

Fundamentals

1.) $p = .5$
 $q = .5$

$$P(3) = p^3 q^2 \frac{5!}{3! 2!} = \frac{1}{2^5} \times 10 = \frac{5}{16}$$

$$= .5^5 \times 10$$

$$5 \times .5^4 = 5 \times .25^2 = \frac{1.25}{4} = \frac{5}{16}$$

Extra credit: I don't know

2.) $H(p_1, \dots, p_N; q_1, \dots, q_N)$

for canonical p.f. we have

$$Q_N(\beta) = \int dq_1 \dots dq_N \int dp_1 \dots dp_N [L(q_1(t), \dots, q_N(t))]$$

$$\exp \left[- \int_0^\beta dt \left(\sum_{i=1}^N \frac{1}{2} \dot{q}_i^2(t) + V(q_1(t), \dots, q_N(t)) \right) \right]$$

to obtain grand canonical

$$\tilde{Q}_N(\beta) = \sum_N e^{\beta \mu N} Q_N(\beta)$$

3.) time-correlation function in canonical ensemble

$$\frac{1}{Q} \int dq_1 \dots dq_N dp_1 \dots dp_N e^{-\beta H(p_1, \dots, p_N; q_1, \dots, q_N)} A(p_1, \dots, p_N; q_1, \dots, q_N) \left(e^{-i \hat{L} t} A(p_1^c, \dots, p_N^c; q_1, \dots, q_N) \right)$$

where $Q = \int dq_1 \dots dq_N dp_1 \dots dp_N e^{-\beta H(p_1, \dots, p_N; q_1, \dots, q_N)}$

$\hat{L}$ - Liouville operator

$$\frac{\partial}{\partial t} i \hat{L} \rho = \rho \{ H, \rho \} \rightarrow \text{Poisson brackets}$$

$$= - \frac{\partial \rho}{\partial p} \frac{\partial H}{\partial q} + \frac{\partial \rho}{\partial q} \frac{\partial H}{\partial p}$$

4-) two coupled harmonic oscillators can be decoupled $\Rightarrow$ if decoupled system is not ergodic and virial / equipartition theorems are not necessarily applicable $\Rightarrow$ applicable if modes can be "freely excited"

Applications

1) probability density: $P(v_x, v_y, v_z) = e^{-\frac{\beta m}{2}(v_x^2 + v_y^2 + v_z^2)}$

normalize $\int dv_x e^{-\frac{\beta m}{2} v_x^2} = \sqrt{\frac{2\pi}{\beta m}}$

$\Downarrow$

$$P(v_x, v_y, v_z) = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{\beta m}{2}(v_x^2 + v_y^2 + v_z^2)}$$

to write energy $P(E)$

$$P(E) = \int dv_x dv_y dv_z \delta\left(E - \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)\right) P(v_x, v_y, v_z)$$

$$= \int v^2 dv (4\pi) \delta\left(E - \frac{m}{2} v^2\right) e^{-\frac{\beta m}{2} v^2} \left(\frac{\beta m}{2\pi}\right)^{3/2}$$

$$= 4\pi \left(\frac{\beta m}{2\pi}\right)^{3/2} \int v^2 dv \delta\left(E - \frac{m}{2} v^2\right) e^{-\frac{\beta m}{2} v^2}$$

define $x = \frac{m}{2} v^2 \Rightarrow \sqrt{\frac{2x}{m}} = v$

$\&$ $dv = \sqrt{\frac{2}{m}} \frac{dx}{2\sqrt{x}}$

$$= 4\pi \left(\frac{\beta m}{2\pi}\right)^{3/2} \int \left(\frac{2x}{m}\right) \sqrt{\frac{2}{m}} \left(\frac{1}{2}\right) \frac{dx}{\sqrt{x}} \delta(E - x) e^{-\beta x}$$

now integrate out δ -fn.

$$\begin{aligned} P(E) &= \frac{2}{\sqrt{\pi}} \left(\frac{\beta \hbar}{2m} \right)^{3/2} \left(\frac{2}{m} \right)^{1/2} \int \frac{dx}{\beta} \sqrt{x} \delta(E-x) e^{-\beta x} \\ &= \frac{2}{\sqrt{\pi}} \beta^{3/2} \sqrt{E} e^{-\beta E} \end{aligned}$$

$$\begin{aligned} 2.) \quad & \int dp dq A(p, q) \left[\exp(-i\hat{L}t) \delta(p, q) \right] \\ &= \int dp dq A(p, q) \left[\sum_{n=0}^{\infty} \frac{t^n (-i\hat{L})^n}{n!} \delta(p, q) \right] \end{aligned}$$

$$-i\hat{L} \delta(p, q) = -\frac{\partial \delta}{\partial p} \frac{\partial H}{\partial q} + \frac{\partial \delta}{\partial q} \frac{\partial H}{\partial p}$$

~~$$\left(\frac{1}{-i\hat{L}} \right)^2 \delta(p, q) = -\frac{\partial^2 \delta}{\partial p^2} \left(\frac{\partial H}{\partial p} \right)^2$$~~

first-order term

$$\int dp dq A(p, q) \left[-\frac{\partial \delta}{\partial p} \frac{\partial H}{\partial q} + \frac{\partial \delta}{\partial q} \frac{\partial H}{\partial p} \right]$$

integration by parts gives

$$\int dp dq \left(\frac{\partial A(p, q)}{\partial p} \frac{\partial H}{\partial q} - \frac{\partial A(p, q)}{\partial q} \frac{\partial H}{\partial p} \right) \delta(p, q)$$

$$\int dp dq [i\hat{L} A(p, q)] \delta(p, q)$$

even terms will not switch sign

$\Rightarrow$

now integrate δ -fu.

$$\begin{aligned} P(E) &= 2\pi \left(\frac{\beta}{\pi}\right)^{3/2} \int dx \sqrt{x} \delta(E-x) e^{-\beta x} \\ &= \frac{2}{\sqrt{\pi}} \beta^{3/2} \sqrt{E} e^{-\beta E} \end{aligned}$$

2.) $\int dp dq A(p, q) [\exp[-i \hat{J} t] \delta(p, q)]$

expand propagator

$$\int dp dq A(p, q) \left[\sum_{n=0}^{\infty} \frac{(-it)^n \hat{J}^n}{n!} \right] \delta(p, q)$$

consider first-order term

$$t \int dp dq A(p, q) [-i \hat{J}] \delta(p, q)$$

$$-i \hat{J} \delta(p, q) = -\frac{\partial \delta(p, q)}{\partial p} \frac{\partial H}{\partial q} + \frac{\partial \delta(p, q)}{\partial q} \frac{\partial H}{\partial p}$$

$$t \int dp dq A(p, q) \left[-\frac{\partial \delta(p, q)}{\partial p} \frac{\partial H}{\partial q} + \frac{\partial \delta(p, q)}{\partial q} \frac{\partial H}{\partial p} \right]$$

integrate
by
parts

first term in p
second term in q

$$t \int dp dq \left[\frac{\partial A(p, q)}{\partial p} \frac{\partial H}{\partial q} - \frac{\partial A(p, q)}{\partial q} \frac{\partial H}{\partial p} \right] \delta(p, q)$$

$$t \int dp dq [(i \hat{J}) A(p, q)] \delta(p, q)$$

upon integration by parts $i \hat{J}$ switches sign

odd terms will switch sign

even terms will not

$$\Rightarrow \int dp dq \left[\sum_{n=0}^{\infty} \frac{(+it)^n \hat{J}^n}{n!} A(p, q) \right] \delta(p, q)$$

$$= \int dp d\bar{p} [\exp[i \hat{J} t]] A(p, a) \delta(p, a)$$

$$3.) \quad Q_1(T) = \sum_{n=-J}^J e^{-\beta \epsilon_n}$$

$$Q_N(T) = Q_1(T)^N$$

$$F = \sum_{n=-J}^J x^n = \quad x = e^{-\beta \epsilon}$$

$$xF = \sum_{n=-J+1}^{J+1} x^n = x^{J+1} - x^{-J} + F$$

$$F(x-1) = x^{J+1} - x^{-J}$$

$$F = \frac{x^{J+1} - x^{-J}}{x-1} = \frac{x^{J+1/2} - x^{-J-1/2}}{x^{1/2} - x^{-1/2}}$$

$$x = e^{-\beta \epsilon}$$

$$\Rightarrow F = \frac{\sinh(\beta \epsilon (J + \frac{1}{2}))}{\sinh(\beta \epsilon / 2)}$$

$$Q_N(T) = \frac{\sinh^N(\beta \epsilon (J + \frac{1}{2}))}{\sinh^N(\beta \epsilon / 2)} \quad - \text{canonical p. f.}$$

internal energy

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N(T) = -\frac{1}{Q_N(T)} \frac{\partial Q_N(T)}{\partial \beta}$$

$$\frac{\partial Q_N}{\partial \beta} = \frac{N \sinh^{N-1}(\beta \epsilon (J + \frac{1}{2})) \cosh(\beta \epsilon (J + \frac{1}{2})) \epsilon (J + \frac{1}{2})}{\sinh^N(\beta \epsilon / 2)}$$

$$- \frac{N \sinh^N(\beta \epsilon (J + \frac{1}{2})) \cosh(\beta \epsilon / 2) \epsilon / 2}{\sinh^{N+1}(\beta \epsilon / 2)}$$

$$\langle E \rangle = -N \frac{\cosh(\beta E(\sigma + 1/2)) E(\sigma + 1/2)}{\sinh(\beta E(\sigma + 1/2))}$$

$$+ N \frac{\cosh(\beta E/2)}{\sinh(\beta E/2)} E/2$$

$$= N \left[\coth(\beta E/2) E/2 - \coth(\beta E(\sigma + 1/2)) E(\sigma + 1/2) \right]$$

entropy

$$\frac{S}{k} = -N \sum_j P_j \ln P_j$$

$$= -N \sum_{n=-J}^J \frac{e^{-\beta E n}}{Q} \ln \frac{e^{-\beta E n}}{Q}$$

$$= -N \sum_{n=-J}^J \frac{e^{-\beta E n}}{Q} (-\beta E n) + N \sum_{n=-J}^J \frac{e^{-\beta E n}}{Q} \ln Q$$

$$= N \beta \langle E \rangle + N \ln Q$$

can also be obtained using $A = \langle E \rangle - TS$

$$A = -kT \ln Q$$

limits

1st, J-limit $\beta \rightarrow \infty$ ($T \rightarrow 0$)

$$\langle E \rangle \rightarrow N \frac{E}{2} - N E(\sigma + 1/2) = -NEJ \Rightarrow \text{ground state energy}$$

(all spins in ground state)

J-finite $\beta \rightarrow 0$ ($T \rightarrow \infty$)

$$\coth(\beta E) \rightarrow \frac{1}{2\beta E}$$

$\langle E \rangle \rightarrow N \left(\frac{1}{2\beta} - \frac{1}{2R} \right) = 0 \Rightarrow$ energy bounded
from above $\Rightarrow$ temperature
can be negative

if $J \rightarrow \infty$ $\langle E \rangle \rightarrow -N(J + \frac{1}{2}) \Rightarrow$ since energy is not
bounded at all (neither from below, nor from
above) $\Rightarrow$ ~~energy~~ temperature is not applicable
as a concept

4.) A.) reservoir analysis or ensemble analysis work

ensemble: $\tilde{\Omega} = \frac{\tilde{N}!}{\prod_{rs} n_{rs}!}$

$$\sum_{rs} n_{rs} = \tilde{N}$$

$$\sum_{rs} n_{rs} E_r = \tilde{N} \bar{E}$$

$$\sum_{rs} n_{rs} V_s = \tilde{N} \bar{V}$$

$\bar{E}$ = average energy

$\bar{V}$ = average volume

minimize under constraints: use Stirling approximation

$$\ln \tilde{\Omega} = \tilde{N} \ln \tilde{N} - \sum_{rs} n_{rs} \ln n_{rs} + \beta \left(\sum_{rs} n_{rs} E_{rs} - \tilde{N} \bar{E} \right) \\ - \alpha \left(\sum_{rs} n_{rs} V_{rs} - \tilde{N} \bar{V} \right)$$

$$\frac{\partial \ln \tilde{\Omega}}{\partial n_{rs}} = -\ln n_{rs} - 1 - \beta E_{rs} - \alpha V_{rs} = 0$$

$$\Rightarrow \frac{n_{rs}}{\tilde{N}} = \frac{e^{-\beta E_r - \alpha V_s}}{\sum_{rs} e^{-\beta E_r - \alpha V_s}}$$

$$P_{rs} = \frac{e^{-\beta E_r - \alpha V_s}}{\sum_{rs} e^{-\beta E_r - \alpha V_s}} \quad \Omega = \sum_{rs} e^{-\beta E_r - \alpha V_s}$$

$$\tilde{G} = \ln \Omega = \ln \sum_{rs} e^{-\beta E_r - \alpha V_s}$$

$$d\tilde{G} = \frac{1}{\Omega} \sum_{rs} e^{-\beta E_r - \alpha V_s} (-d\beta E_r)$$

$$+ \frac{1}{\Omega} \sum_{rs} e^{-\beta E_r - \alpha V_s} (-d\alpha V_s)$$

$$+ \frac{1}{\Omega} \sum_{rs} e^{-\beta E_r - \alpha V_s} (-\beta dE_r)$$

$$d\tilde{G} = -d\beta \bar{E} - d\alpha \bar{V} + \beta \frac{\sum_{rs} e^{-\beta E_r - \alpha V_s} dE_r}{\Omega}$$

$$d(\tilde{G} + \beta \bar{E} + \alpha \bar{V}) = -\beta d\bar{E} - \alpha d\bar{V} - \beta \frac{\sum_{rs} e^{-\beta E_r - \alpha V_s} dE_r}{\Omega}$$

$$\text{identity } \beta = \frac{1}{kT} \quad \alpha = -\frac{P}{kT}$$

$$S = \tilde{G} + \beta \bar{E} + \alpha \bar{V} \rightarrow \text{entropy}$$

↑
work other than
PV-expansion

$$TS = \tilde{G} + \beta \bar{E} + \alpha \bar{V}$$

$$\text{definition of Gibbs free energy: } G = \bar{E} - TS - P\bar{V}$$

$$\tilde{G} = -\bar{E} + TS + P\bar{V} = -G$$

⇒

D.)

$$\tilde{\Omega} = \frac{\tilde{N}}{N n_r!}$$

$$\sum_r n_r = \tilde{N}$$

$$\sum_r n_r V_r = \tilde{N} \bar{V}$$

maximize $\ln \tilde{\Omega}$

$$\ln \tilde{\Omega} + \alpha (\sum_r n_r V_r - \tilde{N} \bar{V})$$

$$\tilde{N} \ln \tilde{N} - \sum_r n_r \ln n_r + \alpha (\sum_r n_r V_r - \tilde{N} \bar{V})$$

$$\Rightarrow Q = \sum_r e^{-\alpha V_r}$$

$$P_r = \frac{e^{-\alpha V_r}}{Q} = \frac{n_r}{\tilde{N}}$$

entropy: $S = \ln \tilde{\Omega}$

$$= \tilde{N} \ln \tilde{N} - \sum_r \frac{\tilde{N} e^{-\alpha V_r}}{Q} \ln \frac{\tilde{N} e^{-\alpha V_r}}{Q}$$

$$= \cancel{\tilde{N} \ln \tilde{N}} - \sum_r \frac{\tilde{N} e^{-\alpha V_r}}{Q} \ln \tilde{N} - \sum_r \frac{\tilde{N} e^{-\alpha V_r}}{Q} \ln e^{-\alpha V_r}$$

$$+ \sum_r \frac{\tilde{N} e^{-\alpha V_r}}{Q} \ln Q$$

$$= -\alpha \bar{V} + \ln Q$$

$$\alpha \rightarrow \frac{P}{kT} \quad (\text{from previous part of exercise})$$