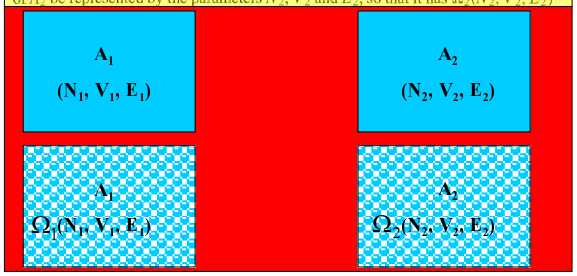
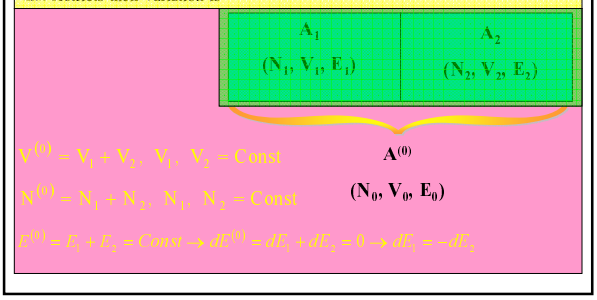
1.2. Contact between statistics and thermodynamics: physical significance of the number $\Omega(N, V, E)$

We consider two physical systems, A_1 and A_2, which are separately in equilibrium; see Fig. 1.1. 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 the parameters N_2, V_2 and E_2, so that it has $\Omega_2(N_2, V_2, E_2)$



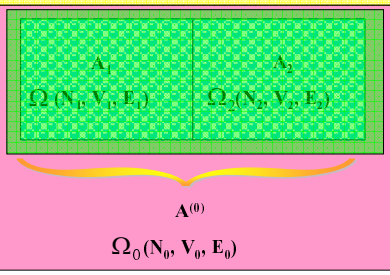
Here, $E^{(0)}$ denotes the energy of the composite system $A^{(0)}(\equiv A_1 + A_2)$; the energy of interaction between A_1 and A_2, if any, is being neglected. Now, at any time t, the the two systems are still separated by a rigid, impenetrable wall, so that the respective volumes V_1 and V_2 and the respective particle numbers N_1 and N_2 remain fixed. The energies E_1 and E_2, however, become variable and the only condition that restricts their variation is



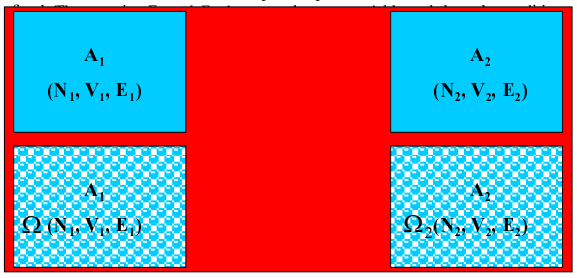
1.2. Contact between statistics and thermodynamics: physical significance of the number $\Omega(N, V, E)$

We consider two physical systems, A_1 and A_2, which are separately in equilibrium; see Fig. 1.1. 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 the parameters N_2, V_2 and E_2, so that it has $\Omega_2(N_2, V_2, E_2)$ possible microstates. The mathematical form of the function Ω_1 may not be the same as that of the function Ω_2, because that ultimately depends upon the nature of the system. We do, of course, believe that all thermodynamic properties of the systems A_1 and A_2 can be derived from the functions $\Omega_1(N_1, V_1, E_1)$ and $\Omega_2(N_2, V_2, E_2)$, respectively.

Here, $E^{(0)}$ denotes the energy of the composite system $A^{(0)}(\equiv A_1 + A_2)$; the energy of interaction between A_1 and A_2, if any, is being neglected. Now, at any time t, the sub-system A_1 is equally likely to be in any one of the $\Omega_1(E_1)$ microstates while the sub-system A_2 is equally likely to be in any one of the $\Omega_2(E_2)$ microstates; therefore, the composite system $A^{(0)}$ is equally likely to be in any one of the $\Omega^{(0)}(E_1, E_2)$ microstates, where



We now bring the two systems into thermal contact with each other, thus allowing the possibility of exchange of energy between the two; this can be done by sliding in a conducting wall and removing the impervious one. For simplicity, the two systems are still separated by a rigid, impenetrable wall, so that the respective volumes V_1 and V_2 and the respective particle numbers N_1 and N_2 remain



$$\Omega_1(E_1, V_1, N_1, E_2, V_2, N_2) =$$

$$\Omega^{(0)}(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E^{(0)} - E_1)$$

$$= \Omega_1(E_1)\Omega_2(E_1)$$

$$= \Omega^{(0)}(E_1)$$

Clearly, the number $\Omega^{(0)}$ itself varies with E_1.

Clearly, the number $\Omega^{(0)}$ itself varies with E_1. The question now arises: at what value of the variable E_1 will the composite system be in equilibrium? In other words, how far will the energy exchange go in order to bring the sub-systems A_1 and A_2 into mutual equilibrium?

We assert that this will happen at that value of E_1 which *maximizes* the number $\Omega^{(0)}(E^{(0)}, E_1)$. The philosophy behind this assertion is that a physical system, left to itself, proceeds naturally in a direction that enables it to assume an ever-

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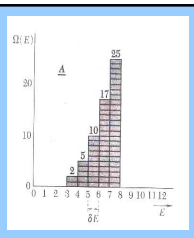
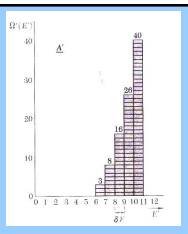


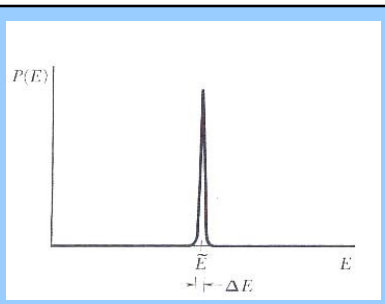
$E^{(0)} = 13$



E	E'	$\Omega(E)$	$\Omega'(E')$	$\Omega^*(E)$
3	10	2	40	80
4	9	5	26	130
5	8	10	16	160
6	7	17	8	136
7	6	25	3	75

محتملترین حالت، که احتمال وقوع آن دو برابر حالت اول است

We assert that this will happen at that value of E_1 which *maximizes* the number $\Omega^{(0)}(E^{(0)}, E_1)$. The philosophy behind this assertion is that a physical system, left to itself, proceeds naturally in a direction that enables it to assume an ever-increasing number of microstates until it finally settles down in a macrostate that affords the *largest possible* number of microstates. Statistically speaking, we regard a macrostate with a larger number of microstates as a more probable state, and the one with the largest number of microstates as the most probable one. Detailed studies show that, for a typical system, the number of microstates pertaining to any macrostate that departs even slightly from the most probable one is "orders of magnitude" smaller than the number pertaining to the latter. Thus, the most probable state of a system is *the* state in which the system spends an "overwhelmingly" large fraction of its time. It is then natural to identify this state with the *equilibrium* state of the system.



شکل عمومی تغییرات P(E) برحسب E

تعداد آن دسته از حالتهای دستگاه $A^{(0)}$ که در آن حالتها انرژی دستگاه A_1 برابر E_1 است.

$$P(E_1) = \frac{\Omega^{(0)}(E_1)}{\Omega^{(0)}_{total}}$$

تعداد کل حالتهای قابل دسترس دستگاه $A^{(0)}$

$$P(E_1) = \frac{\Omega^{(0)}(E_1)}{\Omega^{(0)}_{total}} = C\Omega^{(0)}(E_1) \qquad C^{-1} = \Omega^{(0)}_{total}$$

$$= C\Omega_1(E_1)\,\Omega_2(E_1)$$

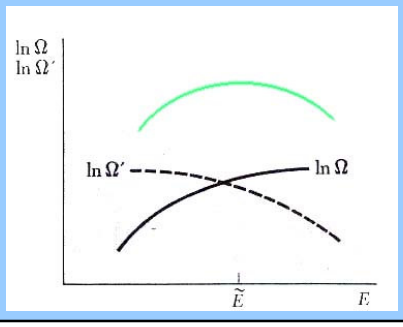
$$= C\Omega_1(E_1)\,\Omega_2\left(E^{(0)} - E_1\right)$$

$$= C\Omega_1(E_1)\,\Omega_2(E_2)$$

$$\ln P(E_1) = \ln C + \ln\Omega_1(E_1) + \ln\Omega_2(E_2)$$

$$\frac{\partial \ln P(E_1)}{\partial E_1} = \frac{1}{P}\frac{\partial P(E_1)}{\partial E_1} = 0$$

ماکزیمم LnP همان ماکزیمم P است.



We assert that this will happen at that value of E_1 which *maximizes* the number $\Omega^{(0)}(E^{(0)}, E_1)$. The philosophy behind this assertion is that a physical system, left to itself, proceeds naturally in a direction that enables it to assume an ever-increasing number of microstates until it finally settles down in a macrostate that affords the *largest possible* number of microstates. Statistically speaking, we regard a macrostate with a larger number of microstates as a more probable state, and the one with the largest number of microstates as the most probable one. Detailed studies show that, for a typical system, the number of microstates pertaining to any macrostate that departs even slightly from the most probable one is "orders of magnitude" smaller than the number pertaining to the latter. Thus, the most probable state of a system is *the* state in which the system spends an "overwhelmingly" large fraction of its time. It is then natural to identify this state with the *equilibrium* state of the system.

گفته فوق را ثابت کنید. (راهنمایی: به کتاب رایف مراجعه کنید و لغت کلیدی تیزی یا **sharpness** توجه کنید.)

$$S^{(0)} = \sum_{\alpha=1}^{2} S_\alpha = S_1 + S_2$$

آنتروپی را حول نقطه تعادل بسط تیلور می دهیم:

$$S^{(0)} = S^{(0)}\Big|_0 + \sum_{\alpha=1}^{2} \frac{\partial S_\alpha}{\partial E_\alpha}\Big|_{N_\alpha, V_\alpha} \Delta E_\alpha$$

$$S^{(0)} - S^{(0)}\Big|_0 = \Delta S^{(0)}$$

$$\Delta S^{(0)} = \frac{\partial S_1}{\partial E_1}\Big|_{N_1, V_1} \Delta E_1 + \frac{\partial S_2}{\partial E_2}\Big|_{N_2, V_2} \Delta E_2$$

$$\Delta S^{(0)} = \left\{ \frac{\partial S_1}{\partial E_1}\Big|_{N_1, V_1} - \frac{\partial S_2}{\partial E_2}\Big|_{N_2, V_2} \right\} \Delta E_1 + \dots$$

$$\Delta S^{(0)} = 0 \Rightarrow \frac{\partial S_1}{\partial E_1}\Big|_{N_1, V_1} - \frac{\partial S_2}{\partial E_2}\Big|_{N_2, V_2} = 0 \Leftrightarrow \beta_1 = \beta_2$$

$$\mathrm{Lop}(\bar{E}_1) = \mathrm{LnC} + \mathrm{Ln}\Omega_1(\bar{E}_1) + \mathrm{Ln}\Omega_2(\bar{E}_2)$$

$$d\mathrm{Lop}(\bar{E}_1) = 0 + \frac{\partial \mathrm{Ln}\Omega_1(\bar{E}_1)}{\partial E_1}\Big|_{V_1, N_1, \bar{E}_1} dE_1 + \frac{\partial \mathrm{Ln}\Omega_2(\bar{E}_2)}{\partial E_2}\Big|_{N_2, V_2, \bar{E}_2} dE_2 = 0$$

$$dE^{(0)} = 0 \Rightarrow dE_1 + dE_2 = 0 \Rightarrow dE_1 = -dE_2$$

$$\left\{ \frac{\partial \mathrm{Ln}\Omega_1(\bar{E}_1)}{\partial E_1}\Big|_{N_1, V_1, \bar{E}_1} - \frac{\partial \mathrm{Ln}\Omega_2(\bar{E}_2)}{\partial E_2}\Big|_{N_2, V_2, \bar{E}_2} \right\} dE_1 = 0$$

$$\beta = \frac{\partial Ln\Omega(E)}{\partial E}\Big|_{N, V, \bar{E}}$$

$$\left\{ \frac{\partial \mathrm{Ln}\Omega_1(\bar{E}_1)}{\partial E_1}\Big|_{N_1, V_1, \bar{E}_1} - \frac{\partial \mathrm{Ln}\Omega_2(\bar{E}_2)}{\partial E_2}\Big|_{N_2, V_2, \bar{E}_2} \right\} dE_1 = 0 \Rightarrow \beta_1 = \beta_2$$

$$\beta_1 = \beta_2$$

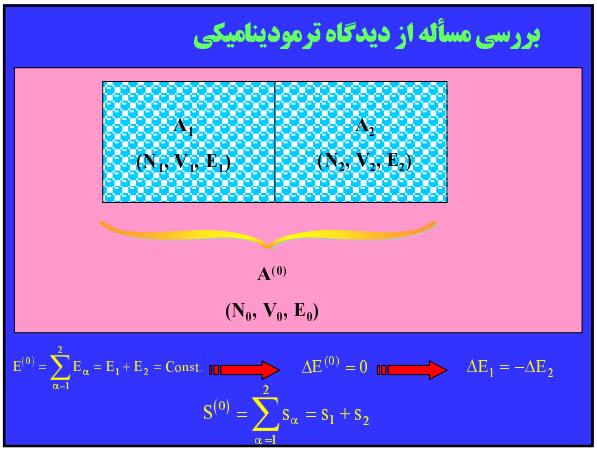
$$\left.\begin{aligned} dE &= dQ - PdV + \mu dN \\ dQ &= TdS \end{aligned}\right\} \Rightarrow dE = TdS - PdV + \mu dN$$

$$\frac{\partial S}{\partial E}\Big|_{V, N} = \frac{1}{T}$$

$$\Delta S^{(0)} = 0 \Rightarrow \frac{\partial S_1}{\partial E_1}\Big|_{N_1, V_1} - \frac{\partial S_2}{\partial E_2}\Big|_{N_2, V_2} = 0 \Rightarrow \beta_1 = \beta_2$$

$$\Rightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

بررسی مسأله از دیدگاه ترمودینامیکی



$$E^{(0)} = \sum_{\alpha=1}^{2} E_\alpha = E_1 + E_2 = \text{Const.} \Rightarrow \Delta E^{(0)} = 0 \Rightarrow \Delta E_1 = -\Delta E_2$$

$$S^{(0)} = \sum_{\alpha=1}^{2} S_\alpha = S_1 + S_2$$

$$\frac{\partial \mathrm{Ln}\Omega_1(E_1)}{\partial E_1}\Big|_{N_1, V_1, \bar{E}_1} = \frac{\partial \mathrm{Ln}\Omega_2(E_2)}{\partial E_2}\Big|_{N_2, V_2, \bar{E}_2}$$

آماری

$$\beta = \frac{\partial Ln\Omega(E)}{\partial E}\Big|_{N, V, \bar{E}}$$

ترمودینامیک

$$\frac{\partial S_1}{\partial E_1}\Big|_{N_1, V_1} = \frac{\partial S_2}{\partial E_2}\Big|_{N_2, V_2}$$

$$\frac{\partial S}{\partial E}\Big|_{V, N} = \frac{1}{T}$$

$$\frac{\Delta(\mathrm{Ln}\Omega(E))}{\Delta S}\Big|_{\bar{E}} = \beta T = \text{const.}$$

$$\frac{\Delta(\mathrm{Ln}\Omega(E))}{\Delta S}\Big|_{\bar{E}} = \beta T = \text{const.} = k$$

$$\frac{(\quad(\quad))}{}\Big|_{\bar{E}} = \beta T = \qquad = k$$

$$S = S_0 + k\mathrm{Ln}\Omega$$

This correspondence was first established by Boltzmann who also believed that, since the relationship between the thermodynamic approach and the statistical approach seems to be of a fundamental character, the constant appearing in (5) must be a *universal constant*. It was Planck who first wrote the explicit formula

$$S = k \ln \Omega, \qquad (6)$$

without any additive constant S_0.

$$\beta = \frac{1}{kT}$$

Now, in the study of the second law of thermodynamics we are told that the law of increase of entropy is related to the fact that the energy content of the universe, in its natural course, is becoming less and less available for conversion into work; accordingly, the entropy of a given system may be regarded as a measure of the so-called disorder or chaos prevailing in the system. Formula (6) tells us how disorder arises microscopically. Clearly, disorder is a manifestation of the largeness of the number of microstates the system can have. The larger the choice of microstates, the lesser the degree of predictability or the level of order in the system. Complete order prevails when and only when the system has no other choice but to be in a unique state ($\Omega = 1$); this, in turn, corresponds to a state of vanishing entropy.

without any additive constant S_0. As it stands, formula (6) determines the *absolute* value of the entropy of a given physical system in terms of the total number of microstates accessible to it in conformity with the given macrostate. The zero of entropy then corresponds to the special state for which only one microstate is accessible ($\Omega = 1$)–the so-called "unique configuration"; the statistical approach thus provides a theoretical basis for the third law of thermodynamics as well. Formula (6) is of fundamental importance in physics; it provides a bridge between the microscopic and the macroscopic.

$$S = k\mathrm{Ln}\Omega$$

$\Omega = 1$ ⟹ $S = k\mathrm{Ln}1 = 0$

که سازگار با قانون سوم ترمودینامیک است، پس انتخاب **S0=0** معقول است.

قانون سوم:

۱) اختلاف آنتروپی بین حالتهای مرتبط با یک فرایند بازگشت پذیر در حد **T=0** به سمت صَفر میل می کند.

۲) رسیدن به دمای صفر با یک تعداد متناهی گامهای بازگشت پذیر امکان پذیر نیست.

در دمای صفر منظم ترین حالت را داریم که معادل با $\Omega = 1$ است.پس **S=0+k(0)=0**.