HW4 Solution

1\. # of way to choose n ortho-H_2 out of N

a) molecules is $\dfrac{N!}{n!\,(N-n)!}$

each ortho-H_2 can have 3 possible spin states, So the # of microstates is

$$\Omega_N(E) = \frac{N!}{n!\,(N-n)!} \cdot 3^n$$

$$S = k_B \ln \Omega_N(E) = k_B \cdot \left[n \ln 3 + N \ln N - n \ln n - (N-n) \ln(\right.$$

$$= k_B \left[\frac{E}{\varepsilon} \ln 3 + N \ln N - \frac{E}{\varepsilon} \ln \frac{E}{\varepsilon} - \left(N - \frac{E}{\varepsilon}\right) \ln\left(N - \frac{E}{\varepsilon}\right. \right.$$

$$T^{-1} = \left.\frac{\partial S}{\partial E}\right|_N = k_B \left[\frac{\ln 3}{\varepsilon} - \ln \frac{E}{\varepsilon} - \frac{1}{\varepsilon} + \ln\left(N - \frac{E}{\varepsilon}\right) + \frac{1}{\varepsilon} \right]$$

$$= \frac{k_B}{\varepsilon} \left[\ln 3 + \ln \frac{N\varepsilon - E}{E} \right]$$

$$\boxed{T = \frac{\varepsilon}{k_B} \Big/ \left[\ln \frac{3(N\varepsilon - E)}{E} \right]}$$

$$\exp\left(\frac{\varepsilon}{k_B T}\right) = \frac{3(N\varepsilon - E)}{E}$$

$$E = \frac{3N\varepsilon}{3 + e^{\varepsilon/k_B T}}$$

$$C_v = \left.\frac{\partial E}{\partial T}\right|_{N,V} = -3N\varepsilon \frac{1}{(3+e^{\varepsilon/k_B T})^2} e^{\varepsilon/k_B T}\left(-\frac{\varepsilon}{k_B T^2}\right)$$

$$\boxed{C_v = N k_B \cdot \left(\frac{\varepsilon}{k_B T}\right)^2 \cdot \frac{3 e^{\varepsilon/k_B T}}{\left(3 + e^{\varepsilon/k_B T}\right)^2}}$$

$T \to 0$ $\quad C_v \sim e^{-\varepsilon/k_B T}$ exponentially small

typical for system with energy g

c) The probability that a given molecule is in one specific ortho-H_2 is the # of ways (N-1) molecules have energy $(n-1)\varepsilon$ divided by # of ways N molecules have energy $n\varepsilon$

$$p = \frac{\Omega_{N-1}((n-1)\varepsilon)}{\Omega_N(n\varepsilon)} = \frac{\frac{(N-1)!}{(n-1)!\,(N-n)!} 3^{n-1}}{\frac{N!}{n!\,(N-n)!} 3^n} = \frac{n}{3N}$$

$$\boxed{p = \frac{E}{3N\varepsilon} = \frac{1}{3 + e^{+\varepsilon/k_BT}}}$$

2) The # of microstates of the system is the # of ways to put n atoms on N interstitial positions

multiplies by

# of ways to put (N-n) atoms on N lattice poin[ts]

$$\Omega(E) = \frac{N!}{n!(N-n)!} \cdot \frac{N!}{(N-n)!\,n!} = \left(\frac{N!}{n!(N-n)!}\right)^2$$

~~Note~~ Note to TA:

No penalty if students missed the power 2.

$$S = k_B \ln \Omega(E) = 2k_B \ln \frac{N!}{n!(N-n)!}$$

$$\boxed{S = 2k_B \left[N\ln N - n\ln n - (N-n)\ln(N-n)\right]}$$

in equilibrium, Helmholtz free energy is minimiz[ed]

$$F = E - TS$$

$$= n\varepsilon - 2k_BT\left\{N\ln N - n\ln n - (N-n)\ln(N\right.$$

$$\frac{\partial \mathcal{F}}{\partial n} = 0 \Rightarrow$$

$$\Vert$$

$$e - 2k_BT\left[-\ln n - 1 + \ln(N-n) + 1\right] = 0$$

$$e = 2k_BT \ln\frac{N-n}{n}$$

$$\frac{N-n}{n} = e^{-e/2k_BT}$$

$$n = \frac{N}{1+e^{-e/2k_BT}}$$

3 Suppose N_+ and N_- are # of links of $0°$ and $180°$ angles respectively.

$$\begin{cases} N_+ - N_- = 2m \\ N_+ + N_- = N \end{cases}$$

$$\Rightarrow \quad N_+ = \frac{N}{2} + m \quad ; \quad N_- = \frac{N}{2} - m$$

The # of ways to arrange N_+ $0°$ angle links is

$$= \frac{N!}{N_+!\,N_-!}$$

~~Note $L_+ = 2md$ and $L_- = -2md$ are both~~

Note that N_- links of $0°$ angle and N_+ links of $180°$ angle ALSO creates polymer with length $2md$.

So the total # of polymers configurations with total length $2md$ is

$$\Omega_N(L) = \frac{2N!}{N_+!\,N_-!}$$

$$\boxed{S = k_B \ln \Omega_N(L) = k_B \ln 2 + k_B\left[N\ln N - \left(\frac{N}{2}+m\right)\ln\left(\frac{N}{2}+m\right) - \left(\frac{N}{2}-m\right)\ln\left(\frac{N}{2}-m\right)\right]}$$

Force on ~~spring~~ polymer

$$F = \left.\frac{\partial \mathcal{F}}{\partial L}\right|_T = \frac{\partial}{\partial L}(-TS) = \frac{T}{2d}\,\frac{\partial S}{\partial m}$$

$$= \frac{T}{2d}\cdot k_B\left[-\ln\left(\frac{N}{2}+m\right) - 1 + \ln\left(\frac{N}{2}-m\right) + 1\right]$$

$$= \frac{k_B T}{2d}\cdot \ln\frac{\frac{N}{2}-m}{\frac{N}{2}+m}$$

$$= \frac{k_B T}{2d}\ln\left(1 - \frac{2m}{\frac{N}{2}+m}\right) \overset{m \ll N}{\simeq} -\frac{k_B T}{2d}\,\frac{4m}{N}$$

$$F = -\frac{k_B T}{d}\frac{L}{Nd}$$

(the minus sign means this is restoration force which opposes expansion).

the spring constant

$$k_s = \frac{|F|}{L} = \frac{k_B T}{N d^2}$$

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$$Z(T,V,N) = \left[Z(T,V,1)\right]^N$$

$$Z(T,V,1) = 3e^{-\beta\varepsilon} + 1$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial}{\partial\beta}\ln\left(1+3e^{-\beta\varepsilon}\right)$$

$$= -N\frac{1}{1+3e^{-\beta\varepsilon}}3e^{-\beta\varepsilon}(-\varepsilon) = N\varepsilon\frac{3e^{-\beta\varepsilon}}{1+3e^{-\beta\varepsilon}}$$

$$= N\varepsilon\frac{3}{e^{\beta\varepsilon}+3}$$

$$C_V = \left.\frac{\partial E}{\partial T}\right|_N = Nk_B\left(\frac{\varepsilon}{k_B T}\right)^2\frac{3e^{\varepsilon/k_B T}}{\left(3+e^{\varepsilon/k_B T}\right)^2}$$

6 a microstate is a state where n left links are open, energy of such state is $\varepsilon_n = n e$.

a)
$$Z = \sum_{n=0}^{N} e^{-\beta \varepsilon_n} = \sum_{n=0}^{N} e^{-\beta n e} = \frac{1-e^{-\beta e (N}}{1-e^{-\beta e}}$$

b)
$$\langle n \rangle = \frac{\langle E \rangle}{e} = -\frac{1}{e}\frac{\partial}{\partial \beta} \ln Z$$

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

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

$$= \frac{e^{-\beta e}}{1-e^{-\beta e}} - \frac{(N+1)\, e^{-\beta e (N+1)}}{1-e^{-\beta e (N+1)}}$$

$k_B T \ll e, \quad \beta e \gg 1$

$$\langle n \rangle \simeq \frac{e^{-\beta e}}{1-e^{-\beta e}} = \frac{1}{e^{\beta e}-1}$$ independent of N