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Arthur V. Tobolsky

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The Microcanonical Ensemble

ARTHUR V. TOBOLSKY

Department of Chemistry, Princeton University, Princeton, New Jersey

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In the usual development of quantum statistical mechanics the microcanonical ensemble is introduced in order to present the basic postulates of this subject with utmost clarity. However practical calculations of elementary problems using the microcanonical ensemble directly are seldom carried out. Either the method of the most probable distribution is introduced, or the canonical ensemble is introduced. Both of these methods require the development of further mathematical and physical concepts.

It is shown here that very elementary methods can be used to develop the thermodynamic properties of monatomic crystals and the "corrected" Boltzmann monatomic gas directly from the basic concepts of the microcanonical ensemble.

For more complex problems, it is shown that the microcanonical ensemble emphasizes the relation between basic concepts in statistical mechanics and certain unsolved problems in the theory of numbers.

IN the development of quantum statistics, the textbooks usually start with a macroscopic system at constant E , V , and N . For a large number N of particles (atoms, molecules), the number of accessible quantum states Ω consistent with these constraints is enormously large and is a very significant property of the assembly.

The microcanonical ensemble consists of the array of all of these Ω quantum states. The basic assumption of statistical mechanics is that all of these accessible quantum states are equally probable, i.e., the probability of quantum state i in the microcanonical ensemble is $P_i = 1/\Omega$. The average value of any mechanical variable, i.e., the pressure, is given by

$$\bar{p} = \sum_{i=1}^{\Omega} P_i p_i = \sum p_i / \Omega. \quad (1)$$

At this point, two definitions of the entropy are introduced

$$S = k \ln \Omega, \quad (2)$$

$$S = -k \sum P_i \ln P_i. \quad (3)$$

In Eqs. (2) and (3) k is Boltzmann's constant. For a microcanonical ensemble, Eqs. (2) and (3) are equivalent since $P_i = 1/\Omega$.

Equation (2) is shown to be reasonable, because as additional quantum states are made available by removal of a barrier, the entropy and Ω both increase. This correlates with the behavior of an isolated system undergoing a spontaneous process.

At this point it is usual to say that although the concepts of quantum statistics are clearly brought to the fore by the microcanonical ensemble the calculation of Ω is quite difficult. For example, Hill¹ says "In practice, except in very simple systems, Ω is not available and the microcanonical equations cannot be utilized. In particular the restriction to constant energy is usually a difficulty. This can be avoided by passing to the canonical ensemble." Hill then uses the canonical ensemble rather than the microcanonical ensemble to make his calculations of the thermodynamic properties of various systems. Mayer and Mayer (Chap. 5 of Ref. 2), on the other hand, calculate Ω for the perfect monatomic gas for the Bose-Einstein, Fermi-Dirac, and Boltzmann cases by using the method of the most probable distribution.

In a sense, the continuity of the argument is somewhat broken by these devices. Either one turns from a consideration of Ω to the consideration of the canonical ensemble partition function; or, one computes Ω somewhat indirectly by the method of the most probable distribution.

It is, however, quite easy to compute Ω directly for an Einstein crystal or for a Boltzmann monatomic gas. From these calculations we can readily define the temperature and also obtain the other thermodynamic properties of these

¹ T. L. Hill, *Introduction to Statistical Thermodynamics* (Addison-Wesley Publishing Company, Reading Massachusetts, 1960), p. 29.

² J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), p. 438.

substances. The meaning of Eq. (2) and its true importance are therefore clarified for the student of quantum statistical mechanics.

The derivations presented below for the Einstein crystal and the Boltzmann gas are not new in principle, but are presented here in a more explicit, direct, and complete manner than in the available textbooks.

This approach makes it possible to formulate Ω for more complex microcanonical ensembles. This results in very simply stated but as yet unsolved problems in the theory of numbers. These rather intriguing relationships are presented in a supplement.

THE EINSTEIN CRYSTAL

Consider first a set of N distinguishable oscillators among which are partitioned N_0 quanta of magnitude $h\nu$. Each oscillator can have 0, 1, 2, 3, 4... quanta corresponding to energies 0, $h\nu$, $2h\nu$, $3h\nu$, $4h\nu$, etc. For the moment the zero-point energy is neglected. The total energy of the assembly is

$$E = N_0 h\nu. \quad (4)$$

The total number of quantum states Ω is equal to the number of different ways that N_0 indistinguishable balls can be placed in N numbered cells. This is a well-known combinatorial problem.^{2,3}

$$\Omega = \frac{(N+N_0-1)!}{(N-1)!N_0!} \approx \frac{(N+N_0)!}{N!N_0!}. \quad (5)$$

By substituting Eq. (5) in (2) using Stirling's formula for factorials of large numbers, one obtains

$$S/k = (N+N_0)\ln(N+N_0) - N\ln N - N_0\ln N_0 \quad (6)$$

The thermodynamic formula most appropriate to the microcanonical ensemble is

$$dS = (dE/T) + (P/T)dV - (\mu/T)dN, \quad (7)$$

where μ is the chemical potential per molecule.

Combining (4) and (7) one obtains

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{h\nu} \left(\frac{\partial S}{\partial N_0}\right)_{V,N}, \quad (8)$$

Introducing the value of S from Eq. (6), then

² W. Feller, *An Introduction to Probability Theory and Its Application* (John Wiley & Sons, Inc., New York, 1957), p. 36.

utilizing (4), there results

$$\frac{1}{T} = \frac{k}{h\nu} \ln\left(1 + \frac{N}{N_0}\right), \quad (9)$$

$$E = N h\nu / (e^{h\nu/kT} - 1). \quad (10)$$

Equation (10) is the Planck-Einstein equation, neglecting zero-point energy.

By substituting Eqs. (10) and (4) into (6), one obtains

$$S = [N h\nu / T (e^{h\nu/kT} - 1)] - N k \ln(1 - e^{-h\nu/kT}). \quad (11)$$

From (10) and (11) and the thermodynamic formula $A = E - TS$ there results

$$A = N k T \ln(1 - e^{-h\nu/kT}). \quad (12)$$

The formulas for the vibrational contribution to the thermodynamic properties of an Einstein crystal of N atoms are given by replacing N by $3N$ in Eqs. (10), (11), and (12); and by adding the zero-point energy $3N h\nu/2$ to the resulting equations for E and A .

Morse⁴ utilizes Eq. (5) to obtain the formula for the entropy shown in (6). However he obtains Eq. (10) relating energy and temperature somewhat indirectly by minimizing the Helmholtz free energy. The use of Eq. (8) is much more direct and natural.

THE BOLTZMANN GAS

Now consider the problem of computing Ω for a Boltzmann monatomic gas. It is first necessary to introduce the formula for the surface of an n -dimensional sphere defined by the equation

$$x_1^2 + x_2^2 + \dots + x_n^2 = r^2. \quad (13)$$

The surface S_n of such a sphere is given by the following approximate formula⁵ for large n .

$$\ln S_n = \frac{1}{2} n \ln(2\pi e r^2/n) + \ln(n/r), \quad (14)$$

where e is the base of the natural logarithms. The first term on the right-hand side is in fact the logarithm of the volume of an n -dimensional sphere. The surface area is derived therefrom by differentiating with respect to r , which gives rise to the second term on the right-hand side. For

⁴ P. M. Morse, *Thermal Physics* (W. A. Benjamin, Inc., New York, 1964), pp. 260-264.

⁵ J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), p. 433.

large n the second term is completely negligible compared with the first term.

Consider a gas of N distinguishable atoms of mass m , occupying a volume V , and whose total energy is E . The $3N$ quantum numbers satisfy the relation

$$n_1^2 + n_2^2 + \dots + n_{3N}^2 = \frac{E}{h^2/8mV^{2/3}} \quad (15)$$

For distinguishable atoms all values $n_1 n_2 \dots n_{3N}$ that satisfy Eq. (15) are allowed. Every set of numbers corresponds to a distinguishable quantum state of the assembly. The total number of quantum states Ω_D corresponding to constant (E, V, N) is therefore the surface area of the positive "octant" of the "sphere" defined by Eq. (15). We must therefore divide S_{3N} by 2^{3N} or by $4^{3N/2}$.

$$\ln \Omega_D = \frac{1}{2}(3N) \ln(4\pi e m V^{2/3} E / 3N h^2) \quad (16)$$

One must now correct for the fact that the atoms are really indistinguishable by dividing by $N!$ This is valid only if the average occupancy of any molecular level is very low; otherwise the Fermi-Dirac or Bose-Einstein treatment must be used. If however the "classical" approximation of dividing by $N!$ is valid, one can evaluate the entropy by Eq. (2).

$$S = k \ln \Omega = k \ln(\Omega_D / N!), \quad (17)$$

$$S = \frac{1}{2}(3Nk) \ln(4\pi e^{5/3} m / 3N^{5/3} h^2) + Nk \ln V + \frac{3}{2} Nk \ln E \quad (18)$$

The temperature can be obtained as follows:
 $1/T = (\partial S / \partial E)_{V, N} = 3Nk / 2E; \quad E = \frac{3}{2} NkT. \quad (19)$

The pressure can be obtained as follows:

$$p/T = (\partial S / \partial V)_{E, N} = Nk / V; \quad pV = NkT. \quad (20)$$

Equations (18), (19), and (20) represent the significant thermodynamic relations for the classical monatomic gas. Equations (19) and (20) are particularly significant since they relate T as defined by Ω , E , V , and N to the ideal gas thermometer.

The classical analog of the calculations for the Boltzmann gas shown here in Eqs. (15)–(20) are carried out by integration in classical phase-space. This calculation is indeed presented in many of the well-known textbooks.⁶

⁶ Reference 5, p. 116.

In summary the properties of gases and crystals can be obtained directly from the number of distinguishable quantum states Ω of macroscopic assemblies.

APPENDIX: OTHER MICROCANONICAL ENSEMBLES

If the number of quanta N_0 to be distributed amongst N distinguishable oscillators is very large compared to N , i.e., if N_0/N is very large, then it is easy to show that Eq. (5) reduces to

$$\Omega = N_0^{N-1} / (N-1)! \approx N_0^N / N! \quad (21)$$

Equation (21) can also be derived by considering Ω to be the area of the base of N dimensional pyramid whose edge has a length N_0 .

Under these conditions, the formulae for E and S corresponding to Eqs. (10) and (11) become

$$E = NkT, \quad (22)$$

$$S = Nk[1 + \ln(kT/h\nu)]. \quad (23)$$

Now consider the number of ways Ω of distributing N_0 indistinguishable quanta amongst N indistinguishable oscillators. This is a number theory or partition problem which has no exact analytic solution. However for N_0/N approaching infinity, there is an asymptotic solution

$$\Omega = N_0^{N-1} / (N-1)! N! \approx N_0^N / (N!)^2. \quad (24)$$

For this value of Ω , the following thermodynamic formulas result:

$$E = NkT, \quad (25)$$

$$S = Nk[2 + \ln(kT/h\nu) - \ln N]. \quad (26)$$

It is interesting to speculate as to whether any actual physical system corresponds to the mathematical solution given in Eqs. (24)–(26), or to the more general problem where N_0/N is not necessarily large.

The problem cited above can be phrased as a problem in number theory: in how many ways can we add exactly N integers to give a sum N_0 , if permutations amongst the integers are not counted as different. For example, if $N=3$ and $N_0=6$, and if we exclude zeros, the distinguishable sets are 114, 123, and 222; therefore $\Omega=3$.

For one dimensional bosons, the computation of Ω can also be considered as a problem in number theory: in how many ways can we add the squares of exactly N integers to give a sum

N_0 ; in this problem permutations of the integers are also not counted as distinct configurations. The quantity N_0 is equal to $E/(h^2/8mL^2)$, where L is the length of the one-dimensional box.

For one-dimensional fermions, the problem would be phrased as above, with the additional restriction that no integer can be used more than once.

For three-dimensional bosons and fermions, the integers discussed above would be replaced by vectors. That is one would consider the sum of squares of exactly N vectors (n_{xi}, n_{yi}, n_{zi})

adding up to exactly N_0 . The vector components are, of course, integers.

All of these problems in number theory are very complex. However since the entropy for the B.-E. and F.-D. cases have been evaluated by other methods, it may be possible to obtain asymptotic solutions to these number-theory problems for large values of N utilizing the inverse relation $\Omega = \exp(S/k)$.

The microcanonical ensemble emphasizes the relation between basic concepts in statistical mechanics and certain number-theory problems.

Emission Spectroscopy as an Elective for Science Majors and Engineers

J. THEODORE PETERS

Drexel Institute of Technology, Philadelphia 4, Pennsylvania

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A plea is made for more colleges and universities to offer emission or atomic spectroscopy as an undergraduate elective. So much of our knowledge today of the mechanism of radiation, of atomic structure, and of properties of atomic nuclei resulted from spectroscopic research. It seems only natural then to expect *more* course offerings in this field. Further evidence is given for the need for more work in higher reaches of theoretical spectroscopy. There is still much to be discovered and checked and tabulated as to emission lines for many of the 102 elements.

FOR several years a course in emission spectroscopy—Physics 16-540—has been offered as an elective for science majors and engineers, juniors and seniors with prerequisites in wave motion, sound and light and, also, atomic physics, by the physics department of Drexel Institute of Technology. For a few years this course was required for graduation for all those majoring in chemistry and physics.

Since 1959, eighty-six students have taken the course in day college. One group of seven from neighboring industries took the course in evening college. Another such course is planned for fall of 1964.

Topics covered usually include:

A brief history of spectroscopy

A study of the prism and grating spectrographs and derivation of equations for resolving power and dispersion for each

A review of lens defects and their corrections

Spectral excitation sources

Limitations of spectroscopy

Cyanogen bands and their control or elimination by use of controlled atmospheres

Balmer equations and others

Spectral series, energy levels, emission and absorption spectra compared

Hurter-Driffield or plate calibration curves and working curves

Exclusion principles and term symbols

Grotrian energy level diagrams

Echelon gratings and Fabry-Perot interferometers

Zeeman and Stark effects.

Two hours of lecture and two of laboratory per week carry three term credits.

The purpose of the laboratory work is three-fold:

To acquaint the student with the instruments used (Fig. 1).

To apply principles of spectrographic analysis in actual qualitative and quantitative work.