# Chapter 3 Statistical Mechanics

Ye Liang

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## 3.1

Assume the system is conservative and the mass of every particle is invariant. We can use the Euler-Lagrange equation to describe the system.

$$L(\mathbf{r}_i, \dot{\mathbf{r}}_i, t) = \sum_i \frac{1}{2} m_i \dot{\mathbf{r}}^2 - U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) \tag{1}$$

Using Euler-Lagrange equation

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{r}}_i} - \frac{\partial L}{\partial \mathbf{r}_i} = 0 \tag{2}$$

The differential equations are

$$m_i \ddot{\mathbf{r}} = -\nabla_i U \tag{3}$$

which is essentially the Newton's second law.

## 3.2

The system with an internal constraint is not ergodic.

## 3.3

The trace of a gas particle in a isolated box. The distribution is uniform if we ignore the possible minor difference near the boundary. In the middle space of the box, where the potential is uniform, the position the classical particle locates when being measured is equally likely.

## 3.4

$$\bar{\Omega}(N, V, E) = \sum_i \Omega_i \delta(E_i) \tag{4}$$

where $\Omega_i$ is the degeneracy of the energy state $E_i$, or the number of states that has energy $E_i$. $\delta(x)$ is the Dirac delta function.

## 3.5

In this system, when $n$ out of $N$ spins flipped up against the field,

$$\Omega = \binom{N}{n} = \frac{N!}{(N-n)!n!} \tag{5}$$

Assume $N$ and $n$ are large enough to apply the Stirling's formula for factor

$$\ln \Omega \approx N \ln N - (N-n)\ln(N-n) - n \ln n \tag{6}$$

The energy of the system is

$$E = -(N-2n)H \tag{7}$$

where $H$ is the uniform field strength.

$$\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = \left(\frac{\partial \ln \Omega}{\partial n}\right)_{N,V} \left(\frac{\partial n}{\partial E}\right)_{N,V} = \frac{1}{2H} \ln\left(\frac{N-n}{n}\right) \tag{8}$$

It can be seen that when $n > N/2$, $\beta < 0$. Easy to see that these states have more spins flipped against the field than those lined up with the field. This is the population inversion. Easy to see these states are not stable solutions in thermodynamics.

## 3.6

$$\begin{aligned}
\left(\frac{\partial(\beta A)}{\partial \beta}\right)_{N,V} \equiv \left(\frac{\partial\left(\dfrac{A}{T}\right)}{\partial\left(\dfrac{1}{T}\right)}\right)_{N,V} &= \left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_{N,V} \left(\frac{dT}{d\left(\frac{1}{T}\right)}\right) \\
&= \left[\frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_{N,V} + A\left(\frac{d\left(\frac{1}{T}\right)}{dT}\right)\right]\left(\frac{dT}{d\left(\frac{1}{T}\right)}\right) \\
&= \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_{N,V}(-T^2) + A \\
&= TS + A = E.
\end{aligned} \tag{9}$$

## 3.7

For simplicity, suppose $\{|v\rangle\}$ are a complete set of eigenvectors of $H$ corresponding to $\{E_i\}$, $v$ for different states. Then

$$\mathrm{Tr}(He^{-\beta H}) = \sum_v E_v e^{-\beta E_v} \tag{10}$$

$$\mathrm{Tr}(e^{-\beta H}) = \sum_v e^{-\beta E_v} = Q \tag{11}$$

Thus

$$\frac{\mathrm{Tr}(He^{-\beta H})}{\mathrm{Tr}(e^{-\beta H})} = \frac{\sum_v E_v e^{-\beta E_v}}{\sum_v e^{-\beta E_v}} = \langle E_v \rangle. \tag{12}$$

## 3.8

$$\begin{aligned}
\ln P(E) &= \ln \Omega(E) - \beta E + C \\
&= \ln \Omega(\langle E \rangle + \delta E) - \beta(\langle E \rangle + \delta E) + C
\end{aligned} \tag{13}$$

$$\ln \Omega(\langle E \rangle + \delta E) = \ln \Omega(\langle E \rangle) + \left.\frac{d \ln \Omega}{dE}\right|_{E=\langle E \rangle} \delta E + \left.\frac{d^2 \ln \Omega}{dE^2}\right|_{E=\langle E \rangle} (\delta E)^2 + O[(\delta E)^3] \tag{14}$$

$$\ln P(E) = C + \ln\Omega(\langle E\rangle) - \beta\langle E\rangle + \left( \left.\frac{d\ln\Omega}{dE}\right|_{E=\langle E\rangle} - \beta \right)\delta E + \left.\frac{d^2\ln\Omega}{dE^2}\right|_{E=\langle E\rangle} (\delta E)^2 + O[(\delta E)^3] \tag{15}$$

$$\ln P(E) \approx C + \ln\Omega(\langle E\rangle) - \beta\langle E\rangle - \frac{1}{k_B T^2 C_V}(\delta E)^2 \tag{16}$$

$$\ln\frac{P(\langle E\rangle + \delta E)}{P(\langle E\rangle)} = -\frac{1}{k_B T^2 C_V}(\delta E)^2 \tag{17}$$

When $\delta E = 10^{-6}\langle E\rangle$, $C_V = \frac{3}{2}Nk_B$,

$$\ln\frac{P(\langle E\rangle + \delta E)}{P(\langle E\rangle)} = -10^{-12} \times \frac{3}{2} \times 0.001 \times 6.022 \times 10^{23} = -9.033 \times 10^{8} \tag{18}$$

$$\therefore\ \frac{P(\langle E\rangle + \delta E)}{P(\langle E\rangle)} = \exp(-9.033 \times 10^{8}) \approx 3.139 \times 10^{-392298206}. \tag{19}$$

## 3.9

(i)

$$\Omega = \frac{N!}{(N-m)!m!} \tag{20}$$

$$\frac{m}{N} = \frac{1}{1+e^{\beta\varepsilon}} \tag{21}$$

$$\begin{aligned}
S =& k_B \ln\Omega = k_B[\ln N! - \ln(N-m)! - \ln m!] \\
\approx& k_B[N\ln N - (N-m)\ln(N-m) - m\ln m] \\
=& -k_B\left( N\ln\frac{N-m}{N} - m\ln\frac{N-m}{m} \right) \\
=& -k_B\left[ N\ln\left(1 - \frac{1}{1+e^{\beta\varepsilon}}\right) - m\ln\left(1+e^{\beta\varepsilon}-1\right) \right] \\
=& Nk_B\left[ \ln\left(1+e^{-\beta\varepsilon}\right) + \frac{\beta\varepsilon}{1+e^{\beta\varepsilon}} \right].
\end{aligned} \tag{22}$$

When $\beta \to +\infty$, $S \to Nk_B\left[\ln(1) + 0\right] = 0$.
(ii)

$$S(E,N) = -k_B\left( N\ln\frac{N-E/\varepsilon}{N} - \frac{E}{\varepsilon}\ln\frac{N-E/\varepsilon}{E/\varepsilon} \right). \tag{23}$$

$$\frac{E}{N\varepsilon} = \frac{1}{1+e^{\beta\varepsilon}}. \tag{24}$$

Thus

$$\beta = \frac{1}{\varepsilon}\ln\left(\frac{N\varepsilon}{E} - 1\right). \tag{25}$$

(iii) When $1 < \dfrac{N\varepsilon}{E} < 2$, $\beta < 0$.

## 3.10

$$\begin{aligned}
S/k_B =& -\beta A + \beta\langle E\rangle \\
=& N\ln(1+e^{-\beta\varepsilon}) + N\frac{\beta\varepsilon}{1+e^{\beta\varepsilon}}.
\end{aligned} \tag{26}$$

This agrees with the result in Exercise 3.9.

## 3.11

Now derive the probability $P_v$ for a system with $\Omega = \Omega(E, X)$,

$$\begin{aligned} P_v \propto \Omega(E - E_v, X - X_v) &\approx \exp\left[\ln\Omega(E,X) - E_v \left(\frac{\partial \ln\Omega}{\partial E}\right)_X \bigg|_{E,X} - X_v \left(\frac{\partial \ln\Omega}{\partial X}\right)_E \bigg|_{E,X}\right] \\ &= \exp\left[\ln\Omega(E,X) - \beta E_v - \xi X_v\right] \end{aligned} \tag{27}$$

Therefore

$$P_v \propto \exp(-\beta E_v - \xi X_v). \tag{28}$$

Define

$$\Xi = \sum_v \exp(-\beta E_v - \xi X_v). \tag{29}$$

Then

$$P_v = \exp(-\beta E_v - \xi X_v)/\Xi. \tag{30}$$

## 3.12

For the microcanonical ensemble,

$$P_v = \frac{1}{\Omega(N,V,E)} \text{ for any } v, \quad \sum_v P_v = 1 \tag{31}$$

$$S = k_B \ln\Omega(N,V,E) = -k_B \ln P_v = -k_B \sum_v P_v \ln P_v. \tag{32}$$

The result is consistent with the Gibbs formula.

## 3.13

Assume

$$S = \sum_v P_v f(P_v) \tag{33}$$

If $S$ is extensive,

$$S_{AB} = S_A + S_B, \tag{34}$$

where

$$S_{AB} = \sum_{v_A}\sum_{v_B} P_{AB}(v_A, v_B) f(P_{AB}(v_A, v_B)), \tag{35}$$

$$S_A = \sum_{v_A} P_A(v_A) f(P_A(v_A)), \quad S_B = \sum_{v_B} P_B(v_B) f(P_B(v_B)), \tag{36}$$

and

$$P_{AB}(v_A, v_B) = P_A(v_A) P_B(v_B) \tag{37}$$

Then we have an equation for function $f(P_v)$

$$\sum_{v_A}\sum_{v_B} P_A(v_A)P_B(v_B) f(P_A(v_A)P_B(v_B)) = \sum_{v_A} P_A(v_A) f(P_A(v_A)) + \sum_{v_B} P_B(v_B) f(P_B(v_B)), \tag{38}$$

$$\sum_{v_A}\sum_{v_B} P_A(v_A)P_B(v_B)f(P_A(v_A)P_B(v_B)) = \sum_{v_A}\sum_{v_B} P_A(v_A)P_B(v_B)f(P_A(v_A)) + \sum_{v_A}\sum_{v_B} P_A(v_A)P_B(v_B)f(P_B(v_B)),$$

$$\sum_{v_A}\sum_{v_B} P_A(v_A)P_B(v_B)\left[f(P_A(v_A)P_B(v_B)) - f(P_A(v_A)) - f(P_B(v_B))\right] = 0 \tag{39}$$

Thus

$$f(P_A(v_A)P_B(v_B)) = f(P_A(v_A)) + f(P_B(v_B)) \tag{40}$$

Therefore $f(x)$ should be

$$f(x) = c \ln x. \tag{41}$$

## 3.14

The constraint for the variance is

$$\sum_v P_v = 1, \quad \sum_v P_v E_v = \langle E \rangle, \quad \sum_v P_v N_v = \langle N \rangle \tag{42}$$

Then we use the Lagrange multipliers $\alpha$, $\beta$ and $\gamma$ for $(\delta S)_{\langle E \rangle, V, \langle N \rangle} = 0$

$$\delta\left[-\sum_v P_v \ln P_v - \alpha\left(\sum_v P_v - 1\right) - \beta\left(\sum_v P_v E_v - \langle E \rangle\right) - \gamma\left(\sum_v P_v N_v - \langle N \rangle\right)\right] = 0 \tag{43}$$

$$(-\ln P_v - 1 - \alpha - \beta E_v - \gamma N_v)\delta P_v = 0 \tag{44}$$

Then

$$P_v = \exp\left[-(1+\alpha) - \beta E_v - \gamma N_v\right] = \Xi^{-1}\exp(-\beta E_v - \gamma N_v) \tag{45}$$

where

$$\Xi = \exp(1+\alpha) = \sum_v \exp(-\beta E_v - \gamma N_v) \tag{46}$$

We find

$$S = -k_B \sum_v P_v \ln P_v = k_B \sum_v P_v \left[\ln \Xi + \beta E_v + \gamma N_v\right] = k_B(\ln \Xi + \beta\langle E \rangle + \gamma \langle N \rangle) \tag{47}$$

Then

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} = k_B \beta \tag{48}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} = k_B \gamma \tag{49}$$

Therefore

$$\beta = \frac{1}{k_B T}, \quad \gamma = -\frac{\mu}{k_B T} = -\beta\mu. \tag{50}$$

$$TS = k_B T \ln \Xi + E - \mu N \tag{51}$$

Thus

$$-k_B T \ln \Xi = E - TS - \mu N = -pV \tag{52}$$

$$\ln \Xi = \beta p V \tag{53}$$

or,

$$\Xi = \exp(\beta p V). \tag{54}$$

## 3.15

(i)

$$P_v = \Xi^{-1} \exp\left(-\beta E^{(v)} + \sum_i \beta\mu_i N_i^{(v)}\right) \tag{55}$$

$$\left(\frac{\partial\langle N_i\rangle}{\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} = \left(\frac{\partial\sum_v P_v N_i^{(v)}}{\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} = \sum_v N_i^{(v)}\left(\frac{\partial P_v}{\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} \tag{56}$$

$$\left(\frac{\partial P_v}{\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} = P_v N_j^{(v)} - P_v\langle N_j\rangle \tag{57}$$

Therefore

$$\left(\frac{\partial\langle N_i\rangle}{\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} = \sum_v P_v N_i^{(v)} N_j(v) - \sum_v P_v N_i^{(v)}\langle N_j\rangle = \langle N_i N_j\rangle - \langle N_i\rangle\langle N_j\rangle = \langle\delta N_i\delta N_j\rangle. \tag{58}$$

(ii)

$$\langle\delta N_i\delta N_l\delta N_j\rangle = \langle N_i N_l N_j\rangle - \langle\delta N_i\delta N_l\rangle\langle N_j\rangle - \langle\delta N_i\delta N_j\rangle\langle N_l\rangle - \langle\delta N_i\delta N_j\rangle\langle N_l\rangle - \langle N_i\rangle\langle N_j\rangle\langle N_l\rangle \tag{59}$$

$$\left(\frac{\partial^2\langle N_i\rangle}{\partial\beta\mu_l\partial\beta\mu_j}\right)_{\beta,\beta\mu_k,V} = \sum_v N_i^{(v)}\left(\frac{\partial^2 P_v}{\partial\beta\mu_l\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} \tag{60}$$

$$\begin{aligned}\left(\frac{\partial^2 P_v}{\partial\beta\mu_l\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} =& (N_j^{(v)} - \langle N_j\rangle)\left(\frac{\partial P_v}{\partial\beta\mu_l}\right)_{\beta,\beta\mu_k,V} - P_v\left(\frac{\partial\langle N_j\rangle}{\partial\beta\mu_l}\right)_{\beta,\beta\mu_k,V} \\ =& (N_j^{(v)} - \langle N_j\rangle)(P_v N_l^{(v)} - P_v\langle N_l\rangle) - P_v\langle\delta N_j\delta N_l\rangle \end{aligned} \tag{61}$$

$$\begin{aligned}&\left(\frac{\partial^2\langle N_i\rangle}{\partial\beta\mu_l\partial\beta\mu_j}\right)_{\beta,\beta\mu_k,V} = \sum_v N_i^{(v)}(N_j^{(v)} - \langle N_j\rangle)(P_v N_l^{(v)} - P_v\langle N_l\rangle) - P_v\langle\delta N_j\delta N_l\rangle \\ =& \sum_v\left[N_i^{(v)}N_j^{(v)}P_v N_l^{(v)} - N_i^{(v)}\langle N_j\rangle P_v N_l^{(v)} - N_i(v)N_j^{(v)}P_v\langle N_l\rangle + N_i^{(v)}\langle N_j\rangle P_v\langle N_l\rangle - N_i^{(v)}P_v\langle\delta N_j\delta N_l\rangle\right] \\ =& \langle N_i N_l N_j\rangle - \langle N_i N_l\rangle\langle N_j\rangle - \langle N_i N_j\rangle\langle N_l\rangle + \langle N_i\rangle\langle N_j\rangle\langle N_l\rangle - \langle N_i\rangle\langle\delta N_j\delta N_l\rangle \\ =& \langle N_i N_l N_j\rangle - \langle\delta N_i\delta N_l\rangle\langle N_j\rangle - \langle\delta N_i\delta N_j\rangle\langle N_l\rangle - \langle N_i\rangle\langle N_j\rangle\langle N_l\rangle - \langle N_i\rangle\langle\delta N_j\delta N_l\rangle \\ =& \langle\delta N_i\delta N_l\delta N_j\rangle. \end{aligned} \tag{62}$$

(iii)

$$\langle(\delta E)^2\rangle = k_B T^2 C_V \tag{63}$$

$$\langle(\delta N)^2\rangle = \left(\frac{\partial^2\ln\Xi}{\partial(\beta\mu)^2}\right)_{\beta,V} = k_B T V\left(\frac{\partial^2 p}{\partial\mu^2}\right)_{T,V} \tag{64}$$

According to the Gibbs-Duhem equation,

$$\left(\frac{\partial p}{\partial\mu}\right)_T = \frac{N}{V} \tag{65}$$

$$\begin{aligned}\left(\frac{\partial^2 p}{\partial\mu^2}\right)_{T,V} =& \frac{1}{V}\left(\frac{\partial N}{\partial\mu}\right)_{T,V} = -\frac{1}{V}\left(\frac{\partial N}{\partial V}\right)_{T,\mu}\left(\frac{\partial V}{\partial\mu}\right)_{T,N} \\ =& -\frac{1}{V}\left(\frac{\partial p}{\partial\mu}\right)_T\left(\frac{\partial V}{\partial p}\right)_{T,N}\left(\frac{\partial p}{\partial\mu}\right)_T \\ =& -\frac{N^2}{V^3}\left(\frac{\partial V}{\partial p}\right)_{T,N} \\ =& \frac{N^2}{V^2}\kappa_T \end{aligned} \tag{66}$$

Therefore

$$\langle(\delta N)^2\rangle = \frac{N^2 k_B T}{V}\kappa_T. \tag{67}$$

# 3.16

For ideal gas,

$$C_V = \frac{3}{2}Nk_B, \quad \kappa_T = \frac{V}{Nk_BT}, \quad E = \frac{3}{2}Nk_BT \tag{68}$$

$$\langle(\delta E)^2\rangle = k_B T^2 C_V = \frac{3}{2}Nk_B^2T^2 \tag{69}$$

$$\frac{\sqrt{\langle(\delta E)^2\rangle}}{E} = \frac{1}{\sqrt{3N/2}} \approx 1.05 \times 10^{-11} \tag{70}$$

$$\langle(\delta N)^2\rangle = \frac{N^2 k_B T}{V}\frac{V}{Nk_BT} = N \tag{71}$$

$$\frac{\sqrt{\langle(\delta N)^2\rangle}}{N} = \frac{1}{\sqrt{N}} \approx 1.29 \times 10^{-11} \tag{72}$$

# 3.17

(a) (i) If $p(x) = \delta(x - x_0)$,

$$\langle gf\rangle = \int_a^b dx g(x)f(x)\delta(x-x_0) = g(x_0)f(x_0) = \left(\int_a^b dx g(x)p(x)\right)\left(\int_a^b dx f(x)p(x)\right) = \langle g\rangle\langle f\rangle. \tag{73}$$

(ii) If arbitrary functions $g$ and $f$ satisfy

$$\langle gf\rangle = \langle g\rangle\langle f\rangle, \tag{74}$$

that is,

$$\int_a^b dx g(x)f(x)p(x) = \left(\int_a^b dx g(x)p(x)\right)\left(\int_a^b dx f(x)p(x)\right) \tag{75}$$

$$\int_a^b dx[f(x) - \langle f\rangle]g(x)p(x) = 0 \tag{76}$$

Since $g$ is arbitrary,

$$[f(x) - \langle f\rangle]p(x) = 0 \tag{77}$$

Because

$$\int_a^b dx p(x) = 1, \tag{78}$$

$\exists x_0 \in [a,b]$ s.t. $p(x_0) \neq 0$. Such $x_0$ comprises a set $A$, $A \neq \varnothing$. Then $\forall x_0 \in A$, $f(x_0) = \langle f\rangle$. Because $f$ is arbitrary, only one such $x_0$ can be guaranteed.

Since

$$\int_a^b dx[f(x) - \langle f\rangle]p(x) = 0, \tag{79}$$

Given an arbitrarily small $\varepsilon > 0$,

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} dx[f(x) - \langle f\rangle]p(x) = 0 \tag{80}$$

and

$$\int_a^b dx p(x) = \int_{x_0-\varepsilon}^{x_0+\varepsilon} dx p(x) = 1. \tag{81}$$

When $x \in (x_0 - \varepsilon, x_0 + \varepsilon)$, $x_0 \in A$, then $\varepsilon \to 0$, $f(x) \to f(x_0) + f'(x_0)(x - x_0)$,

$$\begin{aligned}
\int_{x_0-\varepsilon}^{x_0+\varepsilon} dx[f(x) - \langle f\rangle]p(x) = &\int_{x_0-\varepsilon}^{x_0+\varepsilon} dx[f(x_0) + f'(x_0)(x - x_0) - \langle f\rangle]p(x) \\
=&f'(x_0)\int_{x_0-\varepsilon}^{x_0+\varepsilon} dx(x - x_0)p(x) \\
=&f'(x_0)\left[\int_{x_0-\varepsilon}^{x_0+\varepsilon} dxxp(x) - \int_{x_0-\varepsilon}^{x_0+\varepsilon} dxx_0p(x)\right]
\end{aligned} \tag{82}$$

Then because $f'(x_0)$ can be arbitrary,

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} dxxp(x) = x_0. \tag{83}$$

Thus $p(x) = \delta(x - x_0)$.
(b) (i) If $p(x, y) = p_1(x)p_2(y)$,

$$\iint dxdyf(x)g(y)p(x, y) = \int dxf(x)p_1(x)\int dyg(y)p_2(y) \tag{84}$$

$$\langle f(x)g(y)\rangle = \langle f\rangle\langle g\rangle. \tag{85}$$

(ii) If $\langle f(x)g(y)\rangle = \langle f\rangle\langle g\rangle$ for all $f(x)$ and $g(y)$,

$$\begin{aligned}
\iint dxdyf(x)g(y)p(x, y) = &\iint dxdy_0f(x)p(x, y_0)\iint dx_0dyg(y)p(x_0, y) \\
= &\iint dxdyf(x)g(y)\iint dx_0dy_0p(x, y_0)p(x_0, y)
\end{aligned} \tag{86}$$

Thus

$$p(x, y) = \iint dx_0dy_0p(x, y_0)p(x_0, y) = \int dx_0p(x_0, y)\int dyp(x, y_0) = p_2(y)p_1(x). \tag{87}$$

## 3.18

(a)

$$E_{\{n_i\}} = -\mu H\sum_{i=1}^{N} n_i \tag{88}$$

Using a canonical ensemble,

$$Q = \sum_{\{n_i\}} \exp(-\beta E_{\{n_i\}}) = \sum_{\{n_i\}}\prod_{i=1}^{N} e^{\beta\mu H n_i} = \prod_{i=1}^{N}\left(e^{-\beta\mu H} + e^{\beta\mu H}\right) = [2\cosh(\beta\mu H)]^N. \tag{89}$$

$$U = -\left(\frac{\partial \ln Q}{\partial\beta}\right)_{\mu H,N} = -N\left(\frac{\partial \ln(2\cosh(\beta\mu H))}{\partial\beta}\right)_{\mu H} = -N\mu H\tanh(\beta\mu H) \tag{90}$$

(b)

$$A = -\beta^{-1}\ln Q = -\beta^{-1}N\ln(2\cosh(\beta\mu H)) \tag{91}$$

$$S = \frac{U - A}{T} = -\frac{1}{T}N\mu H\tanh(\beta\mu H) + k_BN\ln(2\cosh(\beta\mu H)) \tag{92}$$

(c) When $T \to 0$, $\beta \to +\infty$.

$$U \to -N\mu H, \quad S \to 0. \tag{93}$$

## 3.19

(a)

$$Q = \sum_{\{n_1\}} \exp(\beta H M_{\{n_i\}}) \tag{94}$$

$$\langle M \rangle = \frac{\partial \ln Q}{\partial \beta H} = N \frac{\partial \ln[2\cosh(\beta\mu H)]}{\partial \beta H} = N\mu \tanh(\beta\mu H). \tag{95}$$

(b) (i)

$$\begin{aligned}\langle M^2 \rangle =& \frac{1}{Q}\frac{\partial^2 Q}{\partial(\beta H)^2} = \frac{1}{Q}[QN\mu^2 \mathrm{sech}^2(\beta\mu H) + QN^2\mu^2\tanh^2(\beta\mu H)] \\ =& N\mu^2\mathrm{sech}^2(\beta\mu H) + N^2\mu^2\tanh^2(\beta\mu H)\end{aligned} \tag{96}$$

$$\langle(\delta M)^2\rangle = \langle M^2\rangle - \langle M\rangle^2 = N\mu^2\mathrm{sech}^2(\beta\mu H). \tag{97}$$

(ii)

$$\chi = \left(\frac{\partial\langle M\rangle}{\partial H}\right)_{\beta,N} = N\beta\mu^2\mathrm{sech}^2(\beta\mu H) \tag{98}$$

Therefore

$$\langle(\delta M^2)\rangle = \chi k_B T. \tag{99}$$

(c) When $T \to 0$,

$$\langle M\rangle \to N\mu, \quad \langle(\delta M)^2\rangle \to 0. \tag{100}$$

## 3.20

When the total magnetization $M$ is fixed, the total energy $E$ is fixed under a given $H$. Then we can use the microcanonical ensemble. The natural variables are $S, N$.

$$\Omega = \frac{N!}{(N-m)!m!} \tag{101}$$

where $m = (N - M/\mu)/2$.

When $N$ is large, we can use the Stirling approximation,

$$\begin{aligned}S = k_B \ln\Omega \approx& -k_B\left(N\ln\frac{N-m}{N} - m\ln\frac{N-m}{m}\right) \\ =& -k_B\left(N\ln\frac{N+M/\mu}{2N} - \frac{N-M/\mu}{2}\ln\frac{N+M/\mu}{N-M/\mu}\right) \\ =& -k_B\left(\frac{N+M/\mu}{2}\ln(N+M/\mu) - \ln(2N) + \frac{N-M/\mu}{2}\ln(N-M/\mu)\right)\end{aligned} \tag{102}$$

$$\beta H = \frac{H}{k_B}\left(\frac{\partial S}{\partial E}\right)_N = -\frac{1}{k_B\mu}\left(\frac{\partial S}{\partial M/\mu}\right)_N = \frac{1}{\mu}\left(\frac{1}{2}\ln(N+M/\mu) + \frac{1}{2} - \frac{1}{2}\ln(N-M/\mu) - \frac{1}{2}\right) = \frac{1}{2\mu}\ln\frac{N+M/\mu}{N-M/\mu} \tag{103}$$

That is,

$$M = N\mu\frac{e^{2\beta\mu H}-1}{e^{2\beta\mu H}+1} = N\mu\tanh(\beta\mu H). \tag{104}$$

## 3.21

(a) When $\mathscr{E} = 0$,

$$\mathscr{H} = \mathscr{H}_0 = -\begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} \tag{105}$$

By diagonalizing matrix $\mathscr{H}$, we obtain the eigenstates under the bases of $|A\rangle$ and $|B\rangle$,

$$|\pm\rangle = \frac{1}{\sqrt{2}}[|A\rangle \pm |B\rangle]. \tag{106}$$

with energy eigenvalues $\mp\Delta$, respectively.

(b) (i)

$$Q = e^{\beta\Delta} + e^{-\beta\Delta} = 2\cosh(\beta\Delta). \tag{107}$$

(ii)

$$\begin{aligned} e^{-\beta\mathscr{H}_0} &= \sum_{n=0} \frac{1}{n!}(\beta\Delta)^n \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}^n \\ &= \sum_{n=0} \frac{1}{(2n+1)!}(\beta\Delta)^{2n+1} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \sum_{n=0} \frac{1}{(2n)!}(\beta\Delta)^{2n} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &= \sinh(\beta\Delta) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \cosh(\beta\Delta) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned} \tag{108}$$

$$\therefore\ Q = \mathrm{Tr}(e^{-\beta\mathscr{H}_0}) = 2\cosh(\beta\Delta). \tag{109}$$

The partition function is the same because the trace of an operator is invariant after a change of basis.

(c) (i)

$$\langle +|m|+\rangle = \frac{1}{2}(\langle A| + \langle B|)m(|A\rangle + |B\rangle) = \frac{1}{2}(\mu + 0 + 0 - \mu) = 0, \tag{110}$$

$$\langle -|m|-\rangle = \frac{1}{2}(\langle A| - \langle B|)m(|A\rangle - |B\rangle) = \frac{1}{2}(\mu + 0 + 0 - \mu) = 0 \tag{111}$$

$$\therefore\ \langle m\rangle = \frac{\langle +|m|+\rangle e^{\beta\Delta} + \langle -|m|-\rangle e^{-\beta\Delta}}{Q} = 0. \tag{112}$$

(ii)

$$\langle +|\mathrm{abs}(m)|+\rangle = \frac{1}{2}(\langle A| + \langle B|)\mathrm{abs}(m)(|A\rangle + |B\rangle) = \frac{1}{2}(|\mu| + 0 + 0 + |-\mu|) = |\mu|, \tag{113}$$

$$\langle -|\mathrm{abs}(m)|-\rangle = \frac{1}{2}(\langle A| - \langle B|)\mathrm{abs}(m)(|A\rangle - |B\rangle) = \frac{1}{2}(|\mu| + 0 + 0 + |-\mu|) = |\mu| \tag{114}$$

$$\therefore\ \langle |m|\rangle = \frac{\langle +|\mathrm{abs}(m)|+\rangle|e^{\beta\Delta} + \langle -|\mathrm{abs}(m)|-\rangle|e^{-\beta\Delta}}{Q} = |\mu|. \tag{115}$$

(iii)

$$\langle m^2\rangle = \frac{\langle +|m^2|+\rangle e^{\beta\Delta} + \langle -|m^2|-\rangle e^{-\beta\Delta}}{Q} = \mu^2. \tag{116}$$

$$\langle(\delta m)^2\rangle = \langle m^2\rangle - \langle m\rangle^2 = \mu^2. \tag{117}$$

(d)

$$\mathscr{H} = \begin{pmatrix} -\mu\mathscr{E} & -\Delta \\ -\Delta & \mu\mathscr{E} \end{pmatrix} \tag{118}$$

(i) The eigenvalues are $\pm\sqrt{\Delta^2+\mu^2\mathscr{E}^2}$.

$$Q=\exp(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2})+\exp(-\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2})=2\cosh(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}). \tag{119}$$

$$\frac{A(\mathscr{E})-A(0)}{N}=-\beta^{-1}\left(\ln\cosh(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2})-\ln\cosh(\beta\Delta)\right). \tag{120}$$

(ii)

$$e^{-\beta\mathscr{H}}=\begin{pmatrix}\cosh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)+\frac{\mu\mathscr{E}\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}} & \frac{\Delta\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}}\\ \frac{\Delta\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}} & \cosh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)-\frac{\mu\mathscr{E}\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}}\end{pmatrix} \tag{121}$$

$$Q=\mathrm{Tr}(e^{-\beta\mathscr{H}})=2\cosh(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}) \tag{122}$$

Then it gives the same free energy of solvation.

(e)

$$m=\begin{pmatrix}\mu & 0\\ 0 & -\mu\end{pmatrix}. \tag{123}$$

$$me^{-\beta\mathscr{H}}=\mu\begin{pmatrix}\cosh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)+\frac{\mu\mathscr{E}\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}} & \frac{\Delta\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}}\\ -\frac{\Delta\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}} & -\cosh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)+\frac{\mu\mathscr{E}\sinh\left(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}\right)}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}}\end{pmatrix} \tag{124}$$

$$\begin{aligned}\langle m\rangle=\frac{\mathrm{Tr}(me^{-\beta\mathscr{H}})}{\mathrm{Tr}(e^{-\beta\mathscr{H}})}&=\frac{2\mu^2\mathscr{E}\sinh(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2})}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}}\Big/2\cosh(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2})\\&=\frac{\mu^2\mathscr{E}}{\sqrt{\Delta^2+\mu^2\mathscr{E}^2}}\tanh(\beta\sqrt{\Delta^2+\mu^2\mathscr{E}^2}).\end{aligned} \tag{125}$$

$$\langle|m|\rangle=\frac{|\mu|\mathrm{Tr}(e^{-\beta\mathscr{H}})}{\mathrm{Tr}(e^{-\beta\mathscr{H}})}=|\mu|. \tag{126}$$

When $\mathscr{E}=0$, $\langle m\rangle=0$, $\langle|m|\rangle=|\mu|$. $\langle m\rangle$ increase with increasing $\mathscr{E}$ because larger external field makes the dipoles more likely to be lined up with the direction of the field.

## 3.22

(a) From the equation (67) we know

$$\langle(\delta\rho)^2\rangle=\langle(\delta N)^2\rangle/V^2=\frac{N^2k_BT}{V^3}\kappa_T \tag{127}$$

where

$$\kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} \tag{128}$$

The equation of the vdW fluid is

$$\beta p=\frac{\rho}{1-b\rho}-\beta a\rho^2, \tag{129}$$

$$\left(\frac{\partial p}{\partial V}\right)_{N,T}=-\frac{\rho}{V}\left(\frac{\partial p}{\partial\rho}\right)_{N,T}=-\frac{\rho}{\beta V}\left[\frac{1}{(1-b\rho)^2}-2\beta a\rho\right] \tag{130}$$

$$\therefore\ \kappa_T = \frac{\beta(1-b\rho)^2}{\rho - 2\beta a\rho^2(1-b\rho)^2} \tag{131}$$

$$\therefore\ \langle(\delta\rho)^2\rangle = \frac{1}{V}\frac{\rho(1-b\rho)^2}{1-2\beta a\rho(1-b\rho)^2} \tag{132}$$

$$\frac{\sqrt{\langle(\delta\rho)^2\rangle}}{\rho} = \frac{1}{\sqrt{\rho V}}\frac{1-b\rho}{\sqrt{1-2\beta a\rho(1-b\rho)^2}}. \tag{133}$$

From this result, it can be seen that when $V \to \infty$, the fluctuation is negligible.
(b)

$$\left(\frac{\partial\beta p}{\partial\rho}\right)_\beta = \frac{1}{(1-b\rho)^2} - 2\beta a\rho, \tag{134}$$

$$\left(\frac{\partial^2\beta p}{\partial\rho^2}\right)_\beta = \frac{2b}{(1-b\rho)^3} - 2\beta a. \tag{135}$$

At the critical point,

$$\frac{1}{(1-b\rho)^2} - 2\beta a\rho = 0 \tag{136}$$

$$\frac{2b}{(1-b\rho)^3} - 2\beta a = 0 \tag{137}$$

The solution of $\rho$ is

$$\rho_c = \frac{1}{3b}. \tag{138}$$

The critical temperature is

$$\beta_c = \frac{27b}{8a}. \tag{139}$$

(c) When $\beta/\beta_c = \frac{1}{1.1}$,

$$\left.\frac{\sqrt{\langle(\delta\rho)^2\rangle}}{\rho}\right|_{\rho=\rho_c} = \frac{1}{10\sqrt{b\rho_c}}\frac{1-b\rho_c}{\sqrt{1-\frac{2}{1.1}\beta_c a\rho_c(1-b\rho_c)^2}} = \frac{1}{10\sqrt{1/3}}\frac{1-1/3}{\sqrt{1-\frac{2}{1.1}\frac{9}{8}(1-1/3)^2}} \approx 0.383 \tag{140}$$

When $\beta/\beta_c = \frac{1}{1.001}$, $\left.\frac{\sqrt{\langle(\delta\rho)^2\rangle}}{\rho}\right|_{\rho=\rho_c} = 3.65$. When $\beta/\beta_c = \frac{1}{1.00001}$, $\left.\frac{\sqrt{\langle(\delta\rho)^2\rangle}}{\rho}\right|_{\rho=\rho_c} = 36.5$.
(d) The density inhomogeneity will cause a reflection, that is, the density difference will change the refractive index. Suppose the refractive index $n$ increases linearly with increasing density in this situation. Thus

$$\frac{\Delta n}{n} \approx \frac{\Delta\rho}{\rho} = \frac{\sqrt{\langle(\delta\rho)^2\rangle}}{\rho}. \tag{141}$$

An empirical estimate of the relative change of the refractive index that can be discerned is $\frac{\Delta n}{n} \sim 0.03$. The estimated $b = 125\text{Å}^3$, $V = 1000^3\text{Å}^3$. Then we obtain $T/T_c - 1 \approx 2\times10^{-4}$.

## 3.23

From Section 3.6 in the textbook we know

$$\langle(\delta N_A)^2\rangle = \sum_{i,j}[\langle n_i n_j\rangle - \langle n_i\rangle\langle n_j\rangle] \tag{142}$$

where we define $n_i = 1$ when the particle $i$ is in the state $A$, $n_i = 0$ if not. Then $N_A = \sum_i n_i$. It can be seen that when $i \neq j$, $\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle = 0$. Thus

$$\langle (\delta N_A)^2 \rangle = \sum_i [\langle n_i^2 \rangle - \langle n_i \rangle^2] \tag{143}$$

Since $n_i$ is either 0 or 1, $n_i^2 = n_i$, $\langle n_i^2 \rangle = \langle n_i \rangle$,

$$\langle (\delta N_A)^2 \rangle = \sum_i (1 - \langle n_i \rangle) \langle n_i \rangle. \tag{144}$$

It can also be seen that $\langle n_i \rangle = \langle N_A \rangle / N = x_A$. Thus

$$\langle (\delta N_A)^2 \rangle = N x_A x_B. \tag{145}$$