4.2 Show that $\sum_N z^N Q_N(V,T)$ can be replaced by the largest term, in the thermodynamic limit

The point is NOT that the largest term is the ONLY ONE that contributes - misconception!

The point is that regarded as a function of N, the terms $z^N Q_N(V,T)$ are roughly constant over the range of N within the contributing range as determined by

$$\langle(\Delta N)^2\rangle = N^2 \frac{kT}{V} \kappa_T \sim N \text{ in the thermodynamic limit}$$

(§4.5, equation 7)

so $\sum_N z^N Q_N \approx M z^{N^*} Q_{N^*}$, and taking the log just adds a constant $\ln M$ that does not come into thermodynamic fcns in thermodynamic limit.

to show this, we have to find how $\ln z^N Q_N$ varies near its maximum.

to find the max: $\frac{\partial}{\partial N} \ln(z^N Q_N) = \ln z + \frac{\partial}{\partial N} \ln Q_N$

so $\ln z = -\frac{\partial}{\partial N} \ln Q_{N^*}$

for the 2nd derivative $\frac{\partial^2}{\partial N} \ln(z^N Q_N) = \frac{\partial^2}{\partial N^2} \ln Q_N$

$\ln Q_N$ is extensive, so an argument could be made that $\frac{\partial^2}{\partial N^2} \ln Q_N$ is $\mathcal{O}(1)$ (not very convincing)

can try special case of ideal gas $Q_N = \frac{1}{N!} Q_1^N$

the $\ln(z^N Q_N) = N \ln z + N \ln Q_1 - (N \ln N - N)$

$\frac{\partial}{\partial N} \quad = \ln z + \ln Q_1 - \ln N$

$\frac{\partial^2}{\partial N^2} \quad = -\frac{1}{N}$ so leading order correction to $\ln z^N Q_N$ is $-\frac{1}{2N}(N-N^*)^2$

absolute decrease is $\mathcal{O}(1)$

relative decrease is $\mathcal{O}(1/N) \to 0$ in thermodynamic limit

Note that with this replacement, the thermodynamic quantities computed in the grand canonical ensemble are the same as those in the canonical ensemble:

$$\ln \mathcal{Q} = N \ln z + \ln Q_N$$

$$P = \frac{kT}{V} \ln \mathcal{Q} = \frac{NkT}{V} \ln z + \frac{kT}{V} \ln Q_N$$

to make this look like canonical $P = \frac{\partial}{\partial V}(kT \ln Q_N)$, we use the fact that $\ln Q_N$ is extensive, so

$$N \frac{\partial \ln Q_N(V,T)}{\partial N} + V \frac{\partial}{\partial V} \ln Q_N(V,T) = Q_N$$

and $\ln z = -\frac{\partial}{\partial N} \ln Q_N$ from previous page

so

$$P = -\frac{NkT}{V} \frac{\partial}{\partial N} \ln Q_N + \frac{kT}{V} N \frac{\partial}{\partial N} \ln Q_N + \frac{kTV}{V} \frac{\partial}{\partial V} \ln Q_N$$

$$= \frac{\partial}{\partial V}(kT \ln Q_N) \quad ✓$$

$$U = -\frac{\partial}{\partial \beta} \ln \mathcal{Q} = -\frac{\partial}{\partial \beta}(N \ln z + \ln Q_N) = -\frac{\partial}{\partial \beta} \ln Q_N \quad ✓$$

$$S = kT \frac{\partial \ln \mathcal{Q}}{\partial T} - Nk \ln z + k \ln \mathcal{Q}$$

$$= kT \frac{\partial (\ln Q_N)}{\partial T} - Nk \ln z + kN \ln z + k \ln Q_N$$

$$= -\frac{\partial}{\partial T}(kT \ln Q_N) \quad ✓$$

4.8 The energy of a single particle is $\frac{p^2}{2m} \pm \mu_B H$

$$\Rightarrow Q_1 = \frac{V}{h^3}\left(2\pi m k T\right)^{3/2}\left(e^{\beta\mu_B H} + e^{-\beta\mu_B H}\right)$$

$$Q_N = \frac{1}{N!} Q_1^N = \frac{1}{N!}\left(\frac{V}{h^3}(2\pi m k T)^{3/2}\left(e^{\beta\mu_B H} + e^{-\beta\mu_B H}\right)\right)$$

The grand partition fcn is

$$\mathcal{Q} = \sum_N z^N Q_N = \sum_N \frac{1}{N!}\left(\frac{zV}{h^3}(2\pi m k T)^{3/2}\left(e^{\beta\mu_B H} + e^{-\beta\mu_B H}\right)\right)^N$$

$$= \exp\left(\frac{zV}{h^3}(2\pi m k T)^{3/2}\left(e^{\beta\mu_0 H} + e^{-\beta\mu_B H}\right)\right)$$

the magnetization is (average $\sum_{i=1}^{N} \vec{\mu}$, E contains $-\vec{H}\cdot\sum_{i=1}^{N}\vec{\mu}$)

$$-\frac{\partial}{\partial H}\ln \mathcal{Q}$$

$$M = \left(\frac{zV}{h^3}(2\pi m k T)^{3/2}\beta\mu_0\left(e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}\right)\right)$$

$$U = -\frac{\partial}{\partial\beta}\ln\mathcal{Q}$$

$$= -\frac{zV}{h^3}\left[\frac{3}{2\beta}\left(e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}\right) + \left(e^{\beta\mu_0 H} - e^{-\beta\mu_0 H}\right)\mu_0 H\right](2\pi m k T)^{3/2}$$

$$= \frac{zV}{h^3}\left[\left(\frac{3kT}{2} - \mu_0 H\right)e^{\beta\mu_0 H} + \left(\frac{3kT}{2} + \mu_0 H\right)e^{-\beta\mu_0 H}\right](2\pi m k T)^{3/2}$$

to calculate the heat given off.

$$Q = T(S_i - S_f) \quad \text{(NOT } U_i - U_f \text{ - work is done by } H!\text{)}$$

let's assume that H is taken to zero at constant z as well as constant V and T

$$TS_i = U_i - NkT\ln z + kT\ln Q$$

$$= \frac{zV}{\lambda^3}\left[\left(\frac{3kT}{2} - \mu_0 H\right)e^{\beta\mu_0 H} + \left(\frac{3kT}{2} + \mu_0 H\right)e^{-\beta\mu_0 H}\right]$$

$$- NkT\ln z$$

$$+ \frac{zV}{\lambda^3}\left[kTe^{\beta\mu_0 H} + kTe^{-\beta\mu_0 H}\right]$$

$$TS_f = \frac{zV}{\lambda^3}3kT - NkT\ln z + \frac{zV}{\lambda^3}\cdot 2kT$$

$$= \frac{zV}{\lambda^3}5kT - NkT\ln z$$

$$\Rightarrow \quad Q = \frac{zV}{\lambda^3}\left[\left(\frac{5kT}{2} - \mu_0 H\right)e^{\beta\mu_0 H} + \left(\frac{5kT}{2} + \mu_0 H\right)e^{-\beta\mu_0 H} - 5kT\right]$$

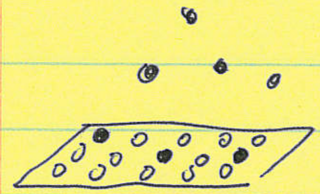
for small H

$$Q \approx \frac{zV}{\lambda^3}\left[-\mu_0 H\cdot\beta\mu_0 H + \frac{5kT}{2}\cdot\frac{(\beta\mu_0 H)^2}{2} - \mu_0 H(\beta\mu_0 H) + \frac{5kT}{2}\frac{(\beta\mu_0 H)^2}{2}\right]$$

$$= \frac{zV}{\lambda^3}\left[kT\left[\frac{5}{2} - 2\right](\beta\mu_0 H)^2\right]$$

$$= \frac{zV}{\lambda^3}\cdot\frac{kT}{2}(\beta\mu_0 H)^2 \quad \text{positive so heat is indeed given off.}$$

4.10



N_0 adsorption centers – distinguishable by position on surface

$\boxed{\text{canonical ensemble}}$ – sum over states w/ N particles

$\binom{N_0}{N}$ distinct ways of putting N particles into N_0 distinguishable sites

for each arrangement, each particle can access a spectrum of states

$$Q_N = \binom{N_0}{N} a(T)^N \quad \text{where} \quad a(T) = \sum_r e^{-\beta E_r}$$

sum over single particle states

$$\mu = \left.\frac{\partial(-kT \ln Q_N)}{\partial N}\right)_{V,T}$$

$$= \frac{\partial}{\partial N}\left(-kT\left(N \ln a(T) + \ln N_0! - \ln N! - \ln(N-N_0)!\right)\right)$$

$$= \frac{\partial}{\partial N}\left(-kT\left(N \ln a(T) + N_0 \ln N_0 - N \ln N - (N_0-N)\ln(N_0-N)\right)\right)$$

$$= -kT\left[\ln a(T) - \ln N - 1 - \ln(N_0 - N) + 1\right]$$

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

$\boxed{\text{grand canonical ensemble}}$ – sum over all states of any N (empty state has energy $= 0$)

$$\mathcal{Q} = \left(1 + z\,a(T)\right)^{N_0}$$

$$N = z\frac{\partial}{\partial z}\ln \mathcal{Q} = z N_0 \frac{\partial}{\partial z}\ln(1 + z\,a(T))$$

$$= z N_0 \frac{a(T)}{1 + z\,a(T)}$$

solve for z: $\frac{N}{N_0}(1 + z\,a(T)) = z\,a(T)$

$$z = \frac{N/N_0}{\left(1 - \frac{N}{N_0}\right)a(T)} \quad \Rightarrow \quad \mu = kT \ln \frac{N/N_0}{\left(1 - \frac{N}{N_0}\right)a(T)} \quad \checkmark$$

Make a plot of N vs μ at a chosen temperature T assuming the adsorbed molecule is a single atom with no internal degrees of freedom.

$$N = e^{\beta\mu} N_0 \frac{a(T)}{1 + Z\, a(T)} \qquad a(T) = 1$$

$$\frac{N}{N_0} = \frac{e^{\beta\mu}}{1 + e^{\beta\mu}}$$

$\to 1$ as $\mu \to \infty$

$= 1/2$ at $\mu = 0$

$\to 0$ as $\mu \to -\infty$