(1) a) Let N_+ be the number of ~~polymers~~ monomers in horizontal orientation and N_- be the number of monomers in ~~...~~ vertical orientation.

$$N_+ + N_- = N$$

$$N_+ a = L \quad \Rightarrow \quad N_+ = L/a$$

$$N_+ = N\ell/a$$

$$N_- = N(1-\ell/a)$$ 1

$$\therefore \; \Omega(L,N) = \frac{N!}{\left(N\frac{\ell}{a}\right)! \; [N(1-\ell/a)]!}$$ 1

$$S = k_B \ln \Omega = \ln N! - \ln\left(N\frac{\ell}{a}\right)! - \ln[N(1-\ell/a)]!$$ 1

$$= \Big[N\ln N - \cancel{N} - \left(\frac{N\ell}{a}\ln\frac{N\ell}{a} - \frac{N\ell}{a}\right) - \left(N\left(1-\frac{\ell}{a}\right)\ln N(1-\ell/a) - N(1-\ell/a)\right)\Big]$$

$$= +N\ln N - N - \frac{N\ell}{a}\ln\frac{N\ell}{a} + \frac{N\ell}{a} - N\left(1-\frac{\ell}{a}\right)\ln N(1-\ell/a) + N(1-\ell/a)\Big]$$ 1

$$= N\ln N - \frac{N\ell}{a}\ln\frac{N\ell}{a} - N(1-\ell/a)\ln N(1-\ell/a)$$

$$= N\ln N - \frac{N\ell}{a}\ln N - N(1-\ell/a)\ln N - \frac{N\ell}{a}\ln\frac{\ell}{a} - N(1-\ell/a)\ln(1-\ell/a)$$

$$S = -N\frac{\ell}{a}\ln\ell/a - N(1-\ell/a)\ln(1-\ell/a).$$ 1

(b) $TdS = dU - FdL$

$$\left.\frac{\partial S}{\partial L}\right)_U = -\frac{F}{T} \qquad \left.\frac{\partial S}{\partial \ell}\right)_U = -\frac{NF}{T}$$ 1

$$\cancel{\left.\frac{\partial S}{\partial \ell}\right) = -\frac{N}{}\left[\frac{1}{a}\ln(1+\right.}$$

$$\left.\frac{\partial S}{\partial \ell}\right) = -Nk_B\left[\frac{1}{a}\ln \ell/a + \frac{1}{a} - \frac{1}{a}\ln(1-\ell/a) - \frac{1}{a}\right]$$

$$= -\frac{Nk_B}{a}\ln\left(\frac{\ell/a}{1-\ell/a}\right)$$ 1

$$\frac{NF}{T} = \frac{Nk_B}{a}\ln\frac{\ell/a}{1-\ell/a}$$ 1

$$\frac{Fa}{k_BT} = \ln\frac{\ell/a}{1-\ell/a} \Rightarrow \frac{\ell}{a} = (1-\ell/a)e^{\beta Fa}$$

$$\frac{\ell}{a}\left(1+e^{\beta Fa}\right) = e^{\beta Fa}$$

$$\frac{\ell}{a} = \frac{e^{\beta Fa}}{1+e^{aF\beta}}$$

$$L = Na\frac{e^{\beta Fa}}{1+e^{\beta Fa}}$$ 2

For High temperatures $\beta \to 0$.

$$L = \frac{Na}{2}\frac{1+\beta Fa}{1+\frac{1}{2}\beta Fa} = \frac{Na}{2}\left(1+\frac{1}{2}\beta Fa\right).$$

$$= \frac{Na}{2}\left(1+\frac{Fa}{2k_BT}\right)$$

c) Canonical Formulation: Since the chain is at a constant temperature T.

difference between the energies Fa. 1

$$Z_N = (1+e^{\beta F a})^N$$ 1

Further constant force ensemble (T, F, N) similar to (T, P, N) and hence Gibb's free energy is the relevant thermodynamic potential.

$$G = U - TS - FL$$

$$dG = -S\,dT - L\,dF$$

$$\left.\frac{\partial G}{\partial F}\right)_T = -L$$ 1

$$G = -k_B T \ln Z_N$$ [Similar to ~~$G = -k_B$~~ the isochoric ensemble we did in class]

$$G = -N k_B T \ln(1+e^{\beta F a})$$

$$\left.\frac{\partial G}{\partial F}\right)_T = -N k_B T \frac{e^{\beta F a}}{1+e^{\beta F a}} \beta a$$

$$L = Na \frac{e^{\beta F a}}{1+e^{\beta F a}}$$

$$l = a \frac{e^{\beta F a}}{(1+e^{\beta F a})}$$ 2

3(a) Total no microstates with the Hamiltonian given

$$\mathcal{H} = \sum_i \frac{l_i^2}{2I}.$$

The microstate is given by $\{\theta_1, \theta_2, \dots \theta_N; l_1, l_2, \dots l_N\}$

Similar to free particle system $\{r_1, r_2, \dots r_N; p_1, \dots p_N\}$.

$$\Omega = \int \prod_i d\theta_i \int \prod_i dp_i \quad 0 \le \mathcal{H} \le E$$

$$= (2\pi)^N \text{ Volume of sphere of radius } \sqrt{2IE}$$ 1

$$= (2\pi)^N \frac{\cancel{2}\,\pi^{N/2}}{\Gamma(N/2+1)} (2IE)^{N/2}$$

$$= (2\pi)^N \frac{\pi^{N/2}}{(N/2)!} (2IE)^{N/2} = (2\pi)^N \frac{(2\pi IE)^{N/2}}{(N/2)!}$$ 1

Use sterling's approximation

$$\ln N! = N\ln N - N = N\ln N - N\ln e$$

$$= N\ln N/e = \ln (N/e)^N$$

$$N! \simeq \left(\frac{N}{e}\right)^N$$

$$\Omega = (2\pi)^N \frac{(2\pi IE)^{N/2}}{\left(\frac{N}{2e}\right)^{N/2}} = (2\pi)^N \left(\frac{4\pi e IE}{N}\right)^{N/2}$$ 1

(b) $$S = k_B \ln \Omega = k_B \left[N\ln 2\pi + \frac{N}{2} \ln\left(\frac{4\pi e IE}{N}\right)\right]$$

$$= N k_B \left[\ln 2\pi + \frac{1}{2} \ln 4\pi e I + \frac{1}{2}\ln E - \frac{1}{2}\ln N\right]$$

$$= N k_B \left[\ln 2\pi\sqrt{4\pi e I} + \frac{1}{2}\ln E - \frac{1}{2}\ln N\right]$$ 2

$$\left.\frac{\partial S}{\partial E}\right)_N = \frac{1}{T} \quad \Rightarrow \quad \frac{1}{T} = \frac{N k_B}{2E}$$

$$E = \frac{1}{2} N k_B T$$ 1

Specific Heat : $\frac{\partial E}{\partial T} = \frac{1}{2} N k_B$ 1

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c) $\rho(l_1, \theta_1 ; l_2, \theta_2 ; \dots \, l_N, \theta_N) = \frac{1}{\Omega}$

$$\rho(l_1, \theta_1) = \frac{\Omega(N-1, E_{N-1})}{\Omega(N, E)} \qquad E_{N-1} = \sum_{i=2}^{N} \frac{l_i^2}{2I}$$ 1

$$E = \frac{l_1^2}{2I} + \sum_{i=2}^{N} \frac{l_i^2}{2I} \qquad E_{N-1} = E - \frac{l_1^2}{2I}$$

$$\rho(l_1, \theta_1) = \frac{(2\pi)^{N-1}}{(2\pi)^N} \left[\frac{4\pi e I E_{N-1}}{(N-1)}\right]^{\frac{(N-1)}{2}} \left(\frac{N}{4\pi e I E}\right)^{N/2}$$ 1

$$= \frac{1}{2\pi} \frac{\left[4\pi e I E \left(1 - \frac{l_1^2}{2IE}\right)\right]^{\left(\frac{N-1}{2}\right)}}{(4\pi e I E)^{N/2}} \frac{N^{N/2}}{(N-1)^{\left(\frac{N-1}{2}\right)}}$$

$$\simeq \frac{1}{2\pi} \frac{(4\pi e I E)^{(N-1)/2}}{(4\pi e I E)^{N/2}} \left(1 - \frac{l_1^2}{2IE}\right)^{\frac{(N-1)}{2}} \frac{N^{N/2}}{\left(\frac{N^{N/2}}{N^{1/2}}\right)}$$

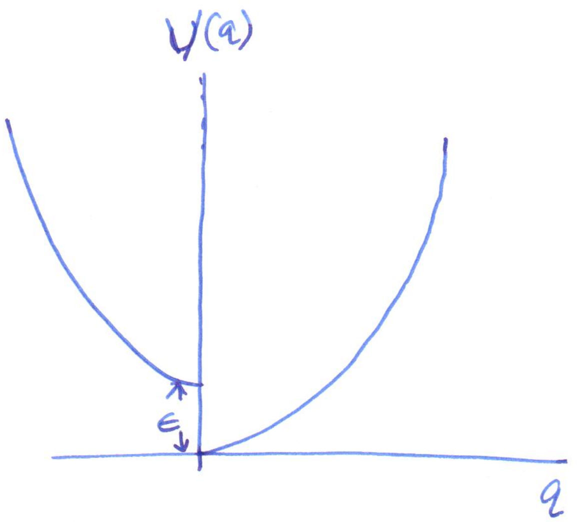
$$\simeq \frac{1}{2\pi} \sqrt{N} \frac{1}{(4\pi e I E)^{1/2}} \left(1 - \frac{l_1^2}{2IE}\right)^{N/2}$$

$$\simeq \frac{1}{2\pi} \sqrt{\frac{N}{4\pi e I \frac{N k_B T}{2}}} \left(1 - \frac{l_1^2}{2I \frac{N}{2} \cdot k_B T}\right)^{N/2}$$ 1

$$\varrho(\ell,\theta) = \frac{1}{2\pi}\frac{1}{\sqrt{2\pi I k_B T}}\, e^{-\ell^2/2I k_B T}$$

$$\varrho(\ell) = \int_0^{2\pi} \varrho(\ell,\theta)\, d\theta = \frac{1}{\sqrt{2\pi I k_B T}}\, e^{-\ell^2/2I k_B T}$$ 1

3



a) Single particle ~~partition~~ function is given by

$$Q = \frac{1}{(2\pi\hbar)}\int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dq \; e^{-\beta h_i(p,q)}$$ 1

$$h_i(p,q) = \frac{p^2}{2m} + V(q)$$

$$= \int_{-\infty}^{+\infty} dp\, e^{-\beta p^2/2m} \int_{-\infty}^{+\infty} dq\, e^{-\beta V(q)}$$

$$= \sqrt{\frac{\pi}{\beta/2m}}\, I(\epsilon) = \left(\frac{2m\pi}{\beta}\right)^{1/2} I(\epsilon)$$

with $I(\epsilon) = \int_{-\infty}^{+\infty} dq\; e^{-\beta V(q)}$

$$I(\epsilon) = \int_{-\infty}^{0} e^{-\beta \frac{m\omega^2}{2} q^2 - \beta\epsilon}\, dq + \int_{0}^{\infty} dq\; e^{-\beta \frac{m\omega^2}{2} q^2}$$ 1

$$= e^{-\beta\epsilon} \frac{1}{2}\sqrt{\frac{2\pi}{\beta m\omega^2}} + \frac{1}{2}\sqrt{\frac{2\pi}{\beta m\omega^2}}$$

$$= \frac{1}{2}\sqrt{\frac{2\pi}{\beta m\omega^2}}\left[1 + e^{-\beta\epsilon}\right]$$ 1

$\epsilon \to 0 \qquad I(0) = \sqrt{\frac{2\pi}{\beta m\omega^2}}$ Classical Harmonic oscillator. as worked out in class.

$\epsilon \to \infty \qquad I(\infty) \qquad I(\infty) = \frac{1}{2}\sqrt{\frac{2\pi}{\beta m\omega^2}}$ Harmonic oscillator can access only half the coordinate space.

$$Q = \left(\frac{2m\pi}{\beta}\right)^{1/2} \frac{1}{2}\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2}\left[1 + e^{-\beta\epsilon}\right]\frac{1}{(2\pi\hbar)}$$

$$= \frac{1}{2}\left(\frac{4\cancel{m}\pi^2}{\beta^2\cancel{m}\omega^2}\right)^{1/2}\left[1 + e^{-\beta\epsilon}\right]\frac{1}{(2\pi\hbar)}$$

$$= \frac{1}{2}\left(\frac{2\pi}{\beta\omega}\right)\frac{1}{(2\pi\hbar)}\left[1 + e^{-\beta\epsilon}\right]$$

$$= \frac{1}{2}\left(\frac{k_B T}{\hbar\omega}\right)\left[1 + e^{-\epsilon/k_B T}\right]$$

$$Z_N = \frac{1}{2^N}\left(\frac{k_B T}{\hbar\omega}\right)^N \left[1+e^{-\epsilon/k_B T}\right]^N .$$ 2

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z_N .$$

$$\ln Z_N = \ln \frac{1}{2^N}\left(\frac{1}{\beta\hbar\omega}\right)^N\left[1+e^{-\beta\epsilon}\right]^N$$

$$= -N\ln 2 - N\ln(\beta\hbar\omega) + N\ln\left[1+e^{-\beta\epsilon}\right]$$

$$\frac{\partial \ln Z_N}{\partial\beta} = -\frac{N\hbar\omega}{\beta\hbar\omega} + \frac{N\, e^{-\beta\epsilon}(-\epsilon)}{1+e^{-\beta\epsilon}}$$

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

$$\langle E\rangle = Nk_BT - \frac{N\epsilon}{1+e^{+\beta\epsilon}}$$

$$u = k_BT - \frac{\epsilon}{1+e^{\beta\epsilon}}$$

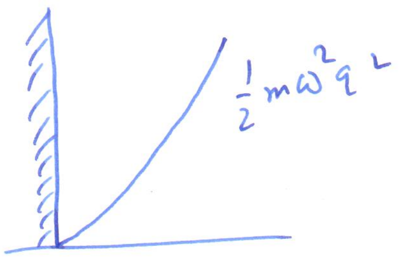
$$u = k_BT - \frac{\epsilon}{1+e^{\beta\epsilon}}$$ 1

$\epsilon \to 0 \qquad u = k_BT$

$\epsilon \to \infty \qquad u = k_BT$ 1

(b) Quantum analog of the problem in the limit of $\epsilon \to \infty$.

$\epsilon \to \infty$ Corresponds to wall at $q = 0$.



Hence ~~at~~ the boundary conditions get's modified.

$\psi(q=0) = 0$

$\psi(q \to \infty) = 0$

As opposed to the free case when $\psi(\pm\infty) \to 0$.

~~Thus~~ Since the Hamiltonian remains the solutions of ψ_n are same except not all n's are allowed. Only those wave functions for which ψ vanishes at $q=0$ survives.

Thus, $n = 1, 3, 5, 7, \ldots$ survives. 2

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega .$$

$$Q = \sum_{n=1,3,5,\ldots} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} = e^{-\beta\hbar\omega/2}\left[e^{-\beta\hbar\omega} + e^{-3\beta\hbar\omega} + e^{-5\beta\hbar\omega} + \cdots\right]$$ 1

$$= e^{-\beta\hbar\omega/2}\, e^{-\beta\hbar\omega}\left[1 + e^{-2\beta\hbar\omega} + e^{-4\beta\hbar\omega} + \cdots\right]$$

$$Q = \frac{e^{-3\beta\hbar\omega/2}}{1 - e^{-2\beta\hbar\omega}}$$ 1

$$Z_N = \left(\frac{e^{-3\beta\hbar\omega/2}}{1-e^{-2\beta\hbar\omega}} \right)^N$$ 1

$$\ln Z_N = -\frac{3}{2} N \beta \hbar\omega - N \ln\left(1-e^{-2\beta\hbar\omega}\right)$$

$$\frac{\partial}{\partial\beta} \ln Z_N = -\frac{3}{2} N \hbar\omega - \frac{N\left(-e^{-2\beta\hbar\omega}\right)}{1-e^{-2\beta\hbar\omega}}(-2\hbar\omega)$$

$$= -\left[\frac{3}{2} N\hbar\omega + \frac{2N\hbar\omega}{e^{2\beta\hbar\omega}-1} \right]$$

$$E = -\frac{\partial \ln Z_N}{\partial\beta} = \frac{3}{2} N\hbar\omega + \frac{2N\hbar\omega}{e^{2\beta\hbar\omega}-1}$$

$$u = \frac{3}{2}\cancel{N}\hbar\omega + \frac{2\hbar\omega}{e^{2\beta\hbar\omega}-1}$$ 2

$\beta \to 0 \quad (T\to\infty)$ $\qquad u = \frac{3}{2}\hbar\omega + \frac{2\hbar\omega}{2\hbar\omega} = \frac{5}{2}\hbar\omega$

$\beta \to \infty \quad (T \to 0)$ $\qquad u = \frac{3}{2}\hbar\omega$ $\qquad$ all oscillators are in ground state $n=1$.