dilute gas

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{\sum_{i<j} v_{ij}}_{V}$$

pair potential

interactions

eg Lennard-Jones potential

$$\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}$$

$$v_{ij} = v(r_{ij})$$

$$= |\vec{r}_i - \vec{r}_j|$$

$$\mathrm{Tr}\, e^{-\beta(H-\mu N)}$$

$$\Xi = \cancel{\sum_{N=0}^{\infty} z^N Z} = \sum_{N=0}^{\infty} \int e^{-\beta(H_N - \mu N)} \frac{d\Gamma_N}{N!\, h^{3N}}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N \qquad Z_N = \frac{1}{N!\, h^{3N}} \int d\Gamma_N\, e^{-\beta H_N}$$

$$= \frac{1}{N!\, h^{3N}} \int dp_1\, dp_2 \cdots dp_{3N}\, e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} \int dq_1\, dq_2 \cdots \int e^{-\beta V_N}$$

$$= \frac{1}{N!\, h^{3N}} \left[\int_{-\infty}^{\infty} dp\, e^{-\frac{\beta p^2}{2m}}\right]^{3N} \underbrace{\int d^3\vec{r}_1\, d^3\vec{r}_2 \cdots d^3\vec{r}_N\, e^{-\beta V_N}}_{Q_N}$$

configuration partition function

$$= \frac{1}{N!\, h^{3N}} \left(\sqrt{2\pi \frac{m}{\beta}}\right)^{3N} Q_N$$

$$= \frac{1}{N!} \left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^{3N} Q_N \qquad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$= \frac{1}{N!\, \lambda^{3N}} Q_N$$

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

z

$z = e^{\beta\mu}$ fugacity

$$Q_0 \overset{\text{def.}}{\equiv} 1$$

$$Q_1 = \int d^3\vec{r}_1\, e^{-\beta \sum_{i<j}} = V$$

$$Q_2 = \int d^3\vec{r}_1\, d^3\vec{r}_2\, e^{-\beta v(|\vec{r}_1 - \vec{r}_2|)}$$

$$Q_3 = \cdots$$

$$\Xi = 1 + \left(\frac{e^{\beta\mu}}{\lambda^3}\right)V + \frac{1}{2}\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2 V \int e^{-\beta V(r)} + \cdots$$

$$\int 4\pi r^2 dr \quad = \quad b$$

Date

$$PV = k_B \Xi = k_B T \ln \Xi = k_B T$$

$$\Psi = -k_B T \ln \Xi, \quad -N = \frac{\partial \Psi}{\partial \mu} = \cancel{\beta \frac{e^{\beta\mu}}{\lambda^3}}$$

$$= -\frac{1}{\beta}\ln \Xi \qquad = -\frac{1}{\beta}\frac{1}{\Xi}\frac{\partial \Xi}{\partial \mu}$$

$$= -\frac{1}{\cancel{\beta}\Xi}\left[\cancel{\beta}\frac{e^{\beta\mu}}{\lambda^3}V + \cancel{\beta}\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2 V b + \cdots\right]$$

$$N = \frac{1}{\Xi}\left[\frac{e^{\beta\mu}}{\lambda^3}V + \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2 V b + \cdots\right] \qquad \alpha = \frac{e^{\beta\mu}}{\lambda^3}$$

$$\Xi = 1 + \alpha V + \frac{\alpha^2}{2} b + \cdots$$

$$\rho = \frac{N}{V}$$

$$\ln \Xi = \ln\left(1 + \alpha V + \frac{\alpha^2 V}{2} b + \cdots\right) \qquad \ln(1+x) = x - \frac{1}{2}x^2 + \frac{x^3}{3}$$

$$= \alpha V + \frac{\alpha^2 V}{2} b - \frac{1}{2}\left(\alpha V + \frac{\alpha^2}{2} V b\right)^2 + \cdots$$

$$= \alpha V + \frac{\alpha^2 V}{2} b - \frac{1}{2}\alpha^2 V^2 + \cdots$$

$$PV = k_B T \ln \Xi = k_B T\left[\alpha V + \alpha^2 \frac{V b}{2} - \frac{1}{2}\alpha^2 V^2 + \cdots\right]$$

$$N = k_B T \frac{\partial \ln \Xi}{\partial \mu} = k_B T\left[\beta \alpha V + \beta\left(\alpha^2 V b - \alpha^2 V^2\right) + \cdots\right]$$

$$= \alpha V + \left(\alpha^2 V b - \alpha^2 V^2\right) + \cdots$$

$$PV = k_B T\left[N - \frac{1}{2}\left(\alpha^2 V b\right) + \frac{1}{2}\left(\alpha^2 V^2\right) + \cdots\right] \qquad \rho = \frac{N}{V}$$

$$P = k_B T\left(\rho - \frac{1}{2}\alpha^2 \rho\left(\frac{b}{V}\right) + \frac{1}{2}\alpha^2 N\right.$$

virial } expansion
cluster }

Ursell & Mayer

Let $e^{-\beta v(r)} = 1 + f(r)$

$$Q_N = \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \prod_{i<j} (1 + f_{ij})$$

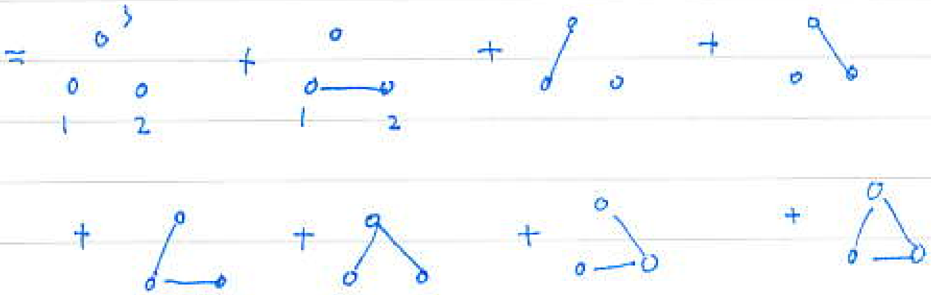
$Q_0 = 1$

f is small

$Q_1 = V$ $\cancel{\ne 0}$

$$Q_2 = \int d^3\vec{r}_1\, d^3\vec{r}_2\, (1 + f_{12}) = V^2 + V \int 4\pi r^2 dr\, f(r)$$

$$Q_3 = \int d^3\vec{r}_1\, d^3\vec{r}_2\, d^3\vec{r}_3\, (1+f_{12})(1+f_{13})(1+f_{23})$$



$$= V^3 + 3V^2 \int 4\pi r^2 dr\, f(r) + 3V \cancel{\int d\vec{r}_2\, d\vec{r}_3\, f(r)} \left[\int 4\pi r^2 dr\, f^2\right]^2$$

$$+ \int d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, f_{12} f_{23} f_{31}$$

let $x = \frac{e^{\beta\mu}}{\lambda^3}$

$$\Xi = 1 + \left(\frac{e^{\beta\mu}}{\lambda^3}\right) \cdot V$$

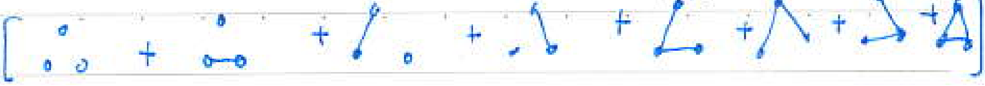
$$+ \frac{1}{2!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2 \left[V^2 + V \int 4\pi r^2 dr\, f(r)\right]$$

$$+ \frac{1}{3!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^3 \left[V^3 + 3V^2 \int 4\pi r^2 dr\, f(r) + 3V \left[\int 4\pi r^2 dr\, f^2\right]^2 + \int d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, f_{12} f_{23} f_{31}\right]$$

$+ \cdots$

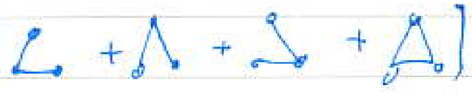
all graphs

$$\Xi = 1 + x\,[$$  $$] + \frac{1}{2!}x^2\,[$$  $$]$$

$$+ \frac{1}{3!}x^3\,[$$  $$]$$

$$+ \frac{1}{4!}x^4\,[\;\cdots\;] + \cdots$$

all connected graphs

$$\ln \Xi = x\,[\circ] + \frac{1}{2!}x^2\,[$$  $$] + \frac{1}{3!}x^3\,[$$  $$] + \cdots$$

check:

$$\Xi = 1 + xV + \frac{1}{2}x^2\Big(V^2 + V\overbrace{\int 4\pi r^2 dr\, f(r)}^{b}\Big)$$

$$+ \frac{1}{3!}x^3\Big(V^3 + 3V^2\int 4\pi r^2 dr\, f(r) + 3V\underbrace{\Big[\int 4\pi r^2 dr\, f\Big]^2}_{b^2} + \overbrace{\int d\vec r_1 d\vec r_2 d\vec r_3\, f_{12} f_{23} f_{31}}^{Vc}\Big)$$

$$+ \frac{1}{4!}x^4(\cdots)$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \frac{x^5}{5} + \cdots$$

$$\ln\Xi = x\cdot V + \frac{1}{2}x^2(V^2 + Vb) + \frac{1}{6}x^3(V^3 + 3V^2 b + 3Vb^2 + cV) + \cdots$$

$$- \frac{1}{2}\big(xV + \frac{1}{2}x^2(V^2+Vb) + O(x^3)\big)^2 + \frac{1}{3}(xV)^3 + \cdots$$

$$= x\cdot V + \frac{1}{2}x^2 Vb + \underbrace{\Big(\frac{1}{6} - \frac{1}{2} + \frac{1}{3}\Big)}_{=0}x^3V^3 + \underbrace{\Big(\frac{1}{6}\cdot 3 - \frac{1}{2}\Big)}_{=0}x^3V^2 b$$

$$1 - 3 + 2 = 0$$

$$+ \frac{1}{6}x^3(3Vb^2 + Vc) + \cdots$$

$$P = \frac{k_B T}{V}\ln\Xi = k_B T\Big[x + \frac{x^2}{2!}\frac{1}{V}V\cdot b + \frac{x^3}{3!}\frac{1}{V}(3Vb^2 + Vc) + \cdots\Big]$$

$$= k_B T\underbrace{\sum_{l=1}^{\infty} x^l b_l}_{=\frac{1}{V}\ln\Xi}$$

$$b_1 = 1$$

$$b_2 = \frac{b}{2}$$

$$b_3 = \frac{1}{3!}(3b^2 + c)$$

$$b_4 = \cdots$$

particle density $\rho = \frac{N}{V} = \frac{1}{V}\frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \mu} = \frac{1}{V}\frac{\partial \ln \Xi}{\partial(\beta\mu)}$

$$= \frac{\partial}{\partial(\beta\mu)}\left[\sum_{l=1}^{\infty} x^l b_l\right] \qquad x = \frac{e^{\beta\mu}}{\lambda^3}$$

$$\frac{\partial}{\partial(\beta\mu)}x^l = l\,x^{l-1}\frac{\partial x}{\partial(\beta\mu)} = l\,x^{l-1}\frac{e^{\beta\mu}}{\lambda^3} = l\,x^l$$

$$\begin{cases} \rho = \sum_{l=1}^{\infty} l\,x^l b_l \\ P = k_BT\sum_{l=1}^{\infty} x^l b_l = k_BT\sum_{l=1} a_l(T)\rho^l \end{cases}$$

virial expansion

$$\rho = x b_1 + 2x^2 b_2 + 3x^3 b_3 + \cdots$$

$$= x + x^2 b + \frac{1}{2}x^3(3b^2 + c) + \cdots$$

$$x = \rho - x^2 b - \frac{1}{2}x^3(3b^2+c) + O(x^4) + \cdot$$

$$= \rho - \left(\rho - x^2 b - \frac{x^3}{2}(3b^2+c)\right)^2 b - \frac{1}{2}\left(\rho - x^2 b + \cdot\right)^3 (3b^2+c) + \cdot$$

$$= \rho - \rho^2 b + 2\rho^3 b^2 - \frac{1}{2}\rho^3(3b^2+c) + \cdot$$

$$= \rho - b\rho^2 + \frac{1}{2}(b^2 - c)\rho^3 + \cdot$$

$$P = k_BT\left(x + x^2\frac{b}{2} + x^3\frac{1}{6}(3b^2+c) + \cdot\right)$$

$$= k_BT\Big(\rho - \rho^2 b + \rho^3\left(\cancel{2b} + \frac{1}{2}b^2 - \frac{c}{2}\right)$$

$$+ \frac{b}{2}(\rho^2 - 2b\rho^3) + \rho^3\frac{1}{6}(3b^2+c) + O(\rho^4)\Big)$$

$$= k_BT\Big[\rho - \frac{b}{2}\rho^2 + \Big[\underbrace{\left(2 - \frac{3}{2} - 1 + \frac{1}{2}\right)}_{0} b^2 + \frac{1}{6}c\Big]\rho^3 + \cdots$$

$$\left(-\frac{1}{2}c + \right.$$

$a_1 = 1$

$a_2 = -\frac{b}{2}$ ← second virial coefficient

$a_3 = -\frac{1}{3}c$

$$= k_BT\Big[\rho - b$$

$$= k_BT\left[\rho - \frac{b}{2}\rho^2 + \frac{-c}{3}\rho^3 + \cdots\right]$$

$$= k_BT\left(\rho - \frac{b}{2}\rho^2 - \frac{c}{3}\rho^3 + \cdots\right)$$

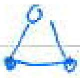
graph inside the integral

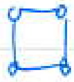
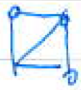
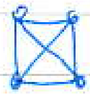
$$a_n = -\frac{1}{n(n-2)!}\frac{1}{V}\left[\boxed{\int d\vec{r}_1 \cdots d\vec{r}_n} \text{ all different } n\text{-point doubly connected graphs}\right]$$

$a_1 = 1$

Date (star graph)

$a_2 = -\frac{1}{2}\frac{1}{V}[$  $]$

$a_3 = -\frac{1}{3}\frac{1}{V}[$  $]$

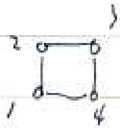
$a_4 = -\frac{1}{4}\cdot\frac{1}{2}\frac{1}{V}[\ 3$  $+ 6$  $+$  $]$

labeling factor

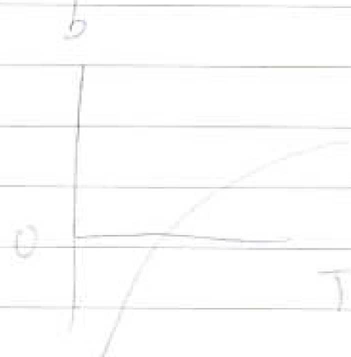
$\circ = \int d\vec{r}_1 \cdot 1 = V$

 $= \int d\vec{r}_1 d\vec{r}_2 \cdot f(|\vec{r}_1 - \vec{r}_2|)$

$f_{ij} = f_{ji}$

 $= \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4\ f_{12} f_{23} f_{34} f_{41}$

Ref Reichl "A modern Course in Statistical physics"



midterm test

5 mark each

10 March 08

Date

1 (a) { triple point of water $T_t = 273.16\,K$ ④
lowest possible $T = 0$ (1)   if 273.15 −1

(b) $U(S,V,N)$ $U(\lambda S, \lambda V, \lambda N) = \lambda U(S,V,N)$

$dU = TdS - pdV + \mu dN$

$\rightarrow U = TS - pV + \mu N$

(c) $\dot{A} = (A, H)$ classical mechanics is poisson bracket

$$(A,B) = \sum_j \left(\frac{\partial A}{\partial q_j}\frac{\partial B}{\partial p_j} - \frac{\partial B}{\partial q_j}\frac{\partial A}{\partial p_j} \right)$$

quantum

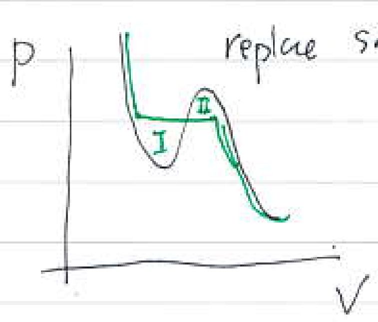
$$(A,B) = \frac{1}{i\hbar}\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)$$

(d) ergodic hypothesis:
time average = phase space average

$$\frac{1}{T}\int_0^T A(t)\,dt = \int d\Gamma\, A(\Gamma)\,\rho(\Gamma)$$ ← equilibrium distribution

no eq. −1

(e) Maxwell construction



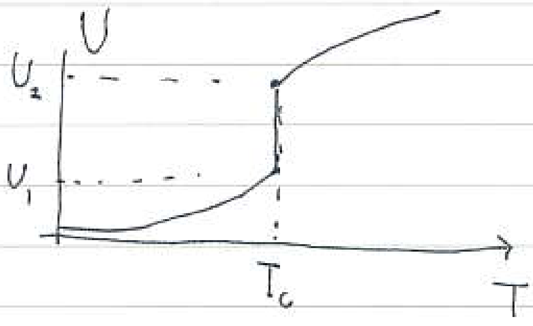
replace smooth curve by flat cut of equal area of I & II.

when $dV = 0$

2\. 7 (a) $\frac{dS}{dU} = \frac{1}{T}$ $\quad \frac{d^2S}{dU^2} = \frac{d}{dU}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{dT}{dU}$

Date $= -\frac{1}{T^2C}$

6 (b)



two phase coexist at T_c

6 (C) 1st order phase transition point at T_c, U_1 jumps to U_2 as T incr

C $\quad \frac{\partial^2 S}{\partial U^2} = 0$ $\quad C \to +\infty$ $\quad U_1$ is in the entire pure phase 1

6 (d) $dQ = TdS \to \delta Q = T_c(S_2 - S_1) = U_2 - U_1$

$$S = \frac{1}{T_c}U + \text{const}$$

$$S_1 = \frac{1}{T_c}U_1 + \text{const}$$

$$S_2 = \frac{1}{T_c}U_2 + \text{const}$$

$$S_2 - S_1 = \frac{1}{T_c}(U_2 - U_1)$$

$\beta p^2 = x^2$

15 mark

3\. (a) $Z = \frac{1}{h^2}\int dp_x \int dp_y \int dx \int dy \, e^{-\beta\left(\frac{1}{2}p_x^2 + p_y^2 + \frac{1}{2}(x^2+y^2+xy)\right)}$

(b) 10 mark

$$= \frac{1}{h^2}\left[\int_{-\infty}^{\infty} dp \, e^{-\beta\frac{p^2}{2}}\right]^2 \int dx \int dy \, e^{-\frac{\beta}{2}(x^2+y^2+xy)}$$

$$= \frac{1}{h^2}\left[\frac{1}{\sqrt{\beta}}\int dx \, e^{-\frac{x^2}{2}}\right]^2 \int$$

$$= \frac{1}{h^2\beta}2\pi \int_{-\infty}^{\infty} dx \, e^{-\frac{\beta x^2}{2}} \int dy \, e^{-\frac{\beta}{2}(\cancel{x}y^2 + xy)}$$

$$= \frac{2\pi}{h^2\beta}\int dx \, e^{-\frac{\beta x^2}{2}} \int dy \, e^{-\frac{\beta}{2}\left[\left(y+\frac{x}{2}\right)^2 - \frac{x^2}{4}\right]}$$

3) $= \frac{2\pi}{h^2\beta} \int dx\, e^{-\frac{\beta}{2}x^2} e^{+\beta\frac{x^2}{8}} \underbrace{\int dy'\, e^{-\frac{\beta}{2}y'^2}}_{\sqrt{\frac{2\pi}{\beta}}}$ $y' = y + \frac{x}{2}$

Date

$-\frac{1}{2} + \frac{1}{8} = \frac{-4}{8} + \frac{1}{8}$

$= \frac{2}{4} + \frac{1}{4}$

$$= \frac{2\pi}{h^2\beta} \sqrt{\frac{2\pi}{\beta}} \int dx\, e^{-\frac{3\beta x^2}{8}}$$

$$Z = \frac{2\pi}{h^2\beta} \sqrt{\frac{2\pi}{\beta}} \sqrt{\frac{2\pi}{3\beta/4}} = \frac{(2\pi)^2}{h^2\beta^2} \sqrt{\frac{4}{3}} = \frac{8\pi^2}{h^2\beta^2\sqrt{3}}$$

$= \frac{1}{4}$

$= -\frac{3}{8}$

$$F = -\frac{1}{\beta}\ln Z = -\frac{1}{\beta}\ln\left(\frac{(2\pi)^2\sqrt{4/3}}{h^2\beta^2}\right) = \frac{2}{\beta}(\ln\beta + \text{const})$$

correct former incorrect ~~defect~~ −7

$e^{-\beta(\mathcal{H}-\mu N)}$

4.

(a) $\Xi = \sum_{N=0}^{\infty} e^{-\beta(-(N-1)\epsilon - \mu N)}$

12

$$= \sum_{N=0}^{\infty} e^{\beta(\epsilon+\mu)N} e^{-\beta\epsilon}$$

$$= \frac{e^{-\beta\epsilon}}{1 - e^{\beta(\epsilon+\mu)}}$$

(b) $\Psi = -\frac{1}{\beta}\ln\Xi = -\frac{1}{\beta}\ln\left[\frac{e^{-\beta\epsilon}}{1-e^{\beta(\epsilon+\mu)}}\right]$

6

$$= -\frac{1}{\beta}\left[\ln e^{-\beta\epsilon} - \ln\left(1-e^{\beta(\epsilon+\mu)}\right)\right]$$

$\langle N\rangle > 0$

$\epsilon+\mu < 0$

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

7

(c) $\langle N\rangle = -\frac{\partial\Psi}{\partial\mu} = -\frac{1}{\beta}\frac{-e^{\beta(\epsilon+\mu)}}{1-e^{\beta(\epsilon+\mu)}}\cdot\beta = \frac{1}{e^{-\beta(\epsilon+\mu)}-1}$

$H + v$

$$\int e^{-\beta a r^3} 4\pi r^2 dr = \int e^{-ar^3} 4\pi \frac{dr^3}{3}$$

$$= \frac{4\pi}{3a}\int_0 e^{-ar^3} d\,ar^3$$

$e^{-\beta H}$ $H = p + a$

$$= \frac{4\pi}{3a} e^{-ar^3}\Big|_R^0$$

$$= \frac{4\pi}{3a\beta}\left[1 - e^{-\beta a R^3}\right]$$

① $Z = \beta^{\frac{3N}{2}} (1-e^{-aR^3})^N$ a small

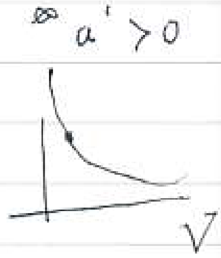
$1 - 1 + aR^3$

$\beta^{\frac{3N}{2}}(1-e^{-a'V})^N$

② $F = -\frac{N}{\beta}\ln(1-e^{-a'V}) + f(T)$ $a' > 0$

$\Rightarrow P = -\frac{\partial F}{\partial V} = \frac{N}{\beta}\frac{-e^{-a'V}(-a')}{1-e^{-a'V}} = \frac{N}{\beta}\frac{a'}{e^{a'V}-1}$

②



$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial\beta}\left[\frac{3N}{2}\ln\beta + V\right] = T$

$\Delta S = \int \frac{dQ}{T} dr$ complicated $aR^3 = \boxed{\frac{4\pi}{3a}R^3} = \frac{4\pi R^3}{3 v_0} = \frac{V}{v_0}$

$\Rightarrow U(\beta, V)$

$\Rightarrow S = -\frac{\partial F}{\partial T} = \frac{\partial f(T)}{\partial T} + N(1-e^{-aV}) + \frac{1}{1-\cdots}$

$\Delta S = -\frac{\partial F}{\partial \beta}\frac{\partial \beta}{\partial T}$ $\frac{1}{T}$ $(-\frac{1}{T^2})$ $(-\beta^2)$

Expansion $\qquad \delta Q = 0, \quad \delta W = 0 \qquad e^x = 1 + x + \frac{x^2}{2}$

$$\delta\, dU = \delta Q - \delta W = 0$$

Date

$$Z = \beta^{\frac{3N}{2}} \left(1 - \left(1 - a'V + \frac{a'^2}{2} V^2\right)\right)^N$$

$$= \beta^{\frac{3N}{2}} \left(a'V + \frac{a'^2}{2} V^2\right)^N$$

$$= \beta^{\frac{3N}{2}} \left(V + \frac{a'}{2} V^2\right)^N$$

$$a' = \beta a$$

$$= \cancel{\beta^{\frac{3N}{2}} V^N \ldots}$$

$$\cancel{S =} \qquad F = -\frac{1}{\beta} \ln Z = -\frac{1}{\beta}\left[\frac{3N}{2} \ln \beta + N \ln\left[V + \frac{a'}{2} V^2\right]\right]$$

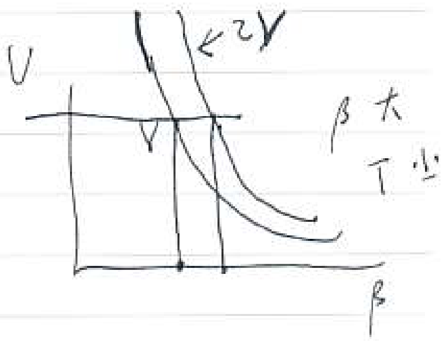
$$1 + \frac{a'}{2} V$$

$$\cancel{S =} \qquad = + kT \frac{3N}{2} \ln T - NkT \ln V - Nk_B T \frac{a'}{2} V$$

$$\cancel{= kT} \; \frac{3N}{2} kT \ln T - NkT \ln V - \frac{N}{2} V a$$

$$\frac{\partial S}{\partial T} = \frac{3N}{2} \ln T + \frac{3N}{2} k - NkT \ln V$$

$$O(a)$$



$$Z = \beta^{\frac{3N}{2}} \left(1 - e^{-\beta a V}\right)^N \cdot \frac{1}{\beta a}$$

$$\left[\int e^{-\beta p^2} dp\right]^3 \int e^{-\beta a r^3} r^2 dr$$

$$\left(\frac{1}{\sqrt{\beta}}\right)^3 \frac{1}{\beta} \int e^{-\beta a r^3} \frac{dr^3}{3} \beta$$

$$\beta^{-\frac{3}{2}-1} \left[e^{-\beta a r^3}\Big|_0^R\right]$$

$$\beta^{-\frac{5}{2}} \left[1 - e^{\beta V}\right]$$

QE 08 $\quad H = \sum_{i=1}^{N} \left(\frac{\vec{p}_i^2}{2m} + V(\vec{r}) \right) \qquad V(r) = \begin{cases} a r^3 & r<R \quad a>0 \\ +\infty & r \geq R \end{cases}$

Date

(a) +3

$$Z = z^N \qquad z = \frac{1}{h^3} \int_{-\infty}^{\infty} d^3\vec{p}\, e^{-\beta \frac{\vec{p}^2}{2m}} \int d^3\vec{r}\, e^{-\beta V(\vec{r})}$$

$$= \frac{1}{h^3} \left(\sqrt{\frac{m}{\beta}}\right)^3 \int_0^R 4\pi r^2 dr\, e^{-\beta a r^3} \qquad (r^3)' = 3r^2$$

$$= \frac{1}{h^3} \left(\frac{m}{\beta}\right)^{\frac{3}{2}} 4\pi \int_0^R e^{-\beta a r^3} d\frac{r^3}{3} \quad (\beta a) \frac{1}{\beta a}$$

$$= \frac{1}{h^3} \left(\frac{m}{\beta}\right)^{\frac{3}{2}} \frac{4\pi}{3} \frac{1}{\beta a} \int_0^R e^{-\beta a r^3} d(\beta a r^3) \qquad V = \frac{4\pi R^3}{3}$$

$$= \frac{1}{h^3} \left(\frac{m}{\beta}\right)^{\frac{3}{2}} \frac{4\pi}{3} \frac{1}{\beta a} \left[1 - e^{-\beta a R^3} \right] \qquad \int_0 e^{-x} dx = -e^{-x} \Big|_0^{\cdots}$$

$$= \text{const}\ T^{\frac{5}{2}} \left[1 - e^{-\frac{a}{k_B T} \frac{3}{4\pi} V} \right]$$

(b) +3

$$P = k_B T \frac{\partial \ln Z}{\partial V} \qquad F = -SdT - pdV \quad F = -k_B T \ln Z$$

$$= k_B T \frac{\partial}{\partial V} \left[\frac{5}{2} \ln T + \ln\left(1 - e^{-\frac{a}{k_B T} \frac{3}{4\pi} V}\right) \right] \cdot N \qquad \frac{\partial F}{\partial V} = -p$$

$$= k_B T N \frac{e^{-\frac{a}{k_B T} \cdot \frac{3}{4\pi} V}}{1 - e^{-\frac{a}{k_B T} \frac{3}{4\pi} V}} \cdot \frac{a}{k_B T} \frac{3}{4\pi}$$

$$= \frac{3a}{4\pi} N \frac{1}{e^{\frac{3aV}{4\pi k_B T}} - 1}$$

if $a \to 0$

$$\frac{3a}{4\pi} \frac{1}{\frac{3a}{4\pi} \frac{V}{k_B T}} = \frac{k_B T N}{V}$$

(c) ↙ correct for adiabatic quasi static process

+2 $dS = \frac{\delta Q}{T}$ $\delta Q = 0$

$\rightarrow \Delta S = 0$

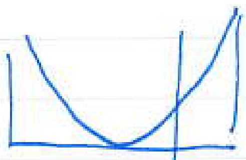
Date

(d) T decrease. $\Delta Q = 0$, $\Delta W = 0$ $\rightarrow \Delta U = 0$

+2 by 1st law of thermodynamics $\Delta U = \Delta Q \cancel{+} \Delta W = 0$

$U = \langle \frac{1}{2} m \vec{v}^2 \rangle + \langle v \rangle = const$

clearly $\langle v \rangle$ is bigger so $\langle \frac{1}{2} m v^2 \rangle$ must be smaller $T \downarrow$.



$R < R'$

$PV = NkT$

ideal gas adiabatic process $S \sim \ln(V T^{\frac{3}{2}})$

$\sim \ln(V^{\frac{5}{2}} P^{\frac{3}{2}})$

$PV^{\frac{5}{3}} = const$

Δ —

$dU = TdS - pdV$

$dS = \frac{dU + pdV}{T} = \frac{C_v dT + \frac{\lambda}{V} ... dV}{T} = 0$?

4 Apr 2008

Langevin Eq. by Fourier method

Date

$$\frac{dv}{dt} = -\gamma v + \frac{R(t)}{m}$$

$\langle R(t) \rangle = 0$

$\langle R(t) R(t') \rangle = C\,\delta(t-t')$

$$\tilde{R}[\omega] = \cancel{\frac{1}{2\pi}} \int_{-\infty}^{\infty} R(t)\, e^{+i\omega t} dt$$

$$\tilde{v}[\omega] = \cancel{\frac{1}{2\pi}} \int_{-\infty}^{\infty} v(t)\, e^{+i\omega t} dt$$

$$v(t) = \int_{-\infty}^{\infty} \tilde{v}[\omega]\, e^{-i\omega t} \frac{d\omega}{2\pi}$$

$$\frac{dv}{dt} = \int_{-\infty}^{\infty} \tilde{v}[\omega](-i\omega)\, e^{-i\omega t} \frac{d\omega}{2\pi}$$

$$\to \quad -i\omega\, \tilde{v}[\omega] + \gamma\, \tilde{v}[\omega] = \frac{\tilde{R}[\omega]}{m}$$

$$\to \quad \tilde{v}[\omega] = \frac{\tilde{R}[\omega]}{m(-i\omega + \gamma)}$$

$$\to \quad |\tilde{v}[\omega]|^2 = \frac{|\tilde{R}[\omega]|^2}{m^2(\omega^2+\gamma^2)} \quad \to \quad I_v[\omega] = \frac{I_v[\omega]}{m^2(\omega^2+\gamma^2)}$$

$\Leftarrow$ Wiener-Kinchin theorem

$$\langle \tilde{v}[\omega]\, \tilde{v}^*[\omega'] \rangle = I_v[\omega]\, \delta(\omega-\omega')$$

where $I_v[\omega] = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle v(t)\, v(0) \rangle e^{-i\omega t} dt$

Similarly $\langle \tilde{R}[\omega]\, \tilde{R}^*[\omega'] \rangle = I_R[\omega]\, \delta(\omega-\omega') \cdot 2\pi$

$$I_R[\omega] = \cancel{\frac{1}{2\pi}} \int_{-\infty}^{\infty} \underbrace{\langle R(t) R(0) \rangle}_{C\,\delta(t)} e^{+i\omega t} dt = \frac{C}{\cancel{2\pi}}$$

$$\langle |\tilde{v}[\omega]|^2 \rangle = I_v[\omega]\, \delta(0) \cdot 2\pi$$

$$\langle |\tilde{R}[\omega]|^2 \rangle = I_R[\omega]\, \delta(0) \cdot 2\pi$$

$$\to \quad I_v[\omega]\, \delta(0) = \frac{I_R[\omega]\, \delta(0)}{m^2(\omega^2+\gamma^2)}$$

$$\to \quad I_v[\omega] = \frac{I_R[\omega]}{m^2(\omega^2+\gamma^2)}$$

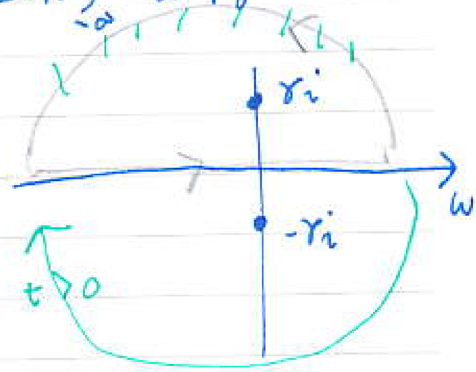
$$I_v[\omega] = \frac{C/\cancel{2\pi}}{m^2(\omega^2+\gamma^2)}$$

$\omega^2+\gamma^2=0$

$\omega = \pm\gamma i$

Date

$$\langle v(t)\,v(0)\rangle = \int_{-\infty}^{\infty} I_v[\omega]\,e^{i\omega t}\,d\omega = \frac{C}{\cancel{2\pi} m^2}\int_{-\infty}^{\infty}\frac{e^{-i\omega t}}{\omega^2+\gamma^2}\frac{d\omega}{2\pi}$$



Residue theorem

$$= \frac{C}{2\pi m^2}\left[\int_{-R}^{R} d\omega + \int dR e^{i\theta}\cdots\right]$$

$\omega = Re^{i\theta}$

$\theta\ [0,\pi]$

$$= \frac{C}{2\pi m^2}\,\cancel{2\pi i}\,(\text{Residue at } \gamma_i)$$

$$\left.\frac{(\omega+i\gamma)\,e^{-i\omega t}}{(\omega+i\gamma)(\omega-i\gamma)}\right|_{\omega\to i\gamma}$$

$$= \frac{C}{\cancel{2\pi} m^2}\cdot\cancel{2\pi i}\,\frac{e^{-\gamma t}}{2i\gamma}$$

$\gamma_i = \gamma i$

$$= \frac{C\,e^{-\gamma t}}{2m^2\gamma} \qquad t>0$$

$$= \frac{e^{-\gamma t}}{2i\gamma} \qquad \omega = i\gamma$$

$$= \frac{k_BT}{m}\,e^{-\gamma t}$$

$C = 2m\gamma k_BT$

$$\frac{a_{-1}}{z-z_0}$$

residue theorem

$$\oint f(z)\,dz = 2\pi i\sum_j \mathrm{Res}(j)$$

inside

right hand path

Res at z_j is $\dfrac{a_{-1}}{z-z_j}$

a_{-1}

Q2. Final exam

Date 6 May 08

$$H = \sum_{i=1}^{N} \varepsilon_i$$

$$\varepsilon_i = \frac{p_i^2}{2m} + u(r_i) \qquad Z = z^N$$

(a) Yes. $T_1 = T_2 = T$

(b) canonical. since total particle number N is fixed.

(c) $e^{-\beta\left(\frac{p^2}{2m} + u(r_i)\right)} d\vec{p}\, d\vec{r}$

$$N_1 + N_2 = N, \qquad N_1 = N_2 e^{\beta u_0}$$

$$\frac{N_1}{N_2} = \frac{1}{e^{-\beta u_0}} = e^{\beta u_0} \qquad N_2(1 + e^{\beta u_0}) = N$$

$$N_2 = \frac{N}{1 + e^{\beta u_0}}$$

$$N_1 = \frac{N e^{\beta u_0}}{1 + e^{\beta u_0}} = \frac{N}{1 + e^{-\beta u_0}}$$

$$N_1 = N \frac{1}{1 + e^{-\beta u_0}} \qquad N_1 + N_2 = N\left[\frac{1}{1 + \frac{1}{x}} + \frac{1}{1+x}\right]$$

$$N_2 = N \frac{1}{1 + e^{\beta u_0}} \qquad = N\left[\frac{x}{x+1} + \frac{1}{1+x}\right]$$

$$\frac{N_1}{N_2} = \frac{\frac{1}{1 + \frac{1}{x}}}{\frac{1}{1+x}} = x \qquad = N\left[\frac{1+x}{1+x}\right] = N$$

$$x = e^{\beta u_0}$$

$$z = C(T)\,[V_1 + V_2 e^{-\beta u_0}]$$

$$F = -k_B T N \ln [V_1 + V_2 e^{-\beta u_0}] + C'(T)$$

Date

$$P_1 = -\frac{\partial F}{\partial V_1} = -\left(-k_B T N \frac{1}{V_1 + V_2 e^{-\beta u_0}}\right) = \frac{kTN}{V(1+e^{-\beta u_0})}$$

$$P_2 = k_B T N \frac{e^{-\beta u_0}}{V_1 + V_2 e^{-\beta u_0}} = \frac{kTN}{V(1+e^{\beta u_0})}$$

$$\begin{bmatrix} e^{k}-\lambda & 1 & 1 \\ 1 & e^{k}-\lambda & 1 \\ 1 & 1 & e^{k}-\lambda \end{bmatrix} = \begin{bmatrix} \alpha+1 & 1 & 1 \\ 1 & \alpha+1 & 1 \\ 1 & 1 & \alpha+1 \end{bmatrix} = (\alpha+1)^3 + 2 - 3(\alpha+1) = 0$$

$$(\alpha+1)^3 - 3\alpha - 1 = 0$$

$$\alpha^3 + 3\alpha^2 + \cancel{3\alpha} \cancel{+1} \cancel{-3\alpha} \cancel{-1} = 0$$

$$\alpha(\alpha^2 + \cancel{8}\alpha + 6) = 0$$

$$\alpha^3 + 3\alpha^2 = 0$$

$$\alpha^2(\alpha+3)$$

$\cancel{\lambda = \alpha}$ $\qquad \lambda = e^{k} - 1 - \alpha$

Q4

(a) $\chi = \beta \int d^d r \, G(r)$

$= \beta \int d^r r^{d-1} \, \cancel{dr} \frac{1}{r^{d-2+\eta}} = \int dr \cdot r^{1-\eta} \qquad r^{1-\eta+1} = L^{2-\eta}$

L

$\chi = \frac{\partial m}{\partial h} \qquad r^{-1+\eta}$

$m = \frac{\partial f}{\partial h}$

$f(t, h, L) = b^{-d} f(b^y t, b^x h, \frac{b}{L})$

$\chi = -\frac{\partial^2 f}{\partial h^2} = -b^{-d} \frac{\partial^2}{\partial h^2} f(b^y t, b^x h, \frac{b}{L})$

$= -f''(t, h, L) \qquad = -b^{-d} b^{2x} \frac{\partial^2}{\partial (b^x h)^2} f(b^y t, b^x h, \frac{b}{L})$

$\chi(t, h, L) = b^{2x-d} \chi(b^y t, b^x h, \frac{b}{L})$

$a = 2x - d \qquad \gamma = \frac{2x-d}{y}$

$= y\gamma \qquad y = \frac{1}{\nu}$

$= \frac{\gamma}{\nu}$

Date

$$\oint_C f(z)\,dz = 2\pi i\,(\text{Sum of enclosed Residues})$$

Residue at z_0 is a_{-1} $\quad f(z) = \cdots + \frac{a_{-1}}{z-z_0} + \cdots$

After contour integral we get

$$F(t) = \frac{C}{4m^2}\left[\frac{e^{-\frac{\gamma}{2}t - i\sqrt{\frac{k}{m}-\frac{\gamma^2}{4}}\,t}}{\gamma\sqrt{\frac{k}{m}-\frac{\gamma^2}{4}}\cdot\left(\frac{i\gamma}{2}-\sqrt{\frac{k}{m}-\frac{\gamma^2}{4}}\right)} + c.c.\right]$$

Q5. $$m\frac{d^2x}{dt^2} = -kx - m\gamma\frac{dx}{dt} + R(t)$$

Date

[a] $$x(t) = \int_{-\infty}^{\infty} \tilde{x}[\omega]\, e^{-i\omega t}\,\frac{d\omega}{2\pi}$$

$$(-i\omega)^2 m\,\tilde{x} = -k\tilde{x} - m\gamma(-i\omega)\tilde{x} + \tilde{R}$$

$$\rightarrow \quad \tilde{x} = \frac{\tilde{R}}{k + im\omega\gamma - \omega^2 m} = \frac{\tilde{R}[\omega]}{k - im\gamma\omega - \omega^2 m}$$

(b)

$$\tilde{F}[\omega] = \frac{C}{|k - im\gamma\omega - \omega^2 m|^2} = \frac{C}{(k-\omega^2 m)^2 + (m\gamma\omega)^2}$$

$$\langle \tilde{x}[\omega]\,\tilde{x}[\omega']^{*} \rangle = \tilde{F}[\omega]\cdot 2\pi\,\delta(\omega-\omega')$$

$$= \frac{1}{k - im\gamma\omega - \omega^2 m}\cdot\frac{1}{(k - im\gamma\omega' - \omega'^2 m)^*}\,\underbrace{\langle \tilde{R}[\omega]\,\tilde{R}[\omega']\rangle}_{\langle\int_{-\infty}^{\infty} R(t)R(t')\rangle e^{i\omega(t-t')}dt\,\cdot\,2\pi\,\delta(\omega-\omega')}$$

← Fourier transf of real time

$$C\,\delta(t-t')$$

$$\tilde{F}[\omega] = \frac{C}{|k - im\gamma\omega - \omega^2 m|^2}$$

$$k - \omega^2 m = \pm i m\gamma\omega$$

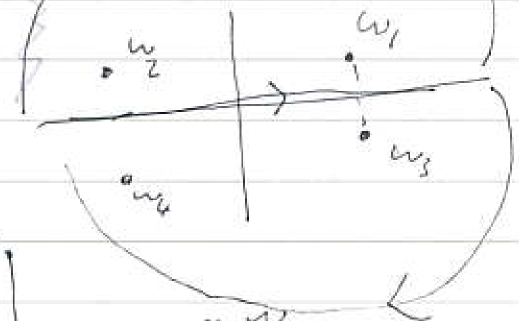
$$m\omega^2 = k \pm im\gamma\omega$$

$$\omega^2 = \frac{k}{m} \pm i\gamma\omega$$

(c) $$F(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\,\frac{C\,e^{-i\omega t}}{|k - im\gamma\omega - \omega^2 m|^2}$$

$$\omega^2 \pm i\gamma\omega - \frac{k}{m} = 0$$

$$\omega = \frac{\mp i\gamma \pm\sqrt{-\gamma^2 + 4\frac{k}{m}}}{2}$$



assume $t>0$ $$= \mp i\frac{\gamma}{2} \pm \sqrt{\frac{k}{m} - \left(\frac{\gamma}{2}\right)^2}$$

$$F(t) = 2\pi i\,\mathrm{Res}\,\frac{C}{|\quad|^2}\,e^{i\omega t}\Big|_{\text{at } \omega_1 \,\&\, \omega_2}$$

$(\omega-\omega_1)(\omega-\omega_2)(\omega-\omega_3)(\omega-\omega_4)$

each ptn is

K Huang proble 8.5 Date 26 Feb 09

grand with respect occupation # (# of phonons)

$$\Xi = \sum_{n=0,1,2\ldots} (e^{\beta\mu})^n Q_n \qquad Q_n = \sum e^{-\beta E_n} \text{ energy of } n \text{ phonons}$$

$$E_n = \hbar\omega n \qquad = g_n e^{-\beta\hbar\omega n}$$

g_n degeneracy

$$\mathcal{H} = \sum_j \hat{a}_j^+ \hat{a}_j \hbar\omega$$

n phonon state

$$\underbrace{\hat{a}_{j_1}^+ \hat{a}_{j_2}^+ \cdots \hat{a}_{j_n}}_{\text{creat } n\text{ - times}} |0\rangle$$

wave fn symmetrized $\varphi_{n_1}(x_1)\,\varphi_{n_2}(x_2)\,\varphi_{n_3}(x_3)$

$$n = \sum_{j=1}^{N} n_j \qquad \hat{\hat{a}}$$

$$g_n = \sum_{\sum_{j=1}^N n_j = n} 1$$

or $\sum e^{-\beta\hbar\omega n_j + \frac{1}{2}\beta\hbar\omega N}$

$$\Xi = \sum_{n=0,1,2\ldots} \sum_{\sum n_j = n} 1\, e^{-\beta\hbar\omega n}$$

$$= \sum_{n_1 n_2 \ldots n_N} e^{-\beta\hbar\omega\sum n_j} = \left(\sum_{n_j=0}^{\infty} e^{-\beta\hbar\omega n_j}\right)^N =$$

$$= \left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)^N \cdot e^{-\beta\frac{1}{2}\hbar\omega N}$$

$\beta \to 0$

N is fixed ...
this gives N oscillators labelled by j
$j = 1, 2, \ldots N$ for the nth oscillator
the # of phonon or photons is n_j in oscillator j

$\sum_j n_j = n$ give the total

$$\frac{1}{\beta\hbar\omega}$$

$$\frac{1}{1-e^{N}e^{-\beta\hbar\omega}}$$

Date

$$= \frac{1}{1-e^{N[1-\beta\hbar\omega+\cdots]}} = \frac{\cdots}{1-e^{N}}$$

total # of particles

$$E = \sum_{k=0}^{\infty} \varepsilon_k n_k \qquad N = \sum_{k=0}^{\infty} n_k$$

energy of 1 particle at energy level k

Each set $\{n_k\}$ is one state

$$\Xi = \sum_{\{n_k\}} e^{-\beta(E_N-\mu N)} = \sum_{\{n_k\}} e^{-\beta\sum_k(\varepsilon_k-\mu)n_k}$$

$$= \prod_k \sum_{n_k=0}^{\infty}\left(e^{-\beta(\varepsilon_k-\mu)}\right)^{n_k} = \prod_k \frac{1}{1-e^{-\beta(\varepsilon_k-\mu)}}$$

Boltzmann stats

$$\Xi_B = \sum_{N=0}^{\infty}\underbrace{\sum}_{\text{fixed } N}\frac{1}{n_1!\,n_2!\,\cdots n_k!\cdots}e^{-\beta(E_N-\mu N)}$$

$N=\sum n_i$ restricted sum

$$= \sum_{\substack{\{n_k\}\\ \text{unrestricted}}}\prod_{k=0}^{\infty}\frac{[e^{-\beta(\varepsilon_k-\mu)}]^{n_k}}{n_k!} = \prod_{k=0}^{\infty} e^{+[e^{-\beta(\varepsilon_k-\mu)}]}$$

$$= e^{\sum_{k=0}^{\infty} e^{-\beta\varepsilon_k}e^{\beta\mu}}$$

$$= \exp\left[e^{\beta\mu}e^{-\beta\hbar\omega_0\frac{1}{2}}\frac{1}{1-e^{-\beta\hbar\omega_0}}\right]$$

$$\Xi = \sum_{N=0}^{\infty}\frac{z^N}{N!}Z_1^N \quad \text{gives same answer}$$

Z_1 1 particle partition fn

for each qua set $\{n_j\}$ the degeny is 1

For Botlzman $g\{n_j\} = \frac{1}{\prod_j n_j!}$ ← exchange the phonon are different is used then

$$\Xi_B = \sum_{n=0,1,2,N} \sum_{\sum_{j=1}^N n_j = n} \frac{e^{-\beta\hbar\omega(\sum_j n_j + \frac{1}{2})} N!}{\prod_j n_j!}$$

$$= \sum_{n_1 n_2 \cdots} \frac{e^{-\beta\hbar\omega n_1}}{n_1! n_2! \cdots} \frac{e^{-\beta\hbar\omega n_2 \cdots}}{n_N!} = \left(\sum_{n_j} \frac{e^{-\beta\hbar\omega(n_j + \frac{1}{2})}}{n_j!}\right)^N$$

$$= e^{-\beta\frac{\hbar\omega}{2}N}\left[\sum_{n_j=0}^{\infty} \frac{(e^{-\beta\hbar\omega})^{n_j}}{n_j!}\right]^N$$

$$= e^{-\beta\frac{\hbar\omega N}{2}} \exp\left[N e^{-\beta\hbar\omega}\right]$$

when $\beta \to 0$ $\quad e^{e^{-\beta\hbar\omega}} = e^{(1-\beta\hbar\omega + \cdots)}$

$$= e^{-\beta\hbar\omega}$$

binom formula

$$(x+y)^n = \sum \frac{n!}{k!(n-k)!} x^k y^{n-k}$$

$$Q_n = \frac{1}{N!}(e^{-\beta\hbar\omega}$$

$$\Xi = \sum_{n=0}^{\infty} \frac{(Ne^{-\beta\hbar\omega})^n}{n!} = e^{Ne^{-\beta\hbar\omega}}$$

If we have $\Xi_B = \sum_{n=0,1,2\ldots} \sum_{\sum_{j=1}^N n_j = n} \frac{n!\, e^{-\beta\hbar\omega\sum_j n_j}}{\prod_j n_j!} e^{-\beta\hbar\omega\frac{1}{2}N}$

$$\sum_{n=0,1,2} \left(\sum_{j=1}^N e^{-\beta\hbar\omega}\right)^n = \sum_{n=0,1,2\ldots} (Ne^{-\beta\hbar\omega})^n \to +\infty$$

$$= \frac{1}{1-e^{Ne^{-\beta\hbar\omega}}} < 0 \quad \text{but convert}$$

Fokker-Planck equations new derivation Date 26 Mar 09

$\frac{dv}{dt} = -\gamma v + \frac{R(t)}{m}$ standard Langevin eq.

for a given realization of the random noise $R(t)$

P : probability of finding the Brownian particle at velocity ~~f~~ v to $v + dv$ is $P(v,t)\,dv$ at time t

$$\int_{-\infty}^{+\infty} P(v,t)\,dv = 1 \quad \text{conservation of probability}$$

$P \propto e^{-\beta \frac{1}{2} m v^2}$ $t \to \infty$

prob. is conserved $\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0$

$\vec{j} = \vec{v} \rho$

$$\frac{\partial P(v,t)}{\partial t} + \frac{\partial}{\partial v}\big(\underbrace{\dot{v} P}_{\text{prob. flux}}\big) = 0$$

think of v as "x"

$$\frac{\partial P(v,t)}{\partial t} + \frac{\partial}{\partial v}\left(\left[-\gamma v + \frac{R(t)}{m}\right] P\right) = 0$$

$\langle P \rangle$ average over noise is the final

$$\frac{\partial P(v,t)}{\partial t} = \gamma \frac{\partial}{\partial v}(vP) - \frac{\partial}{\partial v}\left(\frac{R}{m} P\right)$$

$$= \underline{-\hat{L} P} - \frac{\partial}{\partial v}\left(\frac{R}{m} P\right)$$

formally the same as eqn for v

operator on P acting in v

$$-\hat{L} P = \gamma \frac{\partial}{\partial v}(vP)$$

$P(v,t) = e^{-t\hat{L}} P(v,0)$ if $R = 0$

$$P(v,t) = e^{-t\hat{L}} P(v,0) - \int_0^t d\tau\, e^{-(t-\tau)\hat{L}} \frac{\partial}{\partial v}\left(\frac{R(\tau)}{m} P(\tau)\right)$$

time is τ

$$P(v,t) = e^{-t\hat{L}} p(v,0) - \int_0^t d\tau \, e^{-(t-\tau)\hat{L}} \frac{\partial}{\partial v}\left(\frac{R(\tau)}{m} P(v,\tau)\right)$$

Date

iterate

$$\frac{\partial P(v,t)}{\partial t} = -\hat{L} p(v,t) - \frac{\partial}{\partial v}\left(\frac{R(t)}{m} P(v,t)\right)$$

$$= -\hat{L} p(v,t) - \frac{\partial}{\partial v}\left(\frac{R(t)}{m} e^{-t\hat{L}} p(v,0)\right) \leftarrow \text{disto drop}$$

$$+ \frac{\partial}{\partial v}\left(\frac{R(t)}{m} \int_0^t d\tau \, e^{-(t-\tau)\hat{L}} \frac{\partial}{\partial v}\left(\frac{R(\tau)}{m} P(v,\tau)\right)\right)$$

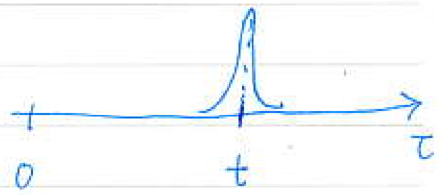
Aveg. over noise $\langle R \rangle = 0$

$$\langle R(t) R(\tau) \rangle = C \, \delta(t-\tau)$$

wick the pair of $R(t)$ with P is zero.

$$\frac{\partial \langle P(v,t)\rangle}{\partial t} = -\hat{L}\langle p(v,t)\rangle + \frac{\partial}{\partial v}\frac{1}{m^2}\int_0^t d\tau \, e^{-(t-\tau)\hat{L}} \underbrace{\langle R(t) R(\tau)\rangle}_{C\,\delta(t-\tau)} \frac{\partial P(v,\tau)}{\partial v}$$

$$= -\hat{L}\langle p(v,t)\rangle + \frac{C}{2m^2}\frac{\partial^2}{\partial v^2}\langle P(v,t)\rangle$$



why $\langle R(t) R(\tau) P(v,\tau)\rangle$

$$= \langle R(t) R(\tau)\rangle \langle P(v,\tau)\rangle \; ?$$

omit $\langle \; \rangle$

$$\rightarrow \frac{\partial P(v,t)}{\partial \tau} = \gamma \frac{\partial}{\partial v}\left(v P(v,t)\right) + \frac{C}{2m^2}\frac{\partial^2}{\partial v^2} P(v,t)$$

$$C = 2m\gamma k_B T$$

$$\frac{C}{2m^2} = \frac{\gamma k_B T}{m}$$

P is a polynml of noise $R(\tau)$

$$P(r,t) \cdots \int_{0\le\tau\le t}^{t} d\tau\, R(\tau) \cdots + \int_{\tau'<\tau} R(\tau')\, R(\tau) \cdots$$

apply Wick then

$$\int_{\tau''<\tau'<\tau} R(\tau'')\, R(\tau')\, R(\tau) + \cdots$$

$$\langle R(t)\, R(\tau)\, P(v,\tau) \rangle \leftarrow \text{time of } R(t') \text{ in } P(v,\tau) \text{ is always smaller than } t$$

$$R(t)\, R(\tau)\; R(\tau')\, R(\tau)$$

$$t < \tau \qquad \tau' < \tau$$

$$\delta(t-t') = \begin{cases} 0 \\ \frac{1}{2\Delta} & \text{if } |t-t'|<\Delta \end{cases}$$

$$R(t)\; R(\tau)\; R(\tau'')\; R(\tau')$$

$$t \geq \tau, \quad \tau' \leq \tau$$

$$\tau \leq t, \quad \tau'' \leq \tau'$$

$$R(t)\, R(\tau)\, \underbrace{R(\tau')\; R(\tau'')}$$

strictly non increasing

$$\int \delta(t-\tau')\, \delta(\tau-\tau'')\, d\tau''\, d\tau'\, d\tau$$

2 conditions needed for the validity of the derivation

1) R is gaussian

2) R is δ-correlated (white) noise.

if we keep $t > \tau$

Gaussian ~~proce~~ process $\langle \underbrace{R\, R \cdots R}_{\text{odd }\#} \rangle = 0$

$$\langle \underbrace{R R \cdots \; R}_{\text{even }\#} \rangle = \sum \langle \;\rangle \langle \;\rangle \langle \;\rangle$$

sum of product all possible pairings

we can assume $t_1 > t_2 > t_3 > t_4 > 0$
if not we permute and rename the variable

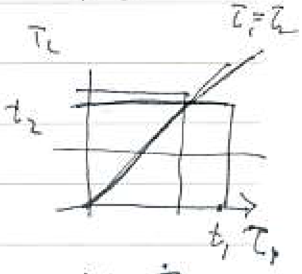
$\langle \delta v(t_1)\, \delta v(t_2)\, \delta(t_3)\, \delta(t_4) \rangle$

$$= \left\langle e^{-\gamma t_1} \int_0^{t_1} \frac{R(\tau_1)}{m} e^{\gamma\tau_1} d\tau_1 \; e^{-\gamma t_2} \int_0^{t_2} \frac{R(\tau_2)}{m} e^{\gamma\tau_2} d\tau_2 \right.$$

$$\left. e^{-\gamma t_3} \int_0^{t_3} \frac{R(\tau_3)}{m} e^{\gamma\tau_3} d\tau_3 \; e^{-\gamma t_4} \int_0^{t_4} \frac{R(\tau_4)}{m} e^{\gamma\tau_4} d\tau_4 \right\rangle$$

3 terms

$$\frac{e^{-\gamma(t_1+t_2+t_3+t_4)}}{m^4} \int_0^{t_1} d\tau_1 \int_0^{t_2} d\tau_2\, e^{\gamma(\tau_1+\tau_2)}\, C\,\delta(\tau_1-\tau_2) \cdot$$



$$\int_0^{t_3} d\tau_3 \int_0^{t_4} d\tau_4\, e^{\gamma(\tau_3+\tau_4)}\, C\,\delta(\tau_3-\tau_4)$$

giving τ_2 using τ_1

+ permutations
12 34
1 23 4
1 23 4

$$= \frac{e^{-\gamma(t_1+t_2+t_3+t_4)}}{m^4} \int_0^{t_2} d\tau_2\, e^{2\gamma\tau_2}\, C^2 \int d\tau_4\, e^{+2\gamma\tau_4}$$

$$\left[\cancel{\frac{1}{2\gamma}\left(1-e^{2\gamma t_2}\right) \frac{\left(1-e^{2\gamma t_4}\right)}{2\gamma}} \right.$$

$$\frac{1}{2\gamma}\left(e^{2\gamma t_2}-1\right) \frac{1}{2\gamma}\left(e^{2\gamma t_4}-1\right)$$

$$= \frac{1}{(2\gamma)^2 m^4} \left\{ e^{-\gamma(t_1+t_2+t_3+t_4)} \left[e^{2\gamma(t_2+t_4)} - e^{2\gamma t_4} - e^{2\gamma t_2} + 1 \right] \right.$$

$$= \frac{1}{(2\gamma)^2 m^4} \left[e^{-\gamma(t_1-t_2+t_3-t_4)} - e^{-\gamma(t_1-t_2+t_3+t_4)} \right.$$

$$\left. - e^{-\gamma(t_1+t_2+t_3-t_4)} + e^{-\gamma(t_1+t_2+t_3+t_4)} \right]$$

or $\langle \delta v_1\, \delta v_2\, \delta v_3\, \delta v_4 \rangle = \frac{C^2}{4\gamma^2 m^4} \left[e^{-\gamma|t_1-t_2| - \gamma|t_3-t_4|} \right.$

long time limit

$$+ e^{-\gamma|t_1-t_3| - \gamma|t_2-t_4|}$$

$$\left. + e^{-\gamma|t_1-t_4| - \gamma|t_2-t_3|} \right]$$

if $t_1 > t_2 > t_3 > t_4$ then

$$\langle \quad \rangle = \frac{C^2}{4\gamma^2 m^4} \left[e^{-\gamma(t_1-t_2) - \gamma(t_3-t_4)} + e^{-\gamma(t_1-t_3) - \gamma(t_2-t_4)} \right.$$

$$\left. + e^{-\gamma(t_1-t_4) - \gamma(t_2-t_3)} \right]$$

Date 6 April 2010

Relation between 2 different form of Boltzmann Eq.
(c.f. S Harris "an introduction to the Theory of the Boltzmann equation)

mass $=1$
$p = v$

symmetric form

$$W(\vec{v}_1 \vec{v}_2 \vec{v}_1{}' \vec{v}_2{}') = \sigma(\chi, V)\, \delta(\vec{v}_1 + \vec{v}_2 - \vec{v}_1{}' - \vec{v}_2{}')\, \delta\!\left(\frac{V^2 - V'^2}{2}\right)$$

momentum conservat

energy conservat

W is my $\sigma(p p_1 | p' p_1')$ on page 251.

where $V = |\vec{v}_2 - \vec{v}_1|$ $\quad V' = |\vec{v}_2{}' - \vec{v}_1{}'|$

χ is scattering angle θ

$$\underbrace{d\vec{v}_1{}'\, d\vec{v}_2{}'}_{6\text{-dimensional integrals}}\, W(\vec{v}_1 \vec{v}_2 \vec{v}_1{}' \vec{v}_2{}')$$

$\vec{v}_1$ is parameter
$\vec{v}_2$ last integral

consider variable change $\qquad d\vec{v} = dv_x\, dv_y\, dv_z$

$$\vec{v}_1{}', \vec{v}_2{}' \to \vec{V}', \vec{V}_c{}'$$

$$\vec{V}' = \vec{v}_2{}' - \vec{v}_1{}'$$

$$\vec{V}_c{}' = \frac{1}{2}(\vec{v}_1{}' + \vec{v}_2{}')$$

Jacob is $\begin{vmatrix} -1 & 1 \\ \frac{1}{2} & \frac{1}{2} \end{vmatrix} = -1$

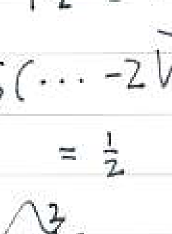
$d\vec{V}_c{}'\, \delta(\cdots - 2\vec{V}_c{}')$
$= \frac{1}{2}$

so $d\vec{v}_1{}'\, d\vec{v}_2{}' = d\vec{V}'\, d\vec{V}_c{}'$

so
$$d\vec{v}_1{}' d\vec{v}_2{}'\, W(\vec{v}_1 \vec{v}_2 \vec{v}_1{}' \vec{v}_2{}') = d\vec{V}'\, d\vec{V}_c{}'\, \sigma(\chi, V)\, \cancel{\delta(\vec{v} - \tfrac{2}{2V})}$$

$$\cancel{\times\, \sigma\, \ldots} \times \left(\delta(\vec{v}_1 + \vec{v}_2 - 2\vec{V}_c{}')\, \delta\!\left(\frac{V^2 - V'^2}{2}\right)\right) \quad \text{integ on } d\vec{V}_c{}'$$

$4\pi R^2 dR$



$$= \frac{1}{2}\, d\vec{V}'\, \sigma(\chi, V)\, \delta\!\left(\frac{V^2 - V'^2}{2}\right)$$

$$= \frac{1}{2}\, d\Omega\, V'^2 dV'\, \sigma(\chi, V)\, \delta\!\left(\frac{V^2 - V'^2}{2}\right)$$

$$= \frac{1}{2}\, d\Omega\, V'^2 dV'\, \sigma(\chi, V)\, \underbrace{\delta\!\left(\frac{(V - V')(V + V')}{2}\right)}_{\frac{1}{V}\delta(V' - V)}$$

$\delta(ax) = \frac{\delta(x)}{|a|}$

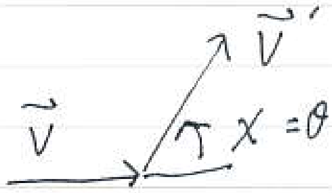
$V' = V$

why extra factor of 2.

$$d\vec{v}_1' \, d\vec{v}_2' \, W(\vec{v}_1 \vec{v}_2 \vec{v}_1' \vec{v}_2') = \frac{1}{2} \, d\Omega \cdot V \, \sigma(\chi, V)$$

To avoid the factor 2 we should define

$$W(\vec{v}_1, \vec{v}_2, \vec{v}_1', \vec{v}_2') = 2\,\sigma(\chi, V)\,\delta(\vec{v}_1 + \vec{v}_2 - \vec{v}_1' - \vec{v}_2')\,\delta\left(\frac{V^2 - V'^2}{2}\right)$$



Example of use of Green-kubo

(1) electric conduction $\vec{J} = \sigma \vec{E}$

current density

applied E-field

electric conductivity

$$\mathcal{H}_I = -\vec{p}\cdot\vec{E}(t)$$

$\hat{A}$ is $\vec{P} = \vec{A}$

dipole moment $\vec{p} = \sum_j e_j \vec{r}_j$

$$\vec{J} = \frac{\partial \vec{P}}{\partial t} = \sum e_j \vec{v}_j$$

$\hat{B}$ is $\dot{\vec{P}} = \dot{\vec{A}} = \hat{B}$

according to Green-kubo

$$\langle \hat{B}(t) \rangle = +\beta \int^{t} dt' \langle B_I(t) ; \dot{A}(t') \rangle \; a(t')$$

$$\langle \hat{J}(t) \rangle = \underbrace{\beta \int_0^t dt' \langle \hat{J}(t) ; \hat{J}(t') \rangle}_{\text{conductance tensor}} \vec{E}(t')$$

thermal current → correlation thermal conductivity

P_{xy} → viscosity η

pressure tensor

Date 25 / 3 / 11

linear response theory

$$H(t) = \hat{H}_0 - a(t)\hat{A}$$

$\uparrow$ scalar field

$$= \hat{H}_0 + \hat{V}$$

e.g. a | $\hat{A}$
E-field | displacement
h field | magnetization
B is | $\langle p(t) \rangle$ polarization
E field | dipole moment

$\vec{E}\cdot\hat{\vec{p}}$

wave function $|\psi\rangle$

$$U(t,t')|\psi(t')\rangle = |\psi(t)\rangle$$

$$i\hbar \frac{\partial U(t,t')}{\partial t} = \hat{H}(t)\, U(t,t')$$

$$\hat{\rho}(t) = \sum_i w_i |\psi_i(t)\rangle\langle\psi_i(t)| = U(t,0)\hat{\rho}(0)U(0,t)$$

$$\rightarrow \quad i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}(t), \hat{\rho}]$$

canonical with H_0

if $a=0$, $\hat{\rho}$ does not change and we assume $\hat{\rho}(0) = \frac{e^{-\beta \hat{H}_0}}{Z}$

$= \hat{B}$

Schrödinger picture

$$\langle \hat{B}(t) \rangle_S = \mathrm{Tr}[\hat{\rho}(t)\hat{B}]$$

change of $\hat{B}$ is purely due to the change of $\hat{\rho}(t)$ in eq. $\hat{B}$ is zero

we assume $\langle \hat{B} \rangle_{H_0} = 0$

interaction picture

$$\hat{B}_I(t) = e^{i\frac{H_0}{\hbar}t}\,\hat{B}\,e^{-i\frac{H_0}{\hbar}t}$$

$$\hat{\rho}_I(t) = e^{+i\frac{H_0}{\hbar}t}\,\hat{\rho}(t)\,e^{-i\frac{H_0}{\hbar}t} \qquad \hat{\rho}_I(0) = \hat{\rho}(0)$$

$$\cancel{i\hbar \partial \hat{\rho}_I} \quad i\hbar \frac{\hat{\rho}_I(t)}{dt} = e^{i\frac{H_0 t}{\hbar}}[-H_0, \hat{\rho}]e^{-i\frac{H_0 t}{\hbar}} + e^{i\frac{H_0 t}{\hbar}}[\hat{H}, \hat{\rho}]e^{-i\frac{H_0 t}{\hbar}}$$

$$= \cancel{-a(t)\hat{A}} = [\hat{V}_I, \hat{\rho}_I]$$

$$\mathrm{Tr}[\hat{\rho}_I(t)\hat{B}_I(t)]$$

Let $\hat{\rho}_I(t) = S(t,0)\hat{\rho}(0)S(0,t)$ compare w/ $\hat{\rho}_I = e^{\cdot\cdot}\rho$

where $S(t,0) = e^{\frac{iH_0t}{\hbar}} U(t,0)$ and $\rho = U(\cdot\cdot)$

$$i\hbar\frac{dS(t,0)}{dt} = - H_0 e^{\frac{iH_0t}{\hbar}} U(t,0) + e^{\frac{iH_0t}{\hbar}}(\hat{H}_0 + \hat{V})U(t,0)$$

$$= \hat{V}_I(t)S(t,0)$$

integr on both side

$$\int_0^t \frac{dS(t,0)}{dt}dt = \frac{1}{i\hbar}\int_0^t V_I(t')S(t',0)dt'$$

$$S(t,0) - 1 = \frac{1}{i\hbar}\int_0^t V_I(t')S(t',0)dt'$$

$$S(t,0) = 1 - \frac{i}{\hbar}\int_0^t V_I(t')S(t',0)dt'$$

iter

$$= \underbrace{1 - \frac{i}{\hbar}\int_0^t V_I(t')dt'}_{\text{Keep only to 1st order}} + \left(\frac{-i}{\hbar}\right)\int_0^t dt' V_I(t')\int^{t'} V(t'')dt'' + \cdots$$

$$\hat{\rho}_I(t) = \left[1 - \frac{i}{\hbar}\int_0^t V_I(t')dt'\right]\rho(0)\left[1 + \frac{i}{\hbar}\int_0^t V_I(t')dt'\right]$$

$$= \rho(0) - \frac{i}{\hbar}\int_0^t [V_I(t'), \rho(0)]dt' + O(V^2)$$

$$V_I = -a(t')\hat{A}_I(t')$$

$$\langle\hat{B}(t)\rangle = \mathrm{Tr}[\hat{\rho}_I(t)\hat{B}_I(t)]$$

$$= \underbrace{\mathrm{Tr}[\rho(0)\hat{B}_I(t)]}_{=0} - \frac{i}{\hbar}\int_0^t dt'\,\mathrm{Tr}\{[V_I(t'), \rho(0)]\hat{B}_I(t)\}$$

$\hat{B}$ inegr is 0

$$\langle \hat{B}(t) \rangle = + \frac{i}{\hbar} \int_0^t dt' \, \mathrm{Tr}\{ [A_I(t'), \rho(0)] \, \hat{B}_I(t) \} \, a(t')$$

$$A_I \rho B_I - \rho A_I B$$

cyclic

$$\rho B_I A_I$$

$$= \frac{i}{\hbar} \int_0^t dt' \, \mathrm{Tr}\{\rho(0) \, [B_I(t), A_I(t')]\} \, a(t')$$

retarded Green's fn

Let $$G_{BA}(t, t') = -\frac{i}{\hbar} \mathrm{Tr}\{\rho(0) [B_I(t), A_I(t')]\}$$

$$= -\frac{i}{\hbar} \langle [B_I(t), A_I(t')] \rangle_{eq} \, \theta(t - t')$$

$$\langle \hat{B}(t) \rangle = - \int_0^t dt \; G(t, t') \, a(t')$$

generalized susceptibility in eq. $G_{BA}(t, t') = G_{BA}(t - t')$

$$\chi(t - t') = - G(t, t')$$

B current
A is driver

$\dot{P} = j = B$

large time limit. In ω space
how current respond to electric field gives conductivity

d ~~B~~

j j correlation gives conductivity

$$\hat{B}[\omega] = - G[\omega] \, a[\omega]$$

Fourier transform

$$\mathrm{Tr}\{\rho(0) [B_I(t), A_I(t')]\} = i\hbar\beta \langle \dot{B}_I(t); \dot{A}_I(t') \rangle$$

$$\beta \langle \dot{a} ; b \rangle = \frac{1}{i\hbar} \langle [a, b] \rangle$$

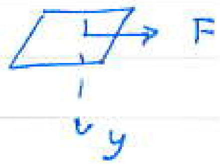
$$\langle \hat{B}(t) \rangle = -\beta \int_0^t dt' \, \langle \dot{B}_I(t); A(t') \rangle \, a(t')$$

$$\langle \dot{a} ; b \rangle = - \langle a ; \dot{b} \rangle$$

Kubo canonical correlation is def as $\langle a ; b \rangle = \frac{1}{\beta} \int_0^{\beta} d\lambda \, Tr\left[\rho(0) e^{\lambda H_0} a \, e^{-\lambda H_0} b\right]$

self diffusion constant $D = \int_0^{\infty} dt \, \langle v_x(t) v_x(0) \rangle$

$J_x = -\kappa \nabla T$



thermal conductivity $\kappa = \frac{V}{k_B T^2} \int_0^{\infty} dt \, \langle J_x(t) J_x(0) \rangle$

viscosity $\eta = \frac{V}{k_B T} \int_0^{\infty} dt \, \langle P_{xy}(t) P_{xy}(0) \rangle$

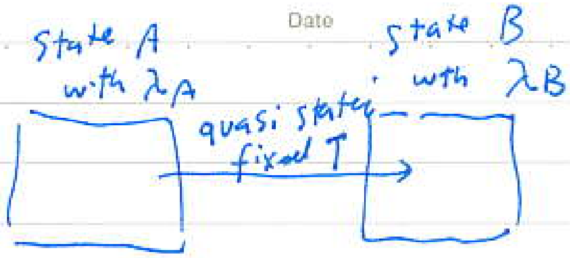
$\frac{F_x}{A} = P_{xy} = -\eta \frac{\partial u_x}{\partial y}$

we have $\langle a ; b \rangle = \langle b ; a \rangle$

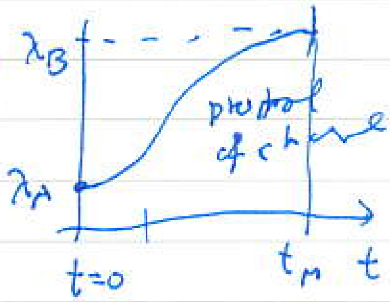
Date

thermodynamics

$H(\lambda)$



fixing T means
the system is in contact with
a bath so that δQ is exchanged!



$$T\,dS \geq \delta Q = -\delta W + dU$$

work done to the system

internal energy change

process that has fixed T

thermodynamic quasi-state process $t_M \to \infty$

$$F = U - TS$$

$$dF = dU - T\,dS$$ true only if T is fixed ?

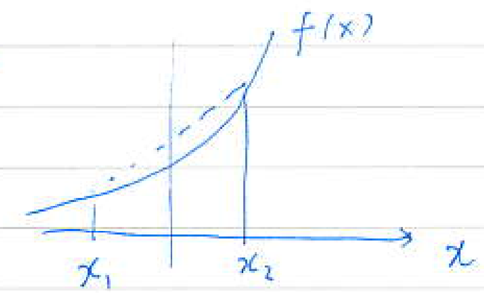
$$\delta W \geq dU - T\,dS = dF$$

integrate $W \geq F_B - F_A = \Delta F$ $=$ if $T_M \to \infty$

Jarzynski equality [PRL 78, 2690 (1997)]

$$\overline{e^{-\beta W}} = e^{-\beta \Delta F}$$ for finite T.

$\overline{e^{x}} \geq e^{\overline{x}}$ exponential function is convex



$$\lambda f(x_1) + (1-\lambda) f(x_2) \geq f(\lambda x_1 + (1-\lambda) x_2)$$

$$\langle f \rangle \geq f(\langle x \rangle)$$

Keep the heat-bath in the picture (Nosé-Hoover or coupled bigger system)

this is more difficult.

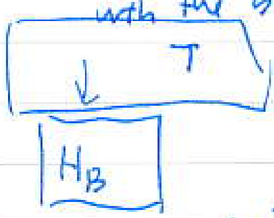
$t < 0$

dis connect during $0 < t < t_M$ evolve according to Hamilton dynamics

$\longrightarrow$

~~H(A~~ $H(\lambda(t))$ system out of equilibrium at t_M but can be reestablished during contact with bath again

re-contact with the bath



Work to the system

$$W = \int_0^{t_M} dt\, \dot{\lambda} \frac{\partial H}{\partial \lambda}$$

$z = \begin{pmatrix} p \\ q \end{pmatrix}$

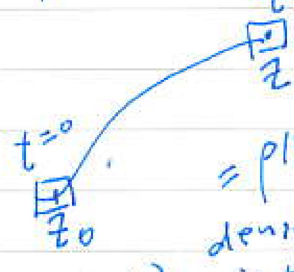
depends on the path of the dynamics in phase space

$z(t)$ is deterministic fixed only by the initial condition $z(0)$

" — " average means average over initial conditions expressed by the begin point

$$\overline{e^{-\beta W}} = \int dz_0\, \rho(z_0, 0)\, e^{-\beta W(z_0, t_M)}$$

$$= \int dz\, \rho(z, t)\, e^{-\beta W(z, t)}$$



$\rho(z_0, 0) = \rho(z, t)$ density is the same

distribution at time t

end point

$$W = \int_0^t dt\, \dot{\lambda} \frac{\partial H}{\partial \lambda} = \int d\lambda \frac{\partial H}{\partial \lambda} = H(\lambda_B, z) - H(\lambda_A, z_0)$$

begin point

$dz_0 = dz$ because hamilton dynamics preserve phase space volume

and ρ satisfies Liouville then $\frac{\partial \rho}{\partial t} = \{H, \rho\}$ or $\frac{D\rho}{Dt} = 0$

$$\overline{e^{-\beta W}} = \int dz\, \rho(z,t)\, e^{-\beta\left(H(\lambda_B, z) - H(\lambda_A, z_0)\right)}$$

$\downarrow$ back to $t=0$

$$= \int dz\, \underbrace{\rho(z_0, 0)\, e^{+\beta H(\lambda_0, z_0)}}\; e^{-\beta H(\lambda_B, z)}$$

$\longleftrightarrow$ cancel

only thing we really need is Jacob $=1$

$$\rho(z_0, 0) = \frac{e^{-\beta H(\lambda_A, z_0)}}{Z_A}$$

$$= \frac{1}{Z_A} \int dz\, e^{-\beta H(\lambda_B z)} = \frac{Z_B}{Z_A} = \frac{e^{-\beta F_B}}{e^{-\beta F_A}}$$

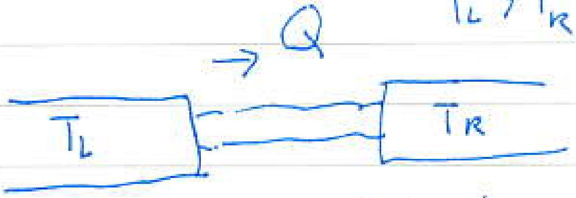
$$F = -k_B T \ln Z$$

$$= e^{-\beta(F_B - F_A)}$$

$$= e^{-\beta \Delta F}$$

Gallavotti-Cohen relation (theorem)

$T_L > T_R$



$$\frac{P(Q)}{P(-Q)} = e^{Q\left(\frac{1}{k_B T_R} - \frac{1}{k_B T_L}\right)}$$

$$= e^{Q(\beta_R - \beta_L)}$$

$P(Q)$ what is the heat transfer ~~fot~~ left lead to right lead during a fixed time t?

$$\beta = \frac{1}{k_B T}$$

A.B Pippard

13 Jan 2014

0-th law of thermodynamics

Date

If, of three bodies, A, B and C, A and B are separately in equilibrium with C, then A and B are in equilibrium with one another.

→ empirical temperature $\theta = \phi(P, V)$ can be defined

bodies in equilibrium have the same temperature

1st law

Energy is conserved if heat is taken into account.

U is a state function.

$$\Delta U = W + Q$$

Clausius

2nd law

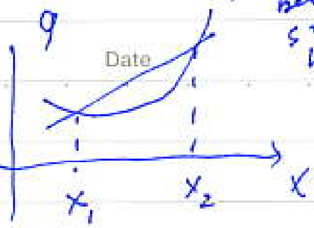
It is impossible to devise an engine which, working in a cycle, shall produce no effect other than the transfer of heat from a colder to a hotter body.

Kelvin

It is impossible to devise an engine which, working in a cycle, shall produce no effect other than the extraction of heat from a reservoir and the performance of an equal amount of mechanical work.

Jensen's inequality if $\varphi(x)$ is a convex function

then $\overline{\varphi(x)} \geq \varphi(\bar{x})$



φ is below the straight line between x_1 & x_2

$$\varphi(\lambda_1 x_1 + \lambda_2 x_2) \leq \lambda_1 \varphi(x_1) + \lambda_2 \varphi(x_2)$$

$0 \leq \lambda_1, \lambda_2 \leq 1$ straight line parametrized by λ

$\lambda_1 + \lambda_2 = 1$

$e^{\pm x}$ is convex $\qquad H = H_0 + H'$

$$Z = \mathrm{Tr}(e^{-\beta H})$$

$$Z_0 = \mathrm{Tr}(e^{-\beta H_0}) \qquad e^{-\beta H} = e^{-\beta H_0} e^{-\beta H'}$$

Jensen inequality $\qquad \langle \ldots \rangle_0 = \dfrac{\mathrm{Tr}(e^{-\beta H_0} \ldots)}{Z_0}$

$$\frac{Z}{Z_0} = \langle e^{-\beta H'} \rangle_0 \geq e^{-\beta \langle H' \rangle_0}$$

divide by $-\beta$

$$\ln Z - \ln Z_0 \geq -\beta \langle H' \rangle_0$$

$$F - F_0 \leq \langle H' \rangle_0 = \langle H - H_0 \rangle_0$$

$$F \leq F_0 + \langle (H - H_0) \rangle_0$$

Feynman - Jensen inequality or Bogoliubov inequality

Ising model

$$H_0 = -h_{eff} \sum_{i=1}^{N} \sigma_i \qquad \left[h_{eff} = Jqm + h\right]$$

not yes

$$F_0 = -k_B T N \ln Z = -k_B T N \ln 2\cosh(\beta h_{eff})$$

determine h_{eff} by minimizing

$$\langle H - H_0 \rangle_0 = \langle -J \sum_{ij} \sigma_i \sigma_j - (h - h_{eff}) \sum_{i=1}^{N} \sigma_i \rangle_0$$

$$= -J \frac{q}{2} N m^2 - (h - h_{eff}) m \cdot N$$

$$m \equiv \langle \sigma_i \rangle_0$$

ψ

$$F \leq -k_B T N \ln(2\cosh(\beta h_{eff})) + \frac{1}{2} J q N m^2 - (h - h_{eff}) \cdot m \cdot N$$

min wrt respect to h_{eff} & m both

1) $\frac{\partial \psi}{\partial h_{eff}} = 0$ $\quad -\frac{N}{\beta} \frac{\sinh(\beta h_{eff})}{2\cosh(\beta h_{eff})} \cdot \beta + m N = 0$

$$\rightarrow \quad m = \tanh(\beta h_{eff})$$

2) $0 = \frac{\partial \psi}{\partial m} = -J q N m - (h - h_{eff}) N = 0$ $\qquad h_{eff} = h + J q m$

~~approx free en is~~

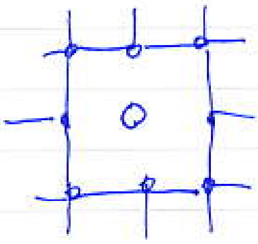
$$F \approx -k_B T N \ln(2\cosh(\beta(h + J q m))) + \frac{1}{2} J q N m^2$$

Cavity method A. Georges "Dynamical mean-field theory..." RMP 68 13 (1996)

$q = 2D$ hypercubic lattice

$k_B T_c = J q$ $\quad$ scale $J \rightarrow J^* = J = \frac{J^*}{2D}$ $\quad J \rightarrow 0$

$$\frac{k_B T_c}{J^*} = 1$$



$$H = -h_0 \sigma_0 - J \sum_{j \in nn\ of\ 0} \sigma_j \sigma_0 + H^0$$

site 0 as well interactions near 0 & nn removed

effective Ham

$$e^{-\beta H_{eff}(\sigma_0)} = \sum_{\text{sum over all except site } \sigma_0} e^{-\beta H(\sigma)}$$

Exact stat mech of cavity

$$Z_0 = \sum_{\sigma_i,\ i \neq 0} e^{-\beta(-\sum \eta_i \sigma_i + H_0)}$$

$$\langle \sigma_i \sigma_j \ldots \sigma_k \rangle_c^{(0)} = \frac{\partial^n \ln Z_0}{\partial \beta\eta_i\, \partial \beta\eta_j \ldots \partial \beta\eta_k}\Bigg|_{\eta_i = 0}$$

Taylor expand $\ln Z_0$

$$\ln Z_0(\eta) = \ln Z_0(\eta_i = 0) + \beta \sum_i \langle \sigma_i \rangle^{(0)} \eta_i + \frac{1}{2}\beta^2 \sum_{ij} \langle \sigma_i \sigma_j \rangle_c^0 \eta_i \eta_j + \cdots$$

$\rightarrow 0 \quad D \to \infty$

$$e^{-\beta H_{eff}(\sigma_0)} = \sum_{\{\sigma_i\}\, i \neq 0} e^{-\beta H(\sigma)}$$

$$= \sum_{\{\sigma_i\}\, i \neq 0} e^{-\beta\left(-h\sigma_0 - \frac{J^*}{2D}\sum_j \sigma_j \sigma_0 + H^0\right)}$$

special case of gen'l cavity hamilt.

$$= e^{\beta h \sigma_0} \sum_{\{\sigma\}} e^{-\beta\left(-\sum_j \sigma_j \eta_j + H_0\right)} \quad \text{with } \eta_j = \begin{cases} \frac{J^*}{2D}\sigma_0 & \text{if } j \in \text{nn. of } 0 \\ 0 & \text{otherwise} \end{cases}$$

take ln, div by $-\frac{1}{\beta}$

$$H_{eff}(\sigma_0) = -h\sigma_0 - \frac{1}{\beta}\left(\ln Z_0(\eta) \;\ldots\right)$$

$$= \text{const} - h\sigma_0 - \sum_{j \in \text{nn } 0} \langle \sigma_j \rangle^0 \eta_j + \cdots$$

as $D \to \infty$ $\quad \langle \sigma_j \rangle^0 = \langle \sigma_j \rangle + O(\frac{1}{D})$

$$H_{eff}(\sigma_0) - h\sigma_0 - \cancel{\Sigma} \langle \sigma_0 \rangle J \cdot q\, \sigma_0 + \cdots$$