Phy127b

Last term: thermodynamics (general);
statistical mechanics of noninteracting particles
(or where the problem could be reduced to non-interacting particles)

This term: interacting particles, phases, and phase transitions

Broad outline: *1) interacting classical gas and liquid-gas transition

*2) order parameter and symmetry breaking - so-called mean field picture of phases of interacting particles
Landau-Ginzburg theory

*3) Second-order phase transitions, Scaling and Renormalization group. Landau-Ginzburg-Wilson theory.

Outline of 1): * perturbative treatment of interactions -
- technique of cummulants

* cluster expansion for gases with strong core repulsion

* ~~[illegible]~~ Van-der-Waals equation and liquid-gas transition

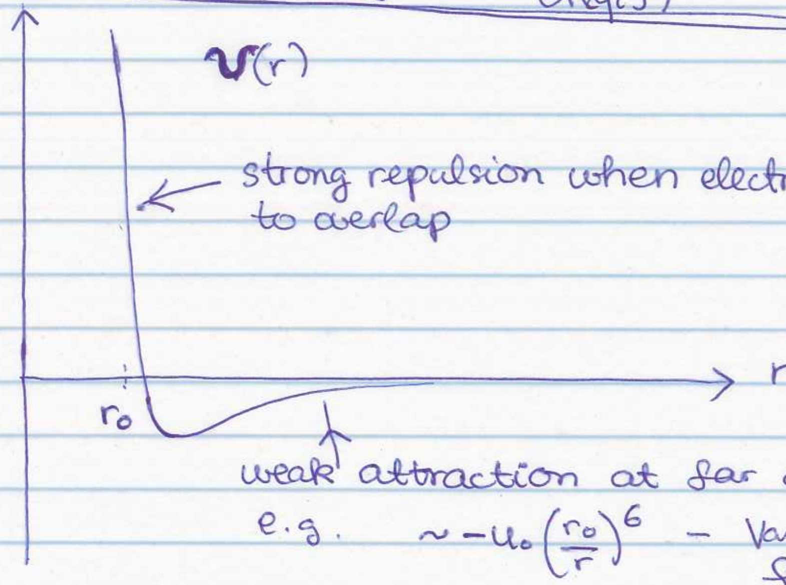
* Non-perturbative techniques: mean field theory and variational method.

Interacting classical gas — perturbative treatment in βU

(cummulant expansion)

$$\boxed{\mathcal{H}(\{\vec{q}_i\},\{\vec{p}_i\}) = \underbrace{\sum_i \frac{\vec{p}_i^{\,2}}{2m}}_{\text{kinetic energy}} + \underbrace{\sum_{i<j}{}' \, v(|\vec{q}_i-\vec{q}_j|)}_{\substack{\text{interactions} \\ U(\{\vec{q}_i\})}}}$$

e.g.



strong repulsion when electronic clouds begin to overlap

weak attraction at far distances, e.g. $\sim -u_0\left(\frac{r_0}{r}\right)^6$ — Van-der-Waals force

Classical canonical ensemble; partition fnctn for N particles

$$\boxed{Z_N} = \frac{1}{N!}\int \prod_i \frac{d^3q_i\, d^3p_i}{h^3}\, e^{-\beta\mathcal{H}(\{\vec{q}_i\},\{\vec{p}_i\})} =$$

$$= \int \prod_i d^3q_i\, e^{-\beta U(\{q_i\})}\ \frac{1}{N!}\prod_{i=1}^{N}\prod_{\mu=x,y,z}\int_{-\infty}^{+\infty}\frac{dp_{i\mu}}{h}\, e^{-\beta\frac{p_{i\mu}^2}{2m}}$$

$$\int_{-\infty}^{+\infty}\frac{dp_{i\mu}}{h}\, e^{-\beta\frac{p_{i\mu}^2}{2m}} = \frac{1}{h}\sqrt{\frac{\pi}{\beta/(2m)}} = \frac{\sqrt{2\pi m k_B T}}{h} \equiv \frac{1}{\lambda(T)}$$

$$\boxed{= \int \prod_i \frac{d^3q_i}{V}\, e^{-\beta U(\{q_i\})}\ \frac{V^N}{N!\,\lambda^{3N}}}$$

$$Z_0 \equiv \frac{V^N}{N!\,\lambda^{3N}}$$ – partition fnctn of non-interacting system

"Configuration integral":

$$\int \prod_i \frac{d^3 q_i}{V} e^{-\beta U(\{q_i\})} = \left\langle e^{-\beta U(\{q_i\})} \right\rangle_0$$

$\langle \ldots \rangle_0$ – is average wrt measure $\prod_i \frac{d^3 q_i}{V}$

(note $\int_V \prod_i \frac{d^3 q_i}{V} 1 = 1$).

Free energy

$$\boxed{F = -k_B T \ln Z = \underbrace{-k_B T \ln Z_0}_{F_0} - k_B T \ln \langle e^{-\beta U} \rangle_0}$$

Cummulant expansion:

$$\langle e^{-\beta U} \rangle_0 = \left\langle 1 - \beta U + \frac{\beta^2}{2} U^2 - \ldots + \frac{(-1)^n \beta^n}{n!} U^n \right\rangle_0 =$$

$$= 1 \underbrace{- \beta \langle U \rangle_0 + \frac{\beta^2}{2} \langle U^2 \rangle_0 - \frac{\beta^3}{3!} \langle U^3 \rangle_0 + \ldots}_{= x}$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \ldots$$

$$\ln \langle e^{-\beta U} \rangle_0 = \left(-\beta \langle U \rangle_0 + \frac{\beta^2}{2} \langle U^2 \rangle_0 - \frac{\beta^3}{3!} \langle U^3 \rangle_0 \right) -$$

to third order in βU

$$- \frac{1}{2} \left(-\beta \langle U \rangle_0 + \frac{\beta^2}{2} \langle U^2 \rangle_0 \right)^2 + \frac{1}{3} \left(-\beta \langle U \rangle_0 \right)^3 + O((\beta U)^4)$$

$$= -\beta \langle U \rangle_0 + \frac{\beta^2}{2} \left(\langle U^2 \rangle_0 - \langle U \rangle_0^2 \right) - \frac{\beta^3}{3!} \left(\langle U^3 \rangle_0 - 3 \langle U^2 \rangle_0 \langle U \rangle_0 + 2 \langle U \rangle_0^3 \right)$$

$$+ O(\beta^4)$$

$$\ln\langle e^{-\beta U}\rangle \equiv \sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} \underbrace{\langle U^l \rangle_{c,0}}_{l\text{-th cummulant}}$$

1st cummulant : $\langle U \rangle_{c,0} \equiv \langle U \rangle_0$

2nd cummulant : $\langle U^2 \rangle_{c,0} \equiv \langle U^2 \rangle_0 - \langle U \rangle_0^2$ | variance

3rd cummulant : $\langle U^3 \rangle_{c,0} \equiv \langle U^3 \rangle_0 - 3\langle U^2 \rangle_0 \langle U \rangle_0 + 2\langle U \rangle_0^3$

... $\langle U^l \rangle_{c,0} \equiv \langle U^l \rangle_0 - \dots$

$$U(\{q_i\}) = \sum_{i<j} v(\vec{q}_i - \vec{q}_j)$$

* $\boxed{\langle U \rangle_{c,0}} = \int \frac{d^3q_1}{V} \frac{d^3q_2}{V} v(q_1 - q_2) \cdot \frac{N\cdot(N-1)}{2} =$

$$\boxed{= \frac{N\cdot(N-1)}{2V} \int d^3\tilde{q}\, v(\tilde{q})}$$

* $\langle U^2 \rangle_{c,0} = \langle U^2 \rangle_0 - \langle U \rangle_0^2 = \sum_{i<j} \sum_{k<l} \Big[\langle v(q_i - q_j) v(q_k - q_l) \rangle - \langle v(q_i - q_j) \rangle \langle v(q_k - q_l) \rangle \Big]$

- If $\{i,j\} \cap \{k,l\} = \emptyset \Rightarrow [\dots] = 0$;
- If $\{i,j\}$ and $\{k,l\}$ have one site in common $\Rightarrow$ still $[\dots] = 0$ because of translational invariance

e.g. $l=j$: $\int \frac{d^3q_i}{V} \frac{d^3q_j}{V} \frac{d^3q_k}{V} v(\underbrace{q_i - q_j}_{\tilde{q}_i}) v(\underbrace{q_k - q_j}_{\tilde{q}_k}) = \int \frac{d^3\tilde{q}_i}{V} v(\tilde{q}_i) \int \frac{d^3\tilde{q}_k}{V} v(\tilde{q}_k)$

- If $\{i,j\} = \{k,l\} \Rightarrow [\dots] = \langle v^2(q_i - q_j) \rangle - \langle v(q_i - q_j) \rangle^2$

$$\boxed{\langle U^2 \rangle_{c,0}} = \sum_{i<j} \left(\langle v^2(q_i - q_j) \rangle - \langle v(q_i - q_j) \rangle^2 \right) =$$

$$= \frac{N\cdot(N-1)}{2}\left(\int \frac{d^3q_i}{V}\frac{d^3q_j}{V} v^2(q_i-q_j) - \left(\int \frac{d^3q_i}{V}\frac{d^3q_j}{V} v(q_i-q_j)\right)^2\right)$$

$$\boxed{= \frac{N\cdot(N-1)}{2}\left(\frac{1}{V}\int d^3\tilde{q}\, v^2(\tilde{q}) - \frac{1}{V^2}\left(\int d^3\tilde{q}\, v(\tilde{q})\right)^2\right)}$$

Remarks: ⊛ $F = F_0 - \frac{1}{\beta}\ln\langle e^{-\beta \mathcal{U}}\rangle = F_0 - \frac{1}{\beta}\Big(-\beta\langle \mathcal{U}\rangle_{c,0} +$

$+\frac{\beta^2}{2}\langle \mathcal{U}^2\rangle_{c,0} + \dots\Big) = F_0 + \langle \mathcal{U}\rangle_{c,0} - \frac{1}{2}\beta\langle \mathcal{U}^2\rangle_{c,0} + \dots$

F - extensive quantity $\left(\begin{array}{l} N \to \alpha N \\ V \to \alpha N \\ F \to \alpha F \end{array}\right)$

$\langle \mathcal{U}\rangle_{c,0} \approx \frac{N^2}{2V}\int d^3\tilde{q}\, v(\tilde{q})$ – extensive quantity

$\langle \mathcal{U}^2\rangle_{c,0} \approx \frac{N^2}{2V}\int d^3\tilde{q}\, v^2(\tilde{q})$ – extensive quantity!

The latter happened because of enormous cancellations between terms in $\langle \mathcal{U}^2\rangle_0$ and $\langle \mathcal{U}\rangle_0^2$

each scales quadratically in system volume, but $\langle \mathcal{U}^2\rangle_0 - \langle \mathcal{U}\rangle_0^2$ scales only linearly

(recall: $\langle E^2\rangle - \langle E\rangle^2 \sim Vol$, $\langle N^2\rangle - \langle N\rangle^2 \sim Vol$, etc.)

The cancellation had to happen because we are calculating extensive quantity! This is very general feature when doing perturbative calculations in many-particle systems and provides useful checks on the calculation. (with reasonably short-range interactions)

Details how this happens are system-specific and need case-by-case work. It is important to keep everything until the very final result, e.g.

$$\langle \mathcal{U} \rangle_0^2 = \left(\int d^3q\, v(q) \left(\frac{N^2}{2V} - \frac{N}{2V} \right) \right)^2$$

tempting to drop as "subleading"

but important to keep since the "leading" term will actually get cancelled in $\langle \mathcal{U}^2 \rangle_0 - \langle \mathcal{U} \rangle_0^2$.

In the present case, the extensivity at each order in β is ensured by the cummulants, e.g.

β^3: $$\langle \mathcal{U}^3 \rangle - 3 \langle \mathcal{U}^2 \rangle \langle \mathcal{U} \rangle + 2 \langle \mathcal{U} \rangle^3$$

Naively, each term is $O(\text{volume}^3)$, but such contributions cancel because of $+1, -3, +2$. More subtle but must happen is that $O(\text{volume}^2)$ terms will also cancel and only $O(\text{volume})$ terms will remain.

MAIN LESSON: Watch for extensivity in perturbative treatments; cummulants $\rightarrow$ extensivity

⊛ Very often such perturbative calculations are visualized in the form of some diagrams, with rules for calculating each diagram, calculating their degeneracies, (multiplicative factors) etc. These are system-specific and it is not particularly useful to memorize such rules, but rather derive them when needed, performing calculations e.g. as above. – Will not try to set this up here.

Diagrams can be useful for performing "resummations", etc – will not do here.

Often extensivity requirements (e.g. realized in cummulants) will lead to cancellations of diagrams containing disconnected pieces, and only connected diagrams remain — useful check to watch out for.

We set up the calculation as organized by $(\beta \mathcal{U}_0)^\ell$.

(*) Actually terms can be written as $(\beta \cdot \mathcal{U}_0)^\ell \times V \times \left(\# + \# \cdot \frac{N}{V} + \dots\right)$

$$\ln Z = \ln Z_0 + V \sum_{p,s} \beta^p \cdot \left(\frac{N}{V}\right)^s \underbrace{D_{p,s}}_{\text{with specific rules for calculating this}} \qquad V \cdot \left(\left(\frac{N}{V}\right)^2 + \# \left(\frac{N}{V}\right)^3 + \dots\right)$$

For gases with very strong core repulsion, working perturbatively in $\beta \mathcal{U}$ does not make much sense, but one can try to reorganize the above series as series in $\frac{N}{V}$. The first term in the series $O\left(V \cdot \frac{N^2}{V^2}\right)$ is obtained by collecting

$$\langle \mathcal{U}^\ell \rangle_c = \underbrace{\int \frac{d^3q_1}{V} \frac{d^3q_2}{V} \left(v(q_1 - q_2)\right)^\ell \cdot \frac{N \cdot (N-1)}{2}}_{\approx \frac{N^2}{2V} \int d^3q \, v(q)^\ell} + \dots$$

$$\sum_{\ell=1}^{\infty} \frac{(-\beta)^\ell}{\ell!} \frac{N^2}{2V} \int d^3q \, v(q)^\ell = \frac{N^2}{2V} \int d^3q \left(e^{-\beta v(q)} - 1\right)$$

$$\boxed{F = F_0 - \frac{N^2}{2V} \cdot \frac{1}{\beta} \int d^3q \left(e^{-\beta v(q)} - 1\right) + \dots \quad O\left(\frac{N^3}{V^2}\right)} = F_0 + \frac{N^2}{V\beta} B_2(T) + \dots$$

$p = p_0 + \frac{N^2}{V^2 \beta} B_2 + \dots = \frac{N k_B T}{V}\left(1 + \frac{N}{V} B_2 + \dots\right)$

— will motivate such series directly in cluster expansion

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = p_0(N, V) - \frac{N^2}{2V^2} \frac{1}{\beta} \left[\int d^3q \left(e^{-\beta v} - 1\right)\right] = \frac{N k_B T}{V} \left[1 - \frac{N}{V} \cdot \frac{1}{2} \int d^3q \left(e^{-\beta v} - 1\right)\right]$$