3.15. Here, $Q_N(V,T) = (1/N!)Q_1^N(V,T)$, while

$$Q_1(V,T) = \int_0^\infty e^{-\beta pc} \frac{V \cdot 4\pi p^2 dp}{h^3} = \frac{8\pi V}{h^3} \frac{1}{\beta^3 c^3},$$

which yields the desired result for Q_N. The thermodynamics of the system now follows straightforwardly.

As regards the density of states, the expression

$$Q_1(V,T) = \int_0^\infty e^{-\beta\varepsilon} g(\varepsilon)\, d\varepsilon = \frac{8\pi V}{h^3} \frac{1}{\beta^3 c^3}$$

leads to

$$g(\varepsilon) = \frac{4\pi V}{h^3 c^3} \varepsilon^2$$

for a single particle, while the expression for $Q_N(V,T)$ leads to

$$g(E) = \frac{1}{N!} \left(\frac{8\pi V}{h^3 c^3} \right)^N \frac{E^{3N-1}}{\Gamma(3N)}$$

for the N-particle system; cf. the expression for $\Sigma(E)$ derived in Problem 2.8.

3.18. We start with eqn. (3.6.2), viz.

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + U^2 , \tag{1}$$

and differentiate it with respect to β, keeping the E_r fixed. We get

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - \langle E^2 \rangle \langle E \rangle + 2U \frac{\partial U}{\partial \beta} .$$

Substituting for $(\partial U / \partial \beta)$ from eqn. (1), we get

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - 3\langle E^2 \rangle U + 2U^3 ,$$

which is precisely equal to $\langle (E-U)^3 \rangle$. As for $\partial^2 U / \partial \beta^2$, we note that, since

$$\left(\frac{\partial U}{\partial \beta}\right)_{E_r} = -kT^2 \left(\frac{\partial U}{\partial T}\right)_V = -kT^2 C_V ,$$

$$\left(\frac{\partial^2 U}{\partial \beta^2}\right)_{E_r} = -kT^2 \left[\frac{\partial}{\partial T}\left(-kT^2 C_V\right)\right]_V = k^2 T^2 \left[2TC_V + T^2 \left(\frac{\partial C_V}{\partial T}\right)_V\right] .$$

Hence the desired result.

For the ideal classical gas, $U = \frac{3}{2} NkT$ and $C_V = \frac{3}{2} Nk$, which readily yield the stated results.

3.29. The partition function of the *anharmonic* oscillator is given by

$$Q_1(\beta)=\frac{1}{h}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-\beta H}dp\,dq \qquad \left\{H=\frac{p^2}{2m}+cq^2-gq^3-fq^4\right\}.$$

The integration over p gives a factor of $\sqrt{2\pi m/\beta}$. For integration over q, we write

$$e^{-\beta cq^2}e^{\beta(gq^3+fq^4)}=e^{-\beta cq^2}\left[1+\beta(gq^3+fq^4)+\frac{1}{2}\beta^2(gq^3+fq^4)^2+\ldots\right];$$

the integration then gives

$$\sqrt{\frac{\pi}{\beta c}}+\beta f\cdot\frac{3}{4}\sqrt{\frac{\pi}{\beta^5c^5}}+\frac{1}{2}\beta^2g^2\cdot\frac{15}{8}\sqrt{\frac{\pi}{\beta^7c^7}}+\ldots\ .$$

It follows that

$$Q_1(\beta)=\frac{\pi}{\beta h}\sqrt{\frac{2m}{c}}\left[1+\frac{3f}{4\beta c^2}+\frac{15g^2}{16\beta c^3}+\ldots\right],$$

so that

$$\ell n\,Q_1(\beta)=const.-\ell n\,\beta+\frac{3f}{4\beta c^2}+\frac{15g^2}{16\beta c^3}+\ldots,$$

whence

$$U(\beta)=\frac{1}{\beta}+\frac{3f}{4\beta^2c^2}+\frac{15g^2}{16\beta^2c^3}+\ldots$$

and

$$C(\beta)=k+\frac{3fk^2T}{2c^2}+\frac{15g^2k^2T}{8c^3}+\ldots\ .$$

Next, the mean value of the displacement q is given by

$$\langle q\rangle=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp(-\beta H)q\,dp\,dq\Big/\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp(-\beta H)dpdq\ .$$

In the desired approximation, we get

$$\langle q\rangle\simeq\beta g\int_{-\infty}^{\infty}e^{-\beta cq^2}q^4\,dq\Big/\int_{-\infty}^{\infty}e^{-\beta cq^2}\,dq$$

$$=\beta g\cdot\frac{3}{4}\sqrt{\frac{\pi}{\beta^5c^5}}\Big/\sqrt{\frac{\pi}{\beta c}}=\frac{3g}{4\beta c^2}\ .$$

3.35. The partition function of the system is given by

$$Q_N = \frac{1}{N!} Q_1^N, \text{ where } Q_1 = \frac{V}{\lambda^3} \cdot Z ,$$

Z being the factor that arises from the rotational/orientational degrees of freedom of the molecule:

$$Z = \int \exp\left[-\beta\left\{\frac{p_\theta^2}{2I} + \frac{p_\varphi^2}{2I\sin^2\theta} - \mu E\cos\theta\right\}\right]\frac{dp_\theta dp_\varphi d\theta d\varphi}{h^2}$$

$$= \int_0^\pi \left(\frac{2\pi I}{\beta}\right)^{1/2}\left(\frac{2\pi I\sin^2\theta}{\beta}\right)^{1/2} e^{\beta\mu E\cos\theta}\,\frac{2\pi d\theta}{h^2}$$

$$= \frac{I}{\beta\hbar^2} \cdot \frac{2\sinh(\beta\mu E)}{\beta\mu E} .$$

The study of the various thermodynamical quantities of the system is now straightforward.

Concentrating on the electrical quantities alone, we obtain for the *net* dipole moment of the system

$$M_z = N\langle\mu\cos\theta\rangle = \frac{N}{\beta}\frac{\partial \ln Z}{\partial E} = N\mu\left[\coth(\beta\mu E) - \frac{1}{\beta\mu E}\right];$$

cf. eqns. (3.9.4 and 6). For $\beta\mu E << 1$,

$$M_z \approx N\mu \cdot \frac{1}{3}\beta\mu E .$$

The polarization P, per unit volume, of the system is then given by

$$P \approx n\mu^2 E / 3kT \qquad (n = N/V) ,$$

and the dielectric constant ε by

$$\varepsilon = \frac{E + 4\pi P}{E} \approx 1 + \frac{4\pi n\mu^2}{3kT}$$

The numerical part of the problem is straightforward.

Observables:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln V/V_Q$$

$$U = \frac{\partial}{\partial \beta}\beta F = \frac{3}{2}NkT$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk\left[\ln\frac{V/N}{V_Q} + 5/2\right]$$

- Suggestive of distributing N indistinguishable particles among V/V_Q cells - i.e. $\Omega \sim (V/V_Q)^N/N!$

validity of classical limit

$\Delta p \Delta x \gg h$ or $\bar{R}$ - interparticle separation $\gg \lambda$ - de Broglie wavelength

$\Rightarrow \bar{R} = (V/N)^{1/3} \gg \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2}$ or $v = V/N \gg V_Q$

estimates: - ideal gas $kT \sim \frac{1}{40}$ eV, $\bar{R} \sim 50$ Å for room temp gas

$$\lambda \sim \left(\frac{(\hbar c)^2 2\pi}{mc^2\ kT}\right)^{1/2} \sim \left(\frac{4\times10^6 \times 6}{20\times10^9/40}\right)^{1/2} \sim 1\ \text{Å}$$

$\bar{R} \gg \lambda$ - classical limit

- electrons in metal $\bar{R} \sim 1$ Å ; λ increased by (mass × temp ratio)$^{1/2}$

$\Rightarrow \lambda \sim 10$ Å - quantum limit

NB mention MB distribution !!

$\bar{v} \sim \sqrt{\frac{kT}{m}}$ $\quad P(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$

3) Einstein Model for crystal lattice

- model: each atom is an independent 3-d simple harmonic oscillator with $E_n = (n+\frac{1}{2})\hbar\omega\beta$

$$Z_{1\,mode} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2}\hbar\omega)} = \frac{1}{2}\operatorname{cosech}\beta\hbar\omega/2 \quad \text{or} \quad \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\hbar\omega\beta}}$$

note the natural scaled variable $\beta\hbar\omega$

$$Z_{tot} = (Z_1)^{3N}$$

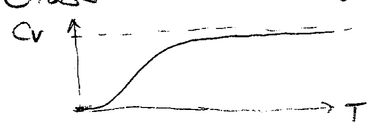
Observables:

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

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

$\rightarrow 3N\hbar\omega/2 \qquad \beta\hbar\omega \gg 1 \qquad$ low temp

$\rightarrow 3NkT \qquad \beta\hbar\omega \ll 1 \qquad$ classical limit (obeys equipartition)



Response fn: $C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$

Note: this fn $\sim e^{-1/T}$ as $T\to 0$. This vanishing of Cv with T is much more rapid than what is observed - a better theory is needed. However the high temp limit is OK