McQuarrie 9-5

$$N_2^{14} + N_2^{15} \rightleftharpoons 2N^{14}N^{15}$$

$$K(T) = \frac{q^2_{N^{14}N^{15}}}{q_{N_2^{14}} q_{N_2^{15}}}$$

$$= \frac{m^3_{N^{14}N^{15}}}{(m_{N_2^{14}} m_{N_2^{15}})^{3/2}} \cdot \overbrace{\frac{4\,\Theta_{r,N_2^{14}}\Theta_{r,N_2^{15}}}{\Theta^2_{r,N^{14}N^{15}}}}^{a} \cdot \overbrace{\frac{(1-e^{-\Theta_{v,N_2^{14}}/T})(1-e^{-\Theta_{v,N_2^{15}}/T})}{(1-e^{-\Theta_{v,N^{14}N^{15}}})^2}}^{\sim 1}$$

$$\cdot \underbrace{e^{-(2\Theta_{v,N^{14}N^{15}} - \Theta_{v,N_2^{14}} - \Theta_{v,N_2^{15}})/2T}}_{b}$$

$$= 1.002 \cdot 4 \cdot a \cdot b$$

$$\Theta_r = \frac{h^2}{8\pi^2 I k}$$

$$a = \frac{\Theta_{r,N_2^{14}}\Theta_{r,N_2^{15}}}{\Theta^2_{r,N^{14}N^{15}}} = \frac{I^2_{N^{14}N^{15}}}{I_{N_2^{14}} I_{N_2^{15}}} = \frac{52.44}{52.50} = 0.9989$$

$$\nu_j = \frac{1}{2\pi}\sqrt{\frac{k_j}{\mu_j}}$$

$$\Theta_{\nu_j} = \frac{h\nu_j}{k} = \frac{h}{2\pi k}\sqrt{\frac{k_j}{\mu_j}}$$

$$2\Theta_{v,N^{14}N^{15}} - \Theta_{v,N_2^{14}} - \Theta_{v,N_2^{15}} = \frac{h k_{N_2}}{2\pi k}\left(2\mu^{-1/2}_{N^{14}N^{15}} - \mu^{-1/2}_{N_2^{14}} - \mu^{-1/2}_{N_2^{15}}\right)$$
$$= 1.7\,K$$

$$b = e^{-1.7K/2T} = e^{-0.85K/T}$$

$$K(T) = 1.002 \cdot 4 \cdot 0.9989 \cdot e^{-0.85K/T}$$

At 300 K, ~~[illegible]~~ $K = 3.99$

Note: mass and rotational effects approximately cancel

McQuarrie 9-12

$3H_2 + N_2 \rightleftharpoons 2NH_3 \qquad T = 400°C = 673K$

$$K_{tr} = \frac{q_{tr}^{(NH_3)\,2}}{q_{tr}^{(N_2)}\, q_{tr}^{(H_2)\,3}} = \left(\frac{2\pi kT}{N_A h^2}\right)^3 \left(\frac{17^2}{28 \cdot 2^3}\right)^{3/2} \cdot \frac{1}{V^2}$$

$$K_{rot} = \frac{q_{rot}^{(NH_3)\,2}}{q_{rot}^{(N_2)}\, q_{rot}^{(H_2)\,3}} = \frac{2 \cdot 2^3}{3^2} \cdot \frac{\left[\sqrt{\pi}\left(\Theta_1^{(NH_3)}\Theta_2^{(NH_3)}\Theta_3^{(NH_3)}\right)^{-1/2}\right]^2}{\left(\Theta^{(N_2)}\Theta^{(H_2)3}\right)} \cdot \frac{1}{T}$$

$$K_{vib} = \frac{q_{vib}^{(NH_3)\,2}}{q_{vib}^{(N_2)}\, q_{vib}^{(H_2)\,3}} = \frac{(1-e^{-3374/T})}{(1-e^{-1360/T})}\left(\frac{1}{(1-e^{-4800/T})}\right)^3 \cdot \frac{(1-e^{-6215/T})}{(1-e^{-2330/T})}$$

$$\Delta U_0 = 2 \cdot 276.8 - 225.1 - 3 \cdot 103.2 = 18.9 \text{ kcal/mol}$$

V = volume/molecule (ideal gas at T + 1 atm)

$K_{tr} = 2.34 \cdot 10^3 / T^5$

$K_{rot} = 6.05 \cdot 10^3 / T$

$$K_{vib} = \begin{cases} 1.48 \text{ at } 900K \\ 1.99 \text{ at } 1200K \\ 1.22 \text{ at } 673K \end{cases}$$

$$K_p = K_{tr} K_{rot} K_{vib}\, e^{\Delta U/RT} = \frac{1.42 \cdot 10^7}{T^6} \cdot 1.22 \cdot e^{9450/T}$$

$= 2.3 \times 10^{-4}$ atm^{-2} at 400K

Q 11-11.

$$C_V = k\int_0^\infty \frac{\left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT}}{\left(1-e^{-h\nu/kT}\right)^2}\, g(\nu)\, d\nu. \qquad \text{, eqn (11-10).}$$

We are interested only in the high temperature limiting form of C_V so we expand the exponentials ($h\nu/kT$ = small)

$$C_V \simeq k\int_0^\infty \frac{\left(\frac{h\nu}{kT}\right)^2\left(1-\frac{h\nu}{kT}+\cdots\right)}{\left(1-1+\frac{h\nu}{kT}-\cdots\right)^2}\, g(\nu)\, d\nu.$$

$$\cong k\int_0^{\nu_{max}} g(\nu)\, d\nu$$

, where we have disallowed $\nu \to \infty$ if we are to have $h\nu/kT$ = small.

Now if we assume that $g(\nu) = 0$ for $\nu > \nu_{max}$ this becomes

$$C_V \simeq k\int_0^{\nu_{max}} g(\nu)\, d\nu$$

But the normalisation condition (eqn 11-23) is just

$$\int_0^{\nu_{max}} g(\nu)\, d\nu = 3N$$

So we have that $C_V \simeq 3Nk$.

Q11-15

For spin waves the dispersion relation is

$$\omega = A k^2 \quad , \text{ where } A = \text{const}.$$

Taking the number of waves with wave number in $(k, k+dk)$ as

$$\omega(k)\, dk = \frac{V}{2\pi^2} k^2 dk$$

we find

$$g(\nu)\, d\nu = \frac{V}{(2\pi A^3)^{1/2}} \nu^{1/2} d\nu$$

If there are S normal modes for these spin waves then normalisation of this frequency distribution requires that

$$\int_0^{\nu_s} g(\nu) d\nu = S$$

We have introduced a cut-off frequency ν_s so that the left hand side will be finite. Thus

$$g(\nu)\, d\nu = \frac{3S}{2\nu_s^{3/2}} \nu^{1/2} d\nu$$

and the heatcapacity is

$$C_V = k \int_0^\infty \frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2} \left(\frac{h\nu}{kT}\right)^2 g(\nu)\, d\nu$$

$$= \frac{3}{2} S k \left(\frac{T}{\theta_s}\right)^{3/2} \int_0^{\theta_s/T} \frac{x^{5/2} e^{-x}}{(1-e^{-x})^2}\, dx .$$

In the low temperature approximation $\theta_s/T \to \infty$ and

$$\int_0^\infty \frac{x^{5/2} e^{-x}}{(1-e^{-x})^2}\, dx = \left(\frac{5}{2}\right)! \, \zeta\left(\frac{5}{2}\right)$$

$$= \frac{105\pi^{1/2}}{8} \zeta\left(\frac{5}{2}\right)$$

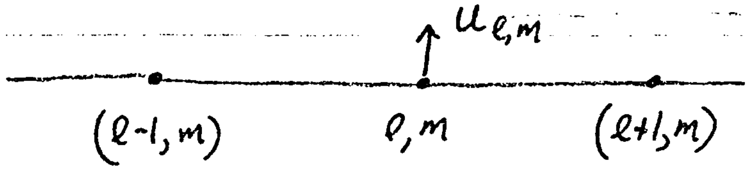
So

$$C_V = \frac{3}{2} S k \cdot \frac{105\pi^{1/2}}{8} \zeta\left(\frac{5}{2}\right) \left(\frac{T}{\theta_s}\right)^{3/2} , \quad T \to 0$$

ie: we have a $T^{3/2}$ dependence for C_V.

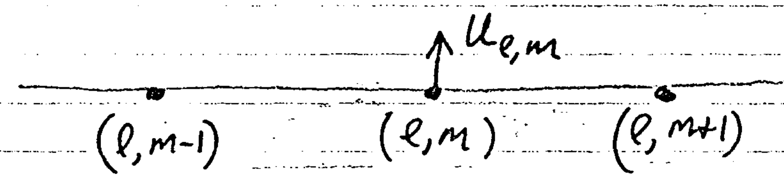
Q11-17. 2-D lattice with transverse modes

Along the m^{th} row we have



Assuming a force constant f the potential energy for interactions along the rows has terms of the form $\frac{f}{2}(u_{\ell,m}-u_{\ell-1,m})^2$

Along the ℓ^{th} column we have



and the potential energy terms are of the form $\frac{f}{2}(u_{\ell,m}-u_{\ell,m-1})$

The Lagrangian is

$$L = K - U$$

$$= \sum_{\ell=1}^{N_\ell}\sum_{m=1}^{N_m}\frac{M}{2}\dot{u}_{\ell,m}^2 - \sum_{\ell=2}^{N_\ell}\sum_{m=2}^{N_m}\frac{f}{2}\Big[(u_{\ell,m}-u_{\ell-1,m})^2 + (u_{\ell,m}-u_{\ell,m-1})^2\Big]$$

where N_ℓ is the number of columns and N_m the number of rows in the lattice.

Lagrange's eqns. are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{u}_{\ell,m}}\right) = \frac{\partial L}{\partial u_{\ell,m}} \quad ; \; \ell = 1, \cdots, N_\ell \; ; \; m = 1, \cdots, N_m$$

$$m \ddot{u}_{\ell,m} = \frac{f}{2} \cdot \frac{\partial}{\partial u_{\ell,m}} \Big\{ (u_{\ell+1,m} - u_{\ell,m})^2 + (u_{\ell,m} - u_{\ell-1,m})^2 + $$

$$+ (u_{\ell,m+1} - u_{\ell,m})^2 + (u_{\ell,m} - u_{\ell,m-1})^2 \Big\}$$

$$= f\left[(u_{\ell+1,m} + u_{\ell-1,m} - 2u_{\ell,m}) + (u_{\ell,m+1} + u_{\ell,m-1} - 2u_{\ell,m})\right]$$

Let's assume a solution of the form

$$u_{\ell m} = e^{i(\ell k_y a + m k_x a + \omega t)}$$

$$\therefore \quad \ddot{u}_{\ell,m} = -\omega^2 u_{\ell,m}$$

and $u_{\ell+1,m} = e^{i k_y a} u_{\ell,m}$, etc.

Substituting those into the eqn. of motion yields

$$-\omega^2 m = f\left[(e^{ik_y a} + e^{-ik_y a} - 2) + (e^{ik_x a} + e^{-ik_x a} - 2)\right]$$

Since $\cos x = \frac{1}{2}\left(e^{ix} + e^{-ix}\right)$ this becomes

$$\omega^2 = \frac{2f}{m}\left\{\left[1-\cos(k_x a)\right] + \left[1-\cos(k_y a)\right]\right\}$$

for x small $\cos x \simeq 1 - \frac{1}{2}x^2$

So

$$\omega^2 \simeq \frac{2f}{m}\left\{\frac{1}{2}(k_x a)^2 + \frac{1}{2}(k_y a)^2\right\}.$$

$$\simeq \frac{f}{m}\cdot\left(k_x^2 + k_y^2\right) a^2$$

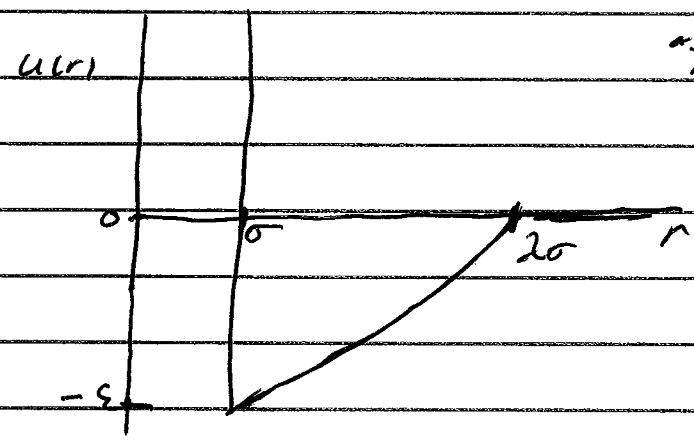
$$= \frac{f}{m} k^2 a^2$$

so $\omega \simeq \left(\frac{f}{m}\right)^{1/2} k a$

4. Q 12-9 I am just going to outline the solution

$$u = \infty \qquad r < \sigma$$
$$= \frac{\varepsilon}{\sigma(\lambda-1)}(r - 2\sigma) \qquad \sigma < r < 2\sigma$$
$$= 0 \qquad r > 2\sigma$$

"Triangle potential"



$$B_2(T) = -2\pi \int_0^{\sigma} (-1) r^2 dr - 2\pi \int_{\sigma}^{2\sigma} \left[e^{\frac{-\beta\varepsilon(r-2\sigma)}{\sigma(\lambda-1)}} - 1 \right] r^2 dr - 2\pi \int_{2\sigma}^{\infty} (0) r^2 dr$$

$$\underbrace{\qquad}_{\frac{2\pi\sigma^2}{3} = b_0} \qquad \underbrace{\qquad}_{A} \qquad \underbrace{\qquad}_{0}$$

A is the tough part, but it is just integration

$$A = -2\pi e^{\frac{+\beta\varepsilon\lambda}{\lambda-1}} \int_{\sigma}^{2\sigma} \left[e^{\frac{-\beta\varepsilon r}{\sigma(\lambda-1)}} - 1 \right] r^2 dr$$

$$v = \frac{r}{\sigma} \qquad r = \sigma v \qquad dr = \sigma\, dv$$

$$A = -2\pi e^{\beta\varepsilon\lambda/\lambda-1} \sigma^3 \int_1^2 \left[e^{av} - 1 \right] v^2 dv \quad \text{where} \quad a = \frac{-\beta\varepsilon}{\sigma(\lambda-1)}$$

$$A = -2\pi\sigma^3 e^{\beta\varepsilon\lambda/\lambda-1}\Big[\underbrace{\int_1^\lambda e^{av} v^2\,dv}_{X} - \underbrace{\int_1^\lambda v^2\,dv}_{-\frac{1}{3}v^3\big|_1^\lambda = \frac{1}{3}(1-\lambda^3)}\Big]$$

Use: $\displaystyle\int x^m e^{ax}\,dx = e^{ax}\sum_{r=0}^{m}(-1)^r \frac{m!\,x^{m-r}}{(m-r)!\,a^{r+1}}$

$$X = e^{ax}\left[\frac{2v^2}{2a} - \frac{2v}{a^2} + \frac{2}{a^3}\right]_1^\lambda$$

Thus $B_2(T) = b_0 - 2\pi\sigma^3 e^{\beta\varepsilon\lambda/\lambda-1}\left(X + \frac{1}{3}(1-\lambda^3)\right)$

Evaluating X will give explicit solution

5. Q12-30 The general expression for $B_2(T)$ ~~[illegible]~~ for monatomic point particles is eq. 12-23 in the text, which can be converted to eq. 12-25:

$$B_2(T) = -2\pi \int_0^\infty [e^{-\beta u} - 1] r^2 dr$$

In our case, however, the molecules are not point particles. They also have dipole moments, and we need to consider the orientation of the dipole vectors. Each vector has a θ and a ϕ, hence $\theta_1, \phi_1, \theta_2, \phi_2$. The energy u depends on θ_1 and θ_2 explicitly, but on only on the difference $\phi = \phi_2 - \phi_1$. Therefore $B_2(T)$ becomes:

$$B_2(T) = -2\pi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \int_{\phi_2=0}^{2\pi} \int_{\phi=0}^{2\pi} \int_{r=0}^{\infty} [e^{-\beta u} - 1] r^2 \sin\theta_1 \sin\theta_2 \, dr \, d\theta_1 d\theta_2 \cdot d\phi \, d\phi_2$$

Since $u = u(\theta_1, \theta_2, \phi, r)$ is independent of ϕ_2, we can immediately integrate for a factor of 2π:

$$B_2(T) = -4\pi^2 \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{r=0}^{\infty} [e^{-\beta u} - 1] r^2 \sin\theta_1 \sin\theta_2 \, dr \, d\theta_1 d\theta_2 \, d\phi$$

Integrating directly using the exponential is tough – analytical solution not obvious. So we proceed by expanding exponential in power series:

$$e^{-\beta u} - 1 = -\beta u + \frac{1}{2}\beta^2 u^2 - \frac{1}{6}\beta^3 u^3 + \frac{1}{24}\beta^4 u^4 + \cdots$$

where $u = \infty, \quad r < \sigma$

$$= -\frac{\mu^2}{r^3}\left[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi\right] \quad r < \sigma$$

By symmetry, the positive and negative contributions cancel in the integrals of odd-power terms. The leading term is therefore the $\beta^2 u^2$ term:

$$e^{-\beta u} - 1 \approx \frac{\mu^4}{r^6}\left[4\cos^2\theta_1\cos^2\theta_2 - 4\sin\theta_1\cos\theta_1\sin\theta_2\cos\theta_2\cos\phi + \sin^2\theta_1\sin^2\theta_2\cos^2\phi\right]$$

Thus:

$$B_2(T) = 4\pi^2 \int_{\theta_1=0}^{\pi}\int_{\theta_2=0}^{\pi}\int_{\phi=0}^{2\pi}\int_{r=0}^{\sigma} r^2 \sin\theta_1\sin\theta_2 \, dr\, d\theta_1\, d\theta_2\, d\phi$$

$$- 4\pi^2 \int_{\theta_1=0}^{\pi}\int_{\theta_2=0}^{\pi}\int_{\phi=0}^{2\pi}\int_{r=\sigma}^{\infty} \frac{1}{2}\beta^2\frac{\mu^4}{r^6}\left[4\cos^2\theta_1\cos^2\theta_2 - 4\sin\theta_1\cos\theta_1\sin\theta_2\cos\theta_2\cos\phi + \sin^2\theta_1\sin^2\theta_2\cos^2\phi\right] \cdot r^2\, dr\, d\theta_1\, d\theta_2\, d\phi \sin\theta_1\sin\theta_2$$

+ higher-order terms

This reduces to

$$B_2(T) = \underbrace{\frac{2\pi}{3}\sigma^3}_{b_0}\left(1 - \frac{1}{3}\frac{\beta^2\mu^4}{\sigma^6} + \ldots\right)$$

... <u>except</u> that I got an extra factor of 8π in my calculation