Chapter 6: Part A
Basic methods and results of statistical mechanics

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$$\boxed{\beta(E) \equiv \frac{\partial \ln \Omega}{\partial E}}$$

$$\boxed{S \equiv k \ln \Omega}$$

$$\boxed{d \ln \Omega = \beta(d\bar{E} + \sum_\alpha \bar{X}_\alpha \, d\bar{x}_\alpha)}$$

$$\bar{X}_\alpha = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial x_\alpha}$$

$$\boxed{\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\
\left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\
\left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p
\end{aligned}}$$

Aim:

- derive general probability statements for a variety of situations

- describe practical methods for calculating macroscopic properties

Ensemble representative of situations of physical interests

- **microcanonical ensemble**
  Isolated system

- **canonical ensemble**
  system in contact with a heat reservoir

- **grand canonical ensemble**
  system in contact with a reservoir exchanging E and N

Ensemble representative of situations of physical interests

6.1 Isolated system

An isolated system with V, N, and the energy is in [E, E+δE]

Fundamental statistical postulate for isolated..

Probability for finding in r state:

$$P_r = \begin{cases} C & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

$$\Sigma P_r = 1$$

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6.1 Isolated system

Probability for finding in r state:

$$P_r = \begin{cases} C & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

$$\Sigma P_r = 1$$

Mean value:

$$\bar{y} = \frac{\sum_k y_k \Omega(y_k)}{\Omega}$$

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6.2 system in contact with a heat reservoir

A<<A’

In equilibrium,

What is the probability for finding in state r of energy E_r ?

$$A^{(0)} = A + A'$$

between $E^{(0)}$ and $E^{(0)} + \delta E$.

$$\boxed{E_r + E' = E^{(0)}}$$

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6.2 system in contact with a heat reservoir

$$E' = E^{(0)} - E_r.$$

If A is in state r, the accessible number for A'

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

Probability to find A in state r is

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

$$\sum_r P_r = 1$$

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6.2 system in contact with a heat reservoir

A<<A’ $\rightarrow$ $E_r \ll E^{(0)}$

Instead of expanding Ω(E’) at E’=E_0

$$\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 E_r \cdots$$

$E_r \lll E^{(0)}$ **Neglect terms of higher order**

$$\left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 \equiv \beta$$

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6.2 system in contact with a heat reservoir

A' is so large that its T is unaffected

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

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

$\Omega'(E^{(0)})$ is just a constant independent of r,

$$P_r = C\, e^{-\beta E_r}$$

Normalization

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

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6.2 system in contact with a heat reservoir

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

Discussion on

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

$$\boxed{P_r = C\, e^{-\beta E_r}}$$

$$E_r \uparrow ==> \Omega(E_0 - E_r) \downarrow$$

The situation is less

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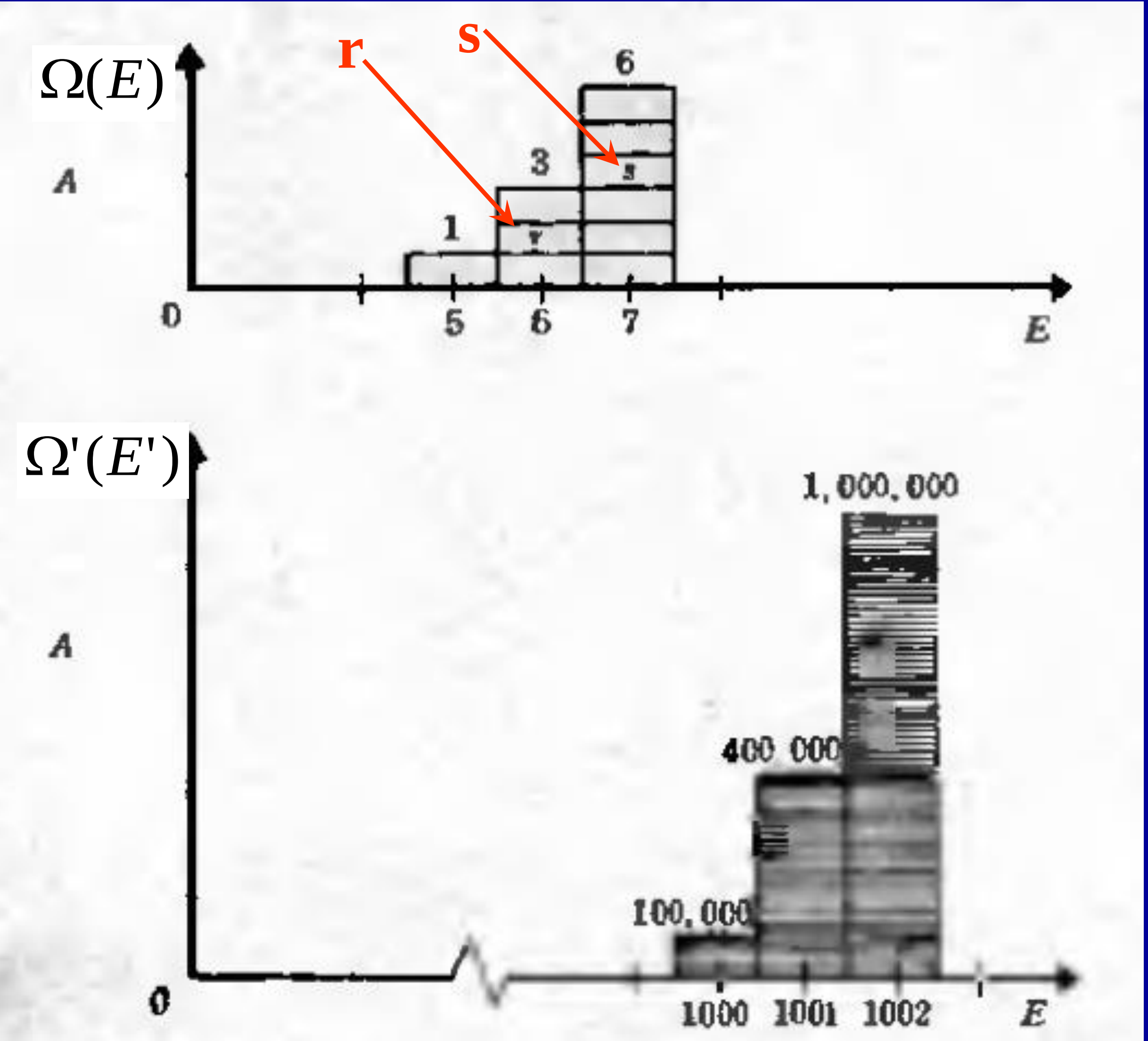
6.2 system in contact with a heat reservoir

example

$\mathrm{Suppose}\, E_0 = 1007$



r state with E=6

s state with E=7

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6.2 system in contact with a heat reservoir

Discussion on $$\boxed{P_r = C\, e^{-\beta E_r}}$$

1, is very general result and is of fundamental important in statistical mechanics;

2, $e^{-\beta E_r}$ is called the "Boltzmann factor", and the probability is known as "canonical distribution".

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6.2 system in contact with a heat reservoir

Discussion on

$$\boxed{P_r = C\, e^{-\beta E_r}}$$

is the probability of finding r state with E_r

Then the total probability for finding E in [E,E+dE]

$$\boxed{P(E) = \sum_r P_r}$$

$$\Rightarrow \boxed{P(E) = C\Omega(E)\, e^{-\beta E}}$$

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6.2 system in contact with a heat reservoir

Discussion on

$$P_r = C\, e^{-\beta E_r}$$

$$P(E) = \sum_r P_r$$

1 2 3 4	5 6 7	8 9	10
E_a	E_b	E_c	E_d

$$P(E_a) = 4 \times \exp(-\beta E_a)$$

$$P(E) = C\Omega(E)\, e^{-\beta E}$$

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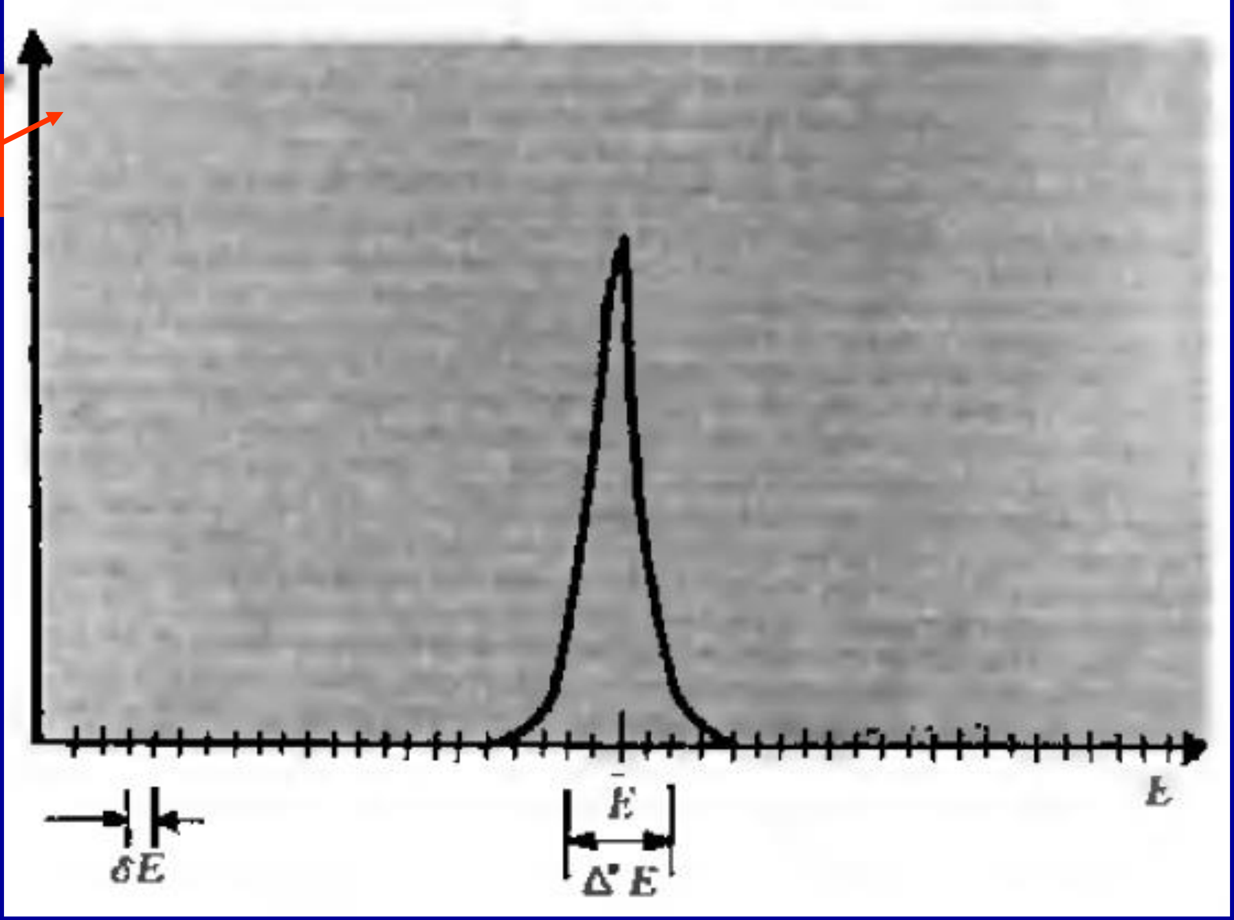
6.2 system in contact with a heat reservoir

Discussion on

$$P(E) = C\Omega(E)\, e^{-\beta E}$$



The larger A is,

The sharper is the maximum P(E)

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6.2 system in contact with a heat reservoir

Mean values

$$\bar{y} = \frac{\sum_r e^{-\beta E_r} y_r}{\sum_r e^{-\beta E_r}}$$

$$\bar{y} = \frac{\sum_E \Omega(E) e^{-\beta E} y(E)}{\sum_E \Omega(E) e^{-\beta E}}$$

Ensemble representative of situations of physical interests

6.3 Simple applications of canonical distribution

Paramagnetism

Every atom have an intrinsic spin ½ either up or down;
Define external H is up.

up $\epsilon_+ = -\mu H$ → $P_+ = C\, e^{-\beta\epsilon_+} = C\, e^{\beta\mu H}$

down $\epsilon_- = +\mu H$ → $P_- = C\, e^{-\beta\epsilon_-} = C\, e^{-\beta\mu H}$

define $$y \equiv \beta\mu H = \frac{\mu H}{kT}$$

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6.3 Simple applications of canonical distribution

Paramagnetism

$$\bar{\mu}_H = \frac{P_+\mu + P_-(-\mu)}{P_+ + P_-} = \mu\,\frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}}$$

$$\bar{\mu}_H = \mu \tanh\frac{\mu H}{kT}$$

The "magnetization" $\bar{M}_0$,

$$\tanh y \equiv \frac{e^y - e^{-y}}{e^y + e^{-y}}$$

$$\bar{M}_0 = N_0\bar{\mu}_H$$

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6.3 Simple applications of canonical distribution

Paramagnetism

Limiting behavior, if y<<1

$$\tanh y \equiv \frac{e^y - e^{-y}}{e^y + e^{-y}}$$

$$= \frac{(1 + y + \cdots) - (1 - y - \cdots)}{2} = y$$

Limiting behavior, if y>>1

$$\tanh y = 1$$

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6.3 Simple applications of canonical distribution

Paramagnetism

for $\mu H / kT \ll 1,$

$$\bar{\mu}_H = \mu \tanh \frac{\mu H}{kT}$$

$$\bar{\mu}_H = \frac{\mu^2 H}{kT}$$

$$\bar{M}_0 = \chi H$$

"magnetic susceptibility"

$$\boxed{\chi = \frac{N_0 \mu^2}{kT}}$$

Curie Law

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6.3 Simple applications of canonical distribution

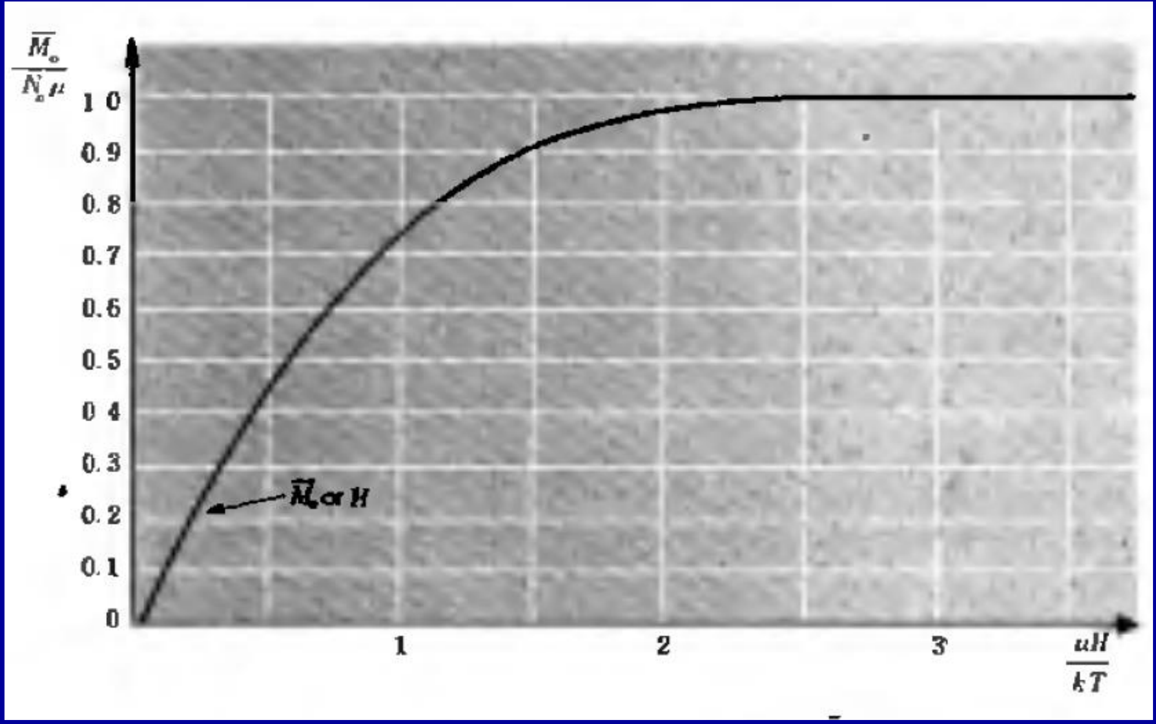
Paramagnetism

$$\bar{\mu}_H = \mu \tanh \frac{\mu H}{kT}$$

for $\mu H / kT \gg 1$,

$$\bar{\mu}_H = \mu$$

$$\bar{M}_0 \rightarrow N_0 \mu$$



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6.3 Simple applications of canonical distribution

Molecule in an ideal gas

T, V, number of molecule is small

Ignore the interaction between molecules

The total energy is the summation of all molecules

energy

$$E = \frac{1}{2} m v^2 = \frac{1}{2} \frac{\mathbf{p}^2}{m}$$

between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$

$\mathbf{p}$ and $\mathbf{p} + d\mathbf{p}$

$$d^3\mathbf{r}\, d^3\mathbf{p} \equiv (dx\, dy\, dz)(dp_x\, dp_y\, dp_z)$$

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6.3 Simple applications of canonical distribution

Molecule in an ideal gas

Probability in [r,r+dr] and [p,p+dp]

$$P(\mathbf{r},\mathbf{p})\, d^3\mathbf{r}\, d^3\mathbf{p} \propto \left(\frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h_0{}^3}\right) e^{-\beta(p^2/2m)}$$

$$\delta r\, \delta p = h_0$$

h_0^3 cell size in phase space

Probability in [p,p+dp]

$$P(\mathbf{p})\, d^3\mathbf{p} = \int_{(r)} P(\mathbf{r},\mathbf{p})\, d^3\mathbf{r}\, d^3\mathbf{p} \propto e^{-\beta(p^2/2m)}\, d^3\mathbf{p}$$

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6.3 Simple applications of canonical distribution

Molecule in an ideal gas

$$\mathbf{v} = \mathbf{p}/m.$$

$P'(\mathbf{v})\, d^3\mathbf{v}$ Probability in [v, v+dv]

$$P'(\mathbf{v})\, d^3\mathbf{v} = P(\mathbf{p})\, d^3\mathbf{p} = C\, e^{-\beta m v^2/2}\, d^3\mathbf{v}$$

C is a constant by normalization

Maxwell distribution for molecule velocity

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6.3 Simple applications of canonical distribution

Molecule in an ideal gas in the presence of gravity

Energy of a molecule:

$$E = \frac{\mathbf{p}^2}{2m} + mgz$$

g is the constant acceleration due to gravity.

Probability in [r,r+dr] and [p,p+dp]

$$P(\mathbf{r},\mathbf{p})\, d^3\mathbf{r}\, d^3\mathbf{p} \propto \frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h_0^3}\, e^{-\beta[(p^2/2m)+mgz]}$$

$$\propto d^3\mathbf{r}\, d^3\mathbf{p}\, e^{-\beta(p^2/2m)}\, e^{-\beta mgz}$$

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6.3 Simple applications of canonical distribution

Molecule in an ideal gas in the presence of gravity

Probability in [p,p+dp]

$$P(\mathbf{p})\, d^3\mathbf{p} = \int_{(\mathbf{r})} P(\mathbf{r},\mathbf{p})\, d^3\mathbf{r}\, d^3\mathbf{p}$$

$$= C\, e^{-\beta(p^2/2m)}\, d^3\mathbf{p}$$

Probability in [z, z+dz]

$$P(z)\, dz = \int_{(x,y)} \int_{(p)} P(\mathbf{r},\mathbf{p})\, d^3\mathbf{r}\, d^3\mathbf{p}$$

$$\boxed{P(z)\, dz = C'\, e^{-\beta mgz}\, dz}$$

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6.3 Simple applications of canonical distribution

Molecule in an ideal gas in the presence of gravity

$$P(z) = P(0)\, e^{-mgz/kT}$$

Sometimes called as "law of atmosphere"

Class-work

P 233 6.6

Homework

P 233   6.1,2,4,5