Ch-4: STATISTICAL MECHANICS || *Kardar Notes*

§4.1

→ $\rho_M(\mu)$ is calculated for eq. ensambles

Liouville's thm justifies the assumption that
"all accessible microstate are equally likely in an equilibrium ensamble."

→ Stat mech (as opposed to the Kinetic theory) doesn't explain how various systems evolve to eq.

§4.2

$\text{đ}Q = 0$ & $\text{đ}W = 0$ MICRO-CANONICAL ENSAMBLE

$\rightarrow dE = 0$ & $dV = 0$

So, $M \equiv (E, \underline{x})$ ← Macroscopic State

μ ← Microstate

$\mathcal{H}(\mu) = E$ ⇒ All microstates are confined to the surface specified.

Assumption: $\exists$ no other conserved quantities, so that all points on the surface are mutually accessible.

Central Postulate:

$$P_{(E,x)}(\mu) = \frac{1}{\Omega(E,x)} \cdot \begin{cases} 1 & \text{for } \mathcal{H}(\mu) = E \\ 0 & \text{else} \end{cases}$$

Remarks

1) a) Points in the phase space are canonically conjugate (x, p)
 b) Change by canonical transformation, $\mu \to \mu'$, leaves phase space volumes invariant.

2) (a) $\Omega(E, x)$ is the SA of the const. E surface
 (b) (i) Subtleties with densities non zero only at E is avoided by using
 $E - \Delta \leq \mathcal{H}(\mu) \leq E + \Delta$
 (ii) $\Omega' \approx (2\Delta)\Omega$ & ∵ Ω grows exponentially, & Δ chosen $\sim O(E^0)$ (or even $O(E^1)$) $\Omega' \sim \Omega$
 (c) (i) $S(E, \underline{x}) = k_B \ln \Omega(E, \underline{x})$

(ii) $\Omega_{tot} = \prod_i \Omega_i$

for i independent sys.

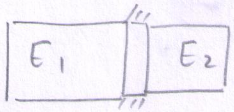
$\Rightarrow$ Entropy is additive — extensive

The zeroth law

assumptions:

1) Interaction of the 2 systems are small

$\rightarrow$ diathermal



$\mu = \mu_1 \otimes \mu_2$

$\mathcal{H}(\mu_1 \otimes \mu_2) = \mathcal{H}_1(\mu_1) + \mathcal{H}_2(\mu_2)$

Note: The joint sys is a micro-canonical ensamble

$$p(\mu_1 \otimes \mu_2) = \frac{1}{\Omega(E)} \begin{cases} 1 & \text{for } \mathcal{H}_1(\mu_1) + \mathcal{H}_2(\mu_2) = E \\ 0 & \text{else} \end{cases}$$

Since E is fixed,

$$\Omega(E) = \int dE_1 \, \Omega_1(E_1)\, \Omega_2(E-E_1) = \int dE_1 \, e^{\frac{S_1(E_1) + S_2(E-E_1)}{k_B}}$$

[We assume Ω depends exponentially on E
Thus $S(E, x) \propto E$ & $E \propto N$] Bad reasoning

$\Rightarrow$ $S \propto$ # particles. Thus Ω is exponentially large
($\because$ S is extensive) (circular?)

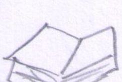
By saddle point, at E_1^* & $E_2^* = E - E_1^*$, we have

$$S(E) = k_B \ln \Omega(E) \approx k_B \ln e^{\frac{S_1(E_1^*) + S_2(E-E_1^*)}{k_B}}$$

$$= (\cancel{k_B})\left(\frac{1}{\cancel{k_B}}\right)\left(S_1(E_1^*) + S_2(E-E_1^*)\right)$$

E_1^* is evaluated by requiring (extremizing the exponent)

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{x_1} = \left.\frac{\partial S_2}{\partial E_2}\right|_{x_2}$$ (am I missing a minus sign?) (No you idiot!)



Read the book for interpretting why the state is expected after eq to be E_1^* & E_2^*

From this we define

$$\left.\frac{\partial S}{\partial E}\right|_x = \frac{1}{T}$$

consistent with the earlier meaning of T.

First Law

Lets look at variations of $S(E, x)$ with x, reversibly.

$đW = J \cdot \delta x$ on the sys.

Thus the internal energy changes to

$E' = E + J \cdot \delta x$

$$\delta(S) = S(E + J \cdot \delta x,\ x + \delta x) - S(E, x)$$

$$= \left(\left.\frac{\partial S}{\partial E}\right|_x J + \left.\frac{\partial S}{\partial x}\right|_E \right) \cdot \delta x$$

Since the prob depends exponentially on S, a first order change in δS would result in a spontaneous change.

Thus
$$\left.\frac{\partial S}{\partial E}\right|_x J_i = - \left.\frac{\partial S}{\partial x_i}\right|_{E,\, x_{i \neq j}}$$

$$\Rightarrow \quad -\frac{J_i}{T} = \left.\frac{\partial S}{\partial x_i}\right|_{E,\, x_{i \neq j}}$$

Now
$$dS(E, x) = \left.\frac{\partial S}{\partial x}\right|_E \cdot dx + \left.\frac{\partial S}{\partial E}\right|_x \cdot dE$$

$$= -\frac{J}{T} \cdot dx + \frac{dE}{T}$$

$$\Rightarrow \quad dE = T\,dS + J \cdot dx$$

Thus we define $đQ = T\,dS$

Second Law

$$\Omega_1(E_1^*, x_1)\, \Omega_2(E_2^*, x_2) > \Omega_1(E_1, x_1)\, \Omega_2(E_2, x_2)$$

$$\Rightarrow \delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geq 0$$

consistent with the second law.

$$\delta S = \left(\left.\frac{\partial S_1}{\partial E_1}\right|_{x_1} - \left.\frac{\partial S_2}{\partial E_2}\right|_{x_2} \right) \delta E_1 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1 \geq 0$$

Shows that heat (energy) flows from hotter to colder.

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stability condition

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§ 4.3 Two-level System

for def^{n}s

N : # impurity atoms
0, ϵ : energy normal/excited

$$\mathcal{H}(\{n_i\}) = \epsilon \sum_{i=1}^{N} n_i \equiv \epsilon N_1$$

where N_1 is the total # of excited impurities

$$p(\{n_i\}) = \frac{1}{\Omega(E,N)} \delta_{\epsilon \sum_{i=1}^{N} n_i, E}$$

$$\Omega(E,N) = {}^{N}C_{N_1} = \frac{N!}{N_1!\,(N-N_1)!}$$

$$S(E,N) = k_B \ln \Omega(E,N) = k_B \ln \frac{N!}{N_1!\,(N-N_1)!}$$

Stirling:

$$\Rightarrow S(E,N) \approx k_B \Big[N \ln N - \cancel{N} - N_1 \ln N_1 + \cancel{N_1} - (N-N_1)\ln(N-N_1) + \cancel{(N-N_1)} \Big]$$

$$= k_B \Big[N \ln N - N_1 \ln N_1 - (N-N_1)\ln(N-N_1) \Big]$$

$$= k_B \Big[(N-N_1)\ln N + N_1 \ln N - N_1 \ln N_1 - (N-N_1)\ln(N-N_1) \Big]$$

$$= k_B \left[N_1 \ln \frac{N}{N_1} + (N-N_1) \ln \frac{N}{N-N_1} \right]$$

$$= - k_B \left[N_1 \ln \frac{N_1}{N} + (N - N_1) \ln \frac{N-N_1}{N} \right]$$

$$= - N k_B \left[\frac{N_1}{N} \ln \frac{N_1}{N} + \frac{N-N_1}{N} \ln \frac{N-N_1}{N} \right]$$

With $N_1 = E/\epsilon$

$$= - N k_B \left[\left(\frac{E}{\epsilon N}\right) \ln \left(\frac{E}{\epsilon N}\right) + \left(1 - \frac{E}{N\epsilon}\right) \ln \left(1 - \frac{E}{N\epsilon}\right) \right.$$

The eq. temp would be

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_N = \frac{-k_B}{\epsilon} \ln \left(\frac{E}{N\epsilon - E}\right)}$$

Verification

$$\frac{\partial S}{\partial E}\Big|_N = -N k_B \left[\left\{ \cancel{\frac{E}{\epsilon N}} \frac{1}{\cancel{\left(\frac{E}{\epsilon N}\right)}} \cdot \cancel{\frac{1}{\epsilon N}} + \left\{ \cancel{\left(1 - \frac{E}{N\epsilon}\right)} \frac{1}{\cancel{\left(1 - \frac{E}{\epsilon N}\right)}} \cdot \cancel{\left(-\frac{1}{N\epsilon}\right)} \right. \right. \right.$$

$$\left. \frac{1}{\epsilon N} \ln \frac{E}{N\epsilon} \right\} + \left(\frac{-1}{\epsilon N}\right) \ln \left(1 - \frac{E}{N\epsilon}\right) \Big\}$$

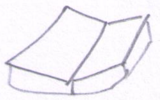
$$= - \frac{\cancel{N} k_B}{\epsilon \cancel{N}} \left[\ln \frac{\frac{E}{N\epsilon}}{1 - \frac{E}{N\epsilon}} \right] = - \frac{k_B}{\epsilon} \ln \left(\frac{E}{N\epsilon - E}\right)$$

$$\Rightarrow \quad e^{\frac{-\epsilon}{T k_B}} = \frac{E}{N\epsilon - E}$$

$$\frac{N\epsilon \; e^{-\frac{\epsilon}{T k_B}}}{1 + e^{-\frac{\epsilon}{T k_B}}} = \boxed{E = \frac{N\epsilon}{e^{\epsilon/T k_B} + 1}}$$

$$C = \frac{dE}{dT} = N k_B \left(\frac{\epsilon}{k_B T}\right)^2 e^{\frac{\epsilon}{k_B T}} \left[e^{\left(\frac{\epsilon}{k_B T} + 1\right)}\right]^{-2}$$

Hint:
(Use $\frac{d(E^{-1})}{dT} = (-1)E^{-2}\frac{dE}{dT}$ to find $\frac{dE}{dT}$)



Consequences of physics from the book.

Prob (Unconditional) for exciting a particular impurity is

$$p(n_1) = \sum_{n_1 \{n_2 \dots n_N\}} P(\{n_i\}) = \frac{\Omega(E - n_1\epsilon, N-1)}{\Omega(E, N)}$$

once energy of one is specified, the rest can be calculated as shown.

$$p(n_1 = 0) = \frac{\Omega(E, N-1)}{\Omega(E, N)} = \frac{(N-1)!}{N_1!(N-N_1-1)!} \cdot \frac{N_1!(N-N_1)!}{N!}$$

$$= 1 - \frac{N_1}{N}$$

and since $n_1 = \{1, 0\}$ are the only options,

$$p(n_1 = 1) = 1 - p(n_1 = 0) = \frac{N_1}{N}$$

putting $N_1 = E/\epsilon$ & $E = \frac{N\epsilon}{e^{\epsilon/TK_B} + 1}$

we have

$$p(n_1 = 0) = \frac{1}{1 + e^{-\epsilon/TK_B}}$$

$$p(n_1 = 1) = \frac{1}{1 + e^{\epsilon/TK_B}} = \frac{e^{-\epsilon/TK_B}}{1 + e^{-\epsilon/TK_B}}$$

§4.4 The ideal gas

(I'll mostly skip all detail & write the eq's only)

N

$\mu = \{p_i, q_i\}$

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i) \right]$$

$$p(\mu) = \frac{1}{\Omega(E,V,N)} \cdot \begin{cases} 1 & \text{for } q_i \in \text{Box}, \ \sum_i \vec{p}_i^{\,2}/2m = E \ (\pm \Delta E) \\ 0 & \text{else} \end{cases}$$

constrained to move on the hyper surface

$$\sum_i \vec{p}_i^{\,2} = 2mE \quad ; \text{ sphere of radius } R = \sqrt{2mE}$$

$$\Delta R = \sqrt{2m/E}\ \Delta E$$

$\exists$ notes on these for details of calculations

Area of d-dim sphere is

$A_d = S_d R^{d-1}$ where S_d is the solid angle.

where $S_d = \dfrac{2\pi^{d/2}}{\Gamma(d/2)}$

proof:

$$I_d = \int_{-\infty}^{\infty} \left(dx\, e^{-x^2}\right)^d = \pi^{d/2}$$

$$I_d = \int_{-\infty}^{\infty} \prod_i dx_i\, e^{-x_i^2} = \int_{\text{all Volume}} dV\, e^{-\sum_i x_i^2}$$

$$= \int_0^{\infty} dR\, S_d R^{d-1} e^{-R^2} = \frac{S_d}{2} \int_0^{\infty} dy\, y^{\frac{d}{2}-1} e^{-y}$$

(using $dV = \underbrace{S_d R^{d-1}}_{\text{Area of sphere } (4\pi r^2 \text{ in 3D})} dR$)

$$= \frac{S_d}{2}\, \Gamma(d/2)$$

equating I_d we get S_d as claimed.

Now the vol. of phase space available

$$\Omega(E, V, N) = \underset{\substack{\uparrow \\ \text{from } q}}{(V^N)} \Big(\underset{\substack{\uparrow \\ \text{from } p}}{\underbrace{S_d R^{d-1}}_{\text{Area}}} \Delta R \Big)$$

$$= V^N \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} (2mE)^{\frac{(3N-1)}{2}} \Delta_R$$

This can be ignored. (explained earlier)

Neglecting terms of order 1, or $\ln E \sim \ln N$ CLARIFY

$$S = k_B \ln \Omega \approx k_B \ln\Big[N\ln V + \frac{3N}{2}\ln(2\pi m E) - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2} \Big]$$

$$= N k_B \ln\left[V \left(\frac{4\pi e m E}{3N} \right)^{3/2} \right]$$

Now, $T\,dS = dE + P\,dV - \mu\,dN$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{3}{2}\frac{N k_B}{E}$$

in Notes for proof

$C_V = \frac{3Nk_B}{2}$ is const

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{N,E} = \frac{N k_B}{V} \Rightarrow PV = N k_B T$$

The unconditional prob. of finding a particle of momentum $\vec{p}_1$ in the gas is

$$p(\vec{p}_1) = \int d^3 \vec{q}_1 \prod_{i=2}^{N} d^3 q_i\, d^3 p_i\, \overbrace{P(\{\vec{q}_i, \vec{p}_i\})}^{1/\Omega(E,V,N)}$$

$$= \frac{V\, \Omega(E - \vec{p}_1^{\,2}/2m, V, N-1)}{\Omega(E, V, N)}$$

Upon using the formula for Ω, we have

$$p(\vec{p}_1) = \frac{V^N \pi^{\frac{3(N-1)}{2}} (2mE - \vec{p}_1^{\,2})^{\left(\frac{3N-4}{2}\right)}}{\left(3\frac{(N-1)}{2} - 1\right)!} \times \frac{\left(\frac{3N}{2}-1\right)!}{V^N \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}$$

$$= \left(1 - \frac{\vec{p}_1^{\,2}}{2mE}\right)^{\frac{3N}{2}-2} \frac{1}{(2\pi m E)^{3/2}} \frac{\left(\frac{3N}{2}-1\right)!}{\left(\frac{3N-1}{2}-1\right)!}$$

(from sterling's aprox., you get)

$$\left(\frac{3N}{2}\right)^{3/2}$$

& in large E limit

$$p(\vec{p}_1) = \left(\frac{3N}{4\pi m E}\right)^{3/2} e^{\left(-\frac{3N}{2}\frac{p_1^2}{2mE}\right)}$$

Maxwell - Boltzman Distribution ; with $E = 3Nk_BT/2$

$$p(\vec{p}_1) = \frac{1}{(2\pi m k_B T)^{3/2}} e^{-\frac{p_1^2}{2mk_BT}}$$

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§ 4.5 MIXING ENTROPY AND THE GIBBS PARADOX

Entropy defined so far is not extensive

$$(E, V, N) \longrightarrow (\lambda E, \lambda V, \lambda N)$$

$$S \longrightarrow \lambda(S + Nk_B \ln \lambda)$$

→ 2 Gases at temp T, V_1 & V_2 volumes.

→ Mixing is clearly irreversible, & must be accompanied by an increase of entropy.

$S_i = S_1 + S_2 = N_1 k_B (\ln V_1 + \sigma_1) + N_2 k_B (\ln V_2 + \sigma_2)$

where $\sigma_\alpha = \ln \left(\frac{4\pi e m_\alpha}{3} \frac{E_\alpha}{N_\alpha} \right)^{3/2}$

↳ Momentum Contribution

Since $\frac{E_\alpha}{N_\alpha} = \frac{3 k_B T}{2}$ for monoatomic,

$\sigma_\alpha (T) = \frac{3}{2} \ln (2\pi e m_\alpha k_B T)$

(don't know why) The temp. is unchanged since

$\frac{3 k_B T_f}{2} = \frac{E_1 + E_2}{N_1 + N_2} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T$

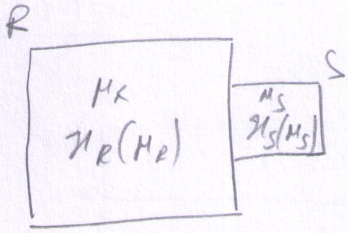
& $S_f = N_1 k_B \ln (V_1 + V_2) + N_2 k_B \ln (V_1 + V_2) + k_B (N_1 \sigma_1 + N_2$

(haven't calculated this)

$(N_1 + N_2) k_B \ln (V_1 + V_2) + k_B (N_1$

§ 4.6 THE CANONICAL ENSAMBLE

$\mu \equiv (T, \underline{x})$



assumption:

$E_{tot} >> E_S$

$$p(\mu_S \otimes \mu_R) = \frac{1}{\Omega_{S\otimes R}(E_{tot})} \cdot \begin{cases} 1 & \text{for } \mathcal{H}_S(\mu_S) + \mathcal{H}_R(\mu_R) = E_{tot} \\ 0 & \text{else} \end{cases}$$

now $\quad p(\mu_S) = \sum_{\{\mu_R\}} p(\mu_S \otimes \mu_R)$

Once μ_S is specified, we have

$$p(\mu_S) = \frac{\Omega_R(E_{tot} - \mathcal{H}_S(\mu_S))}{\Omega_{S\otimes R}(E_{tot})} \propto e^{\frac{1}{k_B} S_R(E_{tot} - \mathcal{H}_S(\mu_S))}$$

Now since $\mathcal{H}_S(\mu_S) << E_{tot}$, we have

$$S_R(E_{tot} - \mathcal{H}_S(\mu_S)) \approx S_R(E_{tot}) - \mathcal{H}_S(\mu_S) \frac{\partial S_R}{\partial E_R} \cdots$$

$$= S_R(E_{tot}) - \frac{\mathcal{H}_S(\mu_S)}{T}$$

Dropping the subscript (cause S_R disappears from the final expression)

$$p_{(T,\underline{x})}(\mu) = \frac{e^{-\beta \mathcal{H}(\mu)}}{Z(T, \underline{x})}$$

where $\quad Z(T, \underline{x}) = \sum_{\{\mu\}} e^{-\beta \mathcal{H}(\mu)}$

$\mathcal{E}$ of course now is a random variable.

$$p(\mathcal{E}) = \sum_{\{\mu\}} p(\mu)\, \delta(\mathcal{H}(\mu) - \mathcal{E}) = \frac{e^{-\beta \mathcal{E}}}{Z} \sum_{\mu} \delta(\mathcal{H}(\mu) -$$

$$\Rightarrow p(\mathcal{E}) = \frac{\Omega(\mathcal{E}) e^{-\beta \mathcal{E}}}{Z} = \frac{1}{Z} e^{\left[\frac{S(\mathcal{E})}{k_B} - \frac{\mathcal{E}}{k_B T}\right]}$$

$$= \frac{1}{Z} e^{-\frac{F(\mathcal{E})}{k_B T}}$$

with $\boxed{F(\mathcal{E}) = \mathcal{E} - TS(\mathcal{E})}$

The distr. is peaked at $\mathcal{E}^*$ that minimizes $F(\mathcal{E})$

$$Z = \sum_{\{\mu\}} p(\mu) = \sum_{\{\mu\}} e^{-\beta \mathcal{H}(\mu)} = \sum_{\mathcal{E}} p(\mathcal{E}) = \sum_{\mathcal{E}} e^{-\beta F(\mathcal{E})}$$

$$\approx e^{-\beta F(\mathcal{E}^*)}$$

The average energy is

$$\langle \mathcal{H} \rangle = \sum_{\{\mu\}} \mathcal{H}(\mu) \frac{e^{-\beta \mathcal{H}(\mu)}}{Z} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{\{\mu\}} e^{-\beta \mathcal{H}(\mu)}$$

$$\Rightarrow \langle \mathcal{H} \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

In thermodynamics,

$$E = F + TS = F - T \left.\frac{\partial F}{\partial T}\right|_x = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = \frac{\partial (\beta F)}{\partial \beta}$$

$$= \frac{\partial \left(\frac{F}{T}\right)}{\partial \left(\frac{1}{T}\right)} =$$

So we get $E = \dfrac{\partial (\beta F)}{\partial \beta}$

& we already had

so we may identify $-\ln Z = \beta F$

$$\Rightarrow \boxed{F(T, \underline{x}) = -k_B T \ln Z(T, \underline{x})}$$

To find how close the average & most probable values are, we ~~have~~ find the variance $\langle \mathcal{H}^2 \rangle_c$

$$Z = \sum_\mu e^{-\beta \mathcal{H}(\mu)}$$

$$-\frac{\partial Z}{\partial \beta} = \sum_\mu \mathcal{H} e^{-\beta \mathcal{H}}$$

$$+\frac{\partial^2 Z}{\partial \beta^2} = \sum_\mu \mathcal{H}^2 e^{-\beta \mathcal{H}}$$

$$\langle \mathcal{H} \rangle_c = \frac{1}{Z} \sum_\mu \mathcal{H} e^{-\beta \mathcal{H}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\langle \mathcal{H}^2 \rangle_c = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2$$

$$= \frac{1}{Z} \sum_\mu \mathcal{H}^2 e^{-\beta \mathcal{H}} - \frac{1}{Z^2} \left(\sum_\mu \mathcal{H} e^{-\beta \mathcal{H}} \right)^2$$

$$= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$= -\frac{\partial}{\partial \beta} \langle \mathcal{H} \rangle$$

In general

$$\langle \mathcal{H}^n \rangle_c = (-1)^n \frac{\partial^n \ln Z}{\partial \beta^n}$$

$$\langle \mathcal{H}^2 \rangle_c = -\frac{\partial \langle \mathcal{H} \rangle}{\partial (1/k_B T)} = k_B T^2 \left. \frac{\partial \langle \mathcal{H} \rangle}{\partial T} \right|_{\underline{x}}$$

$$\Rightarrow \langle \mathcal{H}^2 \rangle_c = k_B T^2 C_{\underline{x}}$$

[I] for details

$p(\varepsilon)$ grows as $\sqrt{\langle \mathcal{H}^2 \rangle_c} \propto N^{1/2}$, Thus the relative error $\dfrac{\sqrt{\langle \mathcal{H}^2 \rangle_c}}{\langle \mathcal{H} \rangle_c}$ goes as $\dfrac{1}{\sqrt{N}}$

Some detail is missing
(1 paragraph)

$$\rho(\varepsilon) = \frac{1}{Z} e^{\frac{-f(\varepsilon)}{k_B T}} \approx$$

§ 4.7 Canonical Examples

(1) Two level system

N impurities

$M = (T, N)$

$$\mathcal{H} = \epsilon \sum_{i=1}^{N} n_i \qquad \text{where } n_i = 0 \text{ or } 1$$

$$\mu \equiv \{n_i\}$$

$$p(\{n_i\}) = \frac{1}{Z} e^{-\beta\epsilon \sum_i n_i}$$

$$Z(T,N) = \sum_{\{n_i\}} e^{-\beta\epsilon \sum_{i=1}^{N} n_i}$$

$$= \left(\sum_{n_1=0}^{1} e^{-\beta\epsilon n_1}\right)\left(\sum_{n_2=0}^{1} e^{-\beta\epsilon n_2}\right) \cdots \left(\sum_{n_N=0}^{1} e^{-\beta\epsilon n_N}\right)$$

$$= \left(1 + e^{-\beta\epsilon}\right)^N$$

$$F(T,N) = -k_B T \ln Z$$

$$= -N k_B T \ln\left(1 + e^{-\epsilon/k_B T}\right)$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_N = \overbrace{N k_B \ln\left(1 + e^{-\epsilon/k_B T}\right)}^{-F/T} +$$

$$N \cancel{k_B} \cancel{T} \left(\frac{\epsilon}{\cancel{k_B} T^{\cancel{2}}}\right) \frac{e^{-\epsilon/k_B T}}{1 + e^{-\epsilon/k_B T}}$$

$$E = F + TS = \frac{N\epsilon}{1 + e^{\epsilon/k_B T}}$$

Also, $E = -\dfrac{\partial \ln Z}{\partial \beta} = -\dfrac{\partial}{\partial \beta} N \ln(1 + e^{-\beta\epsilon}) = -\dfrac{N}{1 + e^{-\beta\epsilon}} \cdot e^{-\beta\epsilon} \cdot (-\epsilon)$

$$= \frac{N\epsilon}{1 + e^{\beta\epsilon}}$$

$p = \prod_i p_i$ (independent probabilities)

Thus the unconditional prob. of excitement is

$$p_i(n_i) = \frac{e^{-\beta\epsilon n_i} \cancel{(1+e^{-\beta\epsilon})^{N-1}}}{(1+e^{-\beta\epsilon})^{\cancel{N}}}$$

(2) The Ideal Gas

$$M \equiv (T, V, N)$$

$$\mu \equiv \{\vec{p}_i, \vec{q}_i\}$$

$$p(\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{Z} e^{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}} \cdot \begin{cases} 1 & \text{for } \{q_i\} \in \text{box} \\ 0 & \text{else.} \end{cases}$$

$$Z(T, V, N) = \int \frac{1}{N!} \prod_{i=1}^{N} \left(\frac{d^3\vec{q}_i \, d^3\vec{p}_i}{h^3}\right) e^{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}}$$

$$= \frac{V^N}{N!} \frac{1}{h^{3N}} \int \prod_{i=1}^{N} (d^3\vec{p}_i) \prod_{i=1}^{N} \left(e^{-\beta \frac{p_i^2}{2m}}\right)$$

use $\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\pi/a}$

$$= \frac{V^N}{N! \cdot h^{3N}} \int \prod_{i=1}^{N} \left(d^3\vec{p}_i \, e^{-\frac{\beta p_i^2}{2m}}\right)$$

and $d^3\vec{p}_i = dp_x\, dp_y\, dp_z$

& $p_i^2 = p_x^2 + p_y^2 + p_z^2$

$$\stackrel{?}{=} \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} = \frac{1}{N!}\left(\frac{V}{\lambda(T)^3}\right)^N$$

where $\lambda(T) = \dfrac{h}{\sqrt{2\pi m k_B T}}$

Now

(I didn't check these)

$$F = -k_B T \ln Z = -N k_B T \ln V + N k_B \ln N - N k_B T - \frac{3N}{2} k_B T \ln\left(\frac{2\pi m k_B T}{h^2}\right)$$

$$= -N k_B T \left[\ln\left(\frac{Ve}{N}\right) + \frac{3}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

Now using

$$dF = -SdT - PdV + \mu dN$$

we can calculate various thermodynamic quantities.

$$-S = \left.\frac{\partial F}{\partial T}\right|_{V,N} = -Nk_B\left[\ln\frac{Ve}{N} + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$- Nk_B \cancel{T}\left(\frac{3}{2}\,\frac{\cancel{h^2}}{\cancel{2\pi m k_B T}}\cdot\frac{\cancel{2\pi m k_B}}{\cancel{h^2}}\right)$$

any way $\quad -S = \dfrac{F-E}{T}$

Thus $\quad \boxed{E = \frac{3}{2}Nk_BT}$

For eq^n of state,

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{Nk_BT}{V} \Rightarrow \boxed{PV = Nk_BT}$$

And $\quad \mu = \left.\dfrac{\partial F}{\partial N}\right|_{T,V} = \dfrac{F}{N} + k_BT$

$$= \frac{E-TS}{N} + \cancel{k_BT}\ \frac{PV}{N}$$

$$= \frac{E - TS + PV}{N}$$

§4.8 The Gibbs Canonical Ensamble

$\mu \equiv (T, J)$

Energy of the combined system is

$$\mathcal{H} - J \cdot x$$

$$p(\mu_s, x) = \frac{e^{-\beta \mathcal{H}(\mu_s) + \beta J \cdot x}}{\mathcal{Z}(T, N, J)}$$

with $\mathcal{Z}$ obviously $= \sum_{\mu_s, x} e^{\beta J \cdot x - \beta \mathcal{H}(\mu_s)}$

Now $\langle x \rangle = k_B T \dfrac{\partial \ln \mathcal{Z}}{\partial J}$

and $x = -\dfrac{\partial G}{\partial J}$ from thermodynamics suggest

$$G(N, T, J) = -k_B T \ln \mathcal{Z}$$

where $G = E - TS - x \cdot J$

Also, H can be evaluated as

$H = E - x \cdot J$

$$-\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \langle \mathcal{H} - J \cdot x \rangle = H$$

Heat capacities at const force maybe evaluated as

$$C_J = \frac{\partial H}{\partial T}$$

Examples

1) The Ideal Gas

isobaric ensemble

$M \equiv (N, T, P)$

$\mu \equiv \{\vec{p}_i, \vec{q}_i\}$

with vol. V

$$p(\{\vec{p}_i, \vec{q}_i\}, V) = \frac{1}{Z} e^{\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta P V\right]} \begin{cases} 1 & \text{for } \{q_i\} \in \text{b} \ldots \text{ of} \ldots \\ 0 & \text{else} \end{cases}$$

pressure, not momentum!

$$Z(N, T, P) = \int_0^\infty dV\, e^{-\beta P V} \underbrace{\int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3\vec{q}_i\, d^3\vec{p}_i}{h^3} e^{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}}}$$

$$= \int_0^\infty dV\, V^N e^{-\beta P V} \frac{1}{N!} \frac{1}{\lambda(T)^{3N}}$$

$$= \frac{1}{N!} \frac{1}{\lambda(T)^{3N}} \int_0^\infty dV\, V^N e^{-\beta P V}$$

$$= \frac{1}{\cancel{N!}} \frac{1}{\lambda(T)^{3N}} \frac{\cancel{N!}}{(\beta P)^{N+1}} = \frac{1}{(\beta P)^{N+1} \lambda(T)^{\ldots}}$$

Ignoring non-extensive contributions,

$$G = -k_B T \ln Z \approx N k_B T \left[\ln P - \frac{5}{2} \ln(k_B T) + \frac{3}{2} \ln\left(\frac{h^{\ldots}}{2\pi \ldots}\right) \ldots\right.$$

Now again, from $dG = -S\,dT + V\,dP + \mu\,dN$

$$V = \left.\frac{\partial G}{\partial P}\right|_{T,N} = \frac{N k_B T}{P} \Rightarrow PV = N k_B T$$

Enthalpy $H = \langle E + PV \rangle$

$$H = -\frac{\partial \ln Z}{\partial \beta} = \frac{5}{2} N k_B T$$

& $C_P = \frac{dH}{dT} = \frac{5}{2} N k_B$

2) Spins

Adding the work done against the external magnetic field we get

$$\mathcal{Z}(N,T,B) = \mathrm{tr}\left[e^{-\beta \mathcal{H} + \beta \vec{B}\cdot\vec{M}} \right]$$

$\to$ \'em'l not μ

Assuming $\mathcal{H} = 0$ (non-interacting spins) we have

where $\vec{M} = \mu_0 \sum_{i=1}^{N} \sigma_i$

$\mu = \{\sigma_i\}$ where σ_i is the ising variable

$$\sigma_i = \{-1, 1\}$$

$$p(\{\sigma_i\}) = \frac{1}{\mathcal{Z}} e^{\beta \mu_0 \vec{B}\cdot \sum_{i=1}^{N} \sigma_i}$$

$$\mathcal{Z} = \sum_{\{\sigma_i\}} e^{\beta \mu_0 \vec{B}\cdot\sum_{i=1}^{N}\sigma_i} = \left(e^{-\beta\mu_0 B} + e^{+\beta\mu_0 B}\right)^N$$

$$= \left[2\cosh(\beta\mu_0 B)\right]^N$$

Thus $G = -k_B T \ln \mathcal{Z} = -N k_B T \ln\left[2\cosh(\beta\mu_0 B)\right]$

Average magnetization is given by

$$M = k_B T \frac{\partial \ln \mathcal{Z}}{\partial B} \leftarrow \text{not } \beta$$

$$\Rightarrow M = -\frac{\partial G}{\partial B} = N\mu_0 \tanh(\beta\mu_0 B)$$

$$\tanh(x) = x - \frac{x^3}{3} + \frac{2x^5}{45} + \ldots$$

$$\Rightarrow M \approx N\mu_0 \beta\mu_0 B$$

Thus, susceptibility

$$\chi(T) = \left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{N\mu_0^2}{k_B T}$$

The Enthalpy is $H = \langle \mathcal{H} - BM \rangle = -BM$

$$C_B = \frac{\partial H}{\partial T} = -B\frac{\partial M}{\partial T}$$

§ 4.9 The grand canonical ensemble

$$M \equiv (T, \mu, \underline{x})$$

$$p(\mu_s) = \frac{e^{[\beta \mu N(\mu_s) - \beta \mathcal{H}(\mu_s)]}}{\mathcal{Q}}$$

$$\mathcal{Q}(T, \mu, x) = \sum_{\mu_s} e^{\beta \mu N(\mu_s) - \beta \mathcal{H}(\mu_s)}$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{(\mu_s | N)} e^{-\beta \mathcal{H}_N(\mu_s)}$$

$$\overset{?}{=} \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, N, x)$$

$$p(N) = \frac{e^{\beta \mu N} Z(T, N, x)}{\mathcal{Q}}$$

$$\langle N \rangle = \frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \beta \mu} = \frac{\partial \ln \mathcal{Q}}{\partial \beta \mu}$$

$$\langle N^2 \rangle_c = \langle N^2 \rangle - \langle N \rangle^2$$

$$= \frac{1}{\mathcal{Q}} \cdot \frac{\partial^2 \ln \mathcal{Q}}{\partial (\beta \mu)^2} - \left(\frac{\partial}{\partial (\beta \mu)} \ln \mathcal{Q} \right)^2$$

$$\overset{?}{=} \frac{\partial^2}{\partial (\beta \mu)^2} \ln \mathcal{Q} = \frac{\partial \langle N \rangle}{\partial (\beta \mu)}$$

The sharpness of the distribution of N allows us to approximate the sum ($\mathcal{Q}$) by its largest value $N = N^* \approx \langle N \rangle$

$$\mathcal{Q}(T, \mu, x) = \lim_{N \to \infty} \sum_{N=0} e^{\beta \mu N} Z(T, N, \underline{x})$$

$$= e^{-\beta(-\mu N^*)} Z(T, N^*, \underline{x}) = e^{-\beta(-\mu N^* + F)}$$

$$= e^{-\beta(-\mu N^* + E - TS)} = e^{-\beta \mathcal{G}}$$

where

$$\boxed{\mathcal{G}(T, \mu, x) = E - TS - \mu N = -k_B T \ln \mathcal{Q}}$$

is the grand potential

Using $d\mathcal{G} = -S dT - N d\mu + J \cdot dx$

we can evaluate S, N, & J by appropriate partial (∂)s.

Ideal gas of non-interacting particles

Final Example

$M \equiv (T, \mu, V)$

$\mu \equiv \{ \vec{p}_1 \vec{q}_1, \quad \ldots \}$ ← indefinite particle

$$\mathcal{Q}(T, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} \underbrace{\frac{1}{N!} \int \left(\prod_{i=1}^{N} \frac{d^3\vec{q}_i \, d^3\vec{p}_i}{h^3} \right) e^{-\beta \sum_i \frac{p_i^2}{2m}}}$$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{N!} \left(\frac{V}{\lambda^3} \right)^N \quad \text{with } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta \mu} V}{\lambda^3} \right)^N$$

$$= \exp\left(\frac{e^{\beta \mu} V}{\lambda^3} \right)$$

$$\mathcal{G}(T, \mu, V) = -k_B T \ln \mathcal{Q} = -k_B T e^{\beta \mu} \frac{V}{\lambda^3}$$

$\therefore$ using $E = TS + J \cdot x + \mu \cdot N$

$$\mathcal{G} = E - TS - \mu \cdot N = J \cdot x = -PV$$

Thus $P = -\frac{\mathcal{G}}{V} = -\frac{\partial \mathcal{G}}{\partial V}\Big|_{\mu, T} = \frac{k_B T e^{\beta\mu}}{\lambda^3}$

$$N = -\frac{\partial \mathcal{G}}{\partial \mu}\Big|_{T, V} = \frac{e^{\beta\mu} V}{\lambda^3}$$

comparing we get eq^n of state

$$P = k_B \frac{TN}{V}$$

---

also

$$k_B T \ln\left(\frac{N\lambda^3}{V}\right) = \mu$$