Lecture 7: Real Liquids & Gasses

Interacting systems of molecules

Before we dealt with ideal gasses, systems in N, V, T ensemble, but

$$\mathcal{H}(\vec{p},\vec{q}) = \sum_{i=1}^{N} |\vec{p}_i|^2/2m$$

Now we will think about systems that interact, namely

$$\mathcal{H}(\vec{p},\vec{q}) = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m + U(\vec{q}_1,\vec{q}_2,\ldots,\vec{q}_N)$$

These interactions could be positive or negative - if negative (attractive) system will condense

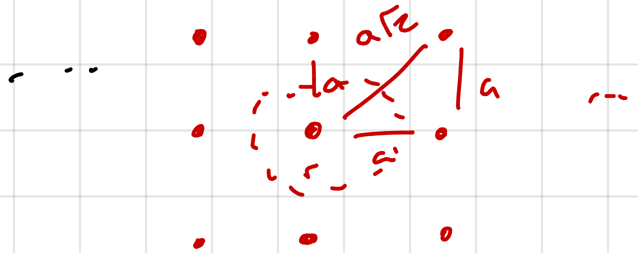
For molecules, typically attractive at long range & repulsive at short range

This means at low enough temps, high press, form a liquid, then solid (phase trans later)

Today we will talk about the structure of liquids and gasses when interactions are turned on (non-ideal)

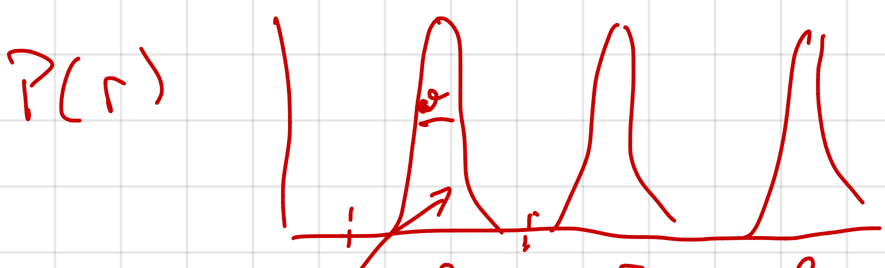
"Structure" means what is the average arrangement of the atoms/molecules

In a solid, we may have (2d) square lattice



how do we characterize this?

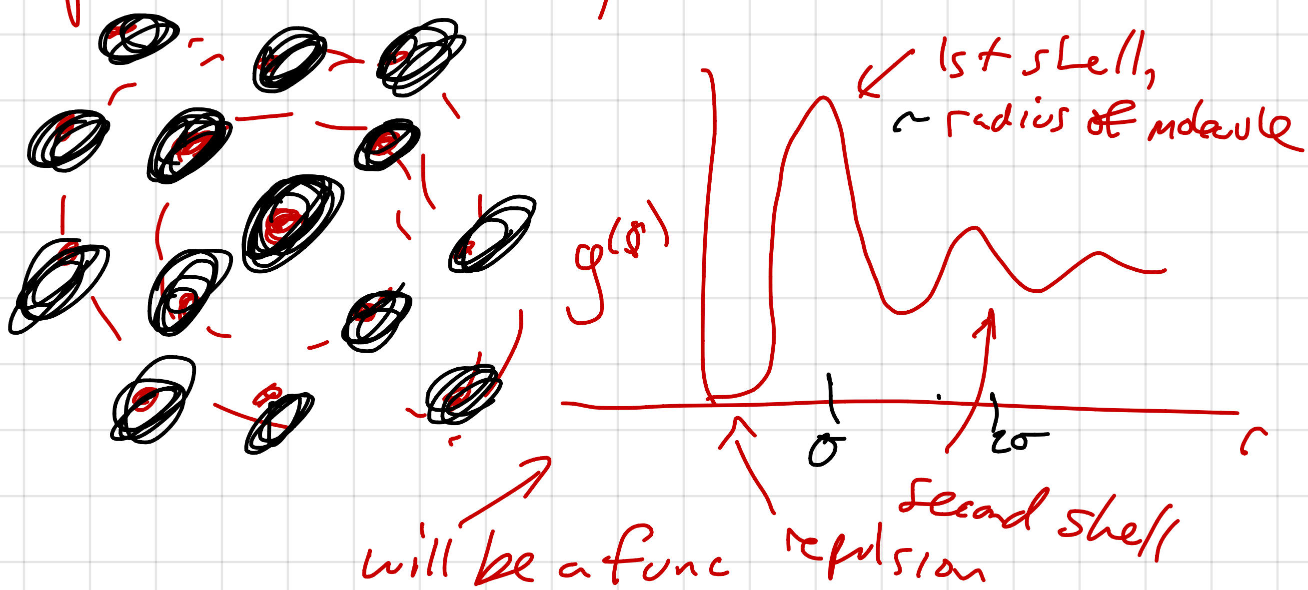
@ T=0



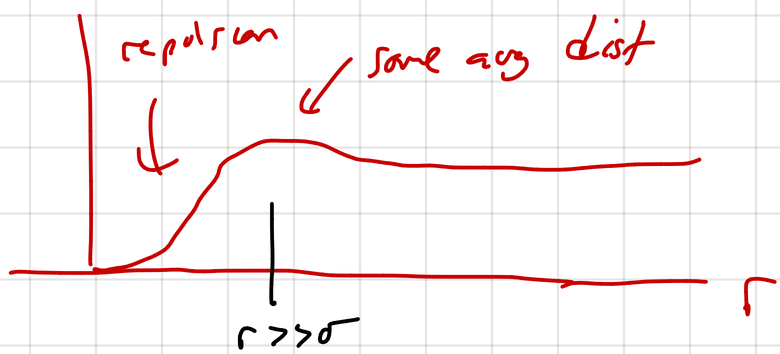
@ T > 0

$$\int_{a-3\sigma}^{a+3\sigma} dr\, P(r) \approx 4$$

In a liquid, as we may be able to predict later, more like



In gas, maybe $g(r)$



These could also depend on angle, but often radially symmetric

Let's see how we can define this function

$$Q(N,V,T) = \frac{1}{N!\, h^{3N}} \int d^N\vec{p} \int d^N\vec{q}\; e^{-\beta\left(\sum \frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q})\right)}$$

$$= \frac{1}{N!} \cdot \frac{1}{\lambda^{3N}} \int_V d^N\vec{q}\; e^{-\beta U(\vec{q})}$$

integrate over box

[aside, Q has $\int_{-\infty}^{\infty} dq_1^x \int_{-\infty}^{\infty} dq_1^y \cdots \int_{-\infty}^{\infty} dq_N^y \int_{-\infty}^{\infty} dq_N^z$

but can define $U(\vec{q}_1, \vec{q}_2, \ldots \vec{q}_N) =$

$$\begin{cases} \infty & \text{if } q_i^\alpha > L/2 \text{ or } q_i^\alpha < -L/2 \\ \tilde{U}(\vec{q}_1, \vec{q}_2, \ldots \vec{q}_N) & \text{otherwise} \end{cases}$$

then $\displaystyle\int_{-\infty}^{\infty} d\vec{q}^{\,N}\, e^{-\beta U(\vec{q})} = \int_{-L/2}^{L/2} dq^{3N}\, e^{-\beta \tilde{U}(q)}$]

Call $\displaystyle Z(N,V,T) = \int_V d\vec{q}^{\,N}\, e^{-\beta U(\vec{q})} = Q \cdot N!\, \lambda^{3N}$

configurational partition function

The prob of finding a particular particle within $d\vec{q}$ of $\vec{q} = (\vec{q}_1, \vec{q}_2, \dots \vec{q}_N)$ is

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

What if we just want to know the prob of finding, eg, 3 particles at positions q_1, q_2, q_3? "Integrate out" other degrees of freedom, like before.

In general, $n < N$

$$P^{(n)}(q_1, q_2, \dots, q_n) = \int d\vec{q}_{n+1} d\vec{q}_{n+2} \dots d\vec{q}_N \, e^{-\beta U(\vec{q})} / Z$$

all N

But we don't care about which n if indistinguishable. Could pick any particle as "1", $N-1$ as "2", $N-2$ as "3"

Hence the prob of finding any particle at $\vec{q}_1$, any at $\vec{q}_2$, ... q_n =

$$\rho^{(n)}(\vec{q}_1, \dots, \vec{q}_n) = \frac{N!}{(N-n)!} \cdot \frac{1}{Z}\int_V d\vec{q}_{n+1} \cdots d\vec{q}_N \, e^{-\beta U(\vec{q})}$$

A nice way of writing the integral

$$\frac{1}{Z}\int dq_{n+1} \dots dq_N e^{-\beta U(q)} = \frac{1}{Z}\int dq^N e^{-\beta U(q)} \delta(q_1 - q_1') \times \delta(q_2 - q_2') \dots \times \delta(q_n - q_n')$$

$$= \frac{1}{Z}\int dq^N e^{-\beta U(q)} \prod_{i=1}^{n} \delta(q_i - q_i')$$

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

thermal average counting # ways this configuration appears

Lets define 1 last quantity,

$$g^{(n)}(q_1, q_2 \dots q_n) = \rho^{(n)}(q_1, \dots, q_n) / \rho^n \quad \text{where } \rho = N/V$$

we'll see why in a second. we will be ingerested in $g^{(1)}, g^{(2)}$, the simplest cases. What is $g^{(1)}$?

$$\int dq\, P^{1}(\vec{q}) = 1 \quad , \text{ prob dist}$$

$$\int dq\, \rho^{(1)}(q) = \int dq\, N P^{(1)}(q) = N$$

← mistake in book

Now, for an "isotropic" system, prob of finding a particle at a particular point has to be a const, cannot depend on position

$$\Rightarrow P^{(1)}(q) = 1/V \,, \quad \rho^{(1)}(q) = N/V = \rho$$

(hence the notation) and $g^{(1)}(\vec{q}) = 1$

Now lets consider $g^{2}(q_1', q_2')$

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

This makes $g^{(2)}$ look like it depends on 2 positions. However, we will see for an isotropic system, only depends on $\vec{r} = \vec{q}_1 - \vec{q}_2$, and often only $|r|$

→ define $R = \frac{1}{2}(q_1 + q_2)$ $\quad r = q_2 - q_1$

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

need $dq_1 dq_2 = \begin{vmatrix} \frac{\partial q_1}{\partial R} & \frac{dq_1}{\partial r} \\ \frac{dq_2}{\partial R} & \frac{dq_2}{\partial r} \end{vmatrix} dR\,dr = \begin{vmatrix} 1 & -\frac{1}{2} \\ 1 & +\frac{1}{2} \end{vmatrix} dR\,dr = dR\,dr$

This means $\int dq_1 dq_2 P^{(2)}(q_1, q_2) = \int d\vec{R}\,d\vec{r}\, P^{(2)}(R, r)$

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

define $g(r) = \frac{1}{V} \int dR\, g^{(2)}(r, R)$ since distrib does not depend on location, then

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

$g(\vec{r})$ says how likely are you to find a position $\vec{r}$ from a tagged particle at the origin

Generally we can also only consider $|r|$, distance away, so we can integrate out angles too

go to spherical where

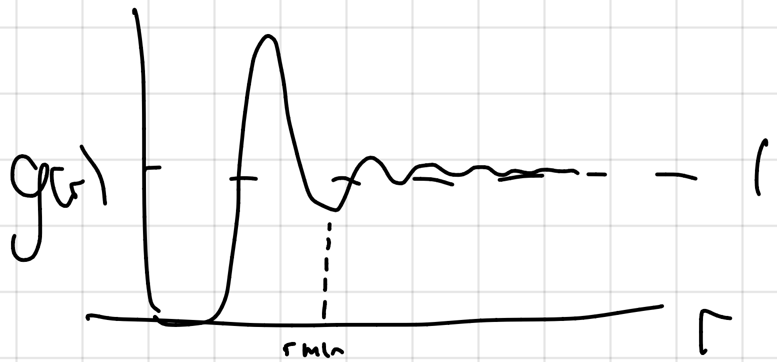
where $x^2+y^2+z^2 = r^2$,
$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

Jacobian is $r^2 \sin\theta \, dr \, d\theta \, d\phi$ & integrating θ & ϕ gives $4\pi r^2 dr$

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

In practice, histogram how often you see a particle between r and $r+\Delta r$ then compare to how many you expect if uniform $\rho\left(\frac{4}{3}\pi(r+\Delta r)^3 - \frac{4}{3}\pi r^3\right) \approx 4\pi\rho r^2 \Delta r$

This $g(r)$ is what was plotted before



goes to 1 as $r \to \infty$ b/c prob seeing a particle between r & $r+\Delta r$ away from another is no more or less than $\frac{1}{4\pi\rho r^2 \Delta r}$

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

$$= (N-1) \approx N$$

$N_1 = 4\pi\rho \int_0^{r_{min}} r^2 g(r)\, dr$, particles in 1st solvation shell, "coordination number"