# Understanding the chemical potential

G. Cook and R. H. Dickerson

## Additional information on Am. J. Phys.

$12 000; vapor cells are available for approximately $250 (rubidium standard cell) to $750 (lithium cell).

[4]M. G. Boshier, D. Berkeland, E. A. Hinds, and V. Sandoghdar, "External-cavity frequency-stabilization of visible and infrared semiconductor lasers for high-resolution spectroscopy," Opt. Commun. **85**, 355–359 (1991).

[5]J. C. Camparo, "The diode laser in atomic physics," Cont. Phys. **26**, 443–477 (1985).

[6]Part T9215 diode laser, Thor Labs, P. O. Box 366, Newton, NJ 07860. Price per laser is approximately $80.

[7]R. D. Mathis Co., 2840 Gundry Ave., Long Beach, CA 90806.

[8]Newark Electronics, 12631 E. Emperial Hwy., Santa Fe Springs, CA 90670.

[9]Part 6-500 transformer, Signal Transformer, 500 Bayview Ave., Inwood, NY 11696.

[10]Part 3344-MSP-A4164 V-60 Turbopump Station with built-in pump and MultiGage Controller, Varian Vacuum Products, 121 Hartwell Ave., Lexington, MA 02173. The station price is approximately $6000.

[11]C. E. Wieman and L. Hollberg, "Using diode lasers for atomic physics," Rev. Sci. Instrum. **62**, 1–20 (1991).

[12]K. C. Harvey and C. J. Myatt, "External-cavity diode-laser using a grazing-incidence diffraction grating," Opt. Lett. **16**, 910–912 (1991).

[13]Part CP1.4-71-10L thermoelectric cooler, Melcor, 1040 Spruce St., Trenton, NJ 08648.

[14]C. C. Bradley, J. Chen, and R. G. Hulet, "Instrumentation for the stable operation of laser diodes," Rev. Sci. Instrum. **61**, 2097–2101 (1990).

[15]K. G. Libbrecht and J. L. Hall, "A low-noise high-speed diode-laser current controller," Rev. Sci. Instrum. **64**, 2133–2135 (1993).

[16]PZT Tube C-5500, 0.035 in. wall, 0.5 in. O.D., 0.5 in. diam, Channel Industries Inc., 839 Ward Dr., Santa Barbara, CA 93111.

[17]P. Horowitz and W. Hill, *The Art of Electronics*, 2nd ed. (Cambridge University Press, Cambridge, 1989), p. 169.

[18]A. Yariv, *Optical Electronics*, 4th ed. (Holt, Rinehart, and Winston).

[19]Part 43 221 holographic grating, Edmund Scientific Co., 101 E. Gloucester Pike, Barrington, NJ 08007.

[20]A. T. Schremer and C. L. Tang, "External-cavity semiconductor-laseer with 1000 GHz continuous piezoelectric tuning range," IEEE Photonics Technol. Lett. **2**, 3–5 (1990).

[21]Part WA-2000 Wavemeter-jr, Burleigh Instruments Inc., P.O. Box E, Fishers, NY 11453. Price is approximately $6000.

[22]MDC Vacuum Products Corp., 23842 Cabot Blvd., Hayward, CA 94545.

[23]M. Kasevich, private communication.

[24]In the presence of moisture, lithium in a nitrogen atmosphere can react to form the nitride. This is an exothermic reaction, which can run away, ruining one's lithium samples. We have seen this happen once, but typically we have no problems filling a leaky glove box with an overpressure of nitrogen from the boil-off of a liquid nitrogen dewar. An argon atmosphere could be used to eliminate this potential problem.

[25]R. Hulet (private communication).

[26]Part E1A53 cartridge heater with thermocouple, type J, style C, Watlow, 12001 Lackland Rd., St. Louis, MO 63146.

[27]Z. Lin, K. Shimizu, M. Zhan, F. Shimizu, and H. Takuma, "Laser cooling and trapping of lithium," Jpn. J. Appl. Phys. **30**, L1324-L1326 (1991).

# Understanding the chemical potential

G. Cook and R. H. Dickerson

*Physics Department, California Polytechnic State University, San Luis Obispo, California 93407*

When teaching thermal physics and statistical mechanics the authors find a lot of confusion among students about the meaning of the chemical potential $\mu$. It seems particularly difficult for students to develop a physical picture of what $\mu$ is. In this paper some simple, pedagogical models are developed to make the meaning of $\mu$ clear, for a few selected systems. © *1995 American Association of Physics Teachers.*

## I. INTRODUCTION

After several years of teaching thermal physics and statistical mechanics to undergraduates, the authors find that there is still a lot of confusion about the meaning of the "chemical potential," $\mu$. Typically, students learn the definition of $\mu$, its properties and consequences, and work problems using it, but often still ask "But what *is* it?" In this paper we try to clarify the meaning of $\mu$.

## II. GENERAL DISCUSSION OF CHEMICAL POTENTIAL

Consider a system which can exchange energy and particles with a reservoir, and the volume of which can change. Energy acquired by the system, through heating, increases its internal energy, $U$, by $TdS$, where $T$ is the temperature of the system, and $S$ is the entropy of the system. If the system expands by volume $dV$ at pressure $p$, the work done by the system is $pdV$. If the system gains $dN$ particles (all of one single type), then $U$ increases by $\mu dN$, where $\mu$ is the chemical potential. The change in the internal energy is then

$$dU = TdS - pdV + \mu dN. \tag{1}$$

This relation is commonly called the thermodynamic identity, valid for infinitesimal, reversible processes.

It follows that

$$\mu = \frac{\partial U}{\partial N}\bigg|_{S,V}. \tag{2}$$

We would like to look at what Eq. (2) tells us for some simple systems.

### A. A system of distinguishable, classical particles

Consider a simple, idealized system. Suppose the single particle energy eigenvalues are quantized in integer multiples of energy $\epsilon$, as shown in Fig. 1. In general, $\epsilon$ will depend on the volume, $V$, of the system, but we will insist on holding $V$
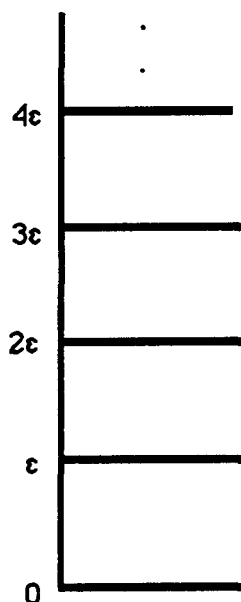
© 1995 American Association of Physics Teachers

Fig. 1. Single particle energy levels for a simple system.



Fig. 2. Variation with temperature of the chemical potential of an ideal Fermi gas, in terms of the Fermi energy, $\epsilon_f$.

constant in this example. We assume that the energy eigenstates are nondegenerate. The system is like that of a collection of simple harmonic oscillators, but with the zero of the single particle energy scale shifted.

Let two distinguishable particles, labeled R and B, make up this system, and assume initially the total energy $U=2\epsilon$. How many microstates are available? We could have

| R | B |
|---|---|
| $2\epsilon$ | $0$ |
| $0$ | $2\epsilon$ |
| $\epsilon$ | $\epsilon$ |

showing that there are three microstates. The entropy of a system can be defined in terms of the Boltzmann constant, multiplied by the logarithm of the number of microstates available, so the entropy for this system is given by

$$S = k \ln g, \tag{3}$$

where $k$ is the Boltzmann constant, and $g$ is the total number of microstates available. Hence, for the system being considered, $S = k \ln 3$.

Let the volume of the system remain fixed, but consider adding another distinguishable particle, labeled W, with zero energy, so that the total energy is still $U=2\epsilon$. We list the available microstates

| R | B | W |
|---|---|---|
| $2\epsilon$ | $0$ | $0$ |
| $0$ | $2\epsilon$ | $0$ |
| $0$ | $0$ | $2\epsilon$ |
| $\epsilon$ | $\epsilon$ | $0$ |
| $\epsilon$ | $0$ | $\epsilon$ |
| $0$ | $\epsilon$ | $\epsilon$ |

The entropy, by Eq. (3), has increased to $S = k \ln 6$.

So what is the chemical potential? According to Eq. (2), *it is calculated as the change in internal energy of the system, when 1 more particle is added, while holding the volume and*
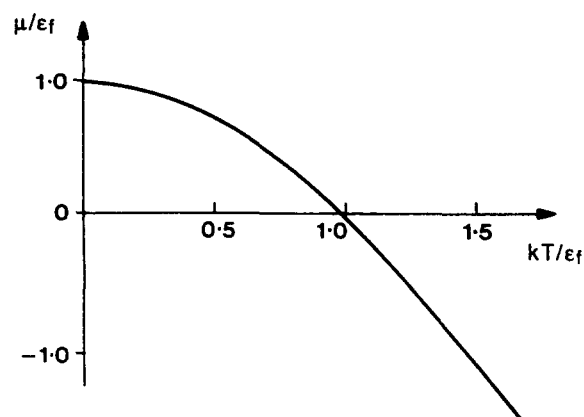
the entropy constant. The only way this can be done for our simple system is to add the W particle with energy $-\epsilon$, or, physically, to add the particle while allowing the internal energy of the system to decrease by $\epsilon$. This makes the total energy $U=\epsilon$, and the available microstates

| R | B | W |
|---|---|---|
| $\epsilon$ | $0$ | $0$ |
| $0$ | $\epsilon$ | $0$ |
| $0$ | $0$ | $\epsilon$ |

Thus the entropy remains constant at $S = k \ln 3$. So, since $\Delta U = -\epsilon$, Eq. (2) gives

$$\mu = -\epsilon.$$

The negative sign in the equation above simply indicates that the system's energy must decrease as a particle is added, so that the entropy remains constant.

## B. Ideal gas

It is standard[1] in statistical physics to calculate the partition function for an ideal gas, and then to use identities involving derivatives of the logarithm of the partition function to determine $U$, $p$, $S$, $\mu$, and so on. This method is explained in detail in many books on statistical mechanics.[1] For an ideal monatomic gas, at temperature $T$, high enough for the gas to behave classically, in a box of volume $V$, *the results for the entropy and chemical potential are as follows*:

$$S = Nk\left[\ln g\frac{V}{N} + \frac{3}{2}\ln\left\{\frac{mU}{3N\pi\hbar^2}\right\} + \frac{5}{2}\right] \tag{4}$$

and

$$\mu = -kT\ln\left[g\frac{V}{N}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}\right], \tag{5}$$

where $g$ is the degeneracy of the particles: $g=2s+1$ for example, for particles of spin $s$.

Equation (4) is known as the Sackur–Tetrode equation. The internal energy is given by

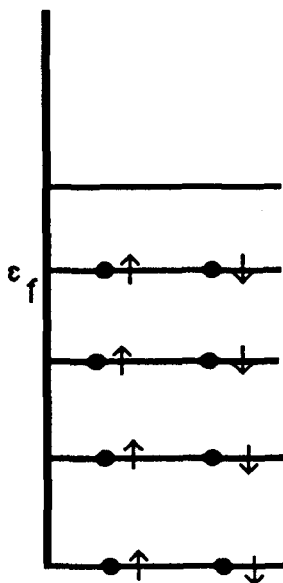$$U = \tfrac{3}{2}NkT, \tag{6}$$

as discussed in many texts.[1]

Fig. 3. Single particle energy states are filled up to the Fermi level. Spacing of energy levels shown is schematic only.
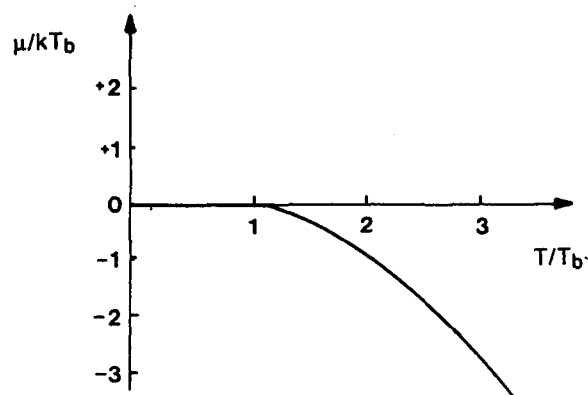


Fig. 4. Variation with temperature of the chemical potential of an ideal Bose gas. $T_b = (3.31\hbar^2/mk)[N/(2s+1)V]^{2/3}$, where $s$ is the spin of the boson and $m$ is the mass of a single particle. $T_b$ is the temperature at which all bosons should be in excited states, leaving the single particle ground state essentially empty.

Students seem to find Eq. (5) surprising. One question they always ask is "Why is it negative?" Actually, in the classical limit, the quantity in square brackets, in Eq. (5), is large, much greater than 1, making $\mu$ a negative number. This is so whenever $T$ is large, and the volume per particle, $V/N$, is large compared to the cube of the thermal de Broglie wavelength, $\lambda = h/p$, where $p^2 = 3mkT$ (which follows from the equipartition theorem). In fact, $\mu$ *must* be negative, because in order to add a particle, while keeping the entropy and volume constant, the particle must carry "negative energy"—or rather, it must be added while the internal energy of the ideal gas is allowed to decrease, by cooling. We demonstrate this by using Eqs. (4) and (6) explicitly.

Let us add a single particle to the system, so that $N \rightarrow N-1$. Let the particle entry to the system involve a change in energy, $\mu$, of $U$, so that the internal energy $U \rightarrow U + \mu$. Then the entropy becomes

$$S' = (N+1)k\left[\ln g\left\{\frac{V}{N+1}\right\} + \frac{3}{2}\ln\left\{\frac{m(U+\mu)}{3(N+1)\pi\hbar^2}\right\} + \frac{5}{2}\right]. \quad (7)$$

We wish to find the value of $\mu$ that makes $S$ in Eq. (4) and $S'$ in Eq. (7) equal, in keeping with Eq. (2). In the classical limit $N$ is large. We use the approximations $1/N \ll 1$, and $|\mu| \ll U$, and expand the logarithms in Eq. (7) to first order. After some algebra (see Appendix A for more detail), we see that the value of $\mu$ that makes the entropy $S' = S$ is precisely that given by Eq. (5). Stated differently, adding a particle to the ideal gas would cause the number of accessible microstates, and hence the entropy, to increase, unless at the same time $U$ is forced to decrease. That is, the only way to hold the entropy of the system constant, is to require $U$ to decrease, which suppresses the number of microstates. Hence, $\mu$ is negative. Or, physically, if you wish to add a particle while holding $S$ constant, the internal energy must be forced to decrease, by cooling the system.

## C. Ideal Fermi gas (Ref. 2)

We have demonstrated that for a classical gas, $\mu < 0$. In the classical limit, i.e., at high temperature and large $N$, both Fermi gases and Bose gases should behave classically; in particular, their chemical potentials should be negative. Having made this point we look at the form of $\mu$ for an ideal Fermi gas, shown in Fig. 2.

Since this form is well documented in many texts,[1] we display only a sketch of it here. At high temperature the form of $\mu$ does indeed approach that of an ideal classical gas. But we see that $\mu > 0$ at low temperature. Why?

At $T = 0$ all the low lying single-particle states are filled, up to the Fermi energy, $\epsilon_f$, in accordance with the Pauli exclusion principle. Each state is shown in Fig. 3, filled with two spin 1/2 fermions, one with spin up, and one with spin down. All states above the Fermi level are empty. There is only one microstate available to the system, and the entropy $S = 0$, in accordance with the third law of thermodynamics.

Let us now add another fermion, at $T = 0$. It must go into a single particle state at, or just above, the Fermi level. So the energy increase of the system is $\Delta U = \epsilon_f$, and thus

$$\mu = \epsilon_f.$$

Note that this is a positive quantity. There is still only one available microstate, so the entropy of the Fermi gas is still zero. Equation (2) shows that this energy really is the chemical potential for this zero temperature Fermi gas.

As the temperature rises, the total internal energy of the system increases, and some of the fermions begin to occupy excited states. The entropy of the system also increases, as the temperature rises, because more microstates become available. Imagine the gas at a very low, but nonzero, temperature, and consider the effect of adding one more particle. To satisfy Eq. (2), the entropy of the system must not increase when the particle is added. The new particle must go into one of the states close to the energy level $\epsilon_f$, since fermions leave these states first, when excited into higher states. In fact, *the new particle must go into a low lying, vacant single particle state*, which will be a little below $\epsilon_f$. The gas must also be cooled a little, to avoid increasing the number of accessible microstates. (Usually, adding a particle to a system causes an increase in the number of accessible

microstates, even if the internal energy of the system remains constant. The reason is that the number of ways of *distributing* the total energy, among the particles, increases. This was shown in Sec. II A). The change in internal energy of the Fermi gas, $\Delta U = \mu$, must therefore be positive, but a little smaller than $\epsilon_f$.

At slightly higher temperatures more fermions are excited into higher single particle states. More of the low lying single particle states become vacant, and the energy of the lowest lying single particle states gets smaller. To add a new particle without increasing the entropy requires the new particle to go into a low lying single particle state, considerably below $\epsilon_f$, while, once again, cooling the gas slightly, to avoid an increase in the number of microstates, and therefore, entropy; hence $\Delta U = \mu$ will be well below $\epsilon_f$. The chemical potential, $\mu$, therefore decreases, from $\epsilon_f$ at $T = 0$, to smaller and smaller values, until $\mu = 0$, just below the temperature $T_f = \epsilon_f/k$, at which even the single particle ground state is unlikely to be occupied.

After this point, $\mu$ becomes negative. If a new particle is added to the system, internal energy must decrease, to comply with the constraint spelled out in Eq. (2), that the entropy remains constant.

As the temperature rises, the gas eventually begins to mimic classical behavior: the chemical potential decreases and becomes increasingly negative. In this way, the behavior of $\mu$ in Fig. 2 can be completely understood.

## D. Ideal Bose gas (Refs. 3 and 4)

A sketch of the chemical potential for an ideal Bose gas is displayed in Fig. 4. The energy scale has been chosen so that the single particle ground state of the system has energy equal to zero. The derivation of $\mu$ as a function of temperature, $T$, is discussed in Appendix B.

At high temperature $\mu$ behaves classically, but at low temperature $\mu \rightarrow 0$. Why?

The answer to this question is easy. As $T \rightarrow 0$ the bosons begin to form a "condensate," that is, they all go into the lowest energy eigenstate available, with $\epsilon = 0$. Bosons do not obey any exclusion principle, so there is nothing to prevent the condensation. At $T = 0$ they are all in the ground state, with zero energy. There is only one available microstate, so $S = k \ln 1 = 0$. If another boson is added to the system, while keeping the entropy constant, it must have zero energy, and go into the ground state too, so $\Delta U = 0$, $\Delta S = 0$, and hence $\mu = 0$.

Consider the Bose gas at very low, but finite, temperature. The internal energy of the gas has increased, and a few bosons are in excited states. Most are still in the ground state. The entropy of the gas has also increased, because the number of microstates available has increased. Consider adding one more particle. For the purpose of calculating $\mu$, Eq. (2) requires that the entropy remain constant. The new particle could be added into the ground state, with zero energy. The number of microstates available to the system probably increases since the number of ways of distributing the given internal energy of the system among the particles present, usually increases when an extra particle is added. At very low temperatures, this increase in the number of microstates is a very small number. Therefore, the entropy of the system would also increase by a small amount. The internal energy of the gas should be allowed to decrease slightly, by cooling the system, so the number of available microstates does not

increase, and the entropy is held fixed. Therefore, the chemical potential is very small in magnitude, at low temperature, and negative.

As the temperature increases, the net internal energy of the Bose system increases. More particles are in excited states, and fewer particles lie in the ground state. If one more, extra, particle is added, it should still go into the ground state with zero energy. Nevertheless, the number of microstates available, and hence the entropy, increases, because the number of ways of distributing the internal energy among the available particles increases. $\mu$ must be negative to compensate for this effect.

The chemical potential of the Bose gas remains close to zero, and negative, until the temperature $T_b$ is reached, at which point the occupancy of the single particle ground state becomes vanishingly small. $T_b$ is called the Bose temperature, or the Bose–Einstein condensation temperature; see Appendix B. The occupancy of the ground state is microscopic at this temperature, and above it (meaning that there may be a few bosons in the ground state, but this number is tiny compared to the number of bosons in the system). $T_b$ is given by

$$T_b = \frac{3.31\hbar^2}{mk}\left(\frac{N}{(2s+1)V}\right)^{2/3}, \qquad (8)$$

where $s$ is the spin of the bosons, $V$ is the volume, and $N$ is the total number of bosons in the system. Equation (8) is obtained[4] by setting the number of particles in excited states equal (essentially) to the total number in the system. See Appendix B for details.

At temperatures higher than $T_b$ the condensate in the ground state is no longer present; if an extra particle is added to the system, even into the ground state, the entropy increases by a large amount because the number of ways of distributing the internal energy between the particles is large, resulting in many more microstates available. The system must be cooled to keep the entropy from increasing. At temperatures higher than $T_b$ this effect predominates. When the condensate has evaporated, $\mu$ becomes rapidly more negative, eventually mimicking ideal gas behavior.

To understand the behavior of $\mu$ shown in Fig. 4 it is crucial to understand the effect the condensation in the ground state has on the system.

To see how this works the reader is invited to do a simple exercise, which demonstrates how $\mu$ stays close to zero at low temperature, below $T_b$, and then becomes rapidly more negative. Consider a system of bosons in which the single particle energy eigenvalues are equally spaced, as shown in Fig. 1, with single particle ground state energy equal to zero (this is a simpler system than the Bose gas, but it shares some of the properties of the gas). Let the number of bosons in the system be $N$, and suppose the temperature is $T = 0$. At zero temperature there is only one microstate available to the system; $U = 0$ and $S = 0$. Consider adding another particle. Add it into the ground state. $\Delta U = 0$ and $\Delta S = 0$, so $\mu = 0$.

Start with $N = 2$. Assume the temperature has increased, so the total internal energy of the system is $\epsilon$. $S = 0$ in this case, also; only one microstate is available. Consider adding another particle. Put it in the ground state making $\Delta U = 0$. There are no new microstates, so $\Delta S = 0$. Hence, $\mu = 0$, still.

Assume $N = 2$, but the temperature has again increased, consistent with $U = 2\epsilon$. The number of available microstates has increased to 2. Consider adding one more particle. Add it

to the ground state with zero energy. Still, the number of available microstates remains constant at two. So $\mu=0$, still.

Keep $N=2$, but allow the temperature to increase, consistent with $U=3\epsilon$. There are only two microstates available and $S=k \ln 2$. Add one more particle with zero energy, keeping $U=3\epsilon$. Suddenly, the number of microstates available to the system has increased, and $\mu$ must begin to go negative.

$\mu$ begins to decrease significantly from zero, only when the temperature increases enough (i.e., above $T_b$) to make the probability of finding the ground state occupied depart significantly from 1.

Repeat this example for $N=3, 4, 5, \ldots$ You will see that as $N$ increases, $T_b$ also increases; $\mu$ stays close to zero until higher and higher temperatures are reached (consistent with higher and higher values of the internal energy of the gas, $U$) as in Eq. (8). At temperatures higher than $T_b$, $\mu$ becomes rapidly more negative.

This simple example demonstrates the behavior of a Bose system.

### E. Photon gas (Refs. 5 and 6)

Photons are bosons with a unique property. The chemical potential of a photon gas in equilibrium in a volume, $V$, and at temperature, $T$, is formally given by $\mu=0$.[5]

The physical reason for setting $\mu=0$ is that the number of photons in the volume cannot be arbitrary; rather, the number of photons is constantly, and automatically, being adjusted so that the photon gas is in thermal equilibrium with the constant temperature walls of the container. That is, the container walls constantly absorb and re-emit photons. Even a gas of photons far out in space does not contain a fixed number of photons, since photons can be annihilated or created in collisions (although the scattering cross section for this process is very small, and photons would have to be annihilated or created in pairs to conserve charge conjugation.[7]) Therefore, when writing the thermodynamic identity for a photon gas the term $\mu dN$, in Eq. (1), should be omitted since $N$ cannot be held fixed anyway. This is formally consistent with setting $\mu=0$.

Further, it is easy to see why $\mu$ should be set equal to 0 by considering distributions. Consider a single photon state of energy $\epsilon$. Suppose the photon gas is in thermal equilibrium at temperature $T$, and that it has chemical potential $\mu$. Photons are spin-1 (in units of $\hbar$) bosons, and should therefore obey Bose–Einstein statistics. The average occupancy of the state of energy $\epsilon$ is therefore given by[6]

$$\langle n(\epsilon) \rangle = \frac{1}{e^{\beta(\epsilon-\mu)}-1},$$

where $\beta=1/kT$ ($k$ is the Boltzmann constant).

This formula is valid for any Bose system. If we now set $\mu=0$, we get

$$\langle n(\epsilon) \rangle = \frac{1}{e^{\beta\epsilon}-1},$$

which is the standard form for the Planck distribution.[6] All thermodynamic quantities can be derived from this equation for the average occupancy of a single photon state of energy $\epsilon$.

For example, the total internal energy of a Bose–Einstein gas is

$$U = \int_0^\infty \epsilon \langle n(\epsilon) \rangle D(\epsilon) d\epsilon = \int_0^\infty \frac{\epsilon D(\epsilon) d\epsilon}{[e^{(\epsilon-\mu)/kT}-1]},$$

where $D(\epsilon)d\epsilon$ is the density of states factor, that is, the number of single particle states with energy between $\epsilon$ and $\epsilon+d\epsilon$.

We set $\mu=0$, and use the density of states factor for a photon gas in a box, $D(\omega)d\omega = V\omega^2 d\omega/\pi^2 c^3$, where a single photon of angular frequency $\omega$ has energy $\epsilon=\hbar\omega$. We get

$$U = \int_0^\infty \hbar\omega \langle n(\omega) \rangle D(\omega) d\omega$$

$$= \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\hbar\omega^3 d\omega}{[\exp(\hbar\omega/kT)-1]},$$

which is the correct expression for the total energy of a photon gas in a box. This integral can be done analytically, of course. The result is the familiar one for blackbody radiation,

$$U = V\left(\frac{8\pi^5 k^4}{15h^3 c^3}\right)T^4.$$

Therefore, the photon gas corresponds to a Bose gas for which $\mu=0$.

### APPENDIX A

We show here that for an ideal gas, setting Eq. (7) and (4) equal and solving for $\mu$ does, indeed, produce Eq. (5) for the chemical potential. With the spin degeneracy factor $g=2s+1$ set to 1 for simplicity, Eq. (7) gives

$$S' = Nk\left(1+\frac{1}{N}\right)\left[\ln\frac{V}{N}\frac{N}{N+1}+\frac{3}{2}\ln\frac{mU}{3N\pi\hbar^2}\frac{1+\dfrac{\mu}{U}}{\dfrac{N+1}{N}}+\frac{5}{2}\right],$$

$$\therefore S' = Nk\left(1+\frac{1}{N}\right)\left[\ln\frac{V}{N}-\ln\left(1+\frac{1}{N}\right)+\frac{3}{2}\ln\frac{mU}{3N\pi\hbar^2}\right.$$
$$\left.+\frac{3}{2}\ln\left(1+\frac{\mu}{U}\right)\right]+Nk\left(1+\frac{1}{N}\right)\left[-\frac{3}{2}\ln\left(1+\frac{1}{N}\right)+\frac{5}{2}\right],$$

$$\therefore S'-S = Nk\left[-\ln\left(1+\frac{1}{N}\right)+\frac{3}{2}\ln\left(1+\frac{\mu}{U}\right)-\frac{3}{2}\ln\left(1+\frac{1}{N}\right)\right]$$
$$+k\left[\ln\frac{V}{N}-\ln\left(1+\frac{1}{N}\right)+\frac{3}{2}\ln\frac{mU}{3N\pi\hbar^2}\right]$$
$$+k\left[\frac{3}{2}\ln\left(1+\frac{\mu}{U}\right)-\frac{3}{2}\ln\left(1+\frac{1}{N}\right)+\frac{5}{2}\right].$$

Use

$$\ln\left(1+\frac{\mu}{U}\right) \approx \frac{\mu}{U},$$

$$\ln\left(1+\frac{1}{N}\right) \approx \frac{1}{N}$$

and drop all terms of order $\mu/U$ and $1/N$ in the expression for $S'-S$. This gives

$$S' - S \approx k \left[ \frac{3\mu N}{2U} + \ln \frac{V}{N} \left( \frac{mU}{3N\pi\hbar^2} \right)^{3/2} \right].$$

Setting $S' - S \approx 0$ and solving for $\mu$ gives the result

$$\mu = -kT \ln \left[ \frac{V}{N} \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right],$$

where we used $U = 3NkT/2$ for a monatomic ideal gas. This result for $\mu$ is Eq. (5).

## APPENDIX B (See Refs. 4 and 6)

For a Bose gas the average occupancy of a single particle state of energy $\epsilon$, at temperature $T$, is

$$\langle n(\epsilon) \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} - 1},$$

where $\beta = 1/kT$.

We choose the zero of the energy scale at the single particle ground state, so $\epsilon = 0$ for that state.

The total number of particles, $N$, in the system is

$$N = \sum \langle n(\epsilon) \rangle.$$

In the continuum limit the summation becomes an integral over the density of states. For a Bose gas of nonrelativistic particles, mass $m$ and spin $s$, the density of states is

$$D(\epsilon) = \frac{(2s+1)V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}.$$

Hence, the number of particles in excited states is given by

$$N_{\text{ex}} = \int_0^\infty \langle n(\epsilon) \rangle D(\epsilon) d\epsilon.$$

Note that the ground state has $\epsilon = 0$, so the occupancy of the ground state is not included in the integral above, since $D(\epsilon) = 0$ at $\epsilon = 0$. Hence, the equation above gives only the number of bosons in excited states. The number of bosons in the ground state must be dealt with separately.[6] The number in the ground state is

$$\langle n(0) \rangle = (2s+1) \frac{1}{e^{-\beta\mu} - 1}.$$

Let the total number of particles in the system be $N$. Then

$$\langle n(0) \rangle + N_{\text{ex}} = N,$$

or

$$(2s+1) \left[ \frac{1}{e^{-\beta\mu} - 1} + \frac{V}{4\pi^2} \left[ \frac{2m}{\hbar^2} \right]^{3/2} \int_0^\infty \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \epsilon^{1/2} d\epsilon \right]$$
$$= N.$$

This equation can be solved numerically for $\mu$ at each temperature $T$. The result is the graph shown in Fig. 4.

The temperature $T_b$ is reached when $N_{\text{ex}} \approx N$. In other words, almost all bosons are in excited states, leaving the occupancy of the ground state vanishingly small. $T_b$ is given by

$$T_b = \frac{3.31\hbar^2}{mk} \left( \frac{N}{(2s+1)V} \right)^{2/3}.$$

[1] Many books in thermal physics and statistical mechanics could be useful here. Examples are: C. Kittel and H. Kroemer, *Thermal Physics*, 2nd ed. (Freeman, New York, 1980), p. 51; P. M. Morse, *Thermal Physics*, 2nd ed. (Benjamin, New York, 1969), p. 239; W. G. V. Rosser, *An Introduction to Statistical Physics*, 2nd ed. (Horwood, Chichester, UK, 1985), p. 109; F. Reif, *An Introduction to Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), p. 201; K. Stowe, *Introduction to Statistical Mechanics and Thermodynamics* (Wiley, New York, 1984), p. 174. A 2nd ed. of this book is planned; D. S. Betts and R. E. Turner, *Introductory Statistical Mechanics* (Addison-Wesley, Wokingham, UK, 1992), p. 192; H. S. Robertson, *Statistical Thermophysics* (Prentice Hall, New Jersey, 1993), p. 146.

[2] As in Ref. 1. See also V. C. Ajuilera-Navarro, G. A. Estevez, and W. Solano-Torres, "On the evaluation of the internal energy and chemical potential of an ideal fermion system," Am. J. Phys. **59**, 452–454 (1991).

[3] V. C. Aguilera-Navarro and G. A. Estevez, "Analytic approximation for the chemical potential of an ideal boson system," Am. J. Phys. **56**, 456–458 (1988).

[4] W. G. V. Rosser, as in Ref. 1 pp. 313–323.

[5] R. E. Kelly, "Thermodynamics of blackbody radiation," Am. J. Phys. **49**, 714–719 (1981).

[6] R. K. Pathria, *Statistical Mechanics* (Pergamon, Oxford, UK, 1972), pp. 175–189. Note especially the footnote labeled "dagger" on p. 189. Equations (7.1.2) and (7.2.1) are especially relevant. A similar, but rather less clear, discussion can be found in the book by W. G. V. Rosser, in Ref. 1), pp. 324–325.

[7] D. Griffiths, *Introduction to Elementary Particles* (Harper and Row, New York, 1987), pp. 128–130.

---

## WRITERS AND LECTURERS

We should not blame young scientists for adopting learned journalese. They are simply following the protocol established and maintained by an unconscious conspiracy of research supervisors and editors who, in turn, learnt these dreadful habits earlier in their careers. What is surprising is that few scientists stop to reflect on what they are doing. Tedious, clotted syntax is thus quite different from other horrors of peer-group communication such as unreadable slides and overheads. Lecturers who announce "You won't be able to see this but ..." do know that they are doing something silly. Writers and speakers or learned journalese, by contrast, have no shame. When did you last hear or read the apology: "I don't like saying things in this way but I feel obliged to ..."?

Bernard Dixon, "Plain words, please," New Scientist **137** (1865), 39 (20 March 1993).