On the use of the statistical definition of entropy to justify Planck's form of the third law of thermodynamics

Salvador Mafé,[a] José A. Manzanares, and Juan de la Rubia
Department of Thermodynamics, Faculty of Physics, University of Valencia, E-46100 Burjasot, Spain

(Received 7 April 1999; accepted 21 December 1999)

The statistical definition of entropy is often used to justify Planck's form of the third law of thermodynamics in a very graphic form. Statements like *for a nondegenerate ground state system at 0 K, the system should be in its lowest energy (ground) state and then $S=0$ according to the statistical definition of entropy* are commonplace in many textbooks. These statements are useful, but might as well be supplemented with more empirical views concerning the physical limits of low temperatures in thermodynamics and the high number of states still accessible for a macroscopic system when the entropy takes small values. The purpose of this note is to emphasize the above points making use of four model systems: the Fermi ideal gas, the confined Bose ideal gas, the photon gas, and the noninteracting particles in a two-level system. Each of these physical systems has a characteristic temperature related to the nature and organization of its microscopic constituents and the third law should perhaps be expressed in terms of the behavior of the system when it approaches this temperature rather than the presumed behavior at exactly $T=0$ K.

I. INTRODUCTION

One of the statistical definitions of entropy,

$$S=k\ln g, \tag{1}$$

connects the entropy S of a system with the number of accessible states g through Boltzmann's constant k, and shows the statistical character of the macroscopic information encapsulated in the *second law* of thermodynamics.[1] It seems intuitive to go a step further and use Eq. (1) to also interpret Planck's form of the *third law* of thermodynamics for a nondegenerate ground state system in a very graphical form, namely, *at 0 K the system should be in its lowest energy (ground) state and then $S=0$ according to Eq. (1)*. However, some empirical views should be added to this interpretation. It has been emphasized previously that there are physical limits on the notion of low temperatures in thermodynamics that can be severe for small systems of experimental interest.[2,3] Indeed, temperature fluctuations may impose a limit on the attainability of low temperatures in finite systems, and should then be mentioned in the context of the third law. Also, the number of states accessible for a macroscopic system can still be very large even when the entropy takes small values.[4,5] Finally, although Eq. (1) may offer a general explanation for the behavior of matter at low temperatures, the actual decrease of entropy with temperature depends very much on the system considered and appears to be related to the quantum principles that rule the behavior of matter at low temperatures.[6,7]

The particular character of the third law of thermodynamics has recently been addressed in a question posed by Blau and Halfpap[8] that received three subsequent answers.[9–11] It seems that this law is better understood in those cases where molecular information on the system under consideration is available.[4–7,10–12] Here, we will explore this question, making use of four model systems that find some applicability in the understanding of the properties of matter at low temperatures: the Fermi ideal gas, the confined Bose ideal gas,[2] the photon gas, and the noninteracting particles in a two-level system. We must say that the conclusions obtained are not entirely new: Some viewpoints similar to ours may be found disseminated over a number of excellent textbooks, specialized articles, and monographs.[2–7,10–17] However, here we have given a simplified presentation that points out important aspects of the problem that are frequently ignored. We emphasize that each physical system has a characteristic temperature related to the nature and organization of its microscopic constituents,[10,16] and that the third law should be expressed in terms of the behavior of the system when it approaches this temperature rather than the presumed behavior at exactly $T=0$ K.

II. PHYSICAL LIMITS ON THERMODYNAMIC TEMPERATURES

Wu and Widom[2] have recently shown that there exist physical limits on the notion of thermodynamic temperature that must be borne in mind when taking the limit $T\rightarrow 0$. We will use their results to calculate the temperature fluctuations[2] that correspond to the systems studied when the entropy takes small values.

It is well known that for a system of heat capacity C, the temperature fluctuations δT can be written as[2,3,17,18]

$$\delta T/T\approx(k/C)^{1/2}, \tag{2}$$

where the condition $\delta T/T\ll 1$ is required for the thermodynamic temperature concept to be unambiguous.[2] Since C is proportional to the number of particles N of the system, the above condition might appear severe only for small systems. In low temperature physics, however, experiments conducted with a reduced number of particles are not uncommon.[2,19,20]

The heat capacities of the ideal Fermi gas,[12,13,17] the confined ideal Bose gas,[2] the photon gas,[12,17,18] and the noninteracting particles in a two-level system[2,5] are (see the Appendix for details):

$$C_F\approx(\pi^2/2)Nk(T/T_F),\quad T/T_F<1, \tag{3a}$$

$$C_b\approx(12\zeta(4)/\zeta(3))Nk(T/T_b)^3,\quad T/T_b<1, \tag{3b}$$

$$C_p=(4\pi^2/15)k(T/T_p)^3, \tag{3c}$$

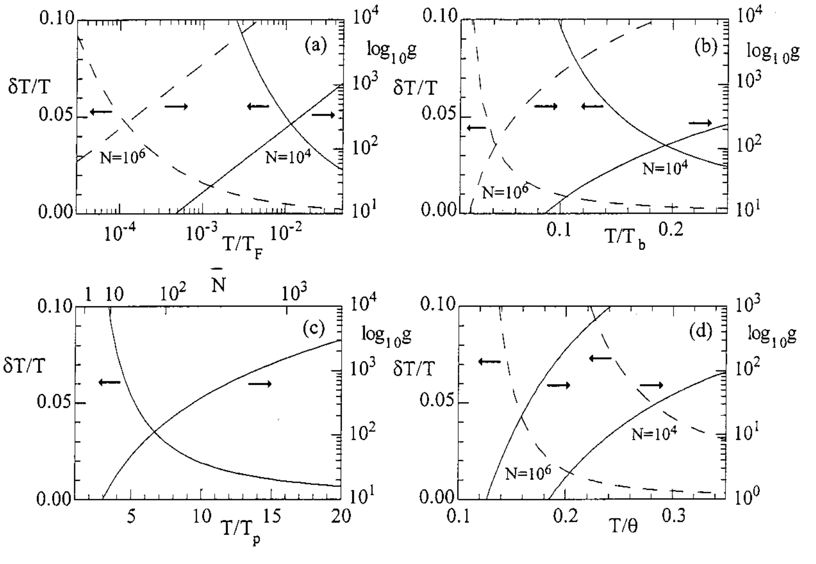

Fig. 1. Number of accessible states g and temperature fluctuations $\delta T/T$ as a function of the relative temperature T/T_{ch} corresponding to (a) the ideal Fermi gas, (b) the confined ideal Bose gas, (c) the photon gas, and (d) the noninteracting particles in a two-level system. The number of particles considered in cases (a), (b), and (d) is $N=10^4$ (continuous lines) and $N=10^6$ (dashed lines). The average number of particles $\overline{N}$ in the photon gas is shown on the upper abscissa scale. The arrows on the curves make reference to the respective (g or $\delta T/T$) ordinate scales.

$$C_\theta = Nk(\theta/T)^2/\cosh^2(\theta/T), \tag{3d}$$

where $T_F=(h^2/8mk)(3N/\pi V)^{2/3}$ is the Fermi temperature[12] for a gas of N fermions of mass m in a volume V, $T_b=(\hbar\omega/k)(N/\zeta(3))^{1/3}$ is the Bose temperature[2] for bound bosons in an oscillator potential of characteristic frequency ω, $T_p=\hbar c/kV^{1/3}$ is a characteristic temperature for a photon gas[2] contained in a volume V, and the temperature $\theta=\Delta\epsilon/2k$ is defined in terms of the energy gap $\Delta\epsilon$ between the two energy levels.

Substituting for these heat capacities in Eq. (2) yields

$$(\delta T/T)_F \approx 0.5(1/N^{1/2})(T_F/T)^{1/2}, \quad T/T_F<1, \tag{4a}$$

$$(\delta T/T)_b \approx 0.3(1/N^{1/2})(T_b/T)^{3/2}, \quad T/T_b<1, \tag{4b}$$

$$(\delta T/T)_p \approx 0.6(T_p/T)^{3/2}, \tag{4c}$$

$$(\delta T/T)_\theta \approx (1/N^{1/2})(T/\theta)\cosh(\theta/T) \tag{4d}$$

for the systems considered.

Figure 1 shows the temperature fluctuations (left ordinate scale) as a function of the ratio of T/T_{ch} for the four systems, T_{ch} being the characteristic temperature of each system. The values $N=10^4$ and $N=10^6$ have been introduced for the number of particles, except for the photon gas, where the average number of photons $\overline{N}=(2\zeta(3)/\pi^2)(T/T_p)^3$ depends on the temperature, and has been shown on the upper abscissa scale of Fig. 1(c). Note that the values considered for T/T_{ch} correspond to low temperatures where the fluctuations are not negligible. $\delta T/T=0.1$ is arbitrarily taken as the upper limit for the values shown in Fig. 1.

Figure 1 shows that the temperature fluctuations reach the value $\delta T/T=0.1$ for *finite* values of T/T_{ch}. Thermodynamic temperatures significantly lower than those in Fig. 1 could only be achieved in systems with a higher number of particles. Moreover, Eq. (2) is quite restrictive for a photon gas.[2] Indeed, a cavity of volume $V=1\ \mathrm{cm}^3$ yields $T_p\approx 0.2\ \mathrm{K}$, so that $T\approx 5T_p\approx 1\ \mathrm{K}$ when $\delta T/T\approx 0.05$ and the average number of photons is only $\overline{N}\approx 20$. In conclusion, Fig. 1 clearly shows that fluctuations impose a limit on the experimental realization of low temperatures in finite small systems, as was previously pointed out by Wu and Widom.[2] Because of fluctuations, the thermodynamic temperature may eventually cease to be well-defined when it is sufficiently low. It might be worth mentioning this empirical view in the context of the unattainability of the absolute zero temperature, although it is true that $T=0$ K is unattainable by any method regardless of the above limitations.

III. THE NUMBER OF STATES ACCESSIBLE FOR A MACROSCOPIC SYSTEM

Except for the photon gas,[10] the model systems considered here yield $S/Nk \ll 1$ for $T/T_{\mathrm{ch}} \ll 1$ when applied to macroscopic systems, in qualitative agreement with experimental data.[6,7] Now, what is the number of states g accessible to the system? This number can be estimated by substituting in Eq. (1) the entropies $S=\int_0^T C(T)\,dT/T$ calculated from the heat capacities in Eqs. (3a)–(3d):

$$S_F/Nk \approx (\pi^2/2)(T/T_F), \quad T/T_F<1, \tag{5a}$$

$$S_b/Nk \approx (4\zeta(4)/\zeta(3))(T/T_b)^3, \quad T/T_b<1, \tag{5b}$$

$$S_p/\overline{N}k = 2\pi^4/(45\zeta(3)), \tag{5c}$$

$$S_\theta/Nk = \ln[2\cosh(\theta/T)] - (\theta/T)\tanh(\theta/T). \tag{5d}$$

Although Eq. (1) applies to a microcanonical ensemble, we have written this equation as $g=\exp(S/k)$ and then proceeded to calculate the entropy S from the heat capacity $C(T)$ (obtained, e.g., in a canonical ensemble) in order to get a crude estimate of the number of microstates g accesible to the equivalent isolated system.[4] (Note that, although in the thermodynamic limit the numerical value of the entropy should be dictated by the thermodynamic state of each system and not by the ensemble used in the calculation, ensembles may not be fully equivalent for finite systems; see the Appendix.)

Figure 1 (right ordinate scales) shows that g is still very large compared to unity even when the temperature is low and the entropy takes relatively small values. For example, when the temperature is so low that $\delta T/T=0.1$, the number of accessible states for a photon gas is still as large as 10^{14} and this value increases up to 10^{53} for the ideal Fermi gas considered here. Therefore, the behavior of the *ideal model systems* at low temperatures should be determined by the quantum nature of the particle distribution functions and the energy spectra, not by the properties of the system ground state[4] or by the energy difference between this ground state and the first excited state.[12] This explains why the consequences of the third law can be detected experimentally at low but *finite* temperatures for macroscopic systems.

IV. QUANTUM ORIGIN OF THE THIRD LAW

Planck's form of the third law of thermodynamics captures the behavior of matter at low temperatures in a pictorial form. The statistical definition of entropy can be used to provide a general justification of this law, although the details of the decrease of the entropy with temperature depend significantly on the particular system considered.[10] Also, for small enough systems the temperature might cease to be well defined when it is sufficiently low.[2] These issues have been emphasized here using four ideal model systems. Three of them (the Fermi, Bose, and photon gases) correspond to *indistinguishable* particles, and the results presented were obtained using the respective *quantum particle distribution functions* together with quasi-continuous energy spectra. The noninteracting particles in a two-level system could be considered as *distinguishable* particles (if we regard them as ideally fixed, which artificially introduces distinguishability) with a *discrete energy spectrum*. It should be mentioned in this context that the entropies derived for the classical ideal gas model using the Boltzmann particle distribution function and for the classical harmonic oscillator model using the continuous energy spectrum do not satisfy the third law.

The forces between particles are certainly crucial in the behavior of matter at low temperatures and should then be taken into account in a statistical mechanical justification of the third law.[11,16] However, the systems of noninteracting particles considered here illustrate some of the underlying physics encapsulated in this law and often constitute useful approximations. The Fermi gas model is used for subsystems of condensed matter (like the free electron gas in solids; note that $T/T_F \ll 1$ at room temperature). The confined Bose gas model constitutes an (admittedly crude) first approximation in Bose–Einstein condensation experiments with ultracold dilute gases. The noninteracting particles in a two-level system provide a useful model for the ideal paramagnetic solid in an external field.

The interaction between particles can sometimes be incorporated in a relatively simple form. Most substances become crystalline solids at low temperatures and their lattice heat capacities can then be approximately described by Debye's theory.[12] The phonons in solids are analyzed as *quasiparticles* with a quasi-continuous energy spectrum and the Bose–Einstein distribution function (a qualitatively similar approach might also be applied to helium,[12] which remains liquid at extremely low temperatures). It is well known that for low enough temperatures, the Debye model leads to a heat capacity proportional to T^3. Some of the results to be obtained using this heat capacity should not then be qualitatively different from those presented here for the confined ideal Bose gas [see Eq. (3b)] when the number of particles is small. Therefore, although we do not claim our results to be general, they might illustrate some trends in real systems.

It is difficult to give a general proof that the entropy of any pure substance in equilibrium vanishes at absolute zero.[6–8,12,14] Derivations of the third law based on statistical mechanics have been given and discussed previously (see, e.g., Wilks[6] and Landsberg[15] as well as references therein). Each physical system considered here has a characteristic temperature[21] ultimately related to the nature and organization of its microscopic constituents,[10,16] and the third law should be expressed in terms of the behavior of the system when it approaches this temperature rather than the presumed behavior at exactly $T=0$ K.

Note finally that since one of the salient features of thermodynamics is its independence from particular microscopic models, the above (system dependent) characteristic temperatures cannot be obtained from thermodynamics. The third law must then be postulated invoking the hypothetical limit $T=0$ K in order to explain the vast amount of experimental data collected for thermodynamic systems at low enough temperatures.[22]

ACKNOWLEDGMENTS

We thank the referees for useful comments that helped to significantly improve the clarity of the original manuscript.

APPENDIX

The heat capacity of the ideal Fermi gas can be derived from the average energy E_F as $C_F=(\partial E_F/\partial T)_V$. For small enough temperatures, $T/T_F<1$, E_F is approximately given by[12,17]

$$E_F \approx (3/5)N\epsilon_F[1+(5\pi^2/12)(T/T_F)^2], \tag{A1}$$

where $T_F=(h^2/8mk)(3N/\pi V)^{2/3}$ and $\epsilon_F=kT_F$ is the Fermi energy.[12]

The confined ideal Bose gas corresponds to bound bosons in an anisotropic oscillator potential of frequencies ω_1, ω_2, and ω_3. This system was chosen because of its theoretical and experimental interest.[2,19] Since it has recently been studied in detail by Wu and Widom,[2] here we will obtain only the heat capacity C_b and the Bose temperature T_b (the interested reader can find the complete derivation in Ref. 2). In the quasiclassical approximation, the grand canonical free energy of the confined ideal Bose gas can be written as[2]

$$\Xi(T,\mu)=kT\int\int(d^3r\,d^3p/h^3)\ln[1-\exp((\mu-h_b)/kT)], \tag{A2}$$

where $\mu<0$ is the chemical potential and

$$h_b(\mathbf{p},\mathbf{r})=p^2/2m+m\mathbf{r}\cdot\hat{\omega}^2\cdot\mathbf{r}/2 \tag{A3}$$

is the one-boson Hamiltonian with

$$\hat{\omega}^2=\begin{pmatrix}\omega_1^2 & 0 & 0\\ 0 & \omega_2^2 & 0\\ 0 & 0 & \omega_3^2\end{pmatrix}. \tag{A4}$$

Expanding the logarithm in a power series, Eq. (A2) gives

$$\Xi(T,\mu)=-\hbar\omega(kT/\hbar\omega)^4\sum_{n=1}^{\infty}(1/n^4)\exp(n\mu/kT) \tag{A5}$$

with $\omega=(\omega_1\omega_2\omega_3)^{1/3}$. Differentiating $\Xi(T,\mu)$ with respect to μ, the number of particles can be obtained as

$$N(T,\mu)=(kT/\hbar\omega)^3\sum_{n=1}^{\infty}(1/n^3)\exp(n\mu/kT). \tag{A6}$$

From Eq. (A6) and following a procedure analogous to the case of the free ideal Bose gas in the thermodynamic limit,[17] the number of bosons in the condensate state is[2]

$$N_0(T) = N[1-(T/T_b)^3], \quad T < T_b\,, \tag{A7}$$

with the critical temperature[2] $T_b = (\hbar\omega/k)[N/\zeta(3)]^{1/3}$, where $\zeta(x)$ is the Riemann zeta function.[7] Also, differentiating $\Xi(T,\mu)$ with respect to T, the entropy is[2]

$$S_b/Nk = (4\zeta(4)/\zeta(3))(T/T_b)^3, \quad T < T_b\,, \tag{A8}$$

from which the heat capacity of Eq. (3b) is readily obtained.

The internal energy of the photon gas can be written as[2,12]

$$E_p = (\pi^2/15)V(kT)^4/(\hbar c)^3 = (\pi^2/15)kT^4/T_p^3, \tag{A9}$$

where $T_p = \hbar c/kV^{1/3}$. Differentiating E_p with respect to T at constant V leads immediately to Eq. (3c).

Finally, it is well-known that the energy of N noninteracting particles in a two-level system is[2,5,17]

$$E_\theta = -Nk\theta\tanh(\theta/T), \tag{A10}$$

where $\theta = \Delta\epsilon/2k$ is a characteristic temperature and $\Delta\epsilon$ is the energy gap between the two energy levels. Again, differentiating E_θ with respect to the temperature yields the heat capacity

$$C_\theta = Nk(\theta/T)^2/\cosh^2(\theta/T). \tag{A11}$$

From the heat capacities of Eqs. (3a)–(3d) the entropy is readily obtained. This entropy is then substituted in Eq. (1) to estimate the number of microstates g accessible to each system (see Fig. 1).[4] Note that Eq. (1) is valid for a microcanonical ensemble, and the entropy S has been calculated here using the heat capacity $C(T)$ derived from other ensembles. Since ensembles are not fully equivalent for finite systems,[23] we must mention that the results of Fig. 1 should be regarded only as very crude estimations.

[a)]Electronic mail: smafe@uv.es

[1] J. L. Lebowitz, ''Boltzmann's entropy and time's arrow,'' Phys. Today, 32–38 (September 1993).

[2] J. Wu and A. Widom, ''Physical limits on the notion of very low temperatures,'' Phys. Rev. E **57** (5), 5178–5183 (1998).

[3] H. Feshbach, ''Small Systems: When does thermodynamics apply?,'' Phys. Today, 9–11 (November 1987).

[4] G. V. Rosser, *An Introduction to Statistical Physics* (Ellis Horwood, Chichester, 1982).

[5] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw–Hill, New York, 1962).

[6] J. Wilks, *The Third Law of Thermodynamics* (Oxford U.P., Oxford, 1961).

[7] J. Wilks, ''The Third Law of Thermodynamics,'' in *Physical Chemistry. An Advanced Treatise*, edited by W. Jost (Academic, New York, 1971).

[8] S. Blau and B. Halfpap, ''Question #34. What is the third law of thermodynamics trying to tell us?,'' Am. J. Phys. **64** (1), 13–14 (1996).

[9] P. T. Landsberg, ''Answer to question #34. What is the third law of thermodynamics trying to tell us?,'' Am. J. Phys. **65** (4), 269–270 (1997).

[10] S. Mafé and J. de la Rubia, ''Answer to question #34. What is the third law of thermodynamics trying to tell us?,'' Am. J. Phys. **66** (4), 277 (1998).

[11] C. Rose-Innes, ''Answer to question #34. What is the third law of thermodynamics trying to tell us?,'' Am. J. Phys. **67** (4), 27 (1999).

[12] K. Huang, *Statistical Mechanics* (Wiley, New York, 1987).

[13] C. Kittel and H. Kroemer, *Thermal Physics* (Freeman, New York, 1980).

[14] T. L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986).

[15] P. T. Landsberg, *Thermodynamics and Statistical Mechanics* (Oxford U.P., Oxford, 1978; reprinted by Dover, New York, 1990).

[16] R. Baierlein, *Thermal Physics* (Cambridge U.P., Cambridge, 1999).

[17] R. K. Pathria, *Statistical Mechanics* (Pergamon, New York, 1972).

[18] E. S. R. Gopal, *Statistical Mechanics and Properties of Matter* (Wiley, New York, 1974).

[19] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, ''Observation of Bose–Einstein condensation in a dilute atomic vapor,'' Science **269**, 198–201 (1995).

[20] C. E. Wieman, ''The Richtmyer memorial lecture: Bose–Einstein condensation in an ultracold gas,'' Am. J. Phys. **64** (7), 847–855 (1996).

[21] Real systems usually have a set of characteristic temperatures. In the case of an ideal gas of diatomic molecules, for example, there exist several characteristic temperatures depending on the degree of freedom (translation, rotation, vibration) probed experimentally. Most of these temperatures are significantly higher than zero.

[22] The above limit provides an origin of entropies, and it is this *operational* aspect that is often emphasized in many thermodynamics textbooks. However, as pointed out previously by many authors (see in particular Refs. 4–6, 10–11, and 14–16), it is interesting to give statistical mechanics justifications of the third law since the behavior of thermodynamic systems at low temperatures points out clearly that this law reflects fundamental properties of natural systems.

[23] K. Burnett, M. Edwards, and Ch. W. Clark, ''The theory of Bose–Einstein condensation of dilute gases,'' Phys. Today, 37–42 (December 1999).