Lecture 17

Finish up Ch 3

Magnetism

Got classical result $M = \rho \mu L\left(\frac{\mu \mathcal{H}}{kT}\right)$

$L(x) = \coth x - \frac{1}{x}$

Compare to quantum

For spin-J particles, got

$$Q_1 = \frac{\sinh x\left(1 + \frac{1}{2J}\right)}{\sinh x/2J}$$

$$x = \frac{(g\mu_B J)\mathcal{H}}{kT}$$

From this, get

$$M = \rho \langle \mu_z \rangle = \frac{\rho}{\beta} \frac{\partial}{\partial \mathcal{H}} \ln Q_1$$

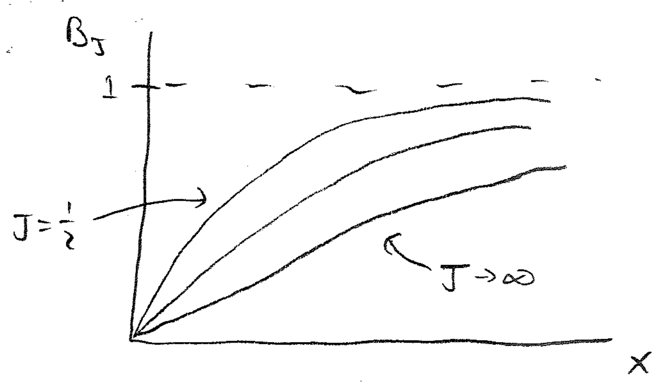
$$= \rho (g\mu_B J) \frac{\partial}{\partial x} \ln Q_1$$

$$= \rho g \mu_B J \left[\left(1 + \frac{1}{2J}\right) \coth x\left(1 + \frac{1}{2J}\right) - \frac{1}{2J} \coth \frac{x}{2J} \right]$$

$$\equiv \rho g \mu_B J \; B_J(x)$$

B_J = Brillouin function of order J

Similar to $L(x)$



For small x, get $B_J(x) \simeq \frac{1}{3}\left(1+\frac{1}{J}\right)x$

and $M \to \rho g \mu_B J \frac{1}{3}\left(1+\frac{1}{J}\right) \frac{g \mu_B J}{kT} \mathcal{H}$

$$= \rho \frac{g^2 \mu_B^2 J(J+1)}{3kT} \mathcal{H}$$

$$= \frac{\rho \hat{\mu}^2}{3kT} \mathcal{H}$$

for $\hat{\mu} = g \frac{\mu_B}{\hbar} \hat{J}$ operator

Looks like classical result with classical $\mu \to$ operator $\hat{\mu}$

Again see Curie law

Can also show pretty easily that $B_J(x) \to L(x)$ as $J \to \infty$, as expected

But in practice, J usually not large

Can actually get J for particles from plot of M vs $\mathcal{H}$.

That's end of Ch 3, & of material for midterm!

Let n_{Ns} = # of systems having N particles and energy E_s

So set $\{n_{Ns}\}$ describes the ensemble

and we require

$$\sum_{N,s} n_{Ns} N = \mathcal{N} \bar{N}$$

$$\sum_{N,s} n_{Ns} E_s = \mathcal{N} \bar{E}$$

Of course, systems are distinguishable, so each set $\{n_{Ns}\}$ corresponds to many possible ensembles

As before, # of permutations is

$$W\{n_{Ns}\} = \frac{\mathcal{N}!}{\prod_{N,s} n_{Ns}!}$$

Most likely state of ensemble is one with largest W.

Maximize W same way as before: Consider $\ln W$, & introduce Lagrange multipliers α, β:

Maximize

$$\ln W - \alpha \sum n_{Ns} N - \beta \sum n_{Ns} E_s$$

w/ respect to all n_{Ns}'s

Chapter 4 - Grand Canonical Ensemble

We saw how much easier canonical ensemble is to use than micro-canonical

$\Rightarrow$ get rid of constraint energy $= E$

Still have constraint particle number $= N$

Sometimes useful to eliminate that as well.

$\Rightarrow$ grand canonical ensemble

For most classical systems, canonical is better

But will need grand canonical to handle quantum statistics

That is main purpose... won't spend much time on classical systems.

Develop math:

Imagine ensemble of $\mathcal{N}$ systems that can exchange both energy & particles with each other.

Total number of particles in all systems $= \mathcal{N}\bar{N}$

Total energy $= \mathcal{N}E$

$\{E_s\}$ = allowed energies for each system as before

$$\frac{\partial}{\partial n_{NS}}\left[\ln \mathcal{N}! - \sum_{NS} \ln n_{NS}! - \alpha \sum n_{NS} N - \beta \sum n_{NS} E_S\right] = 0$$

$$\frac{\partial}{\partial n_{NS}}\left[\ln n_{NS}! - \alpha n_{NS} N - \beta n_{NS} E_S\right] = 0$$

Can take $\mathcal{N} \to \infty$, so n_{NS} is large

$$\ln n_{NS} \to n_{NS} \ln n_{NS} - n_{NS}$$

Gives $\left[\ln n_{NS} + 1 - 1 - \alpha N - \beta E_S\right] = 0$

$$n^*_{NS} = e^{-(\alpha N + \beta E_S)}$$

Or $P_{NS} = \dfrac{n^*_{NS}}{\mathcal{N}} = \dfrac{e^{-(\alpha N + \beta E_s)}}{\sum_{NS} e^{-(\alpha N + \beta E_s)}}$

= Probability for a given system to have N particles & energy E_s

Get α & β by enforcing $\langle N \rangle = \bar{N}$, $\langle E \rangle = \bar{E}$

Or $\bar{N} = \dfrac{\sum_{N,S} N e^{-(\alpha N + \beta E_s)}}{\sum_{NS} e^{-(\alpha N + \beta E_s)}} = -\dfrac{\partial}{\partial \alpha} \ln \sum_{NS} e^{-(\alpha N + \beta E_s)}$

$$\bar{E} = \frac{\sum E_s e^{-(\alpha N + \beta E_s)}}{\sum e^{-(\alpha N + \beta E_s)}} = -\frac{\partial}{\partial \beta} \ln \sum_{NS} e^{-(\alpha N + \beta E_s)}$$

I'll just give you the connection to thermo: find

$$\beta = \frac{1}{kT}$$

$$\alpha = -\frac{\mu}{kT}$$

μ = chemical potential

and

$$-kT \ln \left\{ \sum_{Ns} e^{-(\alpha N + \beta E_s)} \right\} = \Phi$$

= Grand potential

$= -PV$

(or XY in general)

Pathria defines $q = -\Phi/kT = \ln\{ \quad \} = \frac{PV}{kT}$

Also define $$\mathcal{Q} = \sum_{Ns} e^{-(\alpha N + \beta E_s)}$$

= grand partition function

So $\Phi(\mu, V, T) = -kT \ln \mathcal{Q}$

Typically write as $$\mathcal{Q} = \sum_N z^N \sum_s e^{-\beta E_s(N)}$$

for $z = e^{-\alpha} = e^{\mu/kT} = e^{\beta\mu}$
= "fugacity"

But $\sum_s e^{-\beta E_s(N)} = Q_N$

regular partition function

So $\mathcal{Q} = \sum_{N=0}^{\infty} z^N Q_N(V,T)$

$(Q_0 \equiv 1)$

In general, this is harder to deal with than Q_N but in some cases (specifically with identical quantum particles) $\mathcal{Q}$ can be calculated while Q_N can't. We'll see how

For now, just demonstrate g-c ensemble for ideal gas

Know $Q_N = \frac{Q_1^N}{N!}$ $\quad Q_1 = \frac{V}{\lambda^3} = V\left(\frac{2\pi m k T}{h^2}\right)^{3/2}$

So $\mathcal{Q} = \sum_{N=0}^{\infty} z^N \frac{Q_1^N}{N!}$

$= e^{zQ_1}$

Thus $\Phi = -kT \ln \mathcal{Q} = -kT z Q_1 = -PV$

Thermo gives $d\Phi = -SdT - PdV - Nd\mu$

So $N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -\frac{\partial \Phi}{\partial z}\frac{\partial z}{\partial \mu}$

$z = e^{\beta\mu}$

$\frac{\partial z}{\partial \mu} = \beta z$

So $$N = -\beta z \frac{\partial \Phi}{\partial z}$$

$$= -\beta z \frac{\partial}{\partial z}\left(-kTzQ_1\right)$$

$$N = zQ_1$$

Substitute into $\Phi = -kTzQ_1 = -PV$

get $PV = NkT$ ✓

Also gives $$\mu = kT \ln z$$

$$= kT \ln N/Q_1$$

$$= kT \ln \frac{N\Lambda^3}{V}$$

as we've seen before

Then $$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V}$$

$$= \frac{\partial}{\partial T}\left[kT e^{\mu/kT} V \left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]$$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2} V k^{5/2} \frac{\partial}{\partial T}\left[T^{5/2} e^{\mu/kT}\right]$$

$$\left[\frac{5}{2} T^{3/2} e^{\mu/kT} + T^{5/2}\left(-\frac{\mu}{kT^2}\right) e^{\mu/kT}\right]$$

$$= \underbrace{\left(\frac{2\pi m kT}{h^2}\right)^{3/2} V}_{\frac{V}{\Lambda^3}} k \left[\frac{5}{2} - \frac{\mu}{kT}\right] \underbrace{e^{\mu/kT}}_{= \frac{N\Lambda^3}{V}}$$

$$S = Nk\left[\frac{5}{2} - \ln \frac{N\Lambda^3}{V}\right]$$ Sackur-Tetrode

Can also show

$$E = \frac{\partial}{\partial \beta} (\beta \Phi)_{z,V} \quad :$$

$$\frac{\partial}{\partial \beta}(\beta \Phi)_z = \frac{\partial}{\partial \beta}(\beta \phi)_\mu + \frac{\partial}{\partial \mu}(\beta \phi)_\beta \left(\frac{\partial \mu}{\partial \beta}\right)_z$$

Get $\left(\frac{\partial \mu}{\partial \beta}\right)_z$: $\quad z = e^{\beta\mu}$

$$\Rightarrow \mu = \frac{1}{\beta} \ln z$$

$$\left(\frac{\partial \mu}{\partial \beta}\right)_z = -\frac{1}{\beta^2} \ln z = -\frac{\mu}{\beta}$$

So $$\frac{\partial}{\partial \beta}(\beta \Phi)_z = \phi + \beta \left(\frac{\partial \Phi}{\partial \beta}\right)_\mu - \mu \left(\frac{\partial \Phi}{\partial \mu}\right)_\beta$$

$$\frac{\partial \Phi}{\partial \beta} = \frac{\partial \Phi / \partial T}{\partial \beta / \partial T} = -kT^2 \frac{\partial \Phi}{\partial T}$$

$$\frac{\partial}{\partial \beta}(\beta \phi)_z = \phi - T\left(\frac{\partial \Phi}{\partial T}\right)_\mu - \mu \left(\frac{\partial \Phi}{\partial \mu}\right)_T$$

$$= \Phi + TS + \mu N$$

But $\Phi = E - TS - \mu N$

So $$\boxed{\frac{\partial}{\partial \beta}(\beta \phi)_z = E}$$

Here $\Phi = -kTz\,Q_1$

$$E = -z\frac{\partial Q_1}{\partial \beta}$$

$$= -\frac{N}{Q_1}\frac{\partial Q_1}{\partial \beta} \qquad Q_1 \propto \beta^{-3/2}$$

So $\frac{1}{Q_1}\frac{\partial Q_1}{\partial \beta} = -\frac{3}{2}\frac{1}{\beta}$

and $E = \frac{3}{2}NkT$ ✓