Chapter 3
Statistic Thermodynamics

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Constraints and Microstates

- Constraints:

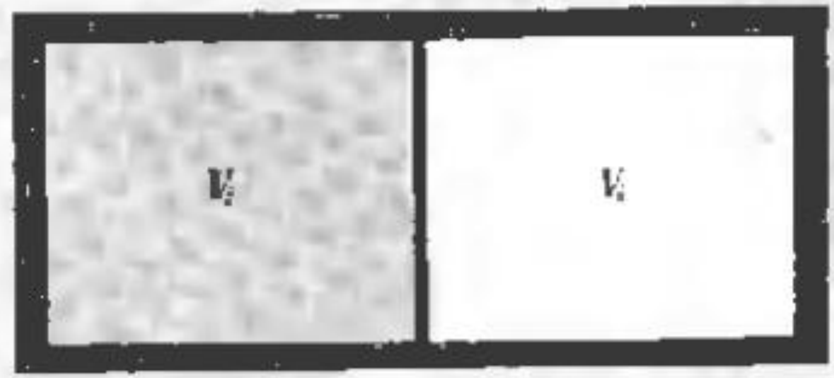
  $\Omega = \Omega\ (y_1, \ldots y_n),\ y = P, V, T\ldots$

- When constraints are removed:
  - $\Omega_f > \Omega_i$, irreversible process
  - $\Omega_f = \Omega_i$, reversible process
  - $P_i = \Omega_i / \Omega_f$

- $P(y) \propto \Omega(y)$

An Example

Fig. 2·3·2 A system consisting of a box divided by a partition into two equal parts, each of volume V_i. The left side is filled with gas; the right side is empty.



$$P_i = \left(\tfrac{1}{2}\right)^N$$

$$N \approx 6 \times 10^{22},$$

What if both sides are filled with equal amount gas?

Thermal interaction between macro systems

- A: E + dE, Ω (E); A’: E’ + dE’, Ω (E’)
- $A^{(0)} \equiv A + A'$, $E + E' = E^{(0)} = \text{constant}$
- $\mathcal{H} = \mathcal{H} + \mathcal{H}' + \mathcal{H}^{(int)}$

Probability of system A and A'

$$P(y) \propto \Omega(y) \qquad P(E) = C\Omega^{(0)}(E)$$

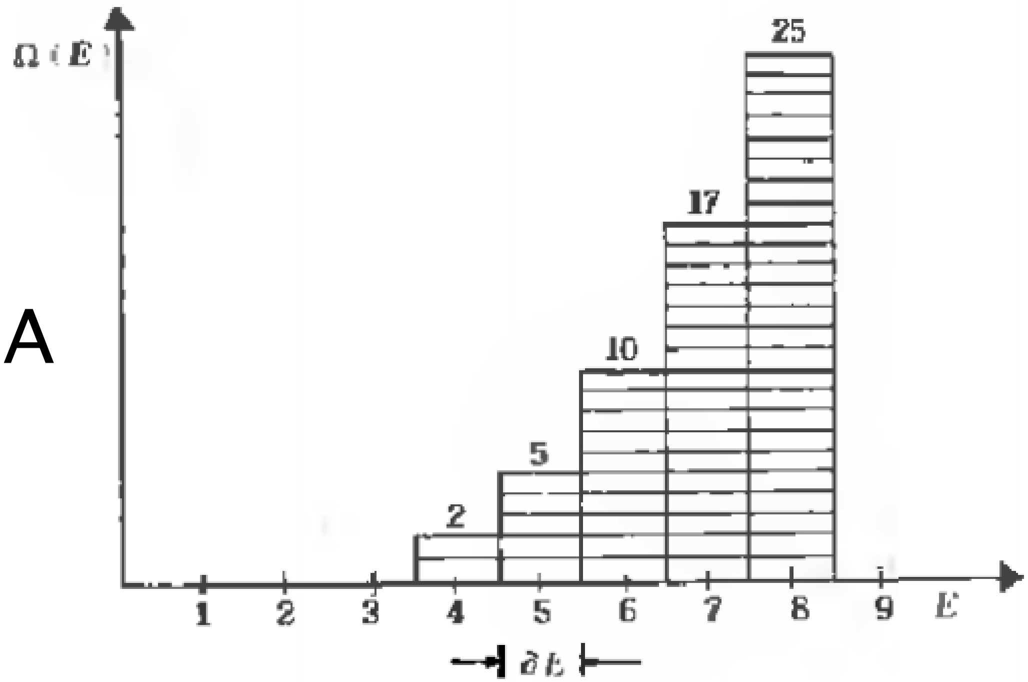
$$P(E) = \frac{\Omega^{(0)}(E)}{\Omega^{(0)}_{tot}}$$

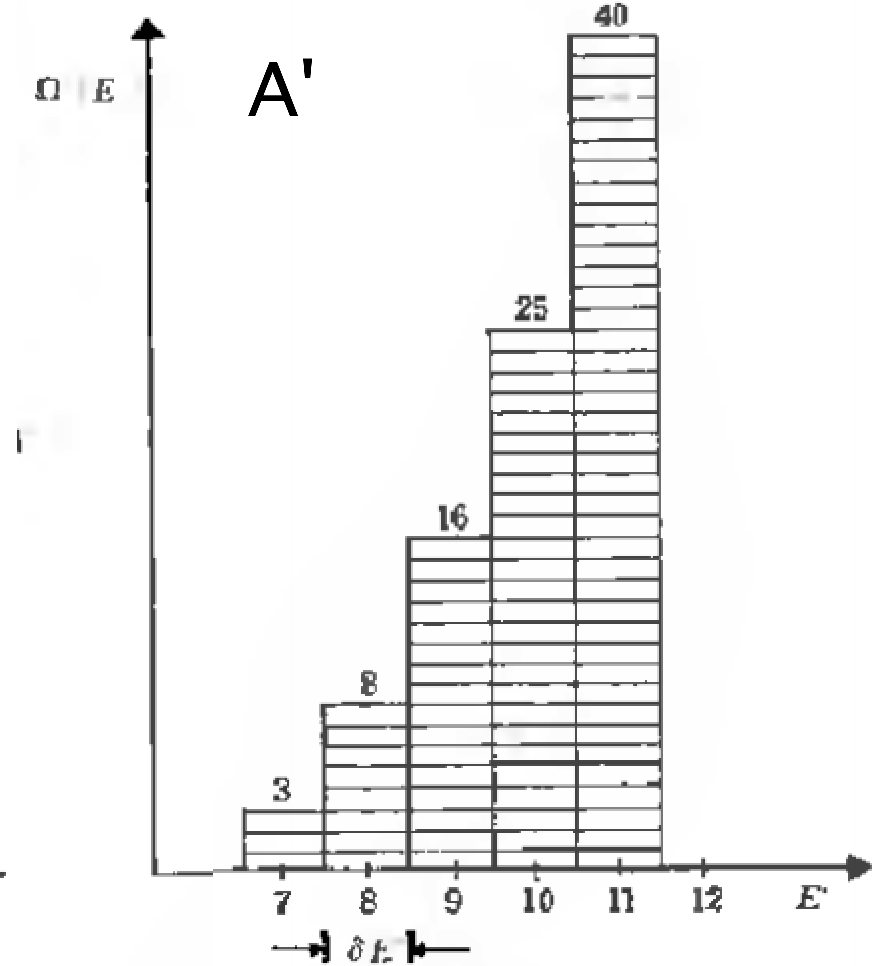
$$\Omega^{(0)}(E) = \Omega(E)\Omega'(E^{(0)} - E)$$

$$P(E) = C\Omega(E)\Omega'(E^{(0)} - E)$$

Example

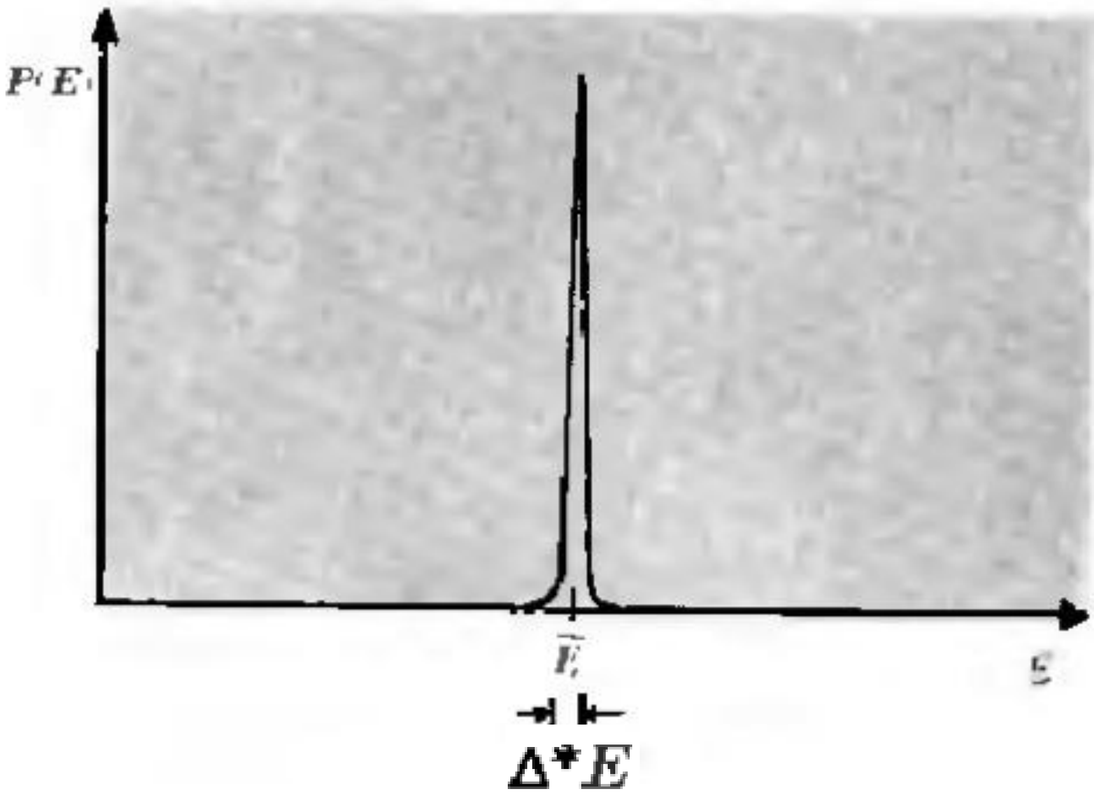
$E^{(0)} = 15$





Suppose $E =$	, then $E' =$	. Here $\Omega(E) =$	, and $\Omega'(E') =$	. Hence $\Omega^{(0)}(E) =$.
4	11	2	40	80
5	10	5	26	130
6	9	10	16	160
7	8	17	8	136
8	7	25	3	75

Sharp maximum of P(E)



$$\Omega \propto E^{f} \text{ and } \Omega' \propto E'^{f'}$$

$$P(E) = C\Omega(E)\Omega'(E^{(0)} - E)$$

$$\Delta^{*}E <<< \bar{E}$$

Energy distribution in equilibrium

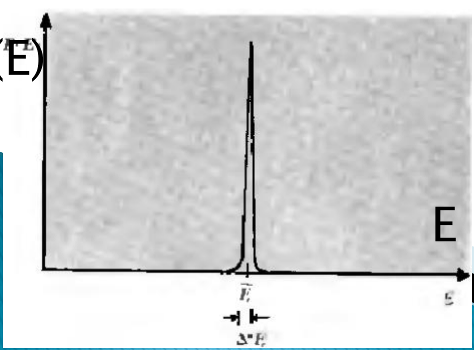
$$\Omega \propto E^{f} \text{ and } \Omega' \propto E'^{f'}$$

$$\ln P \approx f \ln E + f' \ln\left(E^{(0)} - E\right) + \text{constant}$$

$$\ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E')$$

$$\frac{\partial \ln P}{\partial E} = \frac{1}{P}\frac{\partial P}{\partial E} = 0$$, Where E = $\tilde{E}$

P (E)



$$\frac{\partial \ln \Omega(E)}{\partial E} + \frac{\partial \ln \Omega'(E')}{\partial E'}(-1) = 0$$

Energy distribution in equilibrium

$$\frac{\partial \ln \Omega(E)}{\partial E} + \frac{\partial \ln \Omega'(E')}{\partial E'}(-1) = 0$$

$$\beta(\tilde{E}) = \beta'(\tilde{E}')$$, where $$\beta(E) \equiv \frac{\partial \ln \Omega}{\partial E}$$

Reciprocal energy

$P(E)$ is maximum

If a **dimensionless parameter** **T** is introduced:

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

where *k* is some positive constant having the dimensions of energy

T and entropy S

$$\beta(E) \equiv \frac{\partial \ln \Omega}{\partial E} \qquad kT \equiv \frac{1}{\beta} \quad \Rightarrow \quad \frac{1}{T} = \frac{\partial S}{\partial E}$$

Here we define S: $S \equiv k \ln \Omega$

Therefore: when $E = \tilde{E},$ P (E) is a maximum

Ω (E) is a maximum and $S + S' = \text{maximum}$

Here, $T = T'$

S in thermal equilibrium

$$S(\tilde{E}_f) + S'(\tilde{E}_f') \geq S(\tilde{E}_i) + S'(\tilde{E}_i')$$

$$\Delta S \equiv S_f - S_i \equiv S(\tilde{E}_f) - S(\tilde{E}_i)$$
$$\Delta S' \equiv S_f' - S_i' \equiv S(\tilde{E}_f') - S(\tilde{E}_i')$$

$$\Delta S + \Delta S' \geq 0$$

Entropy do not decrease spontaneously.

Heat transfer in equilibrium

$$\bar{E}_f + \bar{E}_f' = \bar{E}_i + \bar{E}_i'$$

$$Q \equiv \bar{E}_f - \bar{E}_i$$
$$Q' \equiv \bar{E}_f' - \bar{E}_i'$$

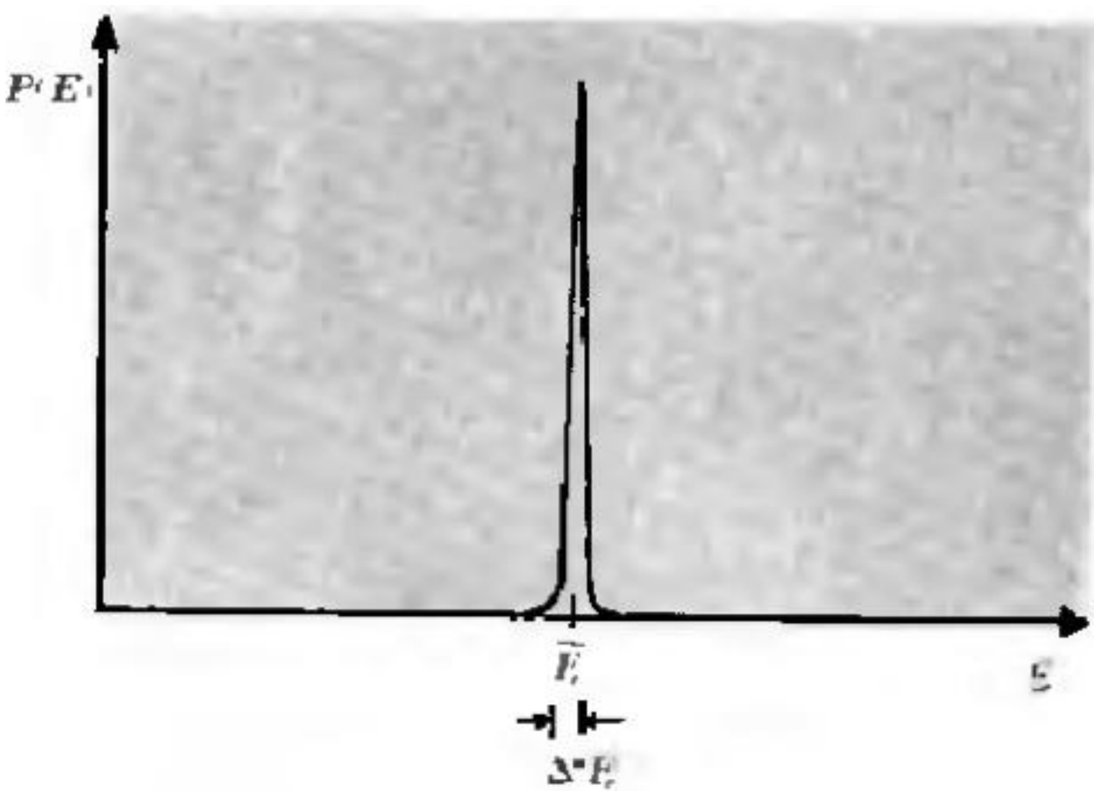
$$Q + Q' = 0$$

- **Heat transfer from hotter system to colder system**
- **Q = Q' = 0, if initial state is in equilibrium**

Temperature

Two systems will remain in equilibrium when placed in thermal contact with each other if and only if they have the same temperature (referred to the same thermometer).

Sharpness of probaility distribution



$$(\mathrm{k}T)^{-1} = \frac{d ln \Omega}{dE}$$

How sharp?

Deal with Tailor series

$$f(a)+\frac{f'(a)}{1!}(x-a)+\frac{f''(a)}{2!}(x-a)^2+\frac{f^{(3)}(a)}{3!}(x-a)^3+\cdots$$

$$\ln\Omega(E)=\ln\Omega(\tilde{E})+\left(\frac{\partial\ln\Omega}{\partial E}\right)\eta+\frac{1}{2}\left(\frac{\partial^2\ln\Omega}{\partial E^2}\right)\eta^2+\cdots$$

$$\beta\equiv\left(\frac{\partial\ln\Omega}{\partial E}\right)\qquad\lambda\equiv-\left(\frac{\partial^2\ln\Omega}{\partial E^2}\right)=-\left(\frac{\partial\beta}{\partial E}\right)$$

$$\ln\Omega(E)=\ln\Omega(\tilde{E})+\beta\eta-\tfrac{1}{2}\lambda\eta^2+\cdots$$

$$\ln\Omega'(E')=\ln\Omega'(\tilde{E}')+\beta'(-\eta)-\tfrac{1}{2}\lambda'(-\eta)^2+\cdots$$

Guassian distribution

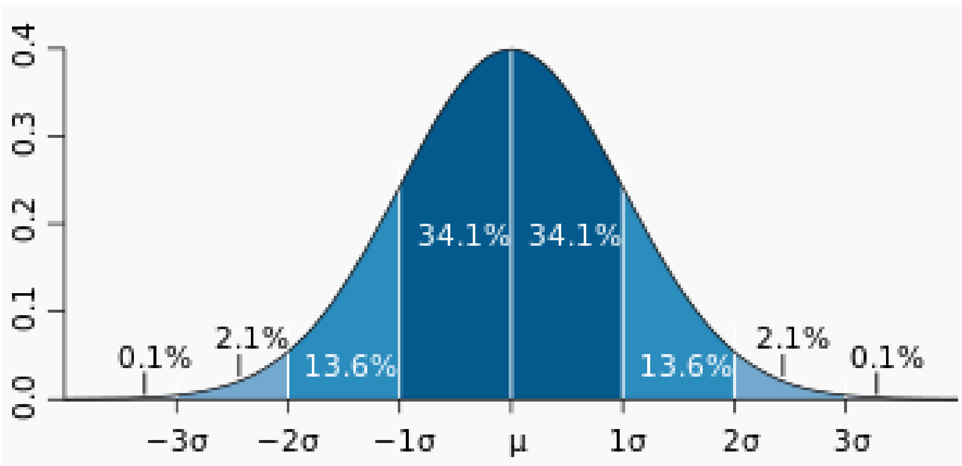
$$\ln\left[\Omega(E)\Omega'(E')\right] = \ln\left[\Omega(\tilde{E})\Omega'(\tilde{E}')\right] + (\beta - \beta')\eta - \tfrac{1}{2}(\lambda + \lambda')\eta^2$$

$$P(E) = C\Omega(E)\Omega'(E^{(0)} - E)$$

$$\ln P(E) = \ln P(\tilde{E}) - \tfrac{1}{2}\lambda_0\eta^2 \qquad \lambda_0 = \lambda + \lambda'$$

$$P(E) = P(\tilde{E})\, e^{-\frac{1}{2}\lambda_0(E-\tilde{E})^2}$$

Guassian distribution



$$P(E) = P(\bar{E})\, e^{-\frac{1}{2}\lambda_0 (E-\bar{E})^2}$$

$$f(x,\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

$$\sigma^2 = \frac{1}{\lambda_0}$$

$$\Delta^* E \sim \sigma$$

n	$F(\mu+n\sigma) - F(\mu - n\sigma)$	i.e. 1 minus …	or 1 in …
1	0.682 689 492 137	0.317 310 507 863	3.151 487 187 53
2	0.954 499 736 104	0.045 500 263 896	21.977 894 5080
3	0.997 300 203 937	0.002 699 796 063	370.398 347 345
4	0.999 936 657 516	0.000 063 342 484	15 787.192 7673
5	0.999 999 426 697	0.000 000 573 303	1 744 277.893 62
6	0.999 999 998 027	0.000 000 001 973	506 797 345.897

Sharp peak

$$\Delta^* E \sim \sigma = \frac{1}{\sqrt{\lambda_0}}$$

$$\lambda = -\left(\frac{\partial^2 \ln \Omega}{\partial E^2}\right) = -\left(\frac{\partial \beta}{\partial E}\right) \qquad \lambda_0 \approx \lambda \approx \frac{f}{\bar{E}^2} = \frac{f}{\bar{E}^2}$$

$$\frac{\Delta^* E}{\bar{E}} \approx \frac{1}{\sqrt{f}}$$