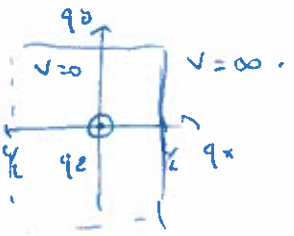
Van der Waal gas:
A gas with interactions!

Setting

- Hamiltonian: $H_N = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} \psi_{ij} + \sum_{i=1}^{N} V[\vec{q}_i]$

$\vec{q}_i, \vec{p}_i \in \mathbb{R}^d \quad (d=3)$

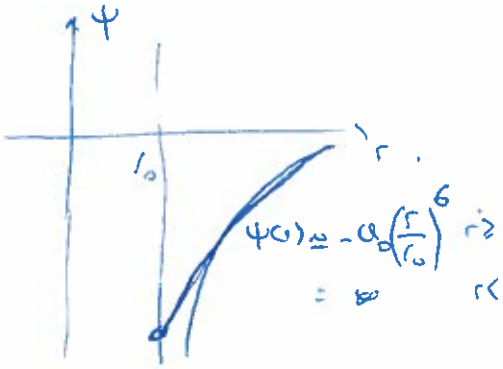
V: wall potential: $V(q_i) = \infty$ if $|q_{i1}| > \frac{L}{2}$, $= 0$ otherwise



ψ_{ij} = Binary interaction

$\psi_{ij} = \psi(r_{ij})$, with $r_{ij} = |q_i - q_j|$

$\psi(r)$:



- Gibbs state:

$$\rho(\vec{q}, \vec{p}) = \frac{1}{N! h^{3N}} \frac{e^{-\beta H(q,p)}}{Z_N}$$

with $Z_N = \frac{1}{N! h^{3N}} \int \pi d\vec{p}\, d\vec{q}\, e^{-\beta H}$.

The objective is to compute free energy, equation of state and discuss mixing experiment for this vdW gas.

Questions:

(1) Introduce $f_{12} = e^{-\beta \psi_{12}} - 1$ and $I = \int f_{12}(\vec{q})\, d\vec{q}$.

Show that the free energy is $F \simeq -k_B T N \left[\log \frac{V}{N\lambda^3} + I \frac{N}{2V} + 1 \right]$

with

$$\lambda = \sqrt{\frac{h^2}{2m \pi k_B T}}$$

$$I = \frac{2a}{k_B T} - 2b \quad \text{, for suitable } a \text{ and } b.$$

Hint: Argue that f_{ij} is a small parameter and expand Z_N to first order in f_{ij}

(2) Deduce the VdW equation of state:

$$p = \frac{k_B T}{v - b} - \frac{a}{v^2} \qquad \text{with} \quad v = \frac{V}{N} \qquad (*)$$

Discuss the meaning of a and b.

(3) Consider again the mixing experiment:

this time with VdW gas instead of a perfect gas

Discuss the irreversibility of this experiment from the point of view of Kelvin, Hamilton and Boltzmann.

In the latter case, please feel free to use/write/adapt the python script `Mixing-Experiment-2.py` (github link on Alexei's webpage) to include collisions between particle.

(4) Bonus: Show that the E.o.S (*) provide a toy model of a first order phase transition.

Hint: Study the isothermal characteristics of (*) in a p-v plane.