Solutions to assignment 4

3.28. (a) When one of the oscillators is in the quantum state n, the energy left for the remaining $(N-1)$ oscillators is $E-\left(n+\frac{1}{2}\right)\hbar\omega$; the corresponding number of quanta to be distributed among these oscillators is $R-n$; see eqn. (3.8.24). The relevant number of microstates is then given by the expression $(R-n+N-2)!/(R-n)!(N-2)!$. Combined with expression (3.8.25), this gives

$$p_n = \frac{(R-n+N-2)!}{(R-n)!(N-2)!} \div \frac{(R+N-1)!}{R!(N-1)!} . \tag{1}$$

It follows that

$$\frac{p_{n+1}}{p_n} = \frac{R-n}{R-n+N-2} \simeq \frac{R}{R+N} = \frac{\bar{n}}{\bar{n}+1} .$$

By iteration, $p_n = p_0\{\bar{n}/(\bar{n}+1)\}^n$.

Going back to eqn. (1), we note that

$$p_0 = \frac{N-1}{R+N-1} \simeq \frac{N}{R+N} = \frac{1}{\bar{n}+1} ,$$

which completes the desired calculation.

(b) The probability in question is proportional to $g_{N-1}(E-\varepsilon)$, i.e. to $(E-\varepsilon)^{\frac{3}{2}(N-1)-1}$. For $1 \ll N$, this is essentially proportional to $(1-\varepsilon/E)^{\frac{3}{2}N}$ and, for $\varepsilon \ll E$, to $e^{-3N\varepsilon/2E}$.

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

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

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

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

whence

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

and

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

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

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

In the desired approximation, we get

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

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

The potential has cq^2 and $-fq^4$ which are even under $q \to -q$, so they don't change $\langle q \rangle$. For $g>0$, $-gq^3$ lowers the potential for $q>0$, so $\langle q \rangle > 0$ if $g>0$.

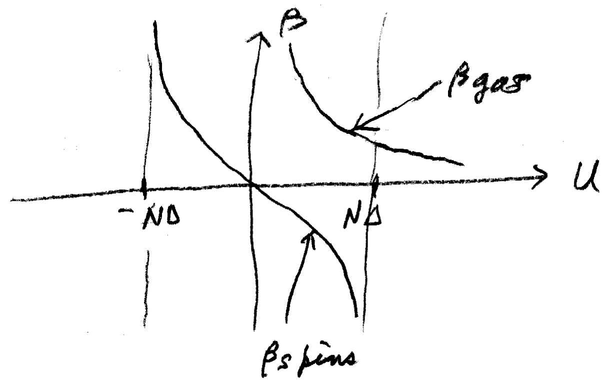
3.41 Want $\beta_{gas} = \beta_{spins}$ at equilibrium

$U_{gas} = \frac{3}{2} N' kT = \frac{3N'}{2\beta}$, so $\beta_{gas} = \frac{3N'}{2U_{gas}}$

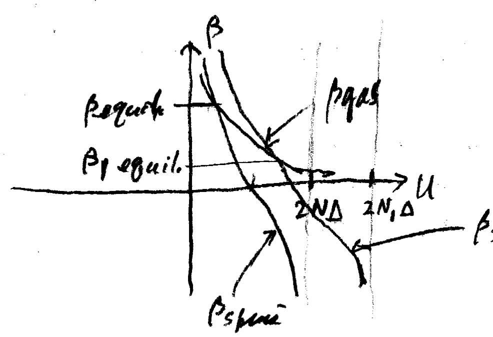
$U_{spins} = N \frac{\Delta e^{-\beta\Delta} + (-\Delta)e^{-\beta(-\Delta)}}{e^{\beta\Delta} + e^{-\beta\Delta}} = -N\Delta \tanh \beta\Delta$

$\beta_{spins} = -\frac{1}{\Delta} \operatorname{arctanh} \frac{U_{spins}}{N\Delta}$

Plot these



They don't intersect! Something is wrong.
Must have the same definition of energy for the lowest state. For the gas, $U_{gas} \to 0$, $\beta \to \infty$, is the lowest state. For the spins, $U_{spins} = -N\Delta$, $\beta \to \infty$, is the lowest state. So add $N\Delta$ to U_{spins} so the zeroes agree.



Of course $T_{equal.} > 0$.

β_1 equil $< \beta_{equil}$, so
$T_1 > T$ for more spins.

4.10 Surface w. N_0 adsorption centers has $N \le N_0$ gas molecules adsorbed on it. Show μ of adsorbed molecules is

$$\mu = kT \ln \frac{N}{(N_0 - N)\, a(T)}, \quad a(T) \text{ - partition funct. of a single adsorbed molecule.}$$

(Neglect intermolecular int. among adsorbed molecules.)

Canonical argument
For adsorbed molecules   Have to assume sites are distinguishable, but empty sites are all equiv., and occupied sites are all equiv.

$$Q_N(N_0, T) = \frac{N_0!}{N!\,(N_0-N)!}\, a^N, \quad Q_1 = a(T) \text{ — one molecule at an occupied site}$$

$$dA = -S\,dT - P\,dV + \mu\,dN$$

$$\left(\frac{\partial A}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial}{\partial N} \ln Q_N\right)_{V,T} = kT \ln \frac{N}{(N_0-N)\,a(T)} \quad \text{from Stirling's approx.}$$

Grand canonical argument: sites are distinguishable

$$\mathcal{Q} = \sum_{N_r, s} e^{-\alpha N_r - \beta E_s}$$

$$\mathcal{Q}(z, N_0, T) = [\mathcal{Q}(z, 1, T)]^{N_0} \qquad \mathcal{Q}(z,1,T) = 1 + e^{-\alpha - \beta E}$$

$$= [1 + z\,a(T)]^{N_0} \qquad = 1 + z a(T)$$

$N_r = 0,\ E_s = 0$ or $N_r = 1,\ E_s = E$

$z = e^{-\alpha} = e^{\frac{\mu}{kT}}$

$$\bar{N} = z \frac{\partial}{\partial z} \ln \mathcal{Q} = N_0 z \frac{\partial}{\partial z} \ln[1 + z a] = \frac{N_0 z a}{1 + z a}$$

$$(1 + z a)\bar{N} = N_0 z a, \quad z(N_0 a - \bar{N} a) = \bar{N}, \quad z = \frac{\bar{N}}{(N_0 - \bar{N})\, a} = e^{\frac{\mu}{kT}}$$

$$\mu = kT \ln \frac{\bar{N}}{(N_0 - \bar{N})\, a(T)}$$

use $\mathcal{Q} = \sum_0^\infty z^N Q_N$ and binomial theorem

$$(1 + z a)^{N_0} = \frac{N_0!\, 1^{N_0-N} (z a)^N}{(N_0-N)!\, N!} \Rightarrow Q_N = \frac{N_0!\, a^N}{(N_0-N)!\, N!}$$

4.11 Equilib. between gaseous phase and adsorbed phase in a one-component system. Show pressure in gaseous phase is

$$P_g = \frac{\theta}{1-\theta} f(T)$$

θ = fraction that are occupied

From 4.11

$$\theta = \frac{\bar{N}}{N_0} = \frac{z\, a_{ad}}{1+z\, a_{ad}}, \quad \text{so} \quad z_{ad} = \frac{1}{a}\frac{\theta}{1-\theta}$$

$$P_{gas} = z_{gas}\, kT f(T), \quad \text{so} \quad z_{gas} = \frac{P_{gas}}{kT f(T)}$$

Then $z_{ad} = z_{gas} \Rightarrow \quad P_{gas} = \frac{kT f(T)}{a} \frac{\theta}{1-\theta}$,

Langmuir's eq.