{aligned}\quad (22)$$

An alternative procedure is to write

$$\langle N \rangle = \left[z \left(\frac{\partial \ln \mathcal{Z}}{\partial z} \right)_{T,V} \right]_{z=1} \quad (23)$$

and

$$\langle N^2 \rangle - \langle N \rangle^2 = \left[z \left(\frac{\partial \langle N \rangle}{\partial z} \right)_{T,V} \right]_{z=1}. \quad (24)$$

With this procedure, I first assume *general* $z \neq 1$, take the needed z derivatives of $\ln \mathcal{Z} = -\sum_s \ln(1 - z e^{-\epsilon_s/kT})$ and $\langle N \rangle$, then set $z = 1$, and finally, convert the sums to integrals. This leads, once again, to Eqs. (21) and (22).

Clearly, the average and variance given by Eqs. (21) and (22) both exist for finite T and V and are of the same order of magnitude. Using Eqs. (21) and (22) in Eq. (19), the relative rms fluctuation in N is

$$f = \frac{2.597 \times 10^{-4} \text{ m}^{3/2} \text{ K}^{3/2}}{\sqrt{VT^3}} = \frac{1.170}{\sqrt{\langle N \rangle}}. \quad (25)$$

Equations (22) and (25) show that $\langle N^2 \rangle - \langle N \rangle^2$ is proportional to $\langle N \rangle$, and the relative fluctuation f is proportional to $1/\sqrt{\langle N \rangle}$. These same properties hold for material gases that satisfy the fluctuation-compressibility theorem, Eq. (8). For example, applying Eq. (8) to air, treated as a classical ideal gas with $\kappa_T = 1/P$, $(kT/V)\kappa_T = 1/\langle N \rangle_{\text{air}}$, and one finds $\langle N^2 \rangle_{\text{air}} - \langle N \rangle_{\text{air}}^2 = \langle N \rangle_{\text{air}}$, or $f_{\text{air}} = 1/\sqrt{\langle N \rangle_{\text{air}}}$. More generally, Eq. (8) can be written as $\langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle \times \text{intensive thermodynamic variable}$.

Returning to the ideal gas, to gain a sense of what this means numerically, consider a room with dimensions 3 m \times 4 m \times 2.5 m and thus $V = 60 \text{ m}^3$. At a typical room temperature of 300 K, the number density of photons is $\langle N \rangle/V = 5.5 \times 10^{14} \text{ m}^{-3}$ and the total photon number is $\langle N \rangle = 3.3 \times 10^{16}$. In contrast, the number density of air molecules at the same temperature and atmospheric pressure is $\langle N \rangle_{\text{air}}/V = 2.5 \times 10^{25} \text{ m}^{-3}$ and the total number of molecules is $\langle N \rangle_{\text{air}} = 1.5 \times 10^{27}$. The relative rms fluctuation for photons and air, respectively, are $f = 5.5 \times 10^{-9}$ and $f_{\text{air}} = 2.6 \times 10^{-14}$. The average number of air molecules

exceeds that for photons by eleven orders of magnitude, and therefore the relative fluctuation for air is much smaller.

The main point is that the variance $\langle N^2 \rangle - \langle N \rangle^2$ exists for the photon gas, and for any finite temperature T the relative fluctuation f vanishes in the thermodynamic limit $V \rightarrow \infty$.

IV. INAPPLICABILITY OF FLUCTUATION-COMPRESSIBILITY THEOREM

Given that the fluctuations in photon number exist, but the isothermal compressibility does not, it is clear that the fluctuation-compressibility theorem, Eq. (8), fails for the photon gas. To understand why, I outline a proof of the fluctuation-compressibility theorem, modeled after Pathria's proof for *material* particles (not photons).³

Consider a macroscopic, open sub-volume of material gas particles embedded within a larger gas. Particles can freely flow into and out of this volume; i.e., N is variable. Because $z = e^{\mu/kT}$ is a variable, $kT(\partial/\partial\mu)_{T,V} = z(\partial/\partial z)_{T,V}$, and thus the variance expression in Eq. (24) can be written as

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} = \frac{kT}{\langle N \rangle^2} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V}. \quad (26)$$

The remainder of the proof proceeds by assuming that V is fixed, but the volume per particle $v \equiv V/\langle N \rangle$ is variable. The right side of Eq. (26) can be written as

$$\begin{aligned}\frac{kT}{\langle N \rangle^2} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} &= kT \left(\frac{v}{V} \right)^2 \left(\frac{\partial (V/v)}{\partial \mu} \right)_{T,V} \\ &= -\frac{kT}{V} \left(\frac{\partial v}{\partial \mu} \right)_{T,V} \\ &= -\frac{kT}{V} \left(\frac{\partial v}{\partial P} \right)_{T,V} \left(\frac{\partial P}{\partial \mu} \right)_{T,V}.\end{aligned}\quad (27)$$

Finally, a more useful expression for $(\partial P/\partial\mu)_{T,V}$ can be obtained using the Gibbs-Duhem equation,

$$d\mu = v dP - s dT, \quad (28)$$

where v and s are the volume and entropy per particle. It follows from Eq. (28) that $(\partial P/\partial\mu)_{T,V} = v^{-1}$, and therefore Eqs. (26) and (27) lead to the fluctuation-compressibility theorem:

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} = \frac{kT}{V} \left(-\frac{1}{v} \right) \left(\frac{\partial v}{\partial P} \right)_{T,V} = \frac{kT}{V} \kappa_T.$$

This completes the proof, which I emphasize holds for a *material* gas.

However, for a photon gas, the proof above fails. Equation (26) must be evaluated at $\mu = 0$ and thus has no remaining μ dependence. Thus, the steps in Eq. (27) that were used for material particles cannot be executed. Further, in the Gibbs-Duhem equation (28), v and P are independent of μ , so the expression, $(\partial P/\partial\mu)_{T,V} = v^{-1}$ that was useful for the material gas does not hold. In fact, for the photon gas P is not a function of μ and Eq. (28) reduces to $dP/dT = s/v = S/V$. The latter equation is consistent with the result obtained by differentiating Eq. (2) and comparing the result with Eq. (3) but is of no help with the proof being attempted.

Other proofs^{4,5} of Eq. (8) fail similarly for the photon gas, and the conclusion is that the standard proofs cannot be used for the photon gas. Moreover, there cannot exist any other proof because, as shown explicitly in Sec. III, for the photon gas the variance of N definitely *does* exist, and as shown in Sec. I, the isothermal compressibility κ_T does *not* exist. Clearly, Eq. (8) does *not* hold for the photon gas.

V. A GEDANKEN EXPERIMENT

The non-existence of the isothermal compressibility can be understood at least in part by envisaging a Gedanken experiment where the photon gas is contained within a vertical cylinder in a gravitational field. A floating (frictionless) piston is the container's ceiling, and the walls are maintained at temperature T . Begin with the piston fixed such that the container volume is V . The number of photons $\langle N \rangle$ adjusts, and the equilibrium pressure $P(T)$ is established in accordance with Eq. (2). If the piston is released so that it can float, thermal equilibrium exists only if the piston weight provides an external pressure equal to $P(T)$.

To measure the compressibility, add an arbitrarily light grain of sand to the piston. One might hope to calculate an approximate value of the compressibility using $\kappa_T \approx -V^{-1} \Delta V / \Delta P$. However, with the walls at fixed temperature, the equilibrium pressure of the photon gas does not change and the extra sand grain causes the piston to drop precipitously to the container floor; i.e., the unstable photon gas collapses to zero volume. During the collapse, the photon gas follows an irreversible path through *non-equilibrium* states. Once equilibrium is re-established, there are zero photons in a zero-volume container.

Thus, an arbitrarily small change in P does *not* lead to a correspondingly small ΔV and there is no way to approximate the isothermal compressibility. The fact that a measurement of the isothermal compressibility κ_T is not possible is consistent with the non-existence of κ_T established on theoretical grounds in Sec. I.

VI. CONCLUDING REMARKS

Because all matter radiates, photons are ubiquitous in the universe. The oldest photons, those in the cosmic microwave background radiation, go back to the big bang. In this respect, photons are indeed *special*. The photon gas is special too in that it is a relatively simple quantum mechanical, relativistic, and thermal model, as evidenced by the occurrence of the fundamental constants h , c , and k in Eqs. (1)–(6). Because photons can be, and are, continually created and annihilated by matter, their total number in a closed box fluctuates continually. Those fluctuations are finite, and the suggestion that the variance of $\langle N \rangle$ does not exist because the isothermal compressibility does not exist is incorrect. I have shown here that specific assumptions used for a material gas to prove the fluctuation-compressibility theorem, namely the proportionality of the variance of $\langle N \rangle$ with the isothermal compressibility, do not hold for photons.

ACKNOWLEDGMENTS

The author grateful to Raj Pathria and Paul Beale for their helpful comments on a first draft of this article.

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¹A detailed discussion and summary of the thermodynamic properties of a photon gas can be found in H. S. Leff, "Teaching the photon gas in introductory physics," *Am. J. Phys.* **70**, 792–797 (2002) and references therein.

²Because P is solely a function of T for the photon gas, $(\partial P / \partial V)_T = 0$. Given this, it is tempting to conclude that $(\partial V / \partial P)_T$ is infinitely large, but this is incorrect. The reason is that the identity $(\partial V / \partial P)_T = 1 / (\partial P / \partial V)_T$ does not hold when the left side is zero. Rather, it is correct to say that $(\partial V / \partial P)_T$ (and thus κ_T) does not exist.

³R. K. Pathria, *Statistical Mechanics*, 2nd ed. (Butterworth-Heinemann, Oxford, 1996), pp. 100–101.

⁴R. Kubo, *Statistical Mechanics* (North Holland-Interscience-Wiley, New York, 1965), pp. 398–399.

⁵K. Huang, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1986), pp. 152–153.

⁶For example, see Ref. 3, p. 172, where after demonstrating that the average number of photons is proportional to VT^3 , it is written that the latter result "cannot be taken at its face value because in the present problem the magnitude of the *fluctuations* in the variable N , which is determined by the quantity $(\partial P / \partial V)^{-1}$, is infinitely large."

⁷It is worth pointing out that fluctuations in energy *are* well defined for a photon gas: the variance in energy is $kT^2 C_v$, and $C_v \propto VT^3$ (see, e.g., Ref. 3, p. 101). This suggests that fluctuations in photon number also exist, contrary to what one might expect from Eqs. (7) and (8). This dichotomy provides further incentive to clarify that the fluctuations in N do indeed exist.

⁸An anonymous reviewer of this manuscript has kindly informed me that a calculation of the fluctuations in N for the photon gas is presented in C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms: Introduction to Quantum Electrodynamics* (Wiley, New York, 1989), pp. 235–236.

⁹Thermal photons are known to have zero chemical potential. See, for example, R. Baierlein, "The elusive chemical potential," *Am. J. Phys.* **69**, 423–434 (2001). Two compelling ways to argue that $\mu = 0$ for thermal photons are: (i) the empirically observed distribution of photon frequencies for blackbody radiation agrees with the prediction for a quantum ideal Bose gas of photons only if the chemical potential μ is set equal to zero; and (ii) using Eqs. (3) and (4) to obtain $S(U, V, N) = (4/3)b^{1/4}V^{1/4}U^{3/4}$, application of the thermodynamic identity $\mu = T(\partial S / \partial N)_{U, V}$ then gives $\mu = 0$.

¹⁰A justification sometimes given for $\mu = 0$ is that the photon number is not fixed, but, rather, is indefinite. See, for example, F. Herrmann and P. Würfel, "Light with nonzero chemical potential," *Am. J. Phys.* **73**, 717–721 (2005). These authors observe that the indefinite number of photons alone is not sufficient to conclude that $\mu = 0$ because particle numbers are not conserved in chemical reactions, where the material constituents have *nonzero* chemical potential. Indeed, the zero chemical potential result holds only for *thermal* photons. For example, if light is in "chemical" equilibrium with the excitations of matter whose chemical potential is *nonzero*—e.g., the electron-hole pairs in a light emitting diode—then the chemical potential of the light must be nonzero too. The full argument, which entails recognition that $\mu_{\text{electron}} + \mu_{\text{hole}} = \mu$, is given by Herrmann and Würfel. See also P. Würfel, "The chemical potential of radiation," *J. Phys. C Solid State Phys.* **15**, 3967–3985 (1982).

¹¹F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), Secs. 9.3–9.7.

¹²This quantum statistics formula for Bose-Einstein single-particle state occupation numbers $\{n_s\}$ can also be found using a counting argument. See, for example, D. ter Haar, *Elements of Statistical Mechanics* (Holt, Rinehart and Winston, New York, 1964), Secs. 4.1–4.3.

¹³See, e.g., J. Honerkamp, *Statistical Physics: An Advanced Approach with Applications* (Springer, Berlin, 1998), pp. 228–233. To see why, note that the single-photon energy is $\epsilon_s = shc\sqrt{V}^{1/3}$, where $V = L^3$ for an assumed cubical volume, with $s \equiv \sqrt{s_x^2 + s_y^2 + s_z^2}$, and where $s_x, s_y,$ and s_z run over the positive integers. The ground state g has $s_x = s_y = s_z = 1$ and $s_g = \sqrt{3}$. Using the result that the average total number of photons $\langle N \rangle \propto V$, it follows that the ratio $\langle n_g \rangle / \langle N \rangle \propto V^{-2/3} \rightarrow 0$ in the thermodynamic limit $V \rightarrow \infty$; i.e., the fraction of photons in the ground (or any other single) state is zero. Note: This argument requires that we set $\mu = 0$ before taking the thermodynamic limit, which is the correct order. If we were to take (incorrectly) the thermodynamic limit first, we would mistakenly "discover" an actually nonexistent singularity for the ground (or any other) state.