Van der Waal's Eqn & Intro to Simulation

Last time, perturbation theory, ie $U(r) = u_0(r) + u_1(r)$
u_1 is small compared to u_0

Have to compute averages like

$\langle e^{-\beta u_1} \rangle_0$ where $\langle a \rangle_0 = \int dr \, a(r) \frac{e^{-\beta u_0(r)}}{Z_0}$

$$A = -k_BT \log Q = \underbrace{-k_BT \log\left[\frac{Z^0}{N! \lambda^{3N}}\right]}_{A_0} \underbrace{- k_BT \log \langle e^{-\beta u_1} \rangle_0}_{A_1}$$

$$A_1 \approx \beta \langle u_1 \rangle_0 - \beta/2 \, \mathrm{Var}_0(u_1)$$

But what is $\langle u_1 \rangle_0$ for small u_1?

Remember $\langle u_0 \rangle_0 = 2\pi N\rho \int_0^\infty dr \, r^2 \, u_0(r) \, g_0(r)$

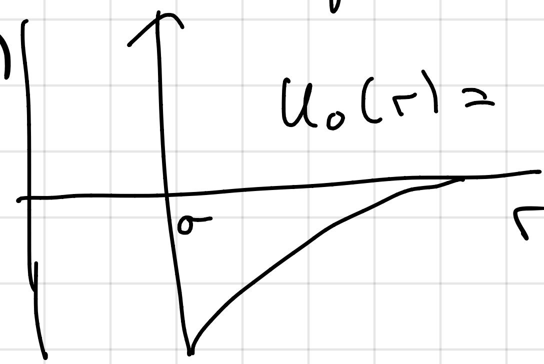
where $g_0(r)$ is $g(r)$ when $u_1 = 0$

same analysis gives $\langle u_1 \rangle_0 = 2\pi N\rho \int_0^\infty dr \, r^2 \, u_1(r) \, \underline{g_0}(r)$

Now know A_1 to low order

Point of perturbation theory is to start with a reference system we can "solve"

Simple potential is hard sphere + attraction $u(r) = u_0 + u_1$

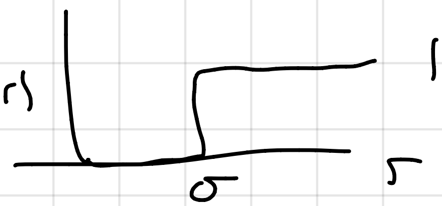


$$u_0(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}$$

in low density limit, for unperturbed $g_0(r) \approx e^{-\beta u_0(r)} = \begin{cases} 0 & r < \sigma \\ 1 & r \geq \sigma \end{cases}$

$$\equiv \Theta(r - \sigma)$$

$g_0(r)$



$$A^{(1)} \approx 2\pi N \rho \int_0^\infty r^2 u_1(r) g_0(r)\, dr = 2\pi N \rho \int_\sigma^\infty r^2 \overbrace{u_1(r)}^{<0}\, dr$$

$$= -aN\rho = -aN^2/V$$

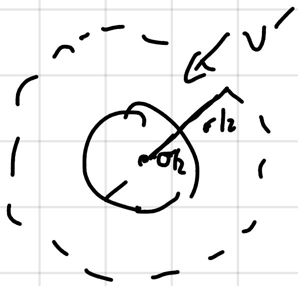
$$a \equiv -2\pi \int_\sigma^\infty r^2 u_1(r)\, dr > 0$$

To get A^0, need $Z^{(0)}$. for ideal gas $Z = V^N$

for low density gas, with repulsion $Z_0 = V_{avail}^{\ N}$

$V_{available} = V - V_{excluded}$

What is $V_{excluded}$ for a hard sphere particle



no particle can be closer than $R = \sigma$, so $V' = 4/3 \pi \sigma^3$

Not obvious, But this double counts exclusion b/c particle i excludes j & vice versa, so

$$V_{excluded} = N \cdot \frac{1}{2} \cdot 4/3 \pi \sigma^3 = N\underbrace{b}_{\frac{2}{3}\pi\sigma^3}$$

$$\Rightarrow Z_0 = (V - Nb)^N$$

$$A \approx -k_B T \log\left[\frac{(V-Nb)^N}{N! \, \Lambda^{3N}}\right] - aN^2/V$$

$$P = -\left(\partial A / \partial V\right) = +k_B T N \cdot \frac{1}{V - Nb} - aN^2/V^2$$

$$= \frac{Nk_BT}{V-Nb} - aN^2/V^2$$

or $\beta P = \dfrac{\rho}{1-\rho b} - a\rho^2\beta$ ⟵ Van der Waal's eqn of state

$$\frac{1}{1-x} = -\frac{d}{dx}\log(1-x) = 1 + x + x^2 + \cdots$$

$$\beta P \approx \rho(1 + \rho b + \rho^2 b^2 + \cdots) - a\rho^2\beta$$

$$\approx \rho + \rho^2 \underbrace{(b - a\beta)}_{B_2} + \rho^3 \underbrace{b^2}_{B_3} + \cdots$$ within VDW approx

Note, Van der Waals eqn of state has a change in behavior corresponding to a critical point. Can predict some "critical behavior" (see pg 175-177) but we will discuss more w/ phase transitions

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These were actually some of the first things people tried to compute with simulations, either to solve problems impossible by hand or to give as inputs to theories [eg equations depending on $g(r)$]

E.g. do system of disks crystallize? first shown on a computer by Alder & Wainright 1957. Crystal actually has more entropy!

How do we do these simulations?

we want to compute quantities like

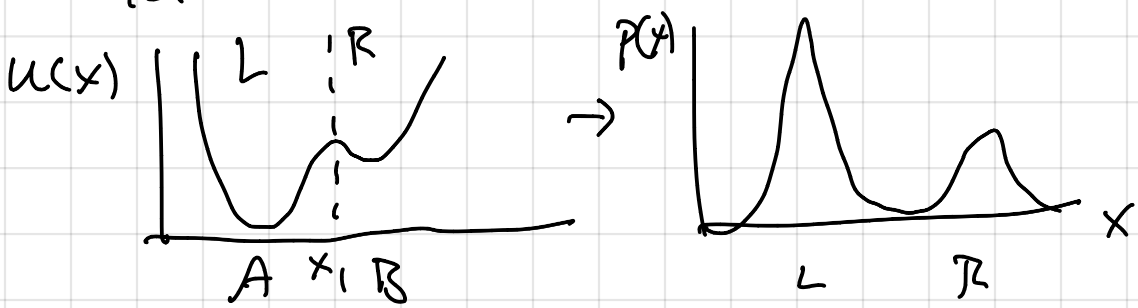
$$\langle A \rangle = \int d\vec{x}\, A(\vec{x})\, P(\vec{x}) \quad \text{where}$$

$P(\vec{x})$ might be something like $e^{-\beta \mathcal{H}(\vec{x})} \Big/ \int d\vec{x}\, e^{-\beta \mathcal{H}(\vec{x})}$

If we know the prob. func., then we can do this integral by "quadrature" (discritization)

$$\langle A \rangle \approx \sum_{i=1}^{N} A(\vec{x}_i)\, P(\vec{x}_i)\, \Delta x$$

Eg



Prob of being on left is $A(x) = \begin{cases} 1 & x < x_1 \\ 0 & x > x_1 \end{cases}$

χ_A, indicator function

however, this does not work in higher dimensions b/c num points is $\left(L/\Delta x \right)^d \sim e^{d \log (L/\Delta x)}$

Idea of both MC & MD: rather than generate x_i on a grid w/ prob 1, generate $x_i \propto P(x)$ somehow

Then $\langle A \rangle \approx \frac{1}{N} \sum_{i=1}^{N} A(x_i)$

One way to do this is to generate a "Markov Chain", rule $x_i \to x_{i+1}$ that only depends on x_i (not $x_1 \ldots x_{i-1}$)

If we also satisfy detailed balance

$$P(x_i)\, P(x_i \to x_{i+1}) = P(x_{i+1})\, P(x_{i+1} \to x_i)$$

$P(x_i \to x_{i+1})$ has 2 parts

$$= P_{gen}(x_i \to x_{i+1})\, P_{acc}(x_i \to x_{i+1})$$

$$P_{acc}(x_i \to x_{i+1}) = \underbrace{\frac{P(x_{i+1})}{P(x_i)} \frac{P_{gen}(x_{i+1} \to x_i)}{P_{gen}(x_i \to x_{i+1})}}_{r(x_i \to x_{i+1})} P_{acc}(x_{i+1} \to x_i)$$

How can we do this? One way, Metropolis rule $P_{acc}(x_i \to x_{i+1}) = \min(1, r(x_i \to x_{i+1}))$

Algorithm

Start @ x_i

→ propose x_{i+1} with prob $P_{gen}(x_i \to x_{i+1})$

gen $r \in (0,1)$

if $r < P_{acc}(x \to x_{i+1})$, move to x_{i+1}

if not, keep x_i (for statistics) as x_{i+1}

Tune P_{acc} to get acept prob. Often move is uniform $x_{i+1} = x_i + \xi \cdot \underset{(0,1)}{r_2}$

For canonical, if uniform gen

$$r(x_i \to x_{i+1}) = P(x_{i+1})/P(x_i) = e^{-\beta(E(x_{i+1}) - E(x_i))}$$

Another more advanced example:

Turns out, const pressure

$$\Delta(N,P,T) = \frac{1}{V_0}\int_0^\infty dV\, e^{-\beta PV} Q(N,V,T)$$

(like how $Q = \frac{1}{\varepsilon_0}\int_0^\infty dE\, e^{-\beta E}\,\Omega(N,V,E)$)

what if we want to do MC & keep const pressure, have to adjust the volume

$$\Delta(N,P,T) \propto \int_0^\infty dV e^{-\beta PV} \int dq^{3N} e^{-\beta u(\vec{q})}$$

$$= \int_0^\infty dV e^{-\beta PV} \cdot V^N \int ds^{3N} e^{-\beta u(\vec{s} V^{1/3})}$$

note: $V^N = e^{N \log V}$

$$= \int_0^\infty dV \int_0^1 ds^{3N} \cdot e^{-\beta(PV + u(sV^{1/3}) - N/\beta \log V)}$$

so now $P(\text{"}x\text{"}) = \exp[-\beta(PV + u - N/\beta \log V)] / \Delta(N,P,T)$

So can make Volume moves,

$V_{i+1} = V_i + \xi$, $\xi \in (-\delta, \delta]$

$$A(V_i \to V_{i+1}) = \min[1, \exp[-\beta P(V_{i+1} - V_i) + N \log(V_{i+1}/V_i) - \beta(\varepsilon_{i+1} - \varepsilon_i)]]$$

$$\varepsilon_{i+1} = u(\vec{s}\, V_{i+1}^{1/3}), \quad \varepsilon_i = u(\vec{s}, V_i^{1/3})$$

This is probably an expensive calculation unless $u(\lambda \vec{q}) = \lambda^n u(\vec{q})$

Conclusion: Monte Carlo is a very powerful (Easy) and general method for sampling from a distribution, not just in chemistry. Useful in statistics, data science, machine learning ...

Downsides: (1) only one thing happens at a time sometimes many moves rejected (inefficient)

(2) Generally good for <u>static</u> properties, not likely any connection to real time, so not good if you want info about kinetics