PHY 407 Chap 14 Solutions

14.4 We have

(a)
$$n_\lambda = \frac{1}{z^{-1}e^{\beta\epsilon_\lambda} \pm 1}$$

For $\lambda^3 n \to 0$, $z \sim \lambda^3 n$, and $z^{-1}e^{\beta\epsilon_\lambda} \gg 1$, so that

$$n_\lambda \approx n\lambda^3 e^{-\beta\epsilon_\lambda} \sim z e^{-\beta\epsilon_\lambda}$$

independent of statistics. From the constraint

$$\sum_\lambda n_\lambda = N$$

we have
$$z \sum_\lambda e^{-\beta\epsilon_\lambda} = N$$

Define $\boxed{Q \equiv \sum_\lambda e^{-\beta\epsilon_\lambda}}$, called the <u>partition function</u>.

Then $\quad zQ = N \quad$ and $\quad z = N/Q$.

(b)

Now
$$U = \sum_\lambda \epsilon_\lambda n_\lambda = z\sum_\lambda \epsilon_\lambda e^{-\beta\epsilon_\lambda}$$

$$\therefore \frac{U}{N} = \frac{z}{N}\sum_\lambda \epsilon_\lambda e^{-\beta\epsilon_\lambda} = \frac{1}{Q}\sum_\lambda \epsilon_\lambda e^{-\beta\epsilon_\lambda}$$

but
$$-\frac{\partial}{\partial\beta}\ln Q = -\frac{1}{Q}\frac{\partial Q}{\partial\beta} = -\frac{1}{Q}\frac{\partial}{\partial\beta}\sum_\lambda e^{-\beta\epsilon_\lambda}$$

$$= -\frac{1}{Q}\sum_\lambda(-\epsilon_\lambda)e^{-\beta\epsilon_\lambda} = \frac{1}{Q}\sum_\lambda \epsilon_\lambda e^{-\beta\epsilon_\lambda}$$

$$\therefore \boxed{\frac{U}{N} = -\frac{\partial}{\partial\beta}\ln Q}$$

$\boxed{12.4}$ cont'd

(c) For a polyatomic molecule

$$\epsilon = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib}$$

$$\therefore Q = \sum_{\alpha\beta\gamma} \exp\left\{-\beta\left(\epsilon_\alpha^{trans} + \epsilon_\beta^{rot} + \epsilon_\gamma^{vib}\right)\right\}$$

$$= \sum_\alpha e^{-\beta\epsilon_\alpha^{trans}} \sum_\beta e^{-\beta\epsilon_\beta^{rot}} \sum_\gamma e^{-\beta\epsilon_\gamma^{vib}}$$

$$= Q_{trans}\, Q_{rot}\, Q_{vib}$$

$$\therefore \frac{U}{N} = -\frac{\partial}{\partial\beta}\left(\ln\left(Q_{trans} Q_{rot} Q_{vib}\right)\right)$$

$$= -\frac{\partial}{\partial\beta}\left(\ln Q_{trans} + \ln Q_{rot} + \ln Q_{vib}\right)$$

or $C_V = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_V = C_{trans} + C_{rot} + C_{vib}$.

(14.5) thermal wavelength $\lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}} = \sqrt{\frac{2\pi\hbar^2\beta}{m}}$

$$Q_{trans} = \sum_{\vec{k}} e^{-\frac{\beta\hbar^2k^2}{2m}} = \frac{V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk \exp\left(-\frac{\beta\hbar^2}{2m}k^2\right)$$

$$= \frac{1}{2}\cdot\frac{V}{2\pi^2}\int_{-\infty}^{\infty} dk\, k^2 \exp\left(-\frac{\lambda^2}{4\pi}k^2\right)$$

$$= \frac{V}{4\pi^2}\cdot\frac{\sqrt{\pi}}{2\left(\frac{\lambda^2}{4\pi}\right)^{3/2}} = \frac{V}{\lambda^3}.$$

14.5 (cont'd)

$$c_V = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_V$$

$$\frac{U}{N} = -\frac{\partial}{\partial \beta}\ln Q_{trans} = -\frac{\partial}{\partial\beta}\ln\left(\frac{V}{\lambda^3}\right) = -\frac{\partial}{\partial\beta}\ln V + \frac{\partial}{\partial\beta}\ln\lambda^3$$

$$\therefore \frac{\partial}{\partial T}\left(\frac{U}{N}\right)\Big|_V = \frac{\partial}{\partial T}\left(\frac{\partial}{\partial\beta}\ln\lambda^3\right)_V = 3\frac{\partial}{\partial T}\left(\frac{\partial}{\partial\beta}\ln\lambda\right)_V$$

$$\lambda = \left(\frac{2\pi\hbar^2}{m}\beta\right)^{1/2}$$

$$\therefore \ln\lambda = \frac{1}{2}\ln\left(\frac{2\pi\hbar^2}{m}\right) + \frac{1}{2}\ln\beta$$

$$\therefore c_V = \frac{\partial}{\partial T}\left(\frac{U}{N}\right)_V = \frac{3}{2}\frac{\partial}{\partial T}\left(\frac{\partial}{\partial\beta}\ln\beta\right)_V = \frac{3}{2}\frac{\partial}{\partial T}\left(\frac{1}{\beta}\right)$$

$$= \frac{3}{2}k$$

$$\therefore \frac{c_V}{k} = \frac{3}{2}.$$

14.6

$$Q_{rot} = \sum_{\ell=0}^{\infty}(2\ell+1)e^{-\beta\hbar^2\ell(\ell+1)/2I}$$

(a) for $kT \ll \frac{\hbar^2}{2I}$,

$$Q_{rot} \sim 1 + 3e^{-\beta\hbar^2/I}$$

$$\therefore \ln Q_{rot} \sim \ln(1 + 3e^{-\beta\hbar^2/I}) \sim 3e^{-\beta\hbar^2/I}$$

$$\therefore \frac{U_{rot}}{N} \sim -\frac{\partial}{\partial\beta}\ln Q_{rot} = -\frac{\partial}{\partial\beta}\left(3e^{-\beta\hbar^2/I}\right) = \frac{3\hbar^2}{I}e^{-\frac{\beta\hbar^2}{I}}$$

14.6 (cont'd)

$$\therefore\ C_{rot} = \frac{\partial}{\partial T}\left(\frac{U}{N}\right)_V = \frac{3\hbar^2}{I}\frac{\partial}{\partial\beta}\left(e^{-\beta\hbar^2/I}\right)\frac{\partial\beta}{\partial T}$$

$$= \left(\frac{3\hbar^2}{I}\right)\left(-\frac{\hbar^2}{I}\right)e^{-\beta\hbar^2/I}\left(-\frac{1}{kT^2}\right) \qquad -\frac{1}{k^2T^2}\cdot k = -\beta^2 k$$

or

$$\boxed{\frac{C_{rot}}{k} \simeq 3\left(\frac{\beta\hbar^2}{I}\right)^2 e^{-\beta\hbar^2/I}\ ,\quad kT \ll \frac{\hbar^2}{2I}}$$

(b.) for $kT \gg \hbar^2/2I$, $\frac{\beta\hbar^2}{2I} \ll 1$

$$Q_{rot} \approx \int_0^\infty dl\,(2l)\,e^{-\beta\hbar^2 l^2/(2I)}$$

let $y = \frac{\beta\hbar^2 l^2}{2I}$, then $dy = \frac{\beta\hbar^2}{I}\,l\,dl$

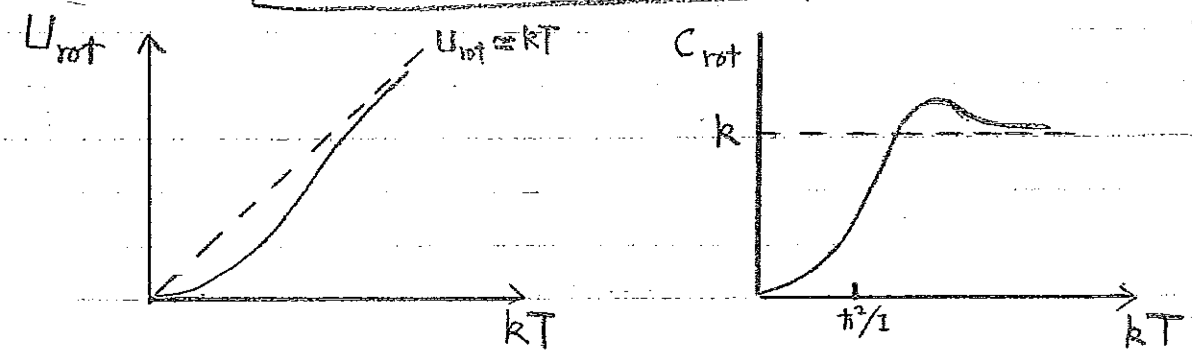
then $2l\,dl = \frac{2I}{\beta\hbar^2}\,dy$.

So $Q_{rot} \approx \int_0^\infty \left(\frac{2I}{\beta\hbar^2}\right)dy\,e^{-y} = \frac{2I}{\beta\hbar^2}$

So $\frac{U_{rot}}{N} = -\frac{\partial}{\partial\beta}\ln Q_{rot} = \frac{\partial}{\partial\beta}\ln\beta = \frac{1}{\beta} = kT$

Thus $\boxed{\frac{C_{rot}}{k} = \frac{\partial}{\partial T}\left(\frac{U_{rot}}{N}\right)_V \approx 1\ ,\quad kT \gg \frac{\hbar^2}{2I}}$

(c)



$\boxed{14.7}$ The vibrational spectrum is

$$\epsilon_n = \hbar\omega\left(n+\frac{1}{2}\right), \quad n=0,1,2,\dots$$

and ω is the vibrational frequency.

(a) $$Q_{vib} = \sum_n e^{-\beta\epsilon_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}$$

set $\alpha \equiv \beta\hbar\omega$, $$= e^{-\frac{\alpha}{2}} \sum_{n=0}^{\infty} e^{-n\alpha} = e^{-\frac{\alpha}{2}}\left(1+e^{-\alpha}+e^{-2\alpha}+\dots\right)$$

$$= \frac{e^{-\frac{\alpha}{2}}}{1-e^{-\alpha}} = \frac{e^{\frac{\alpha}{2}}}{e^{\alpha}-1}$$

$$\therefore \frac{U_{vib}}{N} = -\frac{\partial}{\partial\beta}\ln Q_{vib}$$

$$= -\frac{1}{Q_{vib}}\frac{\partial Q_{vib}}{\partial\alpha}\cdot\frac{d\alpha}{d\beta}$$

$$= \frac{-\hbar\omega(e^{\alpha}-1)}{e^{\alpha/2}}\cdot\frac{d}{d\alpha}\left(\frac{e^{\alpha/2}}{e^{\alpha}-1}\right)$$

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

$$= \frac{-\hbar\omega(e^{\alpha}-1)}{e^{\alpha/2}}\cdot\frac{1}{2}\frac{e^{\alpha/2}}{(e^{\alpha}-1)}\left[1-\frac{2e^{\alpha}}{e^{\alpha}-1}\right],$$

$$\frac{U_{vib}}{N} = \frac{\hbar\omega}{2}\left(\frac{e^{\alpha}+1}{e^{\alpha}-1}\right) \qquad (\alpha\equiv\beta\hbar\omega)$$

$\boxed{14.7}$ (cont'd)

$$\therefore C_{vib} = \frac{\partial}{\partial T}\left(\frac{U}{N}\right)_v = \frac{\partial}{\partial \beta}\left(\frac{U}{N}\right)_v \cdot \left(\frac{d\beta}{dT}\right) \quad , \frac{d\beta}{dT} = -\frac{1}{kT^2}$$

$$= -\left(\frac{1}{kT^2}\right)\frac{\partial}{\partial \beta}\left\{\frac{\hbar\omega}{2}\left(\frac{e^\alpha+1}{e^\alpha-1}\right)\right\}$$

$\alpha = \beta\hbar\omega.$

$$= -\left(\frac{\hbar\omega}{2}\right)\left(\frac{1}{kT^2}\right)\frac{d}{d\alpha}\left(\frac{e^\alpha+1}{e^\alpha-1}\right)\cdot\underbrace{\frac{d\alpha}{d\beta}}_{=\hbar\omega}$$

$$= -\frac{k(\hbar\omega)^2}{2(kT)^2}\left(\frac{e^\alpha}{e^\alpha-1} - \frac{(e^\alpha+1)e^\alpha}{(e^\alpha-1)^2}\right)$$

$$= -\frac{k}{2}(\beta\hbar\omega)^2\frac{e^\alpha}{e^\alpha-1}\underbrace{\left(1-\frac{e^\alpha+1}{e^\alpha-1}\right)}_{\frac{-2}{e^\alpha-1}}$$

$$= k(\beta\hbar\omega)^2\frac{e^\alpha}{(e^\alpha-1)^2} = \frac{k(\beta\hbar\omega)^2 e^\alpha}{e^{2\alpha}(1-e^{-\alpha})^2}$$

$$= k e^{-\alpha}\frac{(\beta\hbar\omega)^2}{(1-e^{-\beta\hbar\omega})^2}$$

$$\therefore \boxed{\frac{C_{vib}}{k} = e^{-\beta\hbar\omega}\left(\frac{\beta\hbar\omega}{1-e^{-\beta\hbar\omega}}\right)^2}$$

Write $\frac{C_{vib}}{k} = e^{-\alpha}\left(\frac{\alpha}{1-e^{-\alpha}}\right)^2$ Consider the limit $T\to\infty$; $\alpha\to 0$

$$\frac{C_v}{k} = e^{-\alpha}\left(\frac{\alpha}{1-(1-\alpha+\frac{\alpha^2}{2}-\cdots)}\right)^2 = e^{-\alpha}\left(\frac{\alpha}{\alpha-\frac{\alpha^2}{2}+\cdots}\right)$$

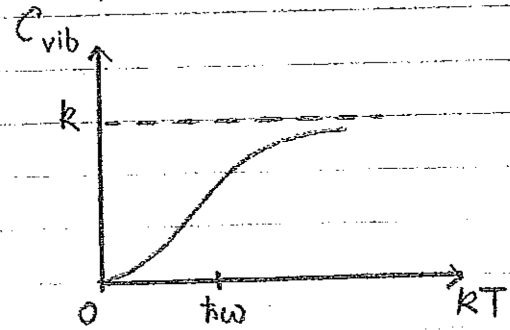
$$= e^{-\alpha}\left(\frac{1}{1-\frac{\alpha^2}{2}+\cdots}\right) \xrightarrow[\alpha\to 0]{} 1$$

$\boxed{14.7}$ (cont'd)

Also, in the limit $T \to 0$, $\alpha \to \infty$

$$\frac{C_{vib}}{k} = e^{-\alpha}\left(\frac{\alpha}{1-e^{-\alpha}}\right)^2 \xrightarrow[\alpha\to\infty]{} \alpha^2 e^{-\alpha} \longrightarrow 0$$

We can plot C_{vib} vs kT qualitatively as follows:



(b) $$\langle n+\tfrac{1}{2}\rangle = \frac{\sum_{n=0}^{\infty}(n+\frac{1}{2})\,e^{-\beta\hbar\omega(n+\frac{1}{2})}}{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}}$$

$$= \frac{1}{Q_{vib}}\left(-\frac{\partial Q_{vib}}{\partial\alpha}\right) \qquad \alpha = \beta\hbar\omega$$

$$= -\frac{\partial}{\partial\alpha}(\ln Q_{vib})$$

$$= -\left(\frac{\partial}{\partial\beta}\ln Q_{vib}\right)\underbrace{\frac{d\beta}{d\alpha}}_{=\hbar\omega}$$

$$= \frac{1}{2}\left(\frac{e^{\alpha}+1}{e^{\alpha}-1}\right) \qquad \text{(from the previous result)}$$

The mean-square fluctuation
$\langle(n+\frac{1}{2})^2\rangle - \langle n+\frac{1}{2}\rangle^2$ is given by

$\boxed{14.7}$ (cont'd)

$$\left\langle \left(n+\tfrac{1}{2}\right)^2 \right\rangle - \left\langle n+\tfrac{1}{2} \right\rangle^2$$

$$= \frac{1}{Q_{vib}} \sum_{n=0}^{\infty} \left(n+\tfrac{1}{2}\right)^2 e^{-\beta\hbar\omega(n+\frac{1}{2})} - \frac{1}{Q_{vib}^2} \left(\sum_{n=0}^{\infty} \left(n+\tfrac{1}{2}\right) e^{-\beta\hbar\omega(n+\frac{1}{2})} \right)^2$$

$$= \frac{1}{Q_{vib}} \left(\frac{\partial^2 Q_{vib}}{\partial \alpha^2} \right) - \frac{1}{Q_{vib}^2} \left(\frac{\partial Q_{vib}}{\partial \alpha} \right)^2$$

$$= \frac{\partial^2}{\partial \alpha^2} \left(\ln Q_{vib} \right) = \frac{\partial}{\partial \alpha} \left(-\frac{1}{2} \left\{ \frac{e^{\alpha}+1}{e^{\alpha}-1} \right\} \right) \quad \text{(from (b))}$$

$$= -\frac{1}{2} \frac{\partial}{\partial \alpha} \left(\frac{e^{\alpha}+1}{e^{\alpha}-1} \right)$$

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

$$= -\frac{1}{2} \cdot \frac{e^{\alpha}}{e^{\alpha}-1} \left(1 - \frac{e^{\alpha}+1}{e^{\alpha}-1} \right)$$

$$= -\frac{1}{2} \cdot \frac{e^{\alpha}}{(e^{\alpha}-1)} \frac{(-2)}{(e^{\alpha}-1)} = \frac{e^{\alpha}}{(e^{\alpha}-1)^2}$$

or $$\boxed{\left\langle \left(n+\tfrac{1}{2}\right)^2 \right\rangle - \left\langle n+\tfrac{1}{2} \right\rangle^2 = \frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\hbar\omega/kT}-1\right)^2}}$$