Fundamental Concepts of Thermal Physics (briefly)

In this appendix we review (or maybe introduce you to) some of the fundamental theoretical concepts of thermal physics needed to understand the theories behind and significance of some of the sophomore physics lab experiments. We adopt a microscopic, quantized point of view from the outset for our description of the composition of our macroscopic systems, because we feel it makes the laws of thermal physics and the concept of entropy much easier to comprehend. The sophomore lab library has several good texts covering these topics, so we will be brief. In particular, much of the material presented here closely follows that in F. Mandl, *Statistical Physics* (2nd ed., 1988, John Wiley & Sons).

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Fundamental Concepts of Thermal Physics (briefly)

- ## *Macroscopic systems, microstates, state variables*

A macroscopic system is one which consists of an enormous number of elementary constituents (such as atoms, conduction electrons, and photons) constantly exchanging energy and momentum among themselves. A macroscopic system typically contains on the order of 10^{20} or more constituent particles and thus would require the specification of a vast number of parameters to fully describe the individual states of these constituents. The number of required parameters is called the number of *degrees of freedom* of the system, and this complete specification may be referred to as a description of the system's *microstate*. Because of the interactions between the system's parts and the interaction of the system with its surroundings, its microstate is continually changing.

Even though a specification of the evolution of such a system's microstate is hopelessly complex, there may be a relatively few macroscopic *state variables* which adequately describe the system's average overall characteristics, such as the number of constituent particles (N), mass density (ρ), volume (V), pressure (P), temperature (T), magnetic polarization $(\vec{M})$, angular momentum $(\vec{J})$, etc., along with other parameters which may describe the influence of external forces on the system, such as gravity or externally-imposed electromagnetic fields. These variables tend to fall into three broad categories: (1) those which specify externally imposed fields or forces; (2) those whose values scale with the overall quantity of material, such as the system's mass and volume; and (3) those which do not scale directly with the size of the system, but may be a function of position within the system, such as pressure and temperature. The latter two categories are termed *extensive* and *intensive* state variables, respectively.

A set of state variables and their values which adequately describe the system's overall characteristics specifies the system's *macrostate*. Generally, there will be many, many microstates of the system which are consistent with this macrostate specification, and there is no practical way to determine which one of these myriad microstates is currently occupied by the system. Thus we are led to a *statistical* description of the microscopic behavior of the system as it relates to the evolution of the system's macrostate. This description is the goal of *thermal physics* (broadly: thermodynamics, statistical mechanics, and kinetic theory).

- ## *Thermal equilibrium*

A macroscopic system may be divided into parts, or subsystems (still of macroscopic size), whose various macrostates may be specified as described above. The values of the overall macroscopic system's extensive state variables will then generally be given by the sum of the subsystems' individual corresponding extensive variable values (if you are careful in your definitions of these subsystem extensive variables), but single values for the system's intensive variables will generally be undefined (since, for example, the pressures and/or temperatures of the subsystems will differ). A full macrostate specification of the system could thus require a careful division into subsystems whose individual macrostates are then listed. Similarly, the microstate of the overall system could be thought of as a function of the subsystems' individual microstates along with terms describing the interactions among the subsystems.

For example, consider an isolated container of volume V filled with a gas of N neon atoms. Assume that the total kinetic energy of all the neon atoms is U and the total angular momentum of the atoms is 0, but the gas is not of uniform density and temperature, and it is full of eddies and currents. An accurate macrostate description of the gas would clearly require not only the specification of the values of V, N, and U (all extensive state variables in this case), but also a whole host of other variables describing the variations in density, temperature, and velocity of small, but still macroscopic, parts of the gas.

If a system (such as the neon gas described above, for example) is isolated from the outside world then the interactions among its constituents and consequent transitions to different microstates will eventually bring it to *thermal equilibrium*, when all its state variables become well-defined and constant (except for incredibly tiny fluctuations about their mean values). In particular, the temperature T will be uniform and constant throughout the system's various subsystems. This temperature equalization is, indeed, one of the hallmarks of thermal equilibrium, and will be discussed further below. At thermal equilibrium a minimal set of macroscopic state variables is required to uniquely specify the macrostate of the system, and all the other state variables' values may be derived from them using the system's *equations of state*.

• *Internal energy, heat, work, and the first law of thermodynamics*

The *internal energy* (U) of a macroscopic system is the sum total of all of its constituents' kinetic and potential energies of various kinds (where $U = 0$ is usually, but not always, taken to correspond to the *ground state* of the system). If the system is isolated, then its internal energy must remain constant, even though its constituents are exchanging energy among themselves as the system's microstate evolves. U is one of a system's extensive state variables, and it is connected to the other state variables (in thermal equilibrium) through the equations of state. A system which is not isolated interacts with its surroundings, and its internal energy will change as it exchanges energy (and possibly constituent particles) with the other systems surrounding it. This energy exchange may result from macroscopic, large-scale interactions such as mechanical work or externally-applied electromagnetic forces, or it may result from the individual, microscopic, nearly independent interactions of its constituent particles with those of another system (without any accompanying large-scale, macroscopic, net force between the systems). This latter interaction is known as *heat transfer*, and its inclusion in the determination of the change in the internal energy of a system is articulated in the *First Law of Thermodynamics*. Note that heat, like work, is a measure of *energy transfer between systems* and is not a state variable.

The internal energy is changed by heat transfer to the system or work performed by the system, so that for an infinitesimal energy transfer

$$dU = đQ - đW \tag{B.1}$$

The symbol $đ$ is used in (B.1) to emphasize that the increments of heat and work are not changes in the system's state variables, but represent energy interactions with the system's surroundings — Q is heat transferred *into* the system, W is mechanical work *performed by* the system. Clearly, the internal energy of a system may be changed by various different combinations of heat transfer and work; the *process* through which the system is changed by interaction with external systems determines this division between heat and work.

- *Statistical weight, entropy, and the second law of thermodynamics*

If a system's internal energy U increases (as it absorbs energy from its surroundings), its temperature T generally rises, and the opposite is true if U decreases. The direction of heat flow between interacting systems is, of course, opposite to the gradient of the temperature, and, as mentioned previously, *thermal equilibrium is reached only when the temperatures of all the various interacting systems are identical* (this final observation is a consequence of the so-called *Zeroth Law of Thermodynamics*). As we shall see, the temperature T is most suitably defined by the *absolute* or *thermodynamic* temperature scale where $T = 0$ only if $U = 0$ (the system is in its ground state).

The ultimate quantum nature of the kinematics of the microscopic particles making up a macroscopic system must be considered when you try to understand the relationship between the ever-changing microstate of a system and its observable macroscopic properties. The microstate of a finite system (however large) with f degrees of freedom may be identified as a point in a $2f$ - dimensional *phase space* of f coordinates q_i and their associated f (conjugate) momenta p_i. Because of the *uncertainty principle*, each microstate cannot be specified with arbitrary accuracy, but must instead occupy a phase space volume of at least $\prod(\Delta q_i \, \Delta p_i) \approx h^f$, where h is Planck's constant. Because of this division of the phase space of possible microstates into finite volumes by the uncertainty principle, the number of possible microstates is *countable*, and, for example, these states may be numbered by an integer index $r \; (r = 0, 1, 2, \ldots)$. If we take the microstates of the system to be its *quantum mechanical eigenstates of the internal energy*, then the states may be indexed in order of increasing internal energy of the system so that $U_0 \le U_1 \le \ldots \le U_r \le U_{r+1} \le \ldots$. In this example $r = 0$ would denote the ground state of the system. Note that it is likely that many of these energy eigenstates are degenerate, so that $U_r = U_{r+1}$ for many values of the index r.

The number of available microstates of a macroscopic system generally grows very, very rapidly as its internal energy is increased. For example, consider the quantum mechanical system of a single, spinless particle in a 1-dimensional box. The number of degrees of freedom in this case is $f = 1$, and the particle's quantum levels in the (infinitely strong) box are equally spaced in momentum. Therefore for energies $U \gg U_0$, its ground state energy, the number of energy levels (microstates) $\le U$ is very nearly $\propto U^{1/2}$. If you have a system of $f \gg 1$ independent particles in the box, then $\Phi(U)$, the total number of different microstates of this combined system with total energy $\le U$, is roughly $\propto U^{Af}$ where A is a constant of order unity. Since for a macroscopic system $f \sim 10^{23}$, $\Phi(U)$ increases at an enormous rate with increasing U.

Consider the number of available microstates of an isolated macroscopic system with fixed (V, N) and with internal energy in the small interval δU about the energy U, with $\delta U \ll U$. Given the result above, the total number of microstates in this energy range $\Omega(U,V,N) \sim f\,\Phi(U)\,\delta U/U$, so that

$$\ln\Omega(U,V,N) \;\sim\; \ln\Phi(U) + \ln f + \ln(\delta U/U)$$

But $\ln\Phi(U,V,N) \sim f \sim 10^{23} \gg \ln f$, so, unless $\delta U/U \sim 10^{-10^{23}}$, an incredibly small energy interval,

$$\ln\Omega(U,V,N) \sim f \sim 10^{23}$$

So $\ln\Omega$ is for all intents and purposes independent of the size of the energy interval δU. These $\Omega(U,V,N)$ microstates represent all the possible states of the system consistent with the constraints (U, V, N), so any macrostate of the system consistent with the given (U, V, N) is associated with some subset of these microstates. *The fundamental postulate of statistical mechanics is that for a macroscopic system over the long term each microstate is equally likely to occur, and the system's actual microstate is continually transitioning in a random fashion between these various states*. A further postulate is that in most macroscopic systems of interest *the macrostate representing thermal equilibrium is associated with all but an incredibly tiny fraction of these microstates*, and that once an isolated system reaches equilibrium the typical fluctuations in the system's state variable values away from their respective means is of order $f^{-1/2} \sim 10^{-10}$ or smaller! General derivations of these postulates in terms of the underlying laws of the classical or quantum dynamics of individual particles are elusive, but the great success of thermal physics theory demonstrates that they must be reasonably valid.

Let a particular macrostate be represented by the set of state variables (U, V, N, α), where α is a list of all the other state variable values required to fully specify this macrostate. Then $\Omega(U,V,N,\alpha)$ is the number of microstates consistent with this macrostate. This number, $\Omega(U,V,N,\alpha)$, is called the *statistical weight* of the macrostate (U, V, N, α); from the postulate stated above, we know that the probability that our isolated system left to itself for a long time will still be found in this macrostate is $\propto \Omega(U,V,N,\alpha)$. We define S, the *entropy* of this macrostate as:

$$S \;\equiv\; k_B \ln\Omega(U,V,N,\alpha) \tag{B.2}$$

where k_B is Boltzmann's constant, 1.38×10^{-23} Joules / Kelvin. Since f, the number of degrees of freedom, is generally $\propto N$, we see that $S \propto \ln\Omega \propto f \propto N$, so the entropy S is *an extensive state variable* of a macroscopic system. Although the thermodynamic concept of entropy was introduced by the German physicist Rudolph Clausius in 1850 (he also first conceived the second law of thermodynamics), the fundamentally microscopic, statistical definition in (B.2) was developed by the Austrian physicist Ludwig Boltzmann in 1877 (who is rightly credited as the "father" of statistical mechanics).

Since the vast majority of the microstates consistent with the given (U, V, N) are associated with the thermal equilibrium macrostate (in accordance with our postulate stated previously), an isolated system left to itself for a long time is overwhelmingly likely to be found in its equilibrium macrostate, and *the entropy is at a maximum for the equilibrium macrostate of an isolated system*. If the system is specially prepared in some non-equilibrium macrostate (U, V, N, α) before it is isolated, then as time goes on interactions among the system's microscopic particles will almost certainly cause the system to evolve through a succession of "nearby" macrostates with ever higher statistical weights until it reaches the thermal equilibrium macrostate. Thus *the entropy S of an isolated system rises as time goes on (except for very tiny fluctuations), until thermal equilibrium is achieved*. This is one way to state the *Second Law of Thermodynamics*. A typical laboratory-sized macroscopic system at thermal equilibrium has $\ln\Omega \sim 10^{23} \sim k_B^{-1}$, so the entropy S at equilibrium is typically within a few orders of magnitude of unity. Because there is usually a unique ground microstate for a typical macroscopic system, equation (B.2) shows that $S = 0$ for a system in its ground state; otherwise $S > 0$.

- *Temperature*

Consider an isolated system (U, V, N) consisting of two subsystems, (U_1, V_1, N_1) and (U_2, V_2, N_2), which are very weakly coupled so that any forces acting between them are weak and slow to affect the state of either. The total system energy $U = U_1 + U_2$, since we may neglect the tiny energy of interaction between the two parts. Similarly, $V = V_1 + V_2$ and $N = N_1 + N_2$. In this case we can consider every microstate of the whole system to factor into the product of the (essentially independent) microstates of the two subsystems, so that for any particular pair of macrostates of the subsystems, it must be true that

$$\begin{aligned} \Omega(U,V,N,U_1,V_1,N_1,\alpha_1,\alpha_2) &= \Omega_1(U_1,V_1,N_1,\alpha_1) \times \Omega_2(U_2,V_2,N_2,\alpha_2) \\ \ln\Omega(U,V,N,U_1,V_1,N_1,\alpha_1,\alpha_2) &= \ln\Omega_1(U_1,V_1,N_1,\alpha_1) + \ln\Omega_2(U_2,V_2,N_2,\alpha_2) \\ \therefore S &= S_1 + S_2 \end{aligned}$$

Now assume that the volume and number of particles in each of the two subsystems are fixed, but the subsystems can slowly exchange energy through heat transfer. When the total system is at thermal equilibrium, then S is at its maximum, and, in particular,

$$\left(\frac{\partial S}{\partial U_1}\right)_{V_1,N_1,V_2,N_2} = 0 = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} + \frac{dU_2}{dU_1}\left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2}$$

$$\therefore \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} \qquad \text{(at equilibrium)} \qquad \text{(B.3)}$$

This equality (B.3) for subsystems in thermal contact and in thermal equilibrium provides the definition of *the absolute (or thermodynamic) temperature* T of any macroscopic system in thermal equilibrium:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{V,N} \tag{B.4}$$

Absolute temperature has the SI unit of *Kelvin*, which is chosen so as to very nearly match the more conventional °*Celsius*. To accomplish this match between the two temperature scales (and definitions) the "triple point" of water is defined to be at 273.16 Kelvin (or +0.01°Celsius), and this in turn determines (using (B.4) and (B.2)) the units of entropy S and the value of Boltzmann's constant, k_B. Note that (B.3) and (B.4) imply the *Zeroth Law* of temperature uniformity at thermal equilibrium stated previously.

Since the total system entropy S in the previous example rises as the system approaches equilibrium, the sign of $\partial S / \partial U_1$ depends on whether U_1 is rising or falling. With the temperature definition (B.4), we see that this implies that heat energy flows from the subsystem with the higher temperature toward the one with the lower temperature, as it should.

• *Canonical ensemble, Boltzmann distribution, partition function*

Let us extend our previous example as follows: our isolated system now consists of an enormous number of identical copies of some small (but still macroscopic) subsystem of fixed volume and number of particles, all in weak thermal contact with each other. The overall isolated system has reached thermal equilibrium at temperature T, but we know that each very small subsystem's internal energy may still fluctuate as its microstate changes and it exchanges energy with its neighbors. Such a system is called a *canonical ensemble* of the identical subsystems (this concept was thoroughly studied by the American mathematical physicist J. W. Gibbs in the early 20th century, who made extensive and lasting contributions the thermal physics).

We wonders (yes, we wonders) what the probability is that, say, the ith subsystem might be found in a *particular* microstate r (with energy U_r) at any particular time, or, equivalently, on average what fraction of the identical subsystems will be in the *particular* microstate r at any given time.

Once we pick a particular subsystem to study we may treat the remaining subsystems as a single, much larger subsystem and then start with our results from the previous section. Since our chosen subsystem is very tiny compared to the combined remainder of the system, we treat the remainder as *a heat bath whose temperature T will remain essentially constant* even though it exchanges relatively tiny bits of its total internal energy with our little subsystem through heat transfer. The heat bath will remain arbitrarily close to thermal equilibrium throughout if it is so large that our subsystem's energy U_r is a fantastically small fraction of the complete isolated system's constant total energy U.

If our little subsystem has energy U_r, then, obviously, the heat bath has energy $U - U_r$, and the statistical weight of the heat bath's macrostate is $\Omega(U - U_r, V, N)$. Since we are given the subsystem's microstate r, the probability for finding this situation must be $p_r \propto \Omega(U-U_r,V,N)$. Consider the log of p_r and the definitions of entropy S and temperature T in (B.2) and (B.4); we can expand our function of $U-U_r$ in a Taylor series about U (we use a Taylor series for $\ln p_r$ rather than p_r itself because $\ln\Omega$ is a much more slowly varying function of U than is Ω. This means that the Taylor series convergence is much better for $\ln\Omega$, and we need keep only its first nontrivial term).

$$\begin{aligned}
p_r \propto\ \Omega(U-U_r,V,N) \quad &\to \quad \ln p_r = \text{constant} + \ln\Omega(U-U_r,V,N) \\
\ln p_r &= \text{constant} + \frac{1}{k_B}S(U-U_r,V,N) \\
&= \text{constant} + \frac{1}{k_B}S(U,V,N) - \frac{U_r}{k_B}\frac{\partial}{\partial U}S(U,V,N) + \ldots \qquad \text{(B.5)} \\
&= \text{constant} + \quad \text{constant} \quad - \frac{U_r}{k_B T} + \ldots \\
\therefore \quad p_r &\propto e^{-U_r/k_B T}
\end{aligned}$$

To normalize the probability p_r we know that the sum of the probabilities for all of the possible microstates for our subsystem must be 1, since the subsystem must be in *some* microstate. Thus for a *system with fixed* (V,N) *in thermal equilibrium with a heat bath at temperature* T,

$$\boxed{\begin{aligned} p_r &= \frac{1}{Z}\ e^{-U_r/k_B T} \\ Z &\equiv \sum_r e^{-U_r/k_B T} \end{aligned}} \qquad \text{(B.6)}$$

(B.6) gives *the probability of finding the system in a* particular *microstate* r *that has energy* U_r. This is the famous *Boltzmann distribution*, and the sum Z over all microstates is called the *partition function*.

One important note about (B.6): the microstate r *represents one particular microstate only*. In general, *there may be many microstates with energy* U_r because the energy eigenstates of the system are *degenerate*. To express the partition function as a sum over energies, you must include the integer factor $g(U_r)$, the degeneracy of the microstates with energy U_r:

$$Z \equiv \sum_{U_r} g(U_r)e^{-U_r/k_B T} \qquad \text{(B.7)}$$

The probability that the system may be in any of the degenerate energy eigenstates is then:

$$p(U_r) = \frac{1}{Z}\ g(U_r)e^{-U_r/k_B T} \qquad \text{(B.8)}$$

- *Equipartition of energy in the classical regime*

Assume we have a macroscopic system with f degrees of freedom in which the separations of consecutive but distinct microstate energies are small compared to k_BT, i.e., if $U_{r+1} \neq U_r$, then $U_{r+1} - U_r \ll k_BT$. In this case we can use the uncertainty principle to estimate the *density* of the system's microstates in its $2f$- dimensional phase space of f coordinates q_i and their associated f (conjugate) momenta p_i as η/h^f, as we mentioned some way back (the constant integer η accounts for any additional spin or polarization degeneracy in the single-particle states). If the system is in equilibrium with a heat bath at temperature T, then we can estimate the value of the partition function Z by approximating the sum in (B.7) with an integral over phase space as follows:

$$Z \approx \int \exp[-E(\vec{q},\vec{p})/k_BT] \; \frac{\eta}{h^f} \, d^f\vec{q} \; d^f\vec{p} \tag{B.9}$$

where the energy is written as a function of the $2f$ phase space coordinates (note that the energy is assumed to not depend on the particles' η internal states). Additionally, if there are, say, N indistinguishable particles involved (such as electrons, helium atoms, etc.), then (B.9) must also be divided by $N!$ to avoid over-counting the states.

The probability of finding the system in a microstate associated with some differential volume of phase space around the point $(\vec{q},\vec{p})$ would then be, in analogy with (B.8),

$$P(\vec{q},\vec{p}) \, d^f\vec{q} \; d^f\vec{p} \; = \; \frac{\exp[-E(\vec{q},\vec{p})/k_BT] \, d^f\vec{q} \; d^f\vec{p}}{\int \exp[-E(\vec{q},\vec{p})/k_BT] \, d^f\vec{q} \; d^f\vec{p}} \tag{B.10}$$

Now suppose that our energy function $E(\vec{q},\vec{p})$ depends purely quadratically on at least one of its $2f$ arguments (either a coordinate q_i or a momentum p_i); in other words, for one argument x_i we have

$$E = a\,x_i^{\,2} + E' \tag{B.11}$$

where neither a nor E' is a function of x_i (although they each may depend on any or all of the $2f-1$ other arguments). Now if we *fix the values of all the other arguments*, then what is the probability distribution for the value of x_i? Clearly,

$$P(x_i)\,dx_i \;\propto\; \exp[-E(\vec{q},\vec{p})/k_BT]\,dx_i \;\propto\; \exp[-a\,x_i^{\,2}/k_BT]\,dx_i \tag{B.12}$$

(B.12) shows that $P(x_i)$ is a normal (Gaussian) distribution with mean 0 and variance $\overline{x_i^{\,2}} = k_BT/2a$. Thus the mean energy contribution to the system stored in the x_i degree of freedom is

$$\overline{a\,x_i^{\,2}} \;=\; \tfrac{1}{2}k_BT \tag{B.13}$$

which has a right-hand side *independent of the values of the other arguments*. A complete integration to determine the mean energy may be immediately integrated with respect to the argument x_i:

$$\overline{E} \;=\; \int E(\vec{q},\vec{p})\,P(\vec{q},\vec{p})\; d^f\vec{q}\; d^f\vec{p} \;=\; \int E'(\vec{q},\vec{p})\,P(\vec{q},\vec{p})\; d\vec{q}\; d\vec{p} \;+\; \tfrac{1}{2}k_B T \qquad \text{(B.14)}$$

where the final integration of E' does not involve the argument x_i.

Therefore, the mean energy of a system in thermal equilibrium at temperature T will include a term equal to $\frac{1}{2}k_B T$ for each degree of freedom satisfying our requirement (B.11) for x_i. This is the statement of *the theorem of equipartition of energy*, valid in the classical regime.

For example, assume we have a classical gas of N independent, free particles in thermal equilibrium at temperature T. If each particle has no internal degree of freedom for storing energy, then its total energy is just due to its center-of-mass motion, $(1/2m)(p_x^2 + p_y^2 + p_z^2)$. Each of the 3 momentum components of each particle is a degree of freedom of the system which satisfies the requirements of (B.11), so each contributes $\frac{1}{2}k_B T$ on average to the total internal energy of our system. Thus, $U = \frac{3}{2}Nk_B T$ for this system. This is the correct expression for the total internal energy of an ideal, monatomic, classical gas; the energy/particle depends only on the temperature, T. The equipartition idea had a long and interesting development in the 19th century due to the efforts of many scientists, but it was first stated in the general form presented here by Boltzmann.

• *Fermions in a box: the ground state of an electron gas*

Now we turn to an important subject for condensed matter physics: the statistical properties of a “gas” of independent, identical, quantum particles subject to *Pauli Exclusion*: no more than one particle at a time may occupy any given single-particle quantum state of the system (such particles are collectively called *fermions*; it turns out that all elementary particles of matter, such as electrons, are fermions). The discussions here and in the next section closely follow that found in Chapter 2 of N. W. Aschroft and N. D. Mermin, *Solid State Physics* (1976, Thomson Learning, Inc.).

In order to apply the principle of Pauli Exclusion when considering a statistical system, one must have some idea of how to organize and count its available single-particle quantum states. Consider first our old friend, the quantum states of an otherwise free particle in a one-dimensional box. The wave functions of the desired single-particle states shall represent *traveling waves with well-defined momenta*, however, and we demand that the boundary conditions imposed by the walls of the box be *periodic* (or *Born-von Karman*): the phase of the wave function for a state must be the same at both walls. Thus the total phase of a wave function across the length L of the box must be an integer multiple of 2π; successive wavenumbers of the momentum eigenstates are separated by $\Delta k = 2\pi/L$. Note that this result is consistent with the *uncertainty principle*: With the particle’s position confined to $\Delta x = L$, successive momentum eigenstates are separated such that $\Delta x\,\Delta k = 2\pi$, so each may be said to occupy a phase space volume of $\Delta x \Delta p = h$, since the particle’s momentum $p = \hbar k$.

The previous result is easy to extend to a 3-dimensional volume $V = L_x L_y L_z$. A momentum eigenstate represented by $\vec{p} = p_x\hat{x} + p_y\hat{y} + p_z\hat{z}$ must occupy a phase space volume of $(\Delta x_i\,\Delta p_i)^3 = h^3$, so, since $\Delta x_i \Delta x_j \Delta x_k = L_x L_y L_z = V$, the momentum eigenstates each occupy a momentum-space volume of $\Delta^3\vec{p} = h^3/V$. If the volume is macroscopic, then these single-particle eigenstates are very densely packed in momentum space — a large momentum-space sphere of radius $p_{max} \gg h/V^{1/3}$ would contain almost exactly $N = (4\pi/3)\,p_{max}^3 (V/h^3)$ possible single-particle states with momenta $\le p_{max}$ in a 3-dimensional box of physical volume V.

A single fermion has an additional, internal degree of freedom determining its quantum state: its *spin polarization*. Fermions must have half-integral total spin quantum numbers; in the case of an elementary fermion such as an electron, this total spin quantum number is $1/2$. Thus an electron has two possible spin polarizations: $\pm 1/2$ (i.e. "spin up" and "spin down"). This extra degree of freedom doubles the number of possible states for an electron so that the number N of single-electron states in a volume V with momenta $\le p_{max}$ given by:

$$N/V = (8\pi/3)\,p_{max}^3 / h^3 \tag{B.15}$$

If these states were all occupied by electrons (only a single electron allowed in each state!), then $n = N/V$ would be the resulting number density of the electrons in V. Conversely, if the volume V contains N independent electrons, then the lowest total kinetic energy state of this N electron system would be obtained by filling the available states starting with the lowest momentum states; the electrons would then occupy the all the available states with momenta $\le p_{max}$ given by (B.15). This would be the *ground state* of the N independent electron system in V; p_{max} is called the *Fermi momentum* of this system.

The kinetic energy of the electrons with momenta p_{max} in this ground state of a system of independent electrons with volume number density $n = N/V$ is called the *Fermi energy*:

$$E_F = \frac{p_{max}^2}{2m} = \left(\frac{3n}{8\pi}\right)^{2/3} \frac{(hc)^2}{2mc^2} \tag{B.16}$$

For example, copper has a conduction electron density of $n = 0.85\times 10^{23}/\mathrm{cm}^3 = 0.085/\text{Å}^3$; with the electron rest energy $mc^2 = 0.51\,\mathrm{MeV}$ and $hc = 12.4\,\mathrm{keV\text{Å}}$, the Fermi energy $E_F = 7\,\mathrm{eV}$. This energy is (not surprisingly) essentially the same as the binding energy of a copper atom's outer valence electron, $7.7\,\mathrm{eV}$, since $1/n$, the volume per conduction electron in solid copper, is nearly equal to the average volume a copper atom's outer valence electron occupies.

The density of single-electron states as a function of electron kinetic energy is straightforward to calculate. From (B.15) it is clear that a thin spherical shell in momentum space with radius p and thickness dp would contain $dn = (dn/dp)\,dp$ single-electron states (per unit physical volume); in terms of energy, the number would be $dn = (dn/dp)\,/(dE/dp)\,dE$. Thus the number of single-electron states per unit volume per unit energy (cf. equation (B.7)) is clearly $g(E) = (dn/dp)\,/(dE/dp)$:

$$g(E) = \frac{dn}{dE} = 8\pi\frac{m}{h^3}p(E) = 8\pi\frac{m^{3/2}}{h^3}\sqrt{2E} = \frac{3}{2}\frac{n}{E_F}\left(\frac{E}{E_F}\right)^{1/2} \qquad (E>0) \qquad \text{(B.17)}$$

The average kinetic energy per electron is thus:

$$n^{-1}\int_0^{E_F} g(E)E\,dE = \frac{3}{5}E_F \qquad \text{(B.18)}$$

This is the average electron kinetic energy for the *ground state* ($T = 0$) of a system of free and independent electrons with volume density n; if the electrons behaved classically, then, of course, their average kinetic energy would be $(3/2)k_BT$, which is 0 in the ground state (see previous section). A classical gas of electrons would require a temperature of $T = (2/5)E_F/k_B$ to have the average kinetic energy of equation (B.18) ($> 3\times10^4\,\text{K}$ for the conduction electrons in copper, with $E_F = 7\,\text{eV}$). Clearly, one would expect that this fact should have a profound influence on the observed electrical and thermal properties of a conductor such as copper.

• *The chemical potential and the Fermi-Dirac distribution*

Now consider the statistics of a system of independent, identical fermions (with a fixed number of particles in a fixed volume V) in thermal equilibrium with a heat bath at temperature $T > 0$. Pick a particular single-particle quantum state j of the system (with particle energy E_j), and ask for the probability f_j that this state is occupied by a particle.

The *microstate* of such a system of particles would be specified by enumerating which single-particle quantum states are occupied and which are empty; the microstate's energy would then be the sum of the energies of the occupied single-particle states (remember, simply swapping two particles doesn't count as forming a different microstate because all of the particles are absolutely identical). The probability of finding a system in thermal equilibrium with a heat bath at temperature T in a particular microstate r with system energy U_r is given by (B.6) to be:

$$p_r = \frac{1}{Z}\,e^{-U_r/k_BT}\;; \qquad Z \equiv \sum_{r'} e^{-U_{r'}/k_BT} \qquad \text{(B.19)}$$

where the partition function Z is a sum over *all* microstates r' of the system. If the system contained N particles, say, then Z would be the sum over all the various ways that the system's N particles could be distributed among all of the system's possible single-particle states (often an infinite number).

Thus, in principle, to determine f_j we would first calculate the value of the N-particle system partition function, Z. Then we would simply pick out that subset of all of the possible N-particle microstates in which the single-particle quantum state j is occupied, calculate each microstate's probability using (B.19), and then sum these probabilities; the result would be f_j. Of course, the set of all microstates of our N-particle system consists of two disjoint subsets: those in which the single-particle quantum state j is occupied, and those in which it is empty — the probability that the single-particle quantum state j is occupied must be 1 minus the probability that it is empty, since these are the only two possibilities.

Now consider *two* otherwise identical systems: one with N particles and the other with N + 1. In the latter system consider the set of microstates in which state j is occupied, whereas consider the set of microstates with empty state j in the N-particle system. Clearly, every microstate in the former set has a corresponding microstate in the latter: namely, the one whose only difference is the occupation status of state j. Order and index the members of the two sets with the index r such that corresponding microstates have the same index value. Obviously, the energy difference between any pair of corresponding microstates is just the energy of the state j, which is E_j. Call the various (N + 1)-particle occupied-j microstate energies U_r; the corresponding N-particle empty-j microstate energies will then be $U_r - E_j$.

Using the set of occupied-j microstates of the (N + 1)-particle system and the empty-j microstates of the N-particle system, the occupation probabilities may be written:

$$\begin{aligned} f_j(N+1) &= \frac{1}{Z(N+1)}\sum_r e^{-U_r/k_B T} \\ f_j(N) &= 1 - \frac{1}{Z(N)}\sum_r e^{-(U_r-E_j)/k_B T} = 1 - e^{E_j/k_B T}\left[\frac{Z(N+1)}{Z(N)}\right] f_j(N+1) \end{aligned} \tag{B.20}$$

We now define a new quantity F in terms of Z as follows:

$$F = -k_B T \ln Z \tag{B.21}$$

F is called the *Helmholtz free energy* of a thermodynamic system (it turns out that for a system in thermodynamic equilibrium $F = U - TS$). This *thermodynamic potential* was first introduced by the nineteenth-century German physicist (and physician) Hermann von Helmholtz. In terms of F the ratio of the two partition functions may be written as $\exp[-(F(N+1)-F(N))/k_B T]$. The change in the free energy introduced by the addition of a particle to a system (at constant T and V) is called the *chemical potential* μ, a concept which is especially useful when considering phase changes and chemical reactions. With the chemical potential, (B.20) may be written as:

$$f_j(N) = 1 - e^{(E_j-\mu)/k_B T} f_j(N+1) \tag{B.22}$$

The expression (B.22) is exact, but we can now make the simple observation that for a macroscopic system (in which $N \sim 10^{22}$, give or take several orders of magnitude), adding one more particle to it should have a tiny impact on the occupation probability of a typical single-particle state j. Thus, it is quite reasonable to assume that to an excellent degree of precision $f_j(N+1) = f_j(N)$. Using this very slight approximation, we achieve our final result, the *Fermi-Dirac distribution*:

$$\boxed{f_j = \frac{1}{e^{(E_j-\mu)/k_BT}+1}} \tag{B.23}$$

The Fermi-Dirac distribution is a major theoretical result fundamental to our understanding of the thermal and electrical behaviors of electrons in conductors and semiconductors. We may draw some immediate conclusions from (B.23):

- If $E_j - \mu \gg k_BT$, then $f_j \approx \exp[-(E_j-\mu)/k_BT]$
- If $\mu - E_j \gg k_BT$, then $f_j \to 1$.
- At $T = 0$: $\mu = E_F$, the Fermi energy

If $E_j - \mu \gg k_BT$ for all but a tiny minority of the lowest-energy single-particle states, and N is much larger than the number of these very low energy states, then for all but these few lowest-energy states it is the case that $f_j \ll 1$. Thus the states occupied by the vast majority of the N particles at any given instant are well-separated in phase space, i.e. the average phase-space separation between nearby particles is $\gg h$. In this case to an excellent approximation the particles behave classically (except that they remain indistinguishable when counting possible microstates). Examples of this situation are: the charge carriers in a typical semiconductor; the electrons in a hot, tenuous plasma; and the molecules in air at standard temperature and pressure.

If, on the other hand, $f_j \sim 1$ for most of the single-particle states actually occupied by a system's particles, then the quantum nature of the particles will be a predominant feature of the system's kinematics. The particles in such a system are called *degenerate*, and quantum effects will have a major impact on the macroscopic characteristics of the system. The most important example of such a system is the behavior of the conduction electrons in a metal.