

1

The Boltzmann distribution law and statistical thermodynamics

1.1 Nature and aims of statistical mechanics

Statistical mechanics is the theoretical apparatus with which one studies the properties of macroscopic systems – systems made up of many atoms or molecules – and relates those properties to the system’s microscopic constitution. One branch of the subject, called statistical thermodynamics, is devoted to calculating the thermodynamic functions of a system of given composition when the forces of interaction within and between the system’s constituent molecules are given or are presumed known. This first chapter is directed toward obtaining the most commonly used formulas of statistical thermodynamics and much of the remainder of the book illustrates their application.

Because the systems to which the theory is applied consist of large numbers of molecules, and are thus systems of a large number of mechanical degrees of freedom, we are not interested in all the details of their underlying microscopic dynamics (and could hardly hope to know them even if we were interested). Instead, it is the systems’ macroscopic properties – among which are the thermodynamic functions – that we wish to understand or to calculate, and these are gross averages over the detailed dynamical states. That is the reason for the word “statistical” in the name of our subject.

A prominent feature in the landscape of statistical mechanics is the Boltzmann distribution law, which tells us with what frequency the individual microscopic states of a system of given temperature occur. An informal statement of that law is given in the next section, where it is seen to be an obvious generalization of two other well known distribution laws: the Maxwell velocity distribution and the “barometric” distribution. We also remark there that the exponential form of the Boltzmann distribution law is consistent with – indeed, is required by – the rule that the probability of occurrence of independent events is the product of the separate probabilities.

In §1.3 we shall find that the normalization constant that occurs in the Boltzmann distribution is related to the system's free energy. That is the key to statistical thermodynamics. Together with a related but simpler observation about the connection between thermodynamic and mechanical energy, it amounts to having found the microscopic interpretation of the first and second laws of thermodynamics.

1.2 The Boltzmann distribution law

The Boltzmann distribution law says that if the energy associated with some state or condition of a system is ε then the frequency with which that state or condition occurs, or the probability of its occurrence, is proportional to

$$e^{-\varepsilon/kT}, \quad (1.1)$$

where T is the system's absolute temperature and where k is the Boltzmann constant, which the reader will already have encountered in the kinetic theory of gases:

$$k = 1.38 \times 10^{-23} \text{ J/K} = 1.38 \times 10^{-16} \text{ erg/K}. \quad (1.2)$$

Many of the most familiar laws of physical chemistry are obvious special cases of the Boltzmann distribution law. An example is the Maxwell velocity distribution. Let v be one of the components of the velocity (v_x or v_y or v_z) of a molecule in a fluid (ideal gas, imperfect gas, or liquid – it does not matter), let m be the mass of the molecule, and let $f(v)dv$ be the probability that v will be found in the infinitesimal range v to $v + dv$. This $f(v)$ is one of the velocity distribution functions that play a prominent part in the kinetic theory of gases. A graph of $f(v)$ is shown in Fig. 1.1. Roughly speaking, it gives the frequency of occurrence of the value v for that chosen velocity component. More precisely, the probability $f(v)dv$ (which is the area under the $f(v)$ curve

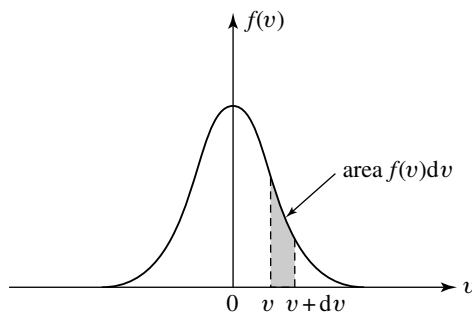


Fig. 1.1

1.2 The Boltzmann distribution law

3

between v and $v + dv$; Fig. 1.1) is the fraction of the time, averaged over long times, that any one molecule has for that one of its velocity components a value in the range v to $v + dv$. (The velocities of the individual molecules continually change with time because the molecules continually collide and otherwise interact with each other.) Alternatively but equivalently, at any one instant the infinitesimal fraction $f(v)dv$ of all the molecules are molecules that have for that component of their velocity a value in the range v to $v + dv$. The velocity distribution function $f(v)$ is

$$f(v) = \sqrt{\frac{m}{2\pi kT}} e^{-mv^2/2kT}. \quad (1.3)$$

The energy associated with that velocity component's having the value v (kinetic energy in this instance) is $\varepsilon = \frac{1}{2}mv^2$, so the Maxwell velocity distribution (1.3) is obviously a special case of the Boltzmann distribution (1.1).

Another special case of the Boltzmann distribution (1.1) is the “barometric” distribution, giving the number density $\rho(h)$ (number of molecules per unit volume) of an ideal gas of uniform temperature T as a function of height h in the field of the earth's gravity. (This could be the earth's atmosphere, say, with the temperature assumed not to vary too much with height – although that is a questionable assumption for the atmosphere.) A column of such a gas of arbitrary cross-sectional area A is depicted in Fig. 1.2. The volume of that part (shown shaded in the figure) that is between h and $h + dh$ is Adh and its mass is then $m\rho(h) Adh$ with m again the mass of a molecule. With the gravitational acceleration g acting downward, that infinitesimal element of the gas, because of its weight, exerts a force $mg \rho(h) Adh$ on the column of gas below it. The excess pressure (force per unit area) at the height h over that at the height $h + dh$ is then

$$p_h - p_{h+dh} = -dp = mg \rho(h)dh. \quad (1.4)$$

This would be true no matter what fluid was in the column; but for an ideal gas the pressure p and number density ρ are related by $p = \rho kT$. [This follows

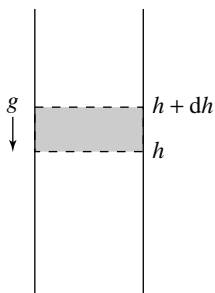


Fig. 1.2

Cambridge University Press

0521811198 - Statistical Mechanics: A Concise Introduction for Chemists

B. Widom

Excerpt

[More information](#)

4

1 Statistical thermodynamics

from the ideal-gas law $pV = nRT$, with n the number of moles and R the gas constant, together with $n = N/N_0$, where N is the number of molecules and N_0 is Avogadro's number, with $k = R/N_0$ (as identified in the kinetic theory of the ideal gas), and with $\rho = N/V$.] Therefore (1.4) becomes a differential equation for $\rho(h)$,

$$d\rho(h)/dh = -(mg/kT)\rho(h). \quad (1.5)$$

The solution, as we may readily verify by differentiation with respect to h , is

$$\rho(h) = \rho(h_0)e^{-mg(h-h_0)/kT} \quad (1.6)$$

where h_0 is an arbitrary fixed reference height. If the gas is a mixture of different species with differing molecular masses m , each has its own distribution (1.6) with its own m .

This is the barometric distribution. Since the probability of finding any specified molecule at the height h is proportional to the number density there, (1.6) is equally well the probability distribution as a function of the height h . Then (1.6) says that the probability of finding a specified molecule at h varies with h as $\exp(-mgh/kT)$. But we recognize mgh as the energy ε (potential energy in this instance) associated with the molecule's being in that state – i.e., at the height h in the earth's gravity. Thus, (1.6) is clearly another special case of the Boltzmann distribution law (1.1).

Exercise (1.1). Spherical particles of diameter $0.5 \mu\text{m}$ and density 1.10 g/cm^3 are suspended in water (density 1.00 g/cm^3) at 20°C . (Particles of such size are called colloidal and a suspension of such particles is a colloid or a colloidal suspension.) Find the effective mass m of the particles, corrected for buoyancy, and then calculate the vertical distance over which the number density of suspended particles decreases by the factor $1/e$. (Historically, in experiments by J. Perrin, who measured the distribution of such particles with height, this was one of the methods by which Boltzmann's constant k was determined – or, equivalently, Avogadro's number N_0 , since $N_0 = R/k$ and the gas constant R is known from simple measurements on gases.)

Solution. The volume of each particle is $(4\pi/3)(0.5/2)^3 10^{-18} \text{ m}^3 = 0.065 \times 10^{-12} \text{ cm}^3$, so the effective mass is $m = (0.065 \times 10^{-12})(1.10 - 1.00) \text{ g} = 6.5 \times 10^{-15} \text{ g}$. From the barometric distribution (1.6), the vertical distance over which the number density decreases by the factor e is kT/mg , which, with $k = 1.38 \times 10^{-16} \text{ erg/K}$, $T = 293 \text{ K}$, $m = 6.5 \times 10^{-15} \text{ g}$, and acceleration due to gravity, $g = 981 \text{ cm s}^{-2}$, is $6.3 \times 10^{-3} \text{ cm}$.

The exponential dependence of the probability on the energy in the distribution law (1.1) is a reflection of the product law for the composition of probabilities of independent events. Suppose ε_1 is the energy associated with some state or condition of the system and ε_2 is that associated with some other condition, and that the occurrences of these two states are independent. For example, we might ask for the chance that one molecule in a fluid has its x -component of velocity in the range v_1 to $v_1 + dv_1$, for which the associated energy is $\varepsilon_1 = \frac{1}{2}mv_1^2$, while another molecule has its x -component of velocity in the range v_2 to $v_2 + dv_2$, for which $\varepsilon_2 = \frac{1}{2}mv_2^2$; or v_1 and v_2 could be the x - and y -components of velocity of the same molecule, these, too, being independent of each other. Then, with the simultaneous occurrence of the two events viewed as a single event, the energy associated with it is $\varepsilon_1 + \varepsilon_2$, while the probability of its occurrence must be the product of the separate probabilities. The probability must therefore be an exponential function of the energy ε , because the exponential is the unique function $F(\varepsilon)$ with the property $F(\varepsilon_1 + \varepsilon_2) = F(\varepsilon_1)F(\varepsilon_2)$:

$$e^{-(\varepsilon_1+\varepsilon_2)/kT} = e^{-\varepsilon_1/kT} e^{-\varepsilon_2/kT}. \quad (1.7)$$

That the parameter determining how rapidly the exponential decreases with increasing energy is the absolute temperature is a law of nature; we could not have guessed that by mathematical reasoning alone.

For the purposes of developing statistical thermodynamics in the next section we shall here apply the distribution law to tell us the frequency of occurrence of the states i , of energy E_i , of a whole macroscopic system. For generality we may suppose these to be the quantum states (although classical mechanics is often an adequate approximation). We should understand, however, that there may be tremendous complexity hidden in the simple symbol i . We may think of it as a composite of, and symbolic for, some enormous number of quantum numbers, as many as there are mechanical degrees of freedom in the whole system, a number typically several times the number of molecules and thus perhaps of the order of 10^{23} or 10^{24} .

For such a macroscopic system in equilibrium at the temperature T , the probability P_i of finding it in the particular state i is, according to the Boltzmann distribution law (1.1),

$$P_i = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}. \quad (1.8)$$

The denominator is the sum of $\exp(-E_i/kT)$ over all states i (and so does not depend on i , which is there just a dummy summation index), and is what

Cambridge University Press

0521811198 - Statistical Mechanics: A Concise Introduction for Chemists

B. Widom

Excerpt

[More information](#)

6

1 Statistical thermodynamics

guarantees that P_i is properly normalized:

$$\sum_i P_i = 1. \quad (1.9)$$

That normalization denominator is called the *partition function* of the system, and is the key to statistical thermodynamics.

1.3 The partition function and statistical thermodynamics

What we identify and measure as the thermodynamic energy U of a macroscopic system is the same as its total mechanical energy E : the sum total of all the kinetic and potential energies of all the molecules that make up the system. Is that obvious? If it now seems obvious it is only because we have given the same name, energy, to both the thermodynamic and the mechanical quantities, but historically they came to be called by the same name only after much experimentation and speculation led to the realization that they are the same thing.

Two key observations led to our present understanding. The energy E of an isolated mechanical system is a constant of the motion; although the coordinates and velocities of its constituent parts may change with time, that function of them that is the energy has a fixed value, E . That is at the mechanical level. At the thermodynamic level, as one aspect of the first law of thermodynamics, it was recognized that if a system is thermally and mechanically isolated from its surroundings – thermally isolated so that no heat is exchanged ($q = 0$) and mechanically isolated so that no work is done ($w = 0$) – then the function U of its thermodynamic state does not change. That is one fundamental property that the mechanical E and the thermodynamic U have in common. The second is that if the mechanical system is not isolated, its energy E is not a constant of the motion, but can change, and does so by an amount equal to the work done on the system: $\Delta E = w$. Likewise, in thermodynamics, if a system remains thermally insulated ($q = 0$), but is mechanically coupled to its environment, which does work w on it, then its energy U changes by an amount equal to that work: $\Delta U = w$. This coincidence of two such fundamental properties is what led to the hypothesis that the thermodynamic function U in the first law of thermodynamics is just the mechanical energy E of a system of some huge number of degrees of freedom: the total of the kinetic and potential energies of the molecules.

If our system is not isolated but is in a thermostat that fixes its temperature T and with which it can exchange energy, then the energy E is not strictly constant, but can fluctuate. Such energy fluctuations in a system of fixed temperature, while often interesting and sometimes important, are of no thermodynamic consequence: the fluctuations in the energy are minute compared with the total

Cambridge University Press

0521811198 - Statistical Mechanics: A Concise Introduction for Chemists

B. Widom

Excerpt

[More information](#)

1.3 The partition function and statistical thermodynamics 7

and are indiscernible at a macroscopic level. Therefore the thermodynamic energy U in a system of fixed temperature T may be identified with the mean mechanical energy \bar{E} about which the system's mechanical energy fluctuates.

That mean energy \bar{E} of a system of given T is now readily calculable from the Boltzmann distribution (1.8):

$$\bar{E} = \frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}, \quad (1.10)$$

and this is what we may now identify as the thermodynamic energy U at the given T . To know the system's energy levels E_i we must know its volume V and also its chemical composition, i.e., the numbers of molecules N_1, N_2, \dots of each chemical species 1, 2, \dots present in the system, for only then is the mechanical system defined. The energy levels E_i are therefore themselves functions of V, N_1, N_2, \dots , and the $\bar{E} (= U)$ obtained from (1.10) is then a function of these variables and of the temperature T . From the identity $d \ln x/dx = 1/x$ and the chain rule for differentiation, we then see that (1.10) implies

$$U(T, V, N_1, N_2, \dots) = \bar{E} = - \left(\frac{\partial}{\partial \frac{1}{kT}} \ln \sum_i e^{-E_i/kT} \right)_{V, N_1, N_2, \dots}. \quad (1.11)$$

The argument of the logarithm in (1.11) is just the normalization denominator in the probability distribution P_i in (1.8). It is called the *partition function*, as remarked at the end of §1.2. It is a function of temperature, volume, and composition. We shall symbolize it by Z , so

$$Z(T, V, N_1, N_2, \dots) = \sum_i e^{-E_i/kT}. \quad (1.12)$$

Equation (1.11) is then

$$U = -k[\partial \ln Z / \partial (1/T)]_{V, N_1, N_2, \dots}. \quad (1.13)$$

Now compare this with the Gibbs–Helmholtz equation of thermodynamics,

$$U = [\partial(A/T) / \partial (1/T)]_{V, N_1, N_2, \dots} \quad (1.14)$$

with A the Helmholtz free energy. We conclude that there is an intimate connection between the free energy A and the partition function Z ,

$$A = -kT \ln Z + T\phi(V, N_1, N_2, \dots) \quad (1.15)$$

where ϕ is some as yet unknown function of just those variables V, N_1, N_2, \dots that are held fixed in the differentiations in (1.13) and (1.14). Because it is

Cambridge University Press

0521811198 - Statistical Mechanics: A Concise Introduction for Chemists

B. Widom

Excerpt

[More information](#)

8

1 Statistical thermodynamics

independent of T , this ϕ does not contribute to those derivatives and thus, so far, could be any function of volume and composition.

In the next chapter, §2.2, and in Chapter 3, §3.2, we shall see from what (1.15) implies for an ideal gas that ϕ is in fact independent of V and is an arbitrary linear function of N_1, N_2, \dots , associated with an arbitrary choice for the zero of entropy. (Since $A = U - TS$ with S the entropy, such an arbitrary additive term in the entropy becomes an arbitrary additive multiple of the absolute temperature T in the free energy, as in (1.15).) We shall then follow the universally accepted convention of taking that arbitrary linear function of N_1, N_2, \dots to be 0. Thus,

$$A = -kT \ln Z. \quad (1.16)$$

In the meantime, since the energy scale also has an arbitrary zero, all the energy levels E_i in the expression (1.12) for Z may be shifted by a common arbitrary amount η , say. There is then an arbitrary factor of the form $\exp(-\eta/kT)$ in Z , which, via (1.13), manifests itself as an arbitrary constant η in U , as expected. The same η also appears as an arbitrary additive constant (in addition to the arbitrary multiple of T) in the free energy A in (1.15) (now associated with the U in $A = U - TS$).

Calculating the partition function Z is the central problem of statistical thermodynamics, and much of the remainder of this book is devoted to calculating it for specific systems. Once the system's partition function has been calculated its Helmholtz free energy A follows from (1.16). That free energy is thus obtained as a function of the temperature, volume, and composition. As a function of just those variables, A is a *thermodynamic potential*; i.e., all the other thermodynamic functions of the system are obtainable from $A(T, V, N_1, N_2, \dots)$ by differentiations alone, no integrations being required. For example, we have the thermodynamic identities

$$S = -(\partial A / \partial T)_{V, N_1, N_2, \dots} \quad (1.17)$$

$$U = A + TS \quad (1.18)$$

$$p = -(\partial A / \partial V)_{T, N_1, N_2, \dots} \quad (1.19)$$

$$\mu_1 = (\partial A / \partial N_1)_{T, V, N_2, N_3, \dots}, \quad \text{etc.} \quad (1.20)$$

in addition to the Gibbs–Helmholtz equation (1.14), yielding the entropy S , energy U , pressure p , and chemical potentials μ_1, μ_2, \dots . (These are molecular rather than molar chemical potentials; they differ from the ones usually introduced in thermodynamics by a factor of Avogadro's number. The molecular chemical potential is the one more frequently used in statistical mechanics, where chemical composition is usually given by numbers of molecules N_1, N_2, \dots rather than numbers of moles n_1, n_2, \dots .)

Cambridge University Press

0521811198 - Statistical Mechanics: A Concise Introduction for Chemists

B. Widom

Excerpt

[More information](#)

1.3 The partition function and statistical thermodynamics

9

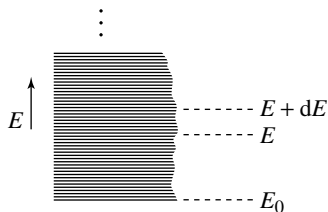


Fig. 1.3

For a macroscopic system, which consists of many, more or less strongly interacting particles, the spacing of the energy levels E_i is usually very much less than the typical thermal energy kT . On any reasonable scale the levels would appear to be almost a continuum. If for no other reason, that would be true because one component of each E_i is the total translational energy of all the molecules, which is then the energy of a large number of particles in a box of macroscopic volume V . But the spacing of particle-in-a-box energy levels decreases with increasing size of the box, as one learns in quantum mechanics, and so is very small when V is of macroscopic size. A consequence of this close spacing of the energy levels E_i is that it is often more convenient and more realistic to treat those levels as though they formed a continuum, and to describe the distribution of the levels as a *density of states*, $W(E)$, such that $W(E) dE$ is the number of states i with energies E_i in the infinitesimal range E to $E + dE$. This is illustrated in Fig. 1.3, which shows, schematically, a near continuum of energy levels starting from the ground state of energy E_0 . The density of these levels at the energy E , that is, the number of states per unit energy at that E , is $W(E)$.

Since all the states in the infinitesimal energy range E to $E + dE$ have essentially the same energy E , that part of the summation over states i in (1.12) that is over the states with energies in that range contributes to the partition function Z just the common $\exp(-E/kT)$ times the number, $W(E) dE$, of those states; and the full sum over i is then the sum (integral) of all these infinitesimal contributions $\exp(-E/kT)W(E) dE$. Thus,

$$Z = \int_{E_0}^{\infty} e^{-E/kT} W(E) dE. \quad (1.21)$$

The density of states, $W(E)$, depends also on the volume and composition of the system, so, expressed more fully, it is a function $W(E, V, N_1, N_2, \dots)$. Equation (1.21) then expresses $Z(T, V, N_1, N_2, \dots)$ as an integral transform (a so-called Laplace transform) of the density of states: multiplying W by $\exp(-E/kT)$ and integrating over all E transforms $W(E)$ into $Z(T)$.

From this same point of view the Boltzmann distribution law, too, may be written in terms of a continuous probability distribution $Q(E)$ rather than in terms of the discrete P_i . The probability $Q(E) dE$ that the system will be found in any of the states i with energies E_i in the range E to $E + dE$ is found by summing the P_i of (1.8) over just those states. Again, $\exp(-E_i/kT)$ has the nearly constant value $\exp(-E/kT)$ for each term of the sum and there are $W(E) dE$ such terms, so from (1.8) and the definition of Z in (1.12), we have $Q(E) dE = Z^{-1} \exp(-E/kT)W(E) dE$, or

$$Q(E) = Z^{-1} W(E) e^{-E/kT}. \quad (1.22)$$

This is the form taken by the Boltzmann distribution law when it is recognized that the energies E_i of the states i of a macroscopic system are virtually a continuum with some density $W(E)$.

We have already remarked that when the temperature of a system is prescribed its energy E fluctuates about its mean energy \bar{E} but that the departures of E from \bar{E} are not great enough to be discernible at a macroscopic level, so that the thermodynamic energy U may be identified with \bar{E} . Since the probability of finding the system's energy in the range E to $E + dE$ when the temperature is prescribed is $Q(E) dE$, this means that the distribution function $Q(E)$ must be very strongly peaked about $E = \bar{E}$, as in Fig. 1.4. The figure shows the distribution to have some width, δE . The energy \bar{E} ($=U$), being an extensive thermodynamic function, is proportional to the size of the system. We may conveniently take the number of its molecules, or total number of its mechanical degrees of freedom, to be a dimensionless measure of the system's size. Call this number N . It will typically be of the order of magnitude of Avogadro's number, say 10^{22} to 10^{24} . Then the mean energy \bar{E} will be of that order of magnitude; i.e., it will be of order $\bar{\epsilon}N$, where the intensive $\bar{\epsilon}$ is the energy per molecule or per degree of freedom. With such a measure N of the system size, the typical energy fluctuations δE (Fig. 1.4) are only of order \sqrt{N} ; i.e., they

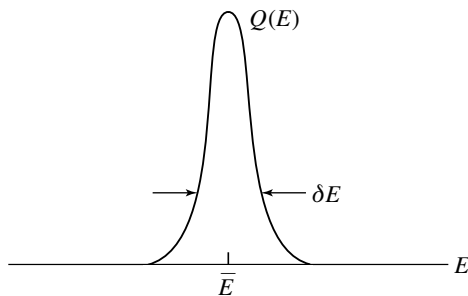


Fig. 1.4