

The Essence of Statistical Mechanics

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0.1 The Definition of Temperature and Entropy

Let A_1 and A_2 be two systems that can exchange energy. Let $\Omega_1(E_1)$ be the number of states of A_1 that have energy E_1 . Let $\Omega_2(E_2)$ be the number of states of A_2 that have energy E_2 . Thinking quantum mechanically we may think of the function Ω as taking on only finite values, that is there is only a finite number N of states of the system. N will be very large. In classical physics, where statistical mechanics was originally developed, one had to introduce the concept of microstates in order to avoid infinity. That is one broke up the infinite states into a finite number of intervals, each considered a single state. Since the final result did not depend on the size of the intervals, other than there must be a large number of them, this subdivision is permissible. We shall suppose that these systems are in equilibrium, and that they form an isolated system, so that together they have constant energy

$$E = E_1 + E_2.$$

We suppose that the system is in one of its most probable states, and in that state A_1 has energy E_1 and A_2 has energy $E_2 = E - E_1$. The number of

states of the combined system, where system A_1 has energy E_1 and system A_2 has energy E_2 , is

$$\Omega_{12} = \Omega_1(E_1)\Omega_2(E_2).$$

Note that Ω_{12} is not the same as the number of states of the system $\Omega(E)$, that have energy E . This latter number is the sum of the Ω_{12} as E_1 takes on all values.

We make the reasonable assumption that there is a constant C so that the probability of A_1 having energy E_1 , and A_2 having energy E_2 is

$$p(E_1) = C\Omega_{12} = C\Omega_1(E_1)\Omega_2(E_2).$$

This is true, for example, if each state of the system is equally likely. For a quantum system of particles, this is not true in general. For example, the Heisenberg uncertainty principle can make the states not equally likely. But we may still apply the method treated here by partitioning the probability space into equally likely small subspaces. These subspaces are then considered single states. So in these cases we have what is called a partition function. In this sense our method here is general.

We suppose that the equilibrium energy E_1 is the most probable energy. Then p is a maximum, and the derivative of p is zero. We shall find the maximum of the logarithm of p , because we want the product to become a sum. Let

$$f(E_1) = \ln p(E_1) = \ln C + \ln \Omega_1(E_1) + \ln \Omega_2(E_2).$$

The derivative is

$$\frac{df(E_1)}{dE_1} = \frac{d(\ln \Omega_1)(E_1)}{dE_1} + \frac{d(\ln \Omega_2)(E_2)}{dE_2} \frac{dE_2}{dE_1}.$$

Setting this to zero and noting that

$$\frac{dE_2}{dE_1} = -1,$$

we have

$$\frac{d(\ln \Omega_1)(E_1)}{dE_1} = \frac{d(\ln \Omega_2)(E_2)}{dE_2}.$$

We define

$$\beta = \frac{\partial(\ln \Omega_1)(E_1)}{\partial E_1} = \frac{\partial(\ln \Omega_2)(E_2)}{\partial E_2}.$$

This quantity characterizes thermal equilibrium of the systems. That is, if β for system one, is equal to β for system two, then the systems are in thermal equilibrium. Two systems are in thermal equilibrium when they are at the same temperature. So β can be taken as a measure of temperature. We introduce a new quantity called the temperature T by

$$T = \frac{1}{\beta k},$$

where k is a constant called Boltzman's constant. The value of k can be determined by considering an ideal gas. One may apply Maxwell's kinetic theory of gases to this special system. One can then identify our T with the temperature that appears in the ideal gas law.

Now given a system with energy E , there are $\Omega(E)$ states of the system in which the system has this energy. We introduce a new quantity called the entropy, which is a function of the energy. It is given as

$$S(E) = k \ln(\Omega(E)).$$

Because

$$\frac{\partial(\ln \Omega)(E)}{\partial E} = \frac{1}{kT},$$

we have

$$\frac{\partial S}{\partial E} = \frac{1}{T}.$$

0.2 Heat

Heat is thermal energy. Let the quantity of heat Q be a quantity of thermal energy transferred to a system. Suppose a system at energy E has an increase of energy Q . Then the entropy is

$$S(E + Q) = k \ln \Omega(E + Q).$$

We have

$$\frac{dS}{dQ} = k \frac{\partial \ln(\Omega(E + Q))}{\partial E}$$

Then for a small addition of heat ΔQ , we have

$$\Delta S = \frac{dS}{dQ} \Delta Q = k \frac{\partial \ln(\Omega(E'))}{\partial E} \Delta Q = k \frac{1}{kT'} \Delta Q = \frac{\Delta Q}{T'},$$

where T' is near the original temperature T . This follows from the mean value theorem. We write this as

$$dS = \frac{dQ}{T}.$$

This is taken as the definition of entropy in thermodynamics.

0.3 Energy Probability Distribution

Suppose that a system A_1 may exchange energy with a much larger system A , so that the energy of system A_1 is much smaller than the energy of system A . Let A and A_1 be in thermal equilibrium at temperature T . We think of A as being the external environment. Let the total energy, E_t , of the two systems be constant. We shall find the probability that the system A_1 has energy E_r . Let $\Omega(E)$ be the number of states of system A , that have energy E . Then if the total energy is E_t , and the energy of A_1 is E_r , then system A may be in any of $\Omega(E_t - E_r)$ states. The probability of system A_1 having energy E_r is the same as the probability of system A being in one of the $\Omega(E_t - E_r)$ states. Therefore the probability of system A_1 having energy E_r is

$$p_r = C_1 \Omega(E_t - E_r),$$

for some constant C_1 . By Taylor's theorem, using the fact that E_r small, we have approximately

$$\begin{aligned} \ln(\Omega(E_t - E_r)) &= \\ \ln(\Omega(E_t)) - \frac{\partial \ln(\Omega)}{\partial E} E_r &= \\ \ln(\Omega(E_t)) - \frac{1}{kT} E_r. \end{aligned}$$

Then

$$\Omega(E_t - E_r) = \Omega(E_t) \exp(-E_r/kT).$$

Now $\Omega(E_t)$ is constant, so we may write

$$p_r = C_2 \exp(-E_r/kT),$$

for some constant C_2 .

Using this result, if the system A_1 has n energy states, then the probability of the system having energy E_r is

$$pr(E_r) = \frac{\exp(-E_r/(kT))}{\sum_{s=1}^n \exp(-E_s/(kT))}.$$

This holds for any system that is in thermal equilibrium with its surrounding environment.

0.4 The Equipartition of Energy

Let a system be in thermal equilibrium at temperature T . Let the energy be a function of n generalized coordinates q_1, \dots, q_n and p_1, \dots, p_n generalized momenta. Suppose that the energy may be written as a sum

$$E = E_1 + E_2,$$

where E_1 is a function of p_1 and E_2 is not a function of p_1 . Then the expected value of E_1 is

$$\bar{E}_1 = \frac{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} E_1 \exp(-\beta E) dq_1 \dots dp_n}{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \exp(-\beta E) dq_1 \dots dp_n}.$$

This simplifies to

$$\bar{E}_1 = \frac{\int_{-\infty}^{\infty} E_1 \exp(-\beta E_1) dp_1}{\int_{-\infty}^{\infty} \exp(-\beta E) dp_1}.$$

If $E_1 = bp_1^2$, then

$$\bar{E}_1 = \frac{\int_{-\infty}^{\infty} bp_1^2 \exp(-\beta bp_1^2) dp_1}{\int_{-\infty}^{\infty} \exp(-\beta bp_1^2) dp_1}.$$

Making the substitution

$$x = \sqrt{\beta b} p_1,$$

we find that the numerator is

$$\frac{1}{\beta \sqrt{\beta b}} \int_{-\infty}^{\infty} x^2 \exp(-x^2) dx,$$

The denominator is

$$\frac{1}{\sqrt{\beta b}} \int_{-\infty}^{\infty} \exp(-x^2) dx.$$

The integral in the denominator may be evaluated as follows. We have

$$\begin{aligned} & \left[\int_{-\infty}^{\infty} \exp(-x^2) dx \right]^2 = \\ & \int_{-\infty}^{\infty} \exp(-x^2) dx \int_{-\infty}^{\infty} \exp(-y^2) dy = \\ & \int_0^{\infty} \exp(-r^2) 2\pi r dr = \pi. \end{aligned}$$

So

$$\int_{-\infty}^{\infty} \exp(-x^2) dx = \sqrt{\pi}.$$

To evaluate the integral in the numerator we introduce the function

$$\begin{aligned} m(s) &= \int_{-\infty}^{\infty} \exp(sx) \exp(-x^2) dx = \\ & \exp(s^2/4) \int_{-\infty}^{\infty} \exp(-(x - s/2)^2) dx = \exp(s^2/4) \sqrt{\pi}. \end{aligned}$$

Taking the second derivative

$$\begin{aligned} m''(s) &= \int_{-\infty}^{\infty} x^2 \exp(sx) \exp(-x^2) dx = \\ & \frac{1}{2} \sqrt{\pi} \exp(s^2/4) (1 + s^2/2). \end{aligned}$$

Letting $s = 0$ we find that

$$\int_{-\infty}^{\infty} x^2 \exp(-x^2) dx = \frac{1}{2} \sqrt{\pi}.$$

Using the values of the two integrals we find

$$\bar{E}_1 = \frac{1}{2\beta} = \frac{1}{2} kT.$$

This generalizes to the equipartition of energy theorem.

Theorem. If the energy is a sum of quadratic terms in each of the $2n$ variables $q_1, \dots, q_n, p_1, \dots, p_n$, of the form

$$E = \sum_{i=1}^n c_i q_i^2 + \sum_{i=1}^n d_i p_i^2,$$

then each energy term has mean energy

$$\frac{1}{2} kT.$$

0.5 The Vibration of Molecules

For many purposes, a vibrating molecule may be considered to be a classical mechanical system. As such, the modes of vibration are controlled by a set of linear differential equations. The solution to these equations may be written in terms of certain fundamental solutions given as eigenvectors of the system. This allows us to characterize the system in terms of certain normal coordinates. The energy of the vibrating system then is given as a sum of quadratic terms involving the normal coordinates. The number of such coordinates is called the degree of freedom of the system. One can consult a work on vibration theory for more details on these techniques. From the partition of energy theorem we find that the average energy is proportional to the product of the degrees of freedom and $\frac{1}{2}kT$. For a monatomic gas there are only three degrees of freedom, namely translation in the x , y , and z directions, so the average energy per molecule is

$$\frac{3}{2}kT.$$

The average energy per mole is obtained by multiplying by Avogadro's number A , that is, the system of one mole has $3A$ degrees of freedom, 3 degrees of freedom for each molecule.

The specific heat is essentially the change in energy with a unit change in temperature. This is the derivative of the energy with respect to the temperature. However, according to the first law of thermodynamics, we must consider not only the increase of internal heat energy, but also the external work done by the system. So there is a distinction between the specific heat at constant pressure C_p , and the specific heat at constant volume C_v . Clearly the specific heat depends on the degrees of freedom of the system. So for example a diatomic molecule has rotational degrees of freedom. This increases the specific heat.

Note that the measured specific heat of a substance gives us information about the number of degrees of freedom of the molecule of the substance and thus gives us information about the molecular structure itself. In **Physics** by Halliday and Resnick, there is a good elementary discussion of the specific heat of gases and tables of values.

It is amazing that the simple arguments presented above give us so much information about the physical world.

0.6 Bibliography

I shall compile a good bibliography later.