11/17

Last time:

Non-ideal gas

$$Z = \underbrace{Z_0}_{\text{ideal gas}} Z_U$$

$$Z_U = \frac{1}{V^N} \int \prod_{i=1}^{N} d^3 r_i \prod_{\substack{\langle \text{pairs} \rangle \\ \langle ij \rangle}} e^{-\beta u_{ij}}$$

At high T or for small u_{ij} $\quad e^{-\beta u_{ij}} \simeq 1 + f_{ij}$

$$\Rightarrow \underline{f_{ij} \simeq e^{-\beta u_{ij}} - 1}$$

useful in homework

$$Z_U = \frac{1}{V^N}\int \prod_{i=1}^{N} d^3r_i \Big(1 + \sum_{\langle i,j\rangle} f_{ij} + \sum_{\substack{\langle i,j\rangle \neq \\ \langle k,l\rangle}} f_{ij} f_{kl} + \dots \Big) =$$

$$= \frac{1}{V^N} \underbrace{\int \prod_{i=1}^{N} d^3r_i}_{V^N} + \frac{V^{N-2}}{V^N} \sum_{\langle i,j\rangle} d^3r_i \cdot d^3r_j \cdot f_{ij} + \dots$$

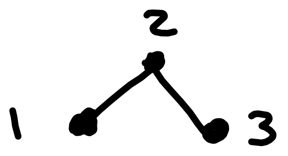
$$b_1 = \frac{1}{V}\int d^3r_1 = 1$$

$$b_2 = \frac{1}{V^2}\,\frac{N(N-1)}{2}\int d^3r_1\, d^3r_2\, f_{12}$$

Now consider a diagram for the integrals

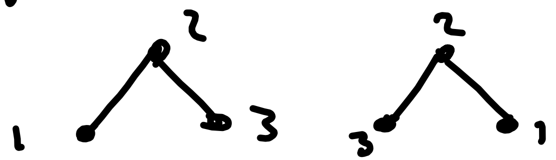
$$\frac{1}{V^N}\int d^3r_1 \dots d^3r_N \sum_{\substack{\langle i,j\rangle \\ \neq \langle k,l\rangle}} f_{ij}\, f_{kl}$$

1) One common molecule:



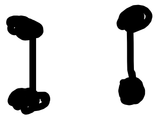
$$= \frac{N(N-1)}{2}(N-2)\frac{1}{V^3}\int d^3r_1\, d^3r_2\, d^3r_3\, f_{12}\, f_{23}$$

Connected diagram



$= 2$

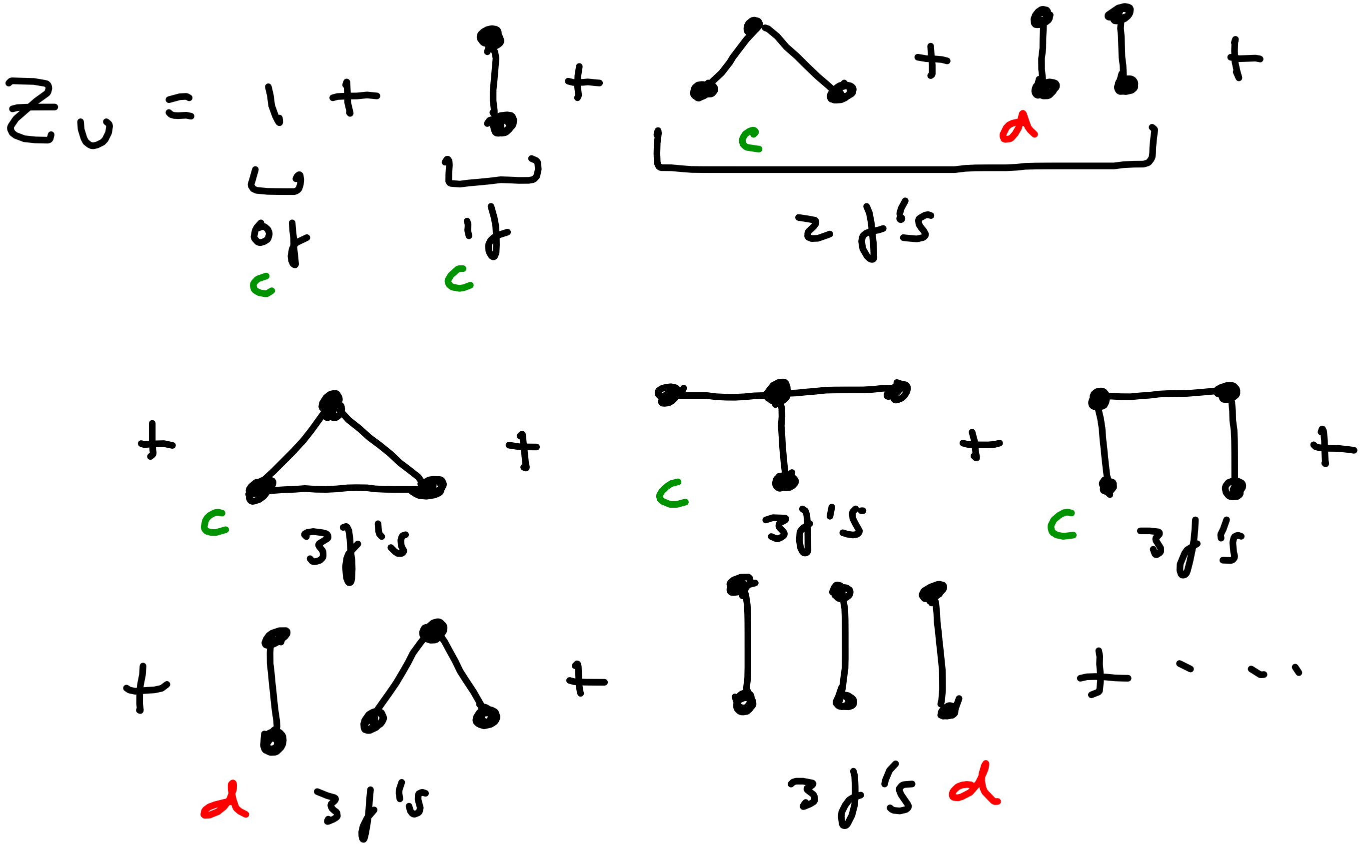
2) no common molecules:



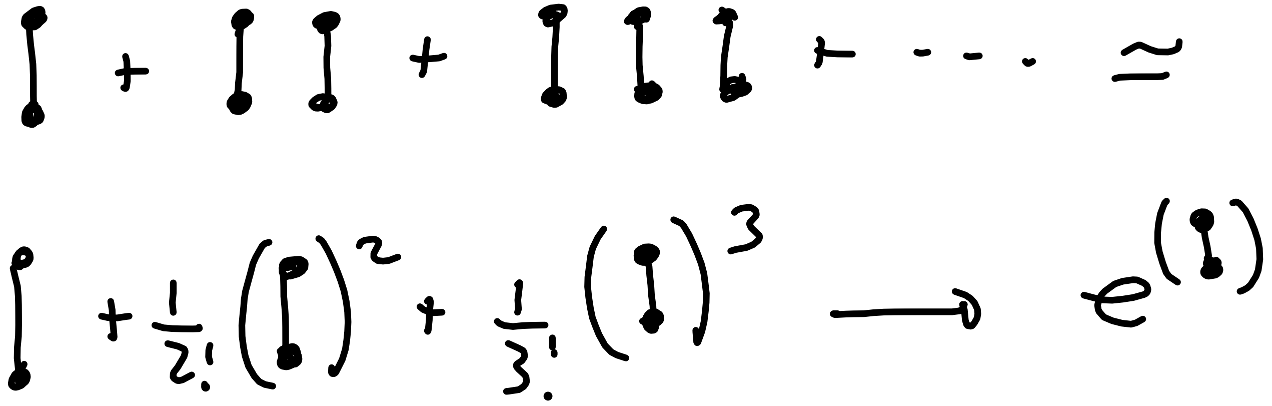
$$= \frac{1}{8}N(N-1)(N-2)(N-3)\frac{1}{V^4}\int d^3r_1\, d^3r_2\, d^3r_3\, d^3r_4\, f_{12}\, f_{34}$$

disconnected diagram

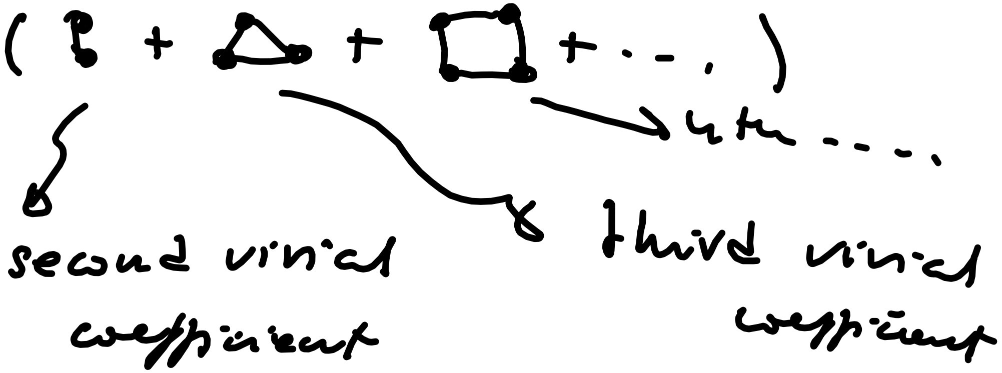
Then



It is possible to see that the disconnected diagrams together with a representative connected one can be summed together:



$Z_v = e$



Only the totally connected diagrams appear. (you remove one molecule and the diagram is still connected).

$$Z = Z_0 Z_v$$

$$F = -kT \ln Z = -kT(\ln Z_0 + \ln Z_v) =$$

$$= -kT \ln Z_0 - kT \ln Z_v$$

Equation of state:

$$\bar{P} = -\frac{\partial F}{\partial V}\Big|_{N,T} = \underbrace{\frac{NkT}{V}}_{\text{ideal result}} + kT\frac{\partial}{\partial V}\left(\overset{\bullet}{\underset{\bullet}{|}} + \triangle + \cdots \right)$$

Second virial coefficient:

$$\text{Consider first } \overset{\bullet}{\underset{\bullet}{|}} = \frac{1}{2}\frac{N^2}{V^2} \int d^3r_1\, d^3r_2\, f_{12} \quad \text{(assuming } N-1 \approx N\text{)}$$

$$\text{If } \bar{r} = \bar{r}_2 - \bar{r}_1 \Rightarrow \bar{r}_2 = \bar{r} + \bar{r}_1$$

$$d^3r_2 = d^3r$$

$$\overset{\bullet}{\underset{\bullet}{|}} = \frac{1}{2}\frac{N^2}{V^2} \overbrace{\int d^3r_1}^{V} \int d^3r\, f(r) = \frac{1}{2}\frac{N^2}{V} \int d^3\bar{r}\, f(r)$$

Remember that we defined $e^{-\beta u_{ij}} = 1 + f_{ij}$

$\therefore \quad f(r) = e^{-\beta u(r)} - 1$

Then

$$\bar{P} = \frac{NkT}{V} + kT \frac{\partial}{\partial V}\left[\frac{1}{2}\frac{N^2}{V}\int d^3r\, f(r)\right] =$$

$$= \frac{NkT}{V} - \frac{k}{2} T \frac{N^2}{V^2}\int d^3r\, f(r) =$$

$$= \frac{NkT}{V}\left[1 - \frac{N}{2V}\int d^3r\, f(r)\right] =$$

But in a previous class we found that

$$B_2 = -\frac{1}{2}\int d^3r\, f(r) = -\frac{1}{2} I(\beta) =$$

$$= -\frac{1}{2}\int_V \left(e^{-\beta u} - 1\right) d^3r$$

Then we found that

$$\bar{P} = \frac{NkT}{V}\left(1 + \frac{N}{V} B_2(T)\right)$$

Higher order virial coefficients:

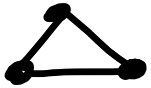
$$\frac{Pv}{kT} = \sum_{\ell=1}^{\infty} B_\ell(T)\left(\frac{\lambda^3}{v}\right)^{\ell-1}$$

$$v = \frac{V}{N} \qquad \lambda = \frac{h}{\sqrt{2\pi m k T}}$$

$B_1 = 1 \equiv$ ●

$$B_2 = -2\pi\int_0^\infty \left(e^{-\beta u} - 1\right) R^2\, dR = -\frac{1}{V}\int d^3r_1\, d^3r_2\, f_{12} =$$

$= -$ ●—●

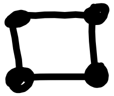
$B_3 = -\frac{2}{3}$  $\equiv -\frac{1}{3}\int d^3r\, d^3r'\, f(r) f(r') \cdot f(r-r')$

(see homework).

$$f(r) = e^{-\beta u(r)} - 1$$

In general:

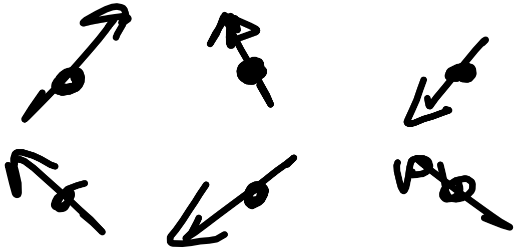
$$B_\ell(T) = \frac{-(\ell-1)}{\ell}\,\frac{1}{(\ell-1)!}$$ (integral given by the ℓ-connected cluster)

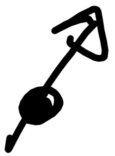
$\ell = 4 \Rightarrow$ 

Ferromagnetism (Reif 10.6):

Interactions between spins:

N identical atoms in a regular lattice





$$\bar{\mu} = \overset{\sim 1}{g}\,\mu_0\,\bar{S}$$

Bohr's magneton

spin

If we turn on a field

$H_0 = (0, 0, H_0)$ the spins will tend to align with it.

Non-interacting atoms:

$$\mathcal{H}_0 = - g\mu_0 \sum_{j=1}^{N} \bar{S}_j \cdot \bar{H}_0 =$$

$$= - g\mu_0 H_0 \sum_{j=1}^{N} S_j^z$$

We solved this problem before and we found that $B_s(\eta)$ (Brillouin function) provided the magnetization as a function of H_0 and T.

However, $M(H_0 = 0) = 0$ which is not the case for a ferromagnet.

Then in a ferromagnet the spins have to interact with each other.

How do they interact?

1) Magnetic interaction among dipoles?

<u>NO</u>!

$\bar{\mu}_1 \cdot \bar{\mu}_2$ dipole interaction

$\frac{\mu_0}{r^3} \sim 1.2 \times 10^{-17}$ erg < 1K

but FM is observed at much higher T.

- Coulomb? YES.
  - charge particles attract or repel each other.
  - spin affects the Coulomb interaction

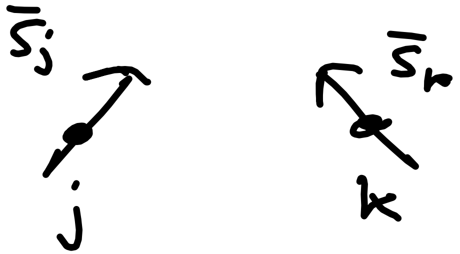
↑↑ electrons with parallel spin cannot be too close to each other due to Pauli's exclusion principle.

↑↓ electrons with ↑↓ spin can be closer to each other.

Exchange interaction:

The (Coulomb) energy of the electrons (or ions will depend on the spin orientation):

① $\mathcal{H}_{jk} = -2 J_{jk} \bar{S}_j \cdot \bar{S}_k$



J_{jk} : the strength decreases with distance because is related to the overlap of the orbitals in neighboring molecules where the electrons are located.

① favors ferromagnetic alignment of the spins if J_{kj} is positive and AF alignment if it is negative.

Simplifications:

$$\mathcal{H}_{jk} = -2J\, S_j^z\, S_k^z$$

we consider only the z-components to avoid dealing with vectors. (this is called Ising interaction while $\bar{S}_i \cdot \bar{S}_j$ is called Heisenberg).

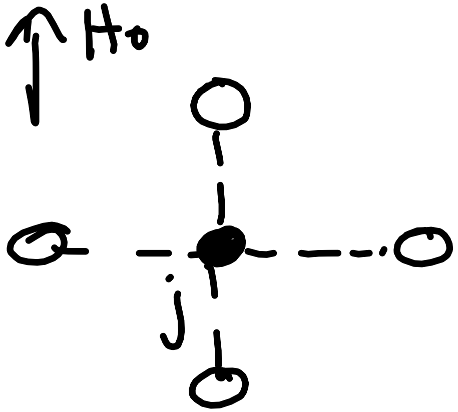
$$\mathcal{H}_{int} = \frac{1}{2}\left(-2J\sum_{j=1}^{N}\sum_{k=1}^{m} S_j^z S_k^z\right)$$

m: number of nearest neighbors of atom j.

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int}$$

Let's find $\langle M \rangle = \langle M(T, H_0) \rangle$

Let's focus on one single atom:



$n = 4$ here

$$\mathcal{H}_j = -g\mu_0 H_0 S_j^z - 2J S_j^z \underbrace{\sum_{k=1}^{n} S_k^z}_{\text{problem}} \tag{2}$$

Approximation!

The effect of the neighboring spins is going to be replaced by an effective field H_m that will be obtained self-consistently.

We will say that

$$2J \left\langle \sum_{k=1}^{n} S_k^z \right\rangle = g\mu_0 H_m \qquad ③$$

H_m : "mean-field", or "effective-field" or "molecular-field".

Then plugging ③ in ② :

$$\mathcal{H}_j = -g\mu_0 (H_0 + \underline{\underline{\underline{H_m}}}) S_{jz}$$

similar to single particle problem but we need to find Hm.

For one single atom:

$$E_m = -g\mu_0(H_0+H_m)m_s \qquad m_s = -S, -S+1, \dots, S$$

$$m_s = \pm\frac{1}{2} \text{ if } S = \frac{1}{2}$$

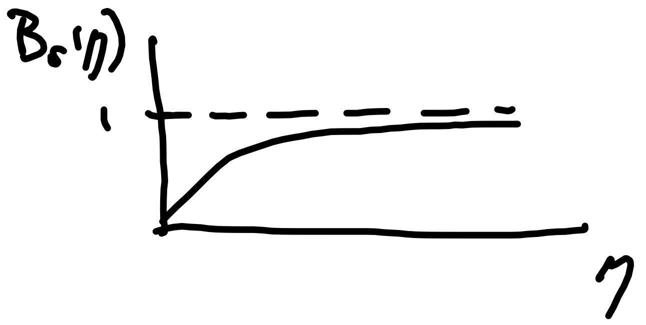
then

$$\langle S_j^z \rangle = S\, B_s(\eta)$$ [Chapter 7 – Look @ older lectures].

with

⊛ $$\eta = \beta g\mu_0(H_0+H_m)$$

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



But what is H_m?

Assume that $\langle S_k^z \rangle = \langle S_j^z \rangle$ for all k.

Then we had that

$$2J \langle \sum_{k=1}^{m} S_k^z \rangle = g\mu_0 H_m$$

$$2J \langle S_j^z \rangle m = g\mu_0 H_m$$

since $\langle S_j^z \rangle = S B_S(\eta)$

$$2J S B_S(\eta) m = g\mu_0 H_m$$

we can use this to find H_m.

Solving for $B_s(y)$ I obtain:

$$B_s(y) = \frac{g\mu_0 H_m}{2JSn}$$

Since $y = \beta g \mu_0 (H_0 + H_m)$ then

$$H_m = \frac{y}{\beta g \mu_0} - H_0 = \frac{1}{\beta g \mu_0}\left(y - \beta g \mu_0 H_0\right)$$

$$B_s(y) = \frac{kT}{2JSn}\left(y - \frac{g\mu_0 H_0}{kT}\right)$$

we'll see how to solve this next time.