

Thermodynamics and Statistical Physics

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Chapter 1

Thermodynamics

Chapter 2

Classical statistical mechanics

Chapter 3

Canonical ensemble and grand canonical ensemble

3.1 Canonical ensemble

3.1.1 Canonical ensemble

Consider an isolated system made up of two subsystems

1: $N_1, V_1, H_1,$

2: N_2, V_2, H_2

with $N = N_1 + N_2, \quad V = V_1 + V_2,$

$$H = H_1(p_1, q_1) + H_2(p_2, q_2)$$

(interactions between two subsystem are negligible)

As discussed before, a decomposition $E = \bar{E}_1 + \bar{E}_2$ of the energy dominates the entropy.

A special case

$$N_2 \gg N_1, \quad \bar{E}_2 \gg \bar{E}_1$$

Let $E = E_1 + E_2$ to be any decomposition of the energy, fluctuating around $E = \bar{E}_1 + \bar{E}_2$.

We are only interested in subsystem 1. The probability of finding system 1 in a state within $dp_1 dq_1$ at (p_1, q_1) is

$$\propto dp_1 dq_1 \Gamma_2(E - E_1)$$

i.e., the density distribution

$$\rho(p_1, q_1) \propto \Gamma_2(E - E_1)$$

Understanding

Since the probability of finding system 1 at (p_1, q_1) and system 2 at (p_2, q_2) is

$$\propto dp_1 dq_1 dp_2 dq_2$$

If we look at only system 1, we should sum up all possible states of system 2,

$$\propto dp_1 dq_1 \int_{E_2=E-E_1} dp_2 dq_2 = dp_1 dq_1 \Gamma_2(E - E_1)$$

Since E_1 fluctuates only around \bar{E}_1 , and $\bar{E}_1 \ll E$

$$\begin{aligned} k \log \Gamma_2(E - E_1) &= k \log \Gamma_2(E) - E_1 \left. \frac{\partial k \log \Gamma(E_2)}{\partial E_2} \right|_{E_2=E} + \dots \\ &= S_2(E) - E_1 \left. \frac{\partial S_2(E_2)}{\partial E_2} \right|_{E_2=E} \\ &= S_2(E) - \frac{E_1}{T} \end{aligned}$$

T is the temperature of the whole system (and therefore also the temperature of system 1)

Omitting the subscript 1.

$$\rho(p, q) \propto e^{-H(p,q)/kT}$$

This is the probability distribution of the so-called canonical ensemble.

Macroscopic conditions:

- N, T fixed.
- In contact with a heat reservoir of temperature T .

such an ensemble is called the canonical ensemble.

We define the partition function

$$Q_N(V, T) \equiv \int d^{3N}p d^{3N}q e^{-H/kT}$$

then the thermodynamics is to be obtained from

$$Q_N(V, T) \equiv e^{-A(V, T)/kT}$$

where $A(V, T)$ is the free energy. To show this

- A is extensive
- A is related to U by $A = U - TS$ with

$$S \equiv - \left(\frac{\partial A}{\partial T} \right)_V.$$

Then

$$\begin{aligned} P &= - \left(\frac{\partial A}{\partial V} \right)_T & S &= - \left(\frac{\partial A}{\partial T} \right)_V \\ U &= A + TS & G &= A + PV \end{aligned}$$

In principle, the integration of $dp dq$ can not extend to $H \geq E$, but we can show that the contribution from this region is negligible small. Therefore, practically the integration extends over all energy. This provides much convenience for calculations in the canonical ensemble.

3.1.2 Energy fluctuation

Questions:

- Why are micro-canonical and canonical ensembles equivalent?
- Why do we need both ensembles?

Reading materials

Any macroscopic observable can be calculated by

$$\langle O \rangle = \frac{1}{Q_N} \int dp dq e^{-H/kT} \cdot O$$

For the energy

$$U = \langle E \rangle = \frac{1}{Q_N} \int dp dq e^{-H/kT} \cdot H$$

i.e.,

$$\int dp dq e^{A/kT - H/kT} (U - H) = 0$$

Then, differentiating both sides with respect to $\beta = \frac{1}{kT}$, we obtain

$$\frac{\partial U}{\partial \beta} + \int dp dq e^{(A-H)/kT} (U - H) (A - H - T \frac{\partial A}{\partial T}) = 0$$

since

$$\beta \frac{\partial A}{\partial \beta} = \beta \frac{\partial A}{\partial T} \frac{\partial T}{\partial \beta} = -T \frac{\partial A}{\partial T}$$

Further

$$\begin{aligned} \therefore S &= - \left(\frac{\partial A}{\partial T} \right)_V \\ U &= A - TS \end{aligned}$$

$$\therefore \frac{\partial U}{\partial \beta} + \langle (U - H)^2 \rangle = 0$$

i.e.,

$$\begin{aligned} \langle H^2 \rangle - \langle H \rangle^2 &= - \frac{\partial U}{\partial \beta} = kT^2 \frac{\partial U}{\partial T} \\ &= kT^2 C_V \end{aligned}$$

$$\begin{aligned} \therefore \langle H \rangle &\sim N \\ C_V &\sim N \end{aligned}$$

As $N \rightarrow \infty$,

$$\frac{\langle H^2 \rangle - \langle H \rangle^2}{\langle H \rangle^2} \rightarrow 0$$

Therefore, both the microcanonical and canonical ensemble are equivalent.

3.1.3 Boltzmann statistical theory

N identical particles

$$H = \sum_i \epsilon_i$$

Now i labels particles

$$\begin{aligned} Q_N(V, T) &= \sum_{p, q} e^{-\beta H} \\ &= \sum_{p, q} \prod_i e^{-\beta \epsilon_i} = \left(\sum_{p_i, q_i} e^{-\beta \epsilon_i} \right)^N \\ &= (Z(\beta, V))^N = e^{-\beta A(V, T)} \end{aligned}$$

$$\begin{aligned}
A(V, T) &= -\frac{N}{\beta} \log Z(\beta, V) = -NkT \log Z(\beta, V) \\
S &= -\left(\frac{\partial A}{\partial T}\right)_V \\
&= Nk \log Z(\beta, V) + \frac{N}{\beta} \frac{\partial \log Z(\beta, V)}{\partial \beta} \frac{\partial \beta}{\partial T} \\
&= Nk \left(\log Z(\beta, V) - \beta \frac{\partial \log Z(\beta, V)}{\partial \beta} \right)
\end{aligned}$$

Comparing $Z(\beta, V)$ here with $Z(\beta, y)$ introduced before, the only difference is that the energy for calculating $Z(\beta, V)$ here is not bonded by the total energy. But this difference is negligible small.

3.2 Some application of canonical ensemble

3.2.1 Equipartition theorem

$$H = \frac{1}{2} \sum_i a_i p_i^2 + U(\{q_i\})$$

then

$$\left\langle \frac{1}{2} a_i p_i^2 \right\rangle = \frac{1}{2} kT$$

Proof:

$$\begin{aligned}
\left\langle \frac{1}{2} a_i p_i^2 \right\rangle &= \frac{\int_{-\infty}^{+\infty} \frac{1}{2} a_i p_i^2 e^{-\beta H} [dp dq]}{\int_{-\infty}^{+\infty} e^{-\beta H} [dp dq]} \\
&= \frac{\int_{-\infty}^{+\infty} \frac{1}{2} a_i p_i^2 e^{-\beta \frac{1}{2} a_i p_i^2} dp_i}{\int_{-\infty}^{+\infty} e^{-\beta \frac{1}{2} a_i p_i^2} dp_i}
\end{aligned}$$

$$\begin{aligned}
\text{numerator} &= \int \frac{1}{2} a_i \cdot p_i^2 \left(\frac{-1}{\beta a_i p_i} \right) d \left(e^{-\beta \frac{1}{2} a_i p_i^2} \right) \\
&= \frac{-1}{2\beta} \left[p_i e^{-\beta \frac{1}{2} a_i p_i^2} \Big|_{-\infty}^{+\infty} - \int e^{-\beta \frac{1}{2} a_i p_i^2} dp_i \right] \\
&= \frac{1}{2} kT \cdot \text{denominator}
\end{aligned}$$

$$\therefore \left\langle \frac{1}{2} a_i p_i^2 \right\rangle = \frac{1}{2} kT$$

Exercise: If $H(\xi \rightarrow \pm\infty) \rightarrow \infty$, then

$$\left\langle \xi \frac{\partial H}{\partial \xi} \right\rangle = kT$$

3.2.2 Ideal gases

$$H = \frac{1}{2m} \sum_i p_i^2$$

$$\begin{aligned}
Q_N(V, T) &= \int d^{3N} p d^{3N} q e^{-\beta \frac{1}{2m} \sum_i p_i^2} \\
&= V^N \left(\int d^3 p e^{-\beta \frac{1}{2m} p^2} \right)^N \\
&= V^N (q(\beta))^N \\
q(\beta) &= \int_{-\infty}^{\infty} dp p^2 e^{-\frac{1}{2mkT} p^2} \int d\Omega \\
&= (\pi 2mkT)^{3/2}
\end{aligned}$$

$$Q_N(V, T) = e^{-A(V, T)/kT}$$

$$\begin{aligned}\therefore A(V, T) &= -kT \log Q_N(V, T) \\ &= -NkT \left(\log V + \frac{3}{2} \log \pi 2mkT \right)\end{aligned}$$

$$\begin{aligned}S &= - \left(\frac{\partial A}{\partial T} \right)_V \\ &= +Nk \left(\log V + \frac{3}{2} \log \pi 2mkT \right) + NkT \cdot \frac{3}{2} \cdot \frac{1}{T} \\ &= +Nk \left(\log V + \frac{3}{2} \log \pi 2mkT + \frac{3}{2} \right)\end{aligned}$$

$$\begin{aligned}P &= - \left(\frac{\partial A}{\partial V} \right)_T \\ &= \frac{NkT}{V}\end{aligned}$$

Equation of state

$$\begin{aligned}U &= A + TS \\ &= -NkT \left(\log V + \frac{3}{2} \log \pi 2mkT - \log V - \frac{3}{2} \log \pi 2mkT - \frac{3}{2} \right) \\ &= \frac{3}{2} NkT\end{aligned}$$

then

$$S = Nk \left(\log V + \frac{3}{2} \log \frac{\pi 4mU}{3N} + \frac{3}{2} \right)$$

Everything is the same as that from the microscopic ensemble.

Here we have neglected the factor $1/N!$ in $Q_N(V, T)$. Since this factor is also not included in $\Sigma(E)$. In general, such a factor is needed.

3.3 Ising model

The Ising model is the simplest model for magnetic materials, exhibiting a phase transition.

This is a square lattice in two-dimensions, describing a crystal. On each lattice site, there is a magnet, described by $S_i = \pm 1$

The Hamiltonian

$$-\frac{1}{kT}H = K \sum_{\langle ij \rangle} S_i S_j + h \sum S_i$$

$\langle ij \rangle$: nearest neighbour

$J = -kTK$: coupling

$\bar{h} = -kTh$: external magnetic field

Canonical ensemble

$$\rho \propto e^{-H/kT}$$

the partition function

$$Z = \sum_{\{S_i\}} e^{-H/kT}$$

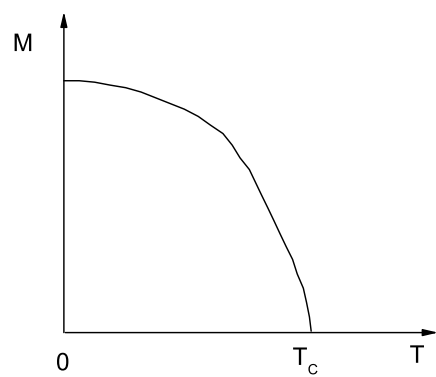
The magnetic field

$$M = \frac{1}{Z} \sum_{\{S_i\}} \frac{1}{N} \sum_i S_i e^{-H/kT}$$

Solvable models

$d = 1$ there is no real phase transition

$d = 2$ too difficult



T

Figure 3.1:

Result: as shown in Fig. 3.1

$$\boxed{h = 0}$$

$$\begin{array}{llll}
 T > T_C & M = 0 & & \\
 T < T_C & M \neq 0 & & \\
 T = T_C & M = 0 & \text{continuous} & \\
 & \partial M / \partial T & \text{discontinuous} & \\
 T \lesssim T_C & M \propto (-\tau)^\beta & \tau = \frac{T - T_C}{T_C} &
 \end{array}$$

Mean-field approximation

How to make approximation

- After approximation, one can perform the calculation
- Clear physical meaning, and at extreme conditions, the approximation should be correct or roughly correct

$$\sum_{\langle ij \rangle} S_i S_j \rightarrow \sum_{\langle ij \rangle} S_i \langle S \rangle = d \langle S \rangle \sum_i S_i$$

$$-\frac{1}{kT} H = -\frac{1}{kT} \sum_i H_i$$

$$-\frac{1}{kT} H_i = Kd \langle S \rangle S_i + h S_i$$

$$Z = Z_i^N \quad Z_i = \sum_{S_i = \pm 1} e^{-\frac{1}{kT} H_i}$$

$$\begin{aligned}
M &= \langle S_i \rangle = \frac{1}{Z_i} \sum_{S_i=\pm 1} S_i e^{-\frac{1}{kT} H_i} \\
&= \tanh(Kd \langle S \rangle + h)
\end{aligned}$$

Self-consistent condition

$$M = \langle S \rangle$$

For $h = 0$,

$$M = \tanh(KdM)$$

Since

$$\tanh x = x - \frac{1}{3}x^3 + \dots$$

$$\therefore M = KdM - \frac{1}{3}(KdM)^3 + \dots$$

Graphical solutions: as shown in Fig. 3.2

For $Kd < 1$, there is only one solution

$$M = 0.$$

For $Kd > 1$, there are two solutions

$$M = 0$$

and

$$M = \pm M_0.$$

In an equilibrium state, the free energy should reach its minimum, and one can prove that $M = \pm M_0$ is a physical solution.

$$\therefore K_C d = 1, \quad K_C = \frac{1}{d}$$

The phase transition takes place.

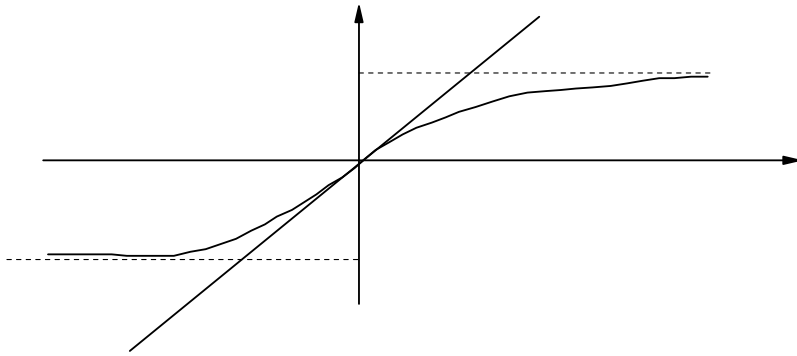


Figure 3.2:

What are the features of the system around K_C ?

$$K = K_C, \quad M = 0$$
$$K = K_C + \Delta K \quad \Delta K \text{ small} \Rightarrow M \text{ small}$$

$$\therefore M = (K_C + \Delta K)dM - \frac{1}{3}(K_C + \Delta M)^3 d^3 M^3$$
$$\approx M + \Delta K dM - \frac{1}{3}M^3 - \Delta K dM^3$$

$$\therefore M = \pm M_0 = \pm \sqrt{3 \frac{\Delta K}{K_C}}$$

Exercise: Derive $\partial M / \partial \Delta K, U$ and C_V at and around K_C discuss their behavior at and around K_C .

Under what conditions is the mean-field approximation almost correct?

- Higher spatial dimensions
- Long-range interactions

Advanced methods in statistical physics:

Approximate methods

- Mean-field methods, and improved mean-field methods
- Variational methods
- Series expansions, (High temperature and low temperature expansions, cumulant expansions. . .)

- Renormalization group methods (Real space, momentum space)

Exact methods

- Numerical solutions
- Monte carlo simulations
- Molecular dynamics

3.4 Grand canonical ensemble

Now we allow the number of particles to be non-conserved. The idea here is similar to that for deriving the canonical ensemble.

Γ space: spanned by (p, q, N) , $N = 0, 1, 2, \dots$

Grand canonical ensemble:

A collection of systems, identical in composition and macroscopic conditions, but existing in different microscopic states and different numbers of particles, without interactions each other.

A member of the ensemble (or a microscopic state), is represented by a point in the Γ space. The density distribution of these points is denoted by $\rho(p, q, N)$

To find $\rho(p, q, N)$, we consider a canonical ensemble of N particles, volume V , and temperature T .

We divide the system into two subsystems:

1: N_1, V_1

2: $N_2 = N - N_1, \quad V_2 = V - V_1$
and assume

$$V_2 \gg V_1, \quad N_2 \gg N_1$$

and designate the coordinates of N_1 , particles in V_1 by $\{p_1, q_1\}$, and those in V_2 by $\{p_2, q_2\}$

$$H(p, q, N) = H(p_1, q_1, N_1) + H(p_2, q_2, N_2)$$

Note that here $H(p_1, q_1, N_1)$ and $H(p_2, q_2, N_2)$ are the same functions evaluated at different values of arguments. This is different from the discussion in canonical ensemble, since we allow interchange of particles in two subsystems.

If a particle moves from V_2 to V_1 we change its coordinates from $\{p_2, q_2\}$, to $\{p_1, q_1\}$.

Reading materials

The partition function of the whole system

$$\begin{aligned} Q_N(V, T) &= \int \frac{dp dq}{N!} e^{-H(p,q)/kT} \\ &= \frac{1}{N!} \int dp_1 dp_2 \sum_{N_1=0}^N \frac{N!}{N_1! N_2!} \int_{V_1} dq_1 \int_{V_2} dq_2 \\ &\quad \cdot \exp[-(H(p_1, q_1, N_1) + H(p_2, q_2, N_2))/kT] \end{aligned}$$

↑

(now dq_1 is restricted to V_1 , dq_2 to V_2 , we need $\sum_{N_1} \dots$)

$$= \sum_{N_1=0}^N \frac{1}{N_1!} \int_{V_1} dp_1 dq_1 e^{-H(p_1, q_1, N_1)/kT} \frac{1}{N_2!} \int_{V_2} dp_2 dq_2 e^{-H(p_2, q_2, N_2)/kT}$$

Therefore

$$\rho(p_1, q_1, N_1) = \frac{Q_{N_2}(V_2, T)}{Q_N(V, T)} \frac{e^{-H(p_1, q_1, N_1)/kT}}{N_1!}$$

$$\frac{Q_{N_2}(V_2, T)}{Q_N(V, T)} = \exp\{-[A(N - N_1, V - V_1, T) - A(N, V, T)]/kT\}$$

Since $N \gg N_1, \quad V \gg V_1$

$$A(N - N_1, V - V_1, T) - A(N, V, T) = -N_1\mu + V_1P$$

where μ and P are respectively the chemical potential and the pressure of the whole system

$$\mu = \left(\frac{\partial A(N_2, V, T)}{\partial N_2} \right)_{N_2=N}$$

$$P = - \left(\frac{\partial A(N, V_2, T)}{\partial V_2} \right)_{V_2=V}$$

- μ is intensive, $\mu = \mu(N, V, T) = \mu\left(\frac{V}{N}, T\right)$
- In equilibrium $\mu = \mu\left(\frac{V_1}{N_1}, T\right)$

end reading materials

Omitting the subscript 1.

$$\rho(p, q, N) = \frac{e^{\beta\mu N}}{N!} e^{-\beta PV - \beta H(p, q)} \quad \beta = \frac{1}{kT}$$

In thermodynamic limit $0 \leq N < \infty$

To obtain thermodynamics, we define the grand partition function

$$Z(\mu, V, T) \equiv \sum_{N=0}^{\infty} e^{\beta\mu N} Q_N(V, T)$$

then

$$\frac{PV}{kT} = \log Z(\mu, V, T)$$

The average number of particles

$$\begin{aligned}\bar{N} &= \langle N \rangle = \frac{1}{Z(\mu, V, T)} \sum_{N=0}^{\infty} N e^{\beta\mu N} Q_N(V, T) \\ &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z(\mu, V, T)\end{aligned}$$

$$\therefore \mu = \mu(\bar{N}, V, T)$$

Eliminating μ from above two equations, we obtain the equation of state

$$P = P(\bar{N}, V, T)$$

To calculate the internal energy, we denote $y = e^{\beta\mu}$,

$$U = -\frac{\partial}{\partial \beta} \log Z(y, V, T) \Big|_{y, V}, \quad U = U(\bar{N}, V, T),$$

then

$$\begin{aligned}C_V &= \left(\frac{\partial U}{\partial T} \right)_{V, \bar{N}} \\ S &= \int_0^T dT \frac{C_V}{T} \\ A &= U - TS\end{aligned}$$

Compared with the canonical ensemble, we have one more parameter μ , or \bar{N}

It is possible to prove that

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} \propto \frac{1}{\langle N \rangle} \xrightarrow{\langle N \rangle \rightarrow \infty} 0$$

therefore, the grand canonical ensemble are equivalent.

3.5 The chemical potential

3.5.1 Thermodynamics

The chemical potential μ is defined such that the free energy changes by $\mu d\bar{N}$, when the number of particles changes by $d\bar{N}$, at constant T and V ,

$$dA = -PdV - SdT + \mu d\bar{N}.$$

Then, we may deduce a generalized form of the first law

$$dU = -PdV + TdS + \mu d\bar{N}$$

That is, μ is the energy carried by one particle, if S and V are kept at constant. When μ is positive, it drives \bar{N} to smaller values, to lower the energy.

For an ideal gas

$$Q_N = V^N (\pi 2mkT)^{3N/2} / N!$$

$$\begin{aligned} A(N, V, T) &= -NkT(\log V + \frac{3}{2} \log \pi 2mkT - \log N + 1) \\ &\quad (\text{since } N! = N \log N - N) \\ &= -NkT(\log \frac{V}{N} + \frac{3}{2} \log \pi 2mkT + 1) \end{aligned}$$

$$\begin{aligned} \mu &= \left(\frac{\partial A}{\partial \bar{N}} \right)_{V,T} \\ &= -kT(\log \frac{V}{N} + \frac{3}{2} \log \pi 2mkT + 1) - NkT(-\frac{1}{N}) \\ &= -kT(\log \frac{V}{N} + \frac{3}{2} \log \pi 2mkT) \end{aligned}$$

Here we should not forget the factor $1/N!$ in Q_N , since it solves the problem of Gibbs, paradox.

Exercise: Derive thermodynamics of an ideal gas, i.e. equation of state,

$$U, C_V, S, A$$

3.5.2 Chemical equilibrium

Suppose there are two kinds of particles in the grand canonical ensemble, and $H = H_1 + H_2$, neglect the interactions,

$$Z = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} Q_{N_1} Q_{N_2} e^{\beta(\mu_1 N_1 + \mu_2 N_2)}$$

$$Q_{N_i} = e^{-A(N_i, V, T)/kT}$$

$$A = \sum_{i=1}^2 A_i$$

$$\mu_i = \left. \frac{\partial A}{\partial N_i} \right|_{T, V \text{ and other } N_j \text{ kept constant}}$$

$$A_i = -kT \log Q_{N_i}$$

e.g., mixture of water and ice, a molecule of water can be converted to that of ice, and vice versa.

Assume that number of total particles is conserved, i.e., $N = N_1 + N_2$ is a constant.

In equilibrium, the free energy reaches its minimum.

$$0 = \delta A = \sum_i \delta A_i = \sum_i \frac{\partial A_i}{\partial N_i} \delta N_i = \sum_i \mu_i \delta N_i$$

From conservation of particle number

$$0 = \delta N = \sum \delta N_i$$

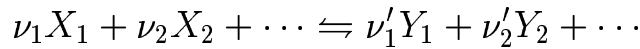
we obtain a condition for equilibrium

$$\mu_1 \delta N_1 + \mu_2 \delta N_2 = \mu_1 \delta N_1 - \mu_2 \delta N_1 = 0$$

i.e., $\mu_1 = \mu_2(V/N, T)$ as shown in Fig. 3.3

reading materials

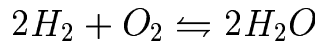
In general, we may have several kinds of particles, and a reaction



We rewrite Y by X , and ν' by ν , then

$$\sum_{i=1}^K \nu_i X_i = 0$$

e.g.,



$$\nu_1 = 2, \nu_2 = 1, \nu_3 = -2$$

Now, conservation of particle number is

$$\frac{\delta N_1}{\nu_1} = \frac{\delta N_2}{\nu_2} = \dots = \frac{\delta N_K}{\nu_K} = \mathbf{const} \equiv \delta N$$

e.g.,

$$\frac{\delta N_{H_2}}{2} = \frac{\delta N_{O_2}}{1} = \frac{\delta N_{H_2O}}{-2}$$

Then, minimizing A

$$0 = \delta A = \sum_i \frac{\partial A_i}{\partial N_i} \delta N_i = \sum_i \mu_i \nu_i \delta N$$

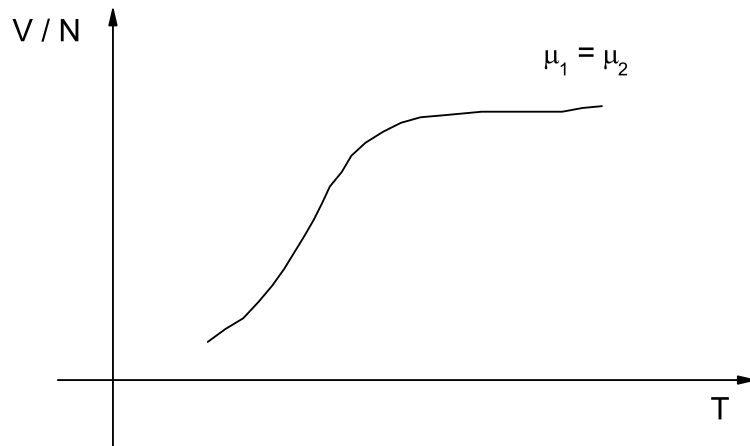


Figure 3.3:

we obtain

$$\sum_{i=1}^K \mu_i \nu_i = 0$$

Exercise:

With the canonical ensemble, prove that if $H(\xi \rightarrow \pm\infty) \rightarrow \infty$, then

$$\langle \xi \frac{\partial H}{\partial \xi} \rangle = kT$$

With the mean-field approximation of the Ising model, derive $\partial M / \partial \Delta K$, U and C_V at and around K_C , and discuss their behavior at and around K_C .

With the grand canonical ensemble, derive thermodynamics of an ideal gas, i.e., equation of state, U , C_V , S , A .

Problems 7.1, 7.2 and 7.3 in the textbook.