

A good summary of Statistical Physics is provided by the Introduction of the “Thermal Physics” by C. Kittel and H. Kroemer, which is mostly reproduced below.

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In order of their appearance, the leading characters in our story are the entropy, the temperature, the Boltzmann factor, the chemical potential, the Gibbs factor, and the distribution functions.

The entropy measures the number of quantum states accessible to a system. A closed system might be in any of these quantum states and (we assume) with equal probability. The fundamental statistical element, the fundamental logical assumption, is that quantum states are either accessible or inaccessible to the system, and the system is equally likely to be in any one accessible state as in any other accessible state. Given  $g$  accessible states, the entropy is defined as  $\sigma = \log g$ . The entropy thus defined will be a function of the energy  $U$ , the number of particles  $N$ , and the volume  $V$  of the system, because these parameters enter the determination of  $g$ ; other parameters may enter as well. The use of the logarithm is a mathematical convenience: it is easier to write  $10^{20}$  than  $\exp(10^{20})$ , and it is more natural for two systems to speak of  $\sigma_1 + \sigma_2$  than of  $g_1 g_2$ .

When two systems, each of specified energy, are brought into thermal contact they may transfer energy; their total energy remains constant, but the constraints on their individual energies are lifted. A transfer of energy in one direction, or perhaps in the other, may increase the product  $g_1 g_2$  that measures the number of accessible states of the combined systems. The fundamental assumption biases the outcome in favor of that allocation of the total energy that maximizes the number of accessible states: more is better, and more likely. This statement is the kernel of the law of increase of entropy, which is the general expression of the second law of thermodynamics.

We have brought two systems into thermal contact so that they may transfer energy. What is the most probable outcome of the encounter? One system will gain energy at the expense of the other, and meanwhile the total entropy of the two systems will increase. Eventually the entropy will reach a maximum for the given total energy. It is not difficult to show (Chapter 2) that the maximum is attained when the value of  $(\partial\sigma/\partial U)_{N,V}$  for one system is equal to the value of the same quantity for the second system. This equality property for two systems in thermal contact is just the property we expect of the temperature. Accordingly, we define the fundamental temperature  $\tau$  by the relation

$$\frac{1}{\tau} \equiv \left( \frac{\partial\sigma}{\partial U} \right)_{N,V} . \quad (1)$$

The use of  $1/\tau$  assures that energy will flow from high  $\tau$  to low  $\tau$ ; no more complicated relation is needed. It will follow that the Kelvin temperature  $T$  is directly proportional to  $\tau$ , with  $\tau = k_b T$ , where  $k_b$  is the Boltzmann constant. The conventional entropy  $S$  is given by  $S = k_b \sigma$ .

Now consider a very simple example of the Boltzmann factor treated in Chapter 3. Let a small system with only two states, one at energy 0 and one at energy  $\epsilon$ , be placed in thermal contact with a large system that we call the reservoir. The total energy of the

combined systems is  $U_0$ ; when the small system is in the state of energy 0, the reservoir has energy  $U_0$  and will have  $g(U_0)$  states accessible to it. When the small system is in the state of energy  $\epsilon$ , the reservoir will have energy  $U_0 - \epsilon$  and will have  $g(U_0 - \epsilon)$  states accessible to it. By the fundamental assumption, the ratio of the probability of finding the small system with energy  $\epsilon$  to the probability of finding it with energy 0 is

$$\frac{P(\epsilon)}{P(0)} = \frac{g(U_0 - \epsilon)}{g(U_0)} = \frac{\exp[\sigma(U_0 - \epsilon)]}{\exp[\sigma(U_0)]} \quad (2)$$

The reservoir entropy  $\sigma$  may be expanded in a Taylor series:

$$\sigma(U - \epsilon) \approx \sigma(U_0) - \epsilon(\partial\sigma/\partial U) = \sigma(U_0) - \epsilon/\tau \quad (3)$$

by the definition (1) of the temperature. Higher order terms in the expansion may be dropped. Cancellation of the term  $\exp[\sigma(U_0)]$ , which occurs in the numerator and denominator of (2) after the substitution of (3), leaves us with

$$P(\epsilon)/P(0) = \exp(-\epsilon/\tau). \quad (4)$$

This is Boltzmann's result. To show its use, we calculate the thermal average energy  $\langle \epsilon \rangle$  of the two state system in thermal contact with a reservoir at temperature  $\tau$ :

$$\langle \epsilon \rangle = \sum_i \epsilon_i P(\epsilon_i) = 0 \cdot P(0) + \epsilon P(\epsilon) = \frac{\epsilon \exp(-\epsilon/\tau)}{1 + \exp(-\epsilon/\tau)}, \quad (5)$$

where we have imposed the normalization condition on the sum of the probabilities:

$$P(0) + P(\epsilon) = 1. \quad (6)$$

The argument can be generalized immediately to find the average energy of a harmonic oscillator at temperature  $\tau$ , and we do this in Chapter 4 as the first step in the derivation of the Planck radiation law.

The most important extension of the theory is to systems that can transfer particles as well as energy with the reservoir. For two systems in diffusive and thermal contact, the entropy will be a maximum with respect to the transfer of particles as well as to the transfer of energy. Not only must  $(\partial\sigma/\partial U)_{N,V}$  be equal for the two systems, but  $(\partial\sigma/\partial N)_{U,V}$  must also be equal, where  $N$  refers to the number of particles of a given species. The new equality condition is the occasion for the introduction of a new quantity, the chemical potential  $\mu$ :

$$-\frac{\mu}{\tau} = \left( \frac{\partial\sigma}{\partial N} \right)_{U,V}. \quad (7)$$

For two systems in thermal and diffusive contact,  $\tau_1 = \tau_2$  and  $\mu_1 = \mu_2$ . The sign in (7) is chosen to ensure that the direction of particle flow as equilibrium is approached is from high chemical potential to low chemical potential.

The Gibbs factor of Chapter 5 is an extension of the Boltzmann factor and allows us to treat systems that can transfer particles. The simplest example is a system with two states, one with 0 particles and 0 energy, and one with 1 particle and energy  $\varepsilon$ . The system is in contact with a reservoir at temperature  $\tau$  and chemical potential  $\mu$ . We extend (3) for the reservoir entropy:

$$\begin{aligned}\sigma(U_0 - \varepsilon; N_0 - 1) &= \sigma(U_0; N_0) - \varepsilon(\partial\sigma/\partial U_0) - 1 \cdot (\partial\sigma/\partial N_0) \\ &= \sigma(U_0; N_0) - \varepsilon/\tau + \mu/\tau\end{aligned}\quad (8)$$

By analogy with (4), we have

$$P(1, \varepsilon)/P(0, 0) = \exp[(\mu - \varepsilon)/\tau]. \quad (9)$$

for the ratio of the probability the system is occupied by 1 particle at energy  $\varepsilon$  to the probability the system is unoccupied, with energy 0. The result (9) after normalization is readily expressed as

$$P(1, \varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/\tau] + 1}. \quad (10)$$

This particular result is known as the Fermi-Dirac distribution function and is used particularly in the theory of metals to describe the electron gas at low temperature and high concentration (Chapter 7).

The classical distribution function used in the derivation of the ideal gas law is just the limit of (10) when the occupancy  $P(1, \varepsilon)$  is much less than 1:

$$P(1, \varepsilon) \cong \exp[(\mu - \varepsilon)/\tau] \quad (11)$$

The properties of the ideal gas are developed from this result in Chapter 6.

The Helmholtz free energy  $F \equiv U - \tau\sigma$  appears as an important computational function, because the relation  $(\partial F/\partial\tau)_{N,V} = -\sigma$  offers the easiest method for finding the entropy, once we have found out how to calculate  $F$  from the energy eigenvalues (Chapter 3). Other powerful tools for the calculation of thermodynamic functions are developed in the text. Most of the remainder of the text concerns applications that are useful in their own right and that illuminate the meaning and utility of the principal thermodynamic functions.

Thermal physics connects the world of everyday objects, of astronomical objects, and of chemical and biological processes with the world of molecular, atomic, and electronic systems. It unites the two parts of our world, the microscopic and the macroscopic.