

Lecture 2: The Statistical Basis of Thermodynamics

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2.1 Microstates and Macrostates

We consider a system composed of N identical particles confined to a space of V . The total energy E would be equal to the sum of the energies of the individual particles.

$$E = \sum_i n_i \epsilon_i \quad (2.1)$$

The specification of the actual values of the parameters N, V, E then defines a *macrostate* of the system. At the molecular level, however, a large number of possibilities still exist because at that level there will be a large number of different ways to make the total state of N, V, E (think out arranging the coins with different sequence of head and tail). Each of the different ways specifies a *microstate* or *complexion* of the given system.

The actual number of all possible microstates (Ω) will be a function of N, V, E . In principle, it is from the magnitude of the number of Ω and from its dependence on the parameters N, V, E , that complete thermodynamics can be derived.

2.2 Multiplicity in Einstein Solids

N : Number of the oscillators.

q : Number of energy states.

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \quad (2.2)$$

It can be simply proved as follows

q circles;

$N - 1$ vertical lines;

how to arrange them?



Exercises

Calculate the multiplicity of an Einstein solid with 5 oscillators and [1,2,3,4,5] units of Energy.

q	$\Omega(5, q)$
1	
2	
3	
4	
5	

2.3 Contact between statistics and thermodynamics

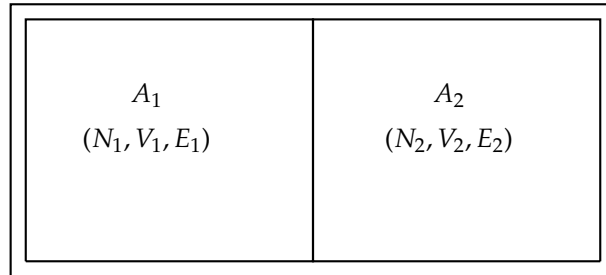


Figure 2.1: A schematic of two physical systems in thermal contact.

Let's first figure out how Ω is related to the thermodynamic quantities. We consider two physical systems, A_1 and A_2 , which are separately in equilibrium. Let the macrostate of A_1 be represented by the parameters N_1, V_1 and E_1 so that it has $\Omega_1(N_1, V_1, E_1)$ possible microstates, and the macrostate of A_2 be represented by $\Omega_2(N_2, V_2, E_2)$. Can we derive some thermodynamic properties from $\Omega_1(N_1, V_1, E_1)$ and $\Omega_2(N_2, V_2, E_2)$?

Let's bring two systems into thermal contact. For simplicity, we only allow the heat exchange between the two, while N, V remain fixed. This means there could be some interchanges between E_1 and E_2 , however, it has to be restricted by the conservation law.

$$E = E_1 + E_2 = \text{const} \quad (2.3)$$

From the microscopic view, the total number of microstates could be expressed as,

$$\Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E - E_1) \quad (2.4)$$

When the system approaches to the equilibrium, what should be the value of \bar{E}_1 . According to the 2nd law, the entropy should reach the maximum. Mathematically, we need to find \bar{E}_1 which satisfies,

$$\left(\frac{\partial \Omega_1(E_1)}{\partial E_1} \right)_{E_1=\bar{E}_1} \Omega_2(E_2) + \left(\frac{\partial \Omega_2(E_2)}{\partial E_2} \right)_{E_2=\bar{E}_2} \frac{\partial E_2}{\partial E_1} \Omega_1(E_1) = 0 \quad (2.5)$$

Remember that $\Delta E_1 = \Delta E_2$ at each time interval, therefore

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{E_1=\bar{E}_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \right)_{E_2=\bar{E}_2} \quad (2.6)$$

Thus, our condition for equilibrium reduces to the equality of parameter β_1 and β_2 :

$$\beta \equiv \left(\frac{\partial \ln \Omega(E)}{\partial E} \right)_{E=\bar{E}} \quad (2.7)$$

or a more complete version as follows,

$$\beta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial E} \right)_{N, V, E = \bar{E}} \quad (2.8)$$

Therefore, we find when two systems are into thermal contact, the exchange of heat continues until the equilibrium E_1, E_2 reach some values. This happens only when the respective values of β_1 and β_2 become equal. It is then natural to expect that the parameter β is somehow related to T . To determine this relationship, we recall the thermodynamic formula

$$\left(\frac{\partial S}{\partial E} \right)_{N, V} = \frac{1}{T} \quad (2.9)$$

Comparing eq. 2.8 and 2.9, we find

$$\left(\frac{\Delta S}{\Delta \ln \Omega} \right) = \frac{1}{\beta T} = \text{const} \quad (2.10)$$

This correspondence was firstly established by Boltzmann. It was Planck who first wrote the explicit formula

$$S = k \ln \Omega \quad (2.11)$$

It means that the absolute value of the entropy of a given physical system in terms of the total number of microstates accessible to it conformity with the given macrostate, which provides a bridge between micro and macroscopic.

2.4 More complete contact

Let's continue to examine a more elaborate exchange between A_1 and A_2 .

not only,

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{E_1 = \bar{E}_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \right)_{E_2 = \bar{E}_2} \quad (2.12)$$

but also

$$\left(\frac{\partial \ln \Omega_1(V_1)}{\partial V_1} \right)_{V_1 = \bar{V}_1} = \left(\frac{\partial \ln \Omega_2(V_2)}{\partial V_2} \right)_{V_2 = \bar{V}_2} \quad (2.13)$$

Our conditions for equilibrium now take the form of an equality between the pair of (β, η)

$$\eta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial V} \right)_{N, E, V = \bar{V}} \quad (2.14)$$

Similarly, there might be exchanges between particles, while need another parameter ζ ,

$$\zeta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial N} \right)_{V, E, N = \bar{N}} \quad (2.15)$$

To determine the physical meaning of the parameters η and ζ , we make use of the thermodynamic identity.

$$dE = TdS - PdV + \mu dN \quad (2.16)$$

so

$$\begin{aligned}\beta &= \frac{1}{kT} \\ \eta &= \frac{P}{kT} \\ \zeta &= -\frac{\mu}{kT}\end{aligned}\tag{2.17}$$

From the macroscopic view, the equilibrium is reached when

$$\begin{aligned}T_1 &= T_2 \\ P_1 &= P_2 \\ \mu_1 &= \mu_2\end{aligned}\tag{2.18}$$

This is identical to the ones following from statistical considerations. The evaluations of P , μ , T indeed requires that energy E be expressed as a function of N, V, E , this should, in principle be possible once S is known.

For instance,

$$\begin{aligned}\left(\frac{\partial S}{\partial E}\right)_{N,V} &= \frac{1}{T} \\ \left(\frac{\partial S}{\partial V}\right)_{N,V} &= \frac{P}{T} \\ \left(\frac{\partial S}{\partial N}\right)_{N,V} &= \frac{-\mu}{T}\end{aligned}\tag{2.19}$$

The rest of thermodynamic quantities follow straightforwardly.

$$\begin{aligned}F &= E - TS \\ G &= F + PV = E - TS - PV = \mu N \\ H &= E + PV = G + TS\end{aligned}\tag{2.20}$$

$$\begin{aligned}C_V &= T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial T}\right)_{N,V} \\ C_P &= T\left(\frac{\partial S}{\partial T}\right)_{N,P} = \left(\frac{\partial H}{\partial T}\right)_{N,P}\end{aligned}\tag{2.21}$$