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 \( \frac{(R-n+N-2)!}{(R-n)! (N-2)!} \). Combined with expression (3.8.25), this gives

\[
P_n = \frac{(R-n+N-2)!}{(R-n)! (N-2)!} \frac{(R+N-1)!}{R!(N-1)!}.
\]

It follows that

\[
P_n = \frac{R-n}{R-n+N-2} \frac{R}{R+N} = \frac{n}{n+1}.
\]

By iteration, \( P_n = P_0 (n/(n+1))^n \).

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

\[
P_0 = \frac{N-1}{R+N-1} = \frac{N}{R+N} = \frac{1}{n+1},
\]

which completes the desired calculation.

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

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

\[
Q(\beta) = \frac{1}{\hbar} \int e^{-\beta H} dp dq \quad \left\{ H = \frac{p^2}{2m} + cq^3 - gq^4 - fq^5 \right\}.
\]

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

\[
e^{-\beta \omega^5} e^{i(\omega^4 q + \omega^3 a)} = e^{-\beta \omega^4} \left[ 1 + \beta (gq^3 + fq^4) + \frac{1}{2} \beta^2 (gq^3 + fq^4)^2 + \ldots \right];
\]

the integration then gives

\[
\sqrt{\frac{\pi}{\beta c}} + \beta f \cdot \frac{3}{4} \sqrt{\frac{\pi}{\beta c^5}} + \frac{15}{16} \frac{\pi}{\beta^2 c^2} + \ldots
\]

It follows that

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

so that

\[
\ln Q(\beta) = \text{const.} - \ln \beta + \frac{3f}{4\beta c^2} + \frac{15g^2}{16\beta^2 c^2} + \ldots.
\]
whence

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

and

\[ C(\beta) = k + \frac{3f k^2 T}{2c^3} + \frac{15g^2 k^2 T}{8c^5} + \ldots \]

Next, the mean value of the displacement \( q \) is given by

\[ \langle q \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-\beta H) q \, dp \, dq \bigg/ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-\beta H) \, dp \, dq. \]

In the desired approximation, we get

\[ \langle q \rangle \approx \beta \int_{-\infty}^{\infty} e^{-\beta q^2} \, dq \bigg/ \int_{-\infty}^{\infty} e^{-\beta q^2} \, dq \]

\[ = \beta \cdot \frac{3}{4 \sqrt{\beta c^3}} \cdot \frac{\pi}{\sqrt{\pi}} = \frac{3g}{4\beta c}. \]

The potential has \( q^2 \) and \( -\frac{g}{\beta} \) which are even under \( q \to -q \), so they don't change \( \langle q \rangle \). For \( g > 0 \), \(-\frac{g}{\beta}\) lowers the potential for \( q > 0 \), so \( \langle q \rangle > 0 \) if \( g > 0 \).
3.4.1 Want $\beta_{\text{gas}} = \beta_{\text{solid}}$ at equilibrium

$$U_{\text{gas}} = \frac{3}{2} k T = \frac{3}{2} \beta_{\text{gas}}$$

$$U_{\text{solid}} = N \frac{\Delta e^{-\beta_{\text{gas}} e^{\beta_{\text{gas}}}} + (-\Delta)e^{-\beta_{\text{gas}} e^{-\beta_{\text{gas}}}}}{e^\beta_{\text{gas}} + e^{-\beta_{\text{gas}}}} = -N \Delta \tanh \beta_{\text{gas}}$$

$$\beta_{\text{gas}} = -\frac{1}{\Delta \tanh \frac{U_{\text{solid}}}{N \Delta}}$$

Plot these

They don't intersect! Something is wrong.

Must have the same definition of energy for the lowest state. For the gas, $U_{\text{gas}} \to 0$, $\beta \to \infty$ is the lowest state. For the solid, $U_{\text{solid}} \to -N \Delta$, $\beta \to 0$, is the lowest state. So add $N \Delta$ to $U_{\text{solid}}$ so the curves agree.

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

$\beta$ varies $< \beta_{\text{equal}}$, so

$T_i > T$ for more solids.
4.10 Surface w. No adsorption occurs here N ≤ N₀, gas molecules adsorbed on it. Show μ of adsorbed molecules as

\[ \mu = kT \ln \frac{N}{(N_0 - N) a (T)} \]

(1) partition function of a simple adsorbed molecule.

(Nearest neighbor approach, among adsorbed molecules.)

For adsorbed molecules, how to assume intermolecular distinguishable, but empty sites are all equal, and occupied sites are all equal.

\[ \frac{q_N}{a_N} = \frac{a_N!}{N! (N_0 - N)!} \]

One molecule at an occupied site

\[ \Delta H = -S \Delta T - P \Delta V + M \Delta N \]

From Sterleng's formula

\[ \ln \frac{(\Delta F)}{(\Delta S)} = -kT \ln \frac{\frac{\Delta F}{\Delta T}}{\Delta S} \]

Grand canonical approach; N is distinguishable, \( w N_0 - \beta E \)

\[ Z(x, N, V) = \left[ \sum_{x, N, V} \right]^{N_0} \]

\[ Z(x, N, V) = 1 + e^{-\beta E} \]

\[ \bar{z} \equiv \frac{\bar{N}}{N} \]

\[ \bar{N} = \frac{N}{V} \]

\[ \bar{z} (\bar{N}, a) = \frac{\bar{N}}{N} \]

\[ \mu = kT \ln \frac{N}{(N_0 - N) a (T)} \]

we let \( \bar{z} = \frac{N}{V} \) and binomial theorem

\[ (1 + az)^N = \sum_{n=0}^{N} \frac{N!}{n!} (z a)^n \]

\[ \Rightarrow \frac{\bar{N}}{N} = \frac{N_0! a \bar{N}}{(N_0 - N)! \bar{N}} \]
Equilib. between gaseous phase and adsorbed phase in a one-component system. Sccow pressure in gaseous phase is

\[ P_g = \frac{\Theta}{1-\Theta} \]

\[ \Theta = \text{fraction treated on occupied} \]

From Eq. 11

\[ \Theta = \frac{N}{N_0} = \frac{2\alpha \tilde{z}}{1 + 2\alpha \tilde{z}} \]

\[ \tilde{z} = \frac{z}{a} \cdot \frac{1}{1 - \Theta} \]

\[ P_{\text{gas}} = \frac{P_{\text{gas}}}{kT + \frac{1}{\gamma}} \text{, so } \tilde{z}_{\text{gas}} = \frac{P_{\text{gas}}}{kT + \frac{1}{\gamma}} \]

Then \[ 2\alpha = 2\tilde{z}_{\text{gas}} \Rightarrow P_{\text{gas}} = \frac{kT + \frac{1}{\gamma}}{a} \cdot \frac{\Theta}{1 - \Theta} \]

Langmuir eq.