The Canonical Ensemble

IN THE preceding chapter we established the basis of ensemble theory and made a somewhat detailed study of the microcanonical ensemble. In that ensemble the macrostate of the systems was defined through a fixed number of particles N, a fixed volume V and a fixed energy E [or, preferably, a fixed energy range $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$]. The basic problem then consisted in determining the number $\Omega(N, V, E)$, or $\Gamma(N, V, E; \Delta)$, of *distinct* microstates accessible to the system. From the asymptotic expressions of these numbers, complete thermodynamics of the system could be derived in a straightforward manner. However, for most physical systems, the mathematical problem of determining these numbers is quite formidable. For this reason alone, a search for an alternative approach within the framework of the ensemble theory seems necessary.

$$\left\{ \begin{array}{lcl} \Omega\ (N, V, E) & \Longrightarrow & H = E \\ \Sigma\ (N, V, E) & \Longrightarrow & H \leq E \\ \Gamma\ (N, V, E) & \Longrightarrow & (E-1/2\Delta) \leq H \leq (E+1/2\Delta) \end{array} \right\}$$

IN THE preceding chapter we established the basis of ensemble theory and made a somewhat detailed study of the microcanonical ensemble. In that ensemble the macrostate of the systems was defined through a fixed number of particles N, a fixed volume V and a fixed energy E [or, preferably, a fixed energy range $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$]. The basic problem then consisted in determining the number $\Omega(N, V, E)$, or $\Gamma(N, V, E; \Delta)$, of *distinct* microstates accessible to the system. From the asymptotic expressions of these numbers, complete thermodynamics of the system could be derived in a straightforward manner. However, for most physical systems, the mathematical problem of determining these numbers is quite formidable. For this reason alone, a search for an alternative approach within the framework of the ensemble theory seems necessary.

Physically, too, the concept of a fixed energy (or even an energy range) for a system belonging to the real world does not appear satisfactory. For one thing, the total energy E of a system is hardly ever measured; for another, it is hardly possible to keep its value under strict physical control. A far better alternative appears to be to speak of a fixed temperature T of the system–a parameter which is not only directly observable (by placing a "thermometer" in contact with the system) but also controllable (by keeping the system in contact with an appropriate "heat reservoir"). For most purposes, the precise nature of the reservoir is not very relevant; all one needs is that it should have an infinitely large heat capacity, so that, irrespective of energy exchange between the system and the reservoir, an overall constant temperature can be maintained. Now, if the reservoir consists of an infinitely large number of mental copies of the given system we have once again an ensemble of systems–this time, however, it is an ensemble in which the macrostate of the systems is defined through the parameters N, V and T. Such an ensemble is referred to as a *canonical* ensemble.

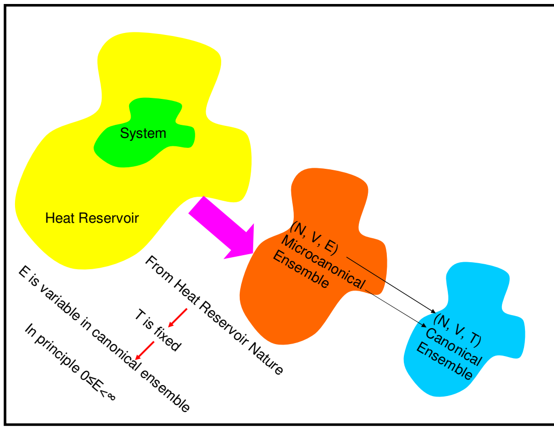
Physically, too, the concept of a fixed energy (or even an energy range) for a system belonging to the real world does not appear satisfactory. For one thing, the total energy E of a system is hardly ever measured; for another, it is hardly possible to keep its value under strict physical control. A far better alternative appears to be to speak of a fixed temperature T of the system–a parameter which is not only directly observable (by placing a "thermometer" in contact with the system) but also controllable (by keeping the system in contact with an appropriate "heat reservoir"). For most purposes, the precise nature of the reservoir is not very relevant; all one needs is that it should have an infinitely large heat capacity, so that, irrespective of energy exchange between the system and the reservoir, an overall constant temperature can be maintained. Now, if the reservoir consists of an infinitely large number of mental copies of the given system we have once again an ensemble of systems–this time, however, it is an ensemble in which the macrostate of the systems is defined through the parameters N, V and T. Such an ensemble is referred to as a *canonical* ensemble.

Physically, too, the concept of a fixed energy (or even an energy range) for a system belonging to the real world does not appear satisfactory. For one thing, the total energy E of a system is hardly ever measured; for another, it is hardly possible to keep its value under strict physical control. A far better alternative appears to be to speak of a fixed temperature T of the system–a parameter which is not only directly observable (by placing a "thermometer" in contact with the system) but also controllable (by keeping the system in contact with an appropriate "heat reservoir"). For most purposes, the precise nature of the reservoir is not very relevant; all one needs is that it should have an infinitely large heat capacity, so that, irrespective of energy exchange between the system and the reservoir, an overall constant temperature can be maintained. Now, if the reservoir consists of an infinitely large number of mental copies of the given system we have once again an ensemble of systems–this time, however, it is an ensemble in which the macrostate of the systems is defined through the parameters N, V and T. Such an ensemble is referred to as a *canonical* ensemble.

در این حالت $\rho = cte$ برقرار نخواهد بود.

$$T = cte \;\rightarrow\; \rho \neq cte \;\Rightarrow\; \rho = e^{-\beta H}$$

در آنسامبل کانونی به مانند آنسامبل میکروکانونی سیال همچنان پایا خواهد ماند و قضیهٔ لیوویل نیز برقرار خواهد بود، در نتیجه ترمودینامیک تعادلی را بحث می کنیم. ولی قید $E-\frac{\Delta}{2} \le E \le E+\frac{\Delta}{2}$ برداشته می شود. یعنی هندسه را کنارمی گذاریم که این هندسه از $E=cte$ ناشی می شود که امکان دارد ما را با هندسهٔ پیچیده ای روبرو کند، در حالی که با در نظر گرفتن $\rho \neq cte$ یعنی $\rho = e^{-\beta E}$ با هندسهٔ کروی ساده روبرو می شویم.



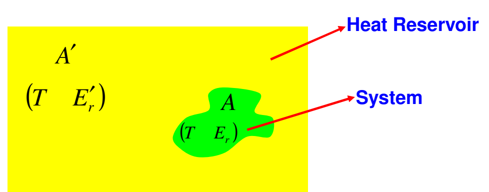
In the canonical ensemble, the energy E of a system is variable; in principle, it can take values anywhere between zero and infinity. The question then arises: what is the probability that, at any time t, a system in the ensemble is found to be in one of the states characterized by the energy value E_r?[1] We denote this probability by the symbol P_r. Clearly, there are two ways in which the dependence of P_r on E_r can be determined. One consists in regarding the system as in equilibrium with a heat reservoir at a *common* temperature T and studying the statistics of the energy exchange between the two. The other consists in regarding the system as a member of a canonical ensemble (N, V, T), in which an energy $\mathscr{E}$ is being shared by $\mathcal{N}$ identical systems constituting the ensemble, and studying the statistics of this sharing process. We expect that in the thermodynamic limit the final result in either case would be the same. Once P_r is determined, the rest follows without difficulty.

In the canonical ensemble, the energy E of a system is variable; in principle, it can take values anywhere between zero and infinity. The question then arises: what is the probability that, at any time t, a system in the ensemble is found to be in one of the states characterized by the energy value E_r?[1] We denote this probability by the symbol P_r. Clearly, there are two ways in which the dependence of P_r on E_r can be determined. One consists in regarding the system as in equilibrium with a heat reservoir at a *common* temperature T and studying the statistics of the energy exchange between the two. The other consists in regarding the system as a member of a canonical ensemble (N, V, T), in which an energy $\mathscr{E}$ is being shared by $\mathcal{N}$ identical systems constituting the ensemble, and studying the statistics of this sharing process. We expect that in the thermodynamic limit the final result in either case would be the same. Once P_r is determined, the rest follows without difficulty.

$$\sum_r n_r = \mathcal{N}$$

$$\sum_r n_r E_r = \mathscr{E} = \mathcal{N} U$$

Equilibrium between a system and a heat reservoir



T is fixed but E_r, E'_r are variables

$$E_r + E'_r = E^{(0)} = const$$

$$\Omega^{(0)}(E_r, E'_r) = \Omega(E_r)\Omega'(E'_r) = \Omega(E_r)\Omega'(E^{(0)} - E_r) = \Omega^{(0)}(E_r)$$

$$P(E_r) = P_r = \frac{\Omega^{(0)}(E_r)}{\Omega^{(0)}_{tot}} = C\Omega^{(0)}(E_r) \qquad C^{-1} = \Omega^{(0)}_{tot}$$

$$P_r = C\Omega^{(0)}(E_r) = C\Omega(E_r)\Omega'(E^{(0)} - E_r) = C\Omega(E_r)\Omega'(E'_r)$$

$$\frac{E_r}{E^{(0)}} = \frac{E^{(0)} - E'}{E^{(0)}} = \left(1 - \frac{E'_r}{E^{(0)}}\right) << 1$$

$$P_r \propto \Omega'(E'_r) = C'\Omega'(E'_r) = C'\Omega'(E^{(0)} - E_r) \qquad C' = C\Omega(E_r)$$

$$\ln\Omega'\left(E^{(0)}-E_r\right)=\ln\Omega'\left(E^{(0)}\right)+\left.\frac{\partial\ln\Omega'}{\partial E'}\right|_{E'=E^{(0)}}\left(-E_r\right)$$

$$\ln\Omega'\left(E^{(0)}-E_r\right)-\ln\Omega'\left(E^{(0)}\right)=\beta\left(-E_r\right)$$

$$\ln\frac{\Omega'\left(E^{(0)}-E_r\right)}{\Omega'\left(E^{(0)}\right)}=-\beta E_r \Longrightarrow \frac{\Omega'\left(E^{(0)}-E_r\right)}{\Omega'\left(E^{(0)}\right)}=e^{-\beta E_r}$$

$$\Omega'\left(E^{(0)}-E_r\right)=C''e^{-\beta E_r} \qquad C''=\Omega'\left(E^{(0)}\right)$$

$$P_r=C'\Omega'\left(E^{(0)}-E_r\right)=C'C''e^{-\beta E_r}=C'''e^{-\beta E_r} \qquad C'''=C'C''$$

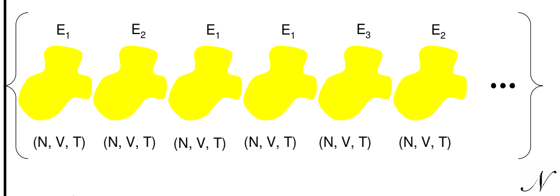
$$\sum_r P_r=1\Rightarrow\sum_r C'''e^{-\beta E_r}=1\Rightarrow C'''\sum_r e^{-\beta E_r}=1\Rightarrow C'''=\frac{1}{\sum_r e^{-\beta E_r}}$$

$$P_r=C'''e^{-\beta E_r}=\frac{1}{\sum_r e^{-\beta E_r}}e^{-\beta E_r}$$

$$P_r=\frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$\sum_r e^{-\beta E_r}$ → **Partition Function**

A system in the canonical ensemble



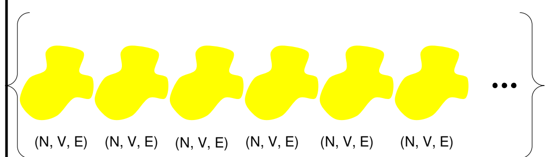
$\mathcal{N}$

$$\begin{cases} 3E_1+2E_2+E_3+\ldots=\mathcal{E}=\mathcal{N}U \\ 3+2+1+\ldots=\mathcal{N} \end{cases}$$

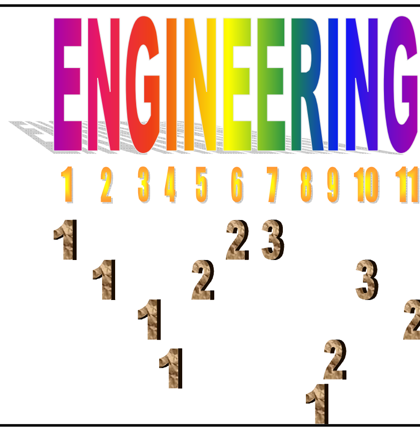
$$\sum_r n_r E_r=\mathcal{E}=\mathcal{N}U$$

$$\sum_r n_r=\mathcal{N}$$

A system in the microcanonical ensemble

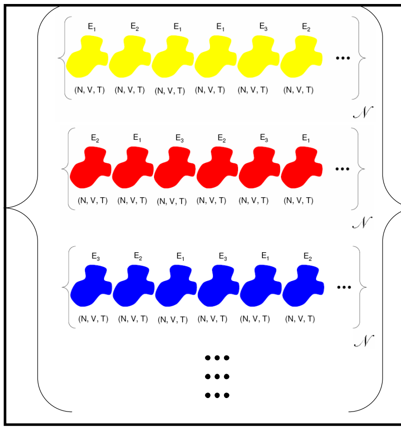


$$\begin{cases} \sum_r n_r\varepsilon_r=E \\ \sum_r n_r=N \end{cases}$$



$$\frac{11!}{3!3!2!2!1!}=277200$$

$$W\{n_i\}=\frac{N!}{n_1!n_2!\ldots n_k!}$$

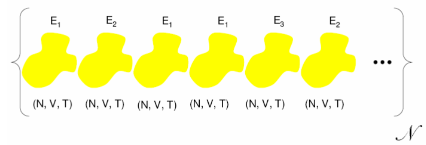


$$\sum_r n_r E_r = \mathcal{E} = \mathcal{N}U$$
$$\sum_r n_r = \mathcal{N}$$

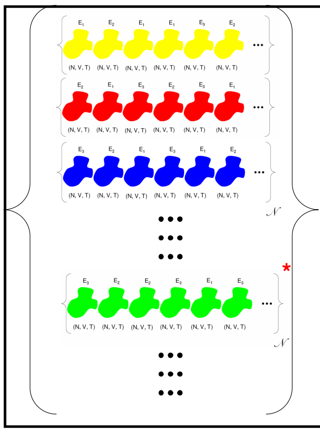
$$\sum_r n_r E_r = \mathcal{E} = \mathcal{N}U$$
$$\sum_r n_r = \mathcal{N}$$

$$\sum_r n_r E_r = \mathcal{E} = \mathcal{N}U$$
$$\sum_r n_r = \mathcal{N}$$

⋮



$$W\{n_r\} = \frac{\mathcal{N}!}{n_0!n_1!n_2!\dots}$$

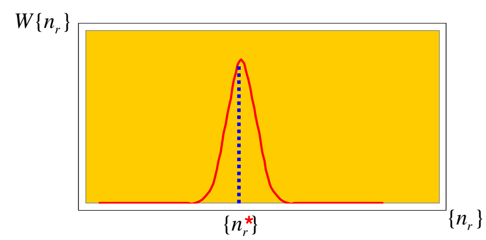


$$\sum_r n_r E_r = \mathcal{E} = \mathcal{N}U$$
$$\sum_r n_r = \mathcal{N}$$
$$\sum_r n_r E_r = \mathcal{E} = \mathcal{N}U$$
$$\sum_r n_r = \mathcal{N}$$
$$\sum_r n_r E_r = \mathcal{E} = \mathcal{N}U$$
$$\sum_r n_r = \mathcal{N}$$

⋮

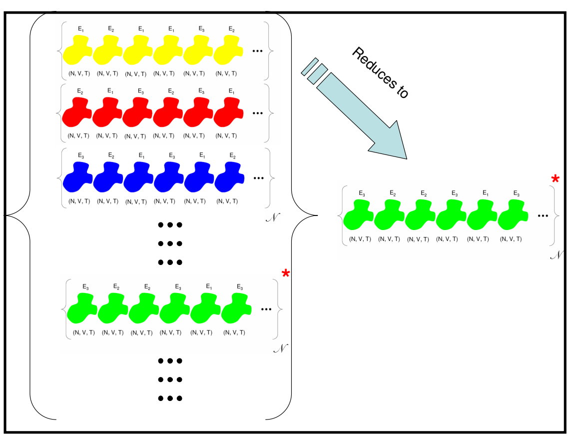
$$\sum_r n_r^* E_r = \mathcal{E} = \mathcal{N}U$$
$$\sum_r n_r^* = \mathcal{N}$$

⋮



$$P_r = \langle n_r \rangle = \frac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}} \approx \frac{n_r^*}{\sum_r n_r^*} = \frac{n_r^*}{\mathcal{N}}$$

$W\{n_r^*\} >>$ All the other $W\{n_r\}$'s



The method of most probable values

$$W\{n_r\} = \frac{\mathcal{N}!}{n_0!n_1!n_2!\dots} = \frac{\mathcal{N}!}{\prod_r n_r!}$$

$$\ln W\{n_r\} = \ln(\mathcal{N}!) - \ln(\prod_r n_r!) = \ln(\mathcal{N}!) - \sum_r \ln(n_r!)$$

$$\ln W\{n_r\} \approx \mathcal{N}\ln\mathcal{N} - \mathcal{N} - \sum_r (n_r \ln n_r - n_r)$$

$$= \mathcal{N}\ln\mathcal{N} - \mathcal{N} - \sum_r n_r \ln n_r + \sum_r n_r$$

$$= \mathcal{N}\ln\mathcal{N} - \mathcal{N} - \sum_r n_r \ln n_r + n$$

$$= \mathcal{N}\ln\mathcal{N} - \sum_r n_r \ln n_r$$

$$W\{n_r\} = \mathcal{N}\ln\mathcal{N} - \sum_r n_r \ln n_r$$

$$\begin{cases} \sum_r n_r E_r = \mathscr{E} = \mathcal{N}U \\ \sum_r n_r = \mathcal{N} \end{cases}$$

$$\delta(\ln W\{n_r\}) = 0 - \sum_r (\ln n_r + n_r \frac{1}{n_r})\delta n_r$$

$$\delta(\ln W\{n_r\}) = -\sum_r (\ln n_r + 1)\delta n_r$$

$$\delta\left[\ln W\{n_r\} - \alpha\sum_r n_r - \beta\sum_r n_r E_r\right] = 0$$

$$\begin{cases} \sum_r n_r = \mathcal{N} \\ \sum_r n_r E_r = \mathscr{E} = \mathcal{N}U \end{cases} \Longrightarrow \begin{cases} \sum_r \delta n_r = 0 \\ \sum_r E_r \delta n_r = 0 \end{cases}$$

$$\sum_r n_r E_r = \mathscr{E} = \mathcal{N}U$$

$$\sum_r (\underbrace{E_r \delta n_r}_{dQ} + \underbrace{n_r \delta E_r}_{dW}) = \underbrace{0}_{d\mathscr{E}}$$

تمرین: فصل 4 کتاب رایف

$$\delta\left[\ln W\{n_r\} - \alpha\sum_r n_r - \beta\sum_r n_r E_r\right] = 0$$

$$\delta \ln W\{n_r\} - \alpha\sum_r \delta n_r - \beta\sum_r n_r \delta E_r = 0$$

$$\delta(\ln W\{n_r\}) = -\sum_r (\ln n_r + 1)\delta n_r$$

$$-\sum_r (\ln n_r + 1)\delta n_r - \alpha\sum_r \delta n_r - \beta\sum_r E_r \delta n_r = 0$$

$$\sum_r (\ln n_r + 1 + \alpha + \beta E_r)\delta n_r = 0$$

$$\ln n_r^* + 1 + \alpha + \beta E_r = 0$$

$$\ln n_r^* = -(1+\alpha) - \beta E_r$$

$$\ln n_r^* = \ln C - \beta E_r$$

$$\ln n_r^* = \ln C - \beta E_r$$

$$\ln n_r^* - \ln C = -\beta E_r$$

$$\ln \frac{n_r^*}{C} = -\beta E_r$$

$$n_r^* = C\exp(-\beta E_r)$$

$$\sum_r n_r^* = \mathcal{N} = \sum_r C e^{-\beta E_r} = C\sum_r e^{-\beta E_r}$$

$$C = \frac{\mathcal{N}}{\sum_r e^{-\beta E_r}}$$

$$n_r^* = \frac{\mathcal{N}}{\sum_r e^{-\beta E_r}} e^{-\beta E_r}$$

$$\frac{n_r^*}{\mathcal{N}} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\sum_r n_r^* E_r = \mathscr{E}$$

$$\sum_r \mathcal{N} \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} E_r = \mathscr{E}$$

$$\mathcal{N} = cte \quad \rightarrow \quad \mathcal{N} \sum_r \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} E_r = \mathscr{E}$$

$$\sum_r \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} E_r = \frac{\mathscr{E}}{\mathcal{N}} = U$$

$$\frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{\mathscr{E}}{\mathcal{N}} = U$$