Lecture 11 - Interacting gasses & liquids, pt 1

Canonical Ensemble, const N, V, T

$$\rho(\vec{q},\vec{p}) = e^{-\beta \mathcal{H}(q,p)} \Big/ \int d\vec{q} \int d\vec{p}\, e^{-\beta \mathcal{H}(\vec{p},\vec{q})}$$

$$\mathcal{H}(\vec{q},\vec{p}) = \underbrace{\sum p_i^2/2m_i}_{\text{ideal gas just this}} + U(\vec{q}_1, \vec{q}_2, \dots \vec{q}_N)$$

U can be positive or negative

Low energy "good", system can condense if U sufficiently negative

Remember

A minimized @ equilibrium and

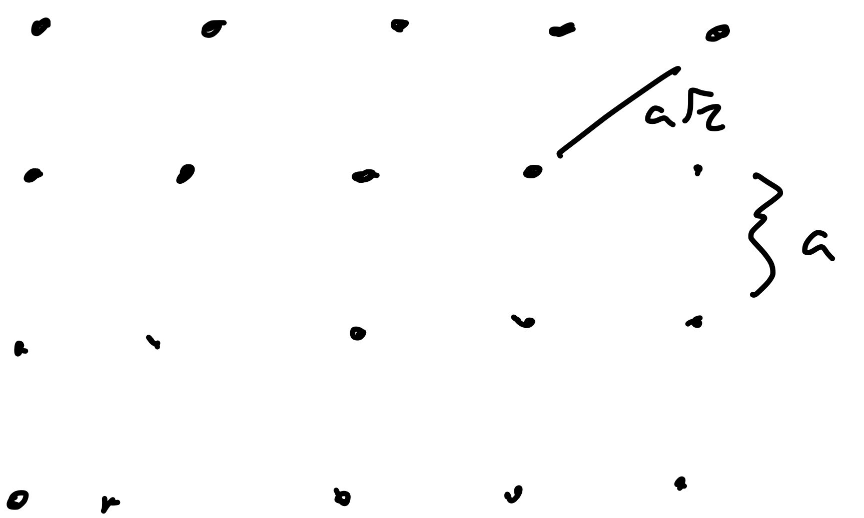
$A = \mathcal{E} - TS$, $T > 0$

At low T, high ρ (or density), tend to get solids or liquids

Will discuss phase transitions later

Now: "structure" of liquids & gasses

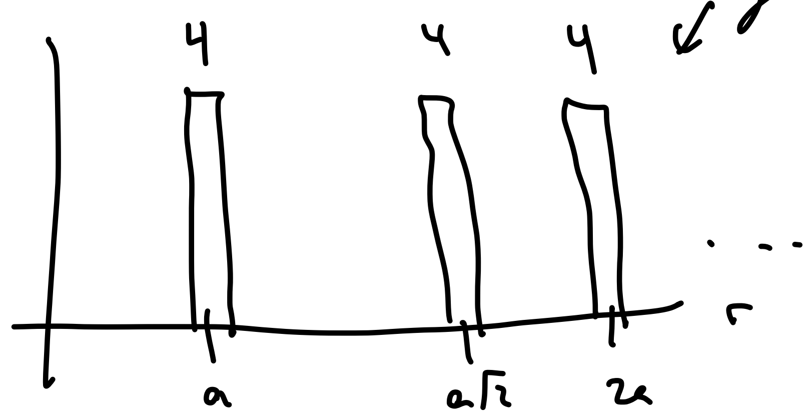
First consider a crystal for contrast



How characterize?

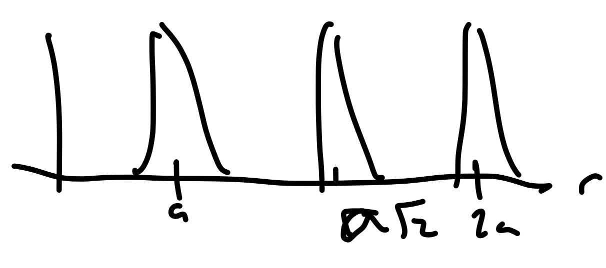
get closer together

$N(r)$



@ $T=0$

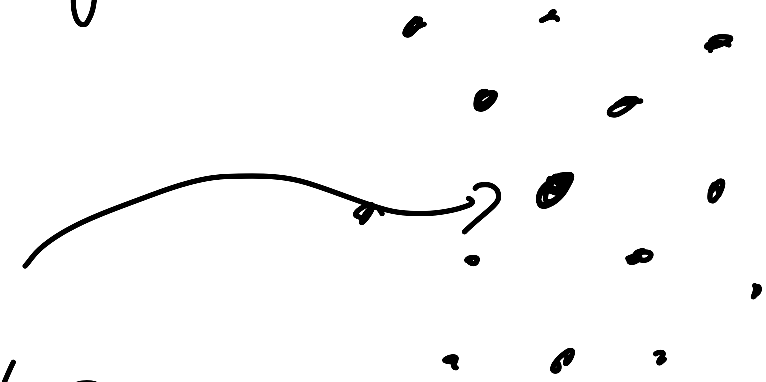
@ $T>0$ $\rho(r)$



$$\int_{a-2\sigma}^{a+2\sigma} dr\ \rho(r) \approx 4$$

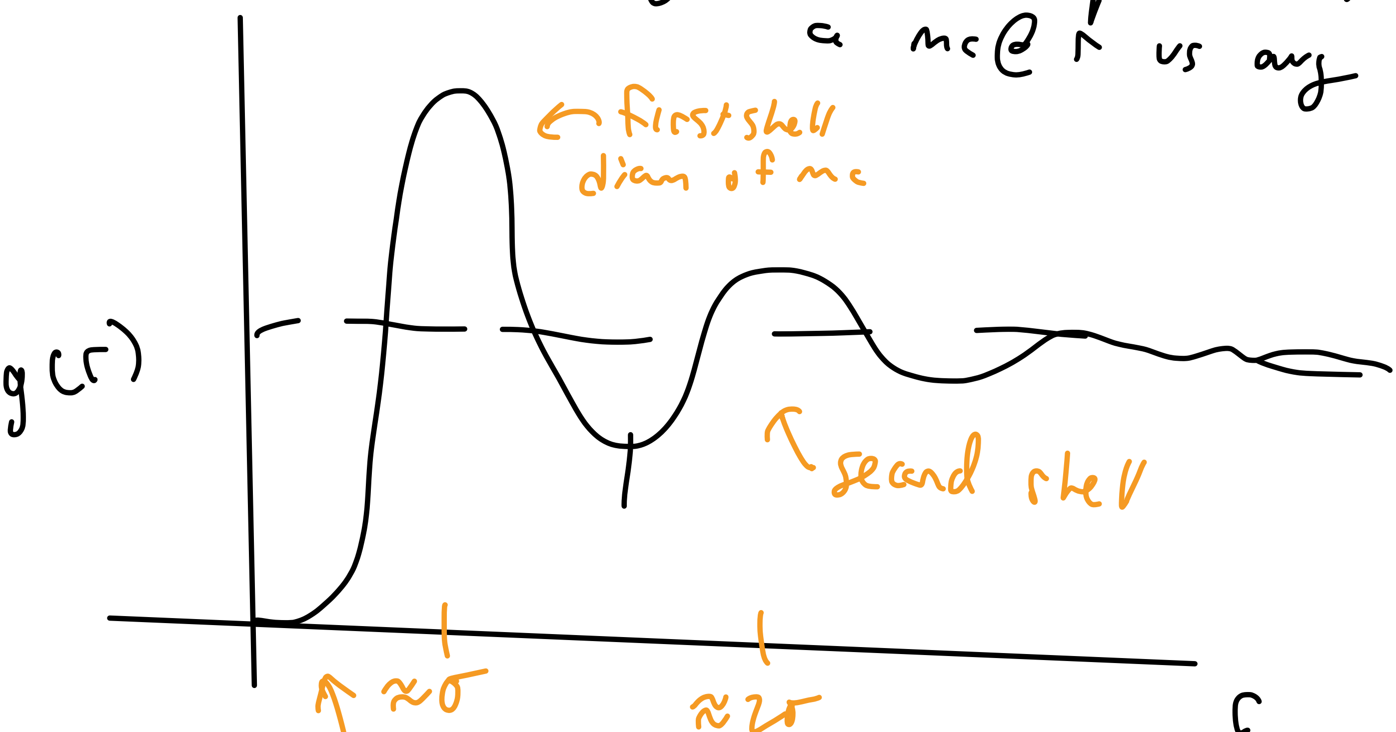
In a liquid

Key properties
isotropic,
trans invariant



look @ avg environment of one molecule. other molecules always moving

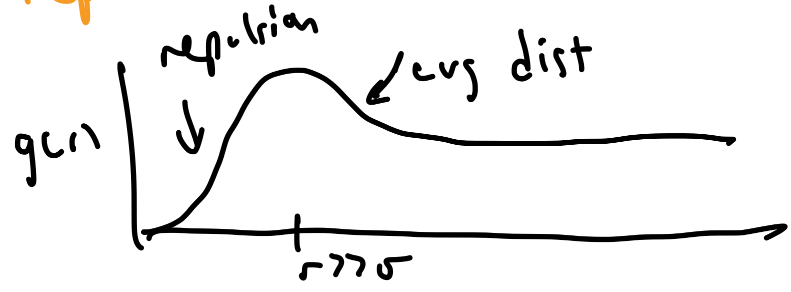
will define $g(r)$, relative prob of finding a mc @ r vs avg



features

repulsion

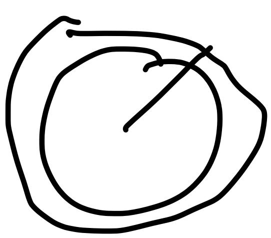
In a gas



$g(r)$ says relative prob of finding at same distance. Can also depend on angles, but often averaged to just distance. Also can be multiple types

In practice, what is this quantity
Stand on particle & histogram # @ dist r

Actually, btwn r and $r+\Delta r$



ideal gas, # in sphere

$$\frac{4}{3}\pi r^3 \rho$$

$$\# \text{ in shell} = \frac{4}{3}\pi (r+\Delta r)^3 \rho - \frac{4}{3}\pi r^3 \rho$$

$$\frac{4}{3}\pi\left(r^3 + 3\Delta r\, r^2 + 3\Delta r^2 r + \Delta r^3\right) \rho - \frac{4}{3}\pi r^3 \rho$$

$$= 4\pi r^2 \Delta r + O(\Delta r^2) \approx 4\pi r^2 \Delta r$$

so $g(r) = \dfrac{h(r)}{4\pi r^2 \Delta r}$ for numerics
$\to 1$ for large r

How do we get from the partition func:

Call $Z_{conf}(N, V, T) = \int d\vec{q}\, e^{-\beta U(\vec{q})}$

just config part, avg over momentum

Prob finding a particular cfg

$$p(\vec{q})\, d\vec{q} = \frac{1}{Z} e^{-\beta U(\vec{q})}\, d\vec{q}_1\, d\vec{q}_2 \ldots d\vec{q}_N$$

if we just want q_1, q_2, q_3 "integrate out" others

define $\rho^{(n)}(q_1 \ldots, q_n) = \int d\vec{q}_{n+1}\, d\vec{q}_{n+2} \ldots d\vec{q}_N\, e^{-\beta U(\vec{q})} / Z$

all N

for $n \subseteq N$.

A nice way to write:

$$P(q_1' \ldots q_n') = \frac{1}{Z} \int d\vec{q}^{\,N}\, \delta(q_1 - q_1')\, \delta(q_2 - q_2') \ldots e^{-\beta U(\vec{q})}$$

$$= \left\langle \prod_{i=1}^{n} \delta(q_i - q_i') \right\rangle_{q_1', q_2' \ldots q_n'}$$

Thermal avg of # ways this can appear

But don't care which mc is at

those pos so define

$$\rho^{(n)}(q_1 \ldots q_n) = \frac{N!}{(N-n)!} P(q_1 \ldots q_n)$$

and $g^{(n)}(q_1 \ldots q_n) = \rho^{(n)} / \rho^n$, $\rho = N/V$

for convenient normalization (next)

will care about simple cases

$\int d\vec{q}\, P^{(1)}(\vec{q}) = 1$ b/c probability

But isotropic so $P^{(1)}(\vec{q}) = \text{const} \Rightarrow P^{(1)} = \frac{1}{V}$

$\rho^{(1)} = N P^{(1)} = N/V$ (hence calling ρ)

@ $g^{(1)} = 1$!

Now $g^{(2)}$, what we usually care about

$$g^{(2)}(\vec{q}_1', \vec{q}_2') = \frac{N(N-1)}{\rho^2} \langle \delta(q_1 - q_1') \delta(q_2 - q_2') \rangle_{q_1', q_2'}$$

Looks like depends on 2 positions, but can't depend where we look so

$$R = \frac{1}{2}(q_1' + q_2') \qquad r = \vec{q}_2' - \vec{q}_1'$$

center coordinates

$$q_1 = \vec{R} - \frac{1}{2}\vec{r} \qquad q_2 = \vec{R} + \frac{1}{2}\vec{r}$$

$$d\vec{q}_1 \, d\vec{q}_2 = d\vec{r}\, d\vec{R} \begin{vmatrix} \frac{\partial q_1}{\partial R} & \frac{\partial q_1}{\partial r} \\ \frac{\partial q_2}{\partial R} & \frac{\partial q_2}{\partial r} \end{vmatrix} = d\vec{r}\, d\vec{R} \begin{vmatrix} 1 & -\frac{1}{2} \\ 1 & \frac{1}{2} \end{vmatrix}$$

$$= d\vec{r}\, d\vec{R}$$

so $\int dq_1 \, dq_2 \, g^{(2)}(q_1, q_2) = \int dR \, dr \, g^{(2)}(\vec{R}, \vec{r})$

$$g^{(2)}(r, R) = \frac{N(N-1)}{\rho^2 Z} \int dq_3 \dots dq_N \, e^{-\beta U(R - \frac{1}{2}r, R + \frac{1}{2}R, \dots)}$$

can't dep on $\vec{R}$

define $g(\vec{r}) = \frac{1}{V}\int d\vec{R} \, g^{(2)}(\vec{r}, \vec{R})$

so $g(\vec{r}) = \frac{N-1}{\rho} \langle \delta(\vec{r}' - \vec{r}) \rangle_{r'}$

How likely are you to find a particle @ displacement $\vec{r}$ from a mc, centered on a molecule @ origin

If prob doesn't depend on angle then spherical coordinates, integrate angles to $4\pi r^2 dr$ as jacobian

so $\int d\theta \int d\phi \, g(\vec{r}) d\vec{r} = 4\pi r^2 dr \, g(r)$

$$\Rightarrow \boxed{g(r) dr = \frac{(N-1)}{4\pi \rho r^2} \langle \delta(r - r') \rangle}$$

$\int dq^{N-2} \int dr \, e^{-\beta U(r, q_3 \ldots q_N)}$

In total, $\rho \int_0^\infty dr \, 4\pi r^2 g(r) dr = N-1 \approx N$

there are the $N-1$ other particles

$N_{coord} = 4\pi \rho \int_0^{r_{min}} r^2 g(r) dr$, first solvation coordination #

In reality, every U depends on all atom positions, In approximation, can say it is pairwise ie

$$U(q_1, q_2 \dots q_n) = \sum_{i>j} u(r_{ij})$$

$$\binom{N}{2} = \frac{N(N-1)}{2}$$ combinations of distances

So $g(r)$ will be closely connected to what $u(r)$ is