Chapter 6: Interacting Classical Systems

Hamiltonian $\hat{H} = \sum_{n=1}^{N} \frac{\vec{p}_n^{\,2}}{2m} + \sum_{n<n'}^{N} u(|\vec{x}_n - \vec{x}_{n'}|)$

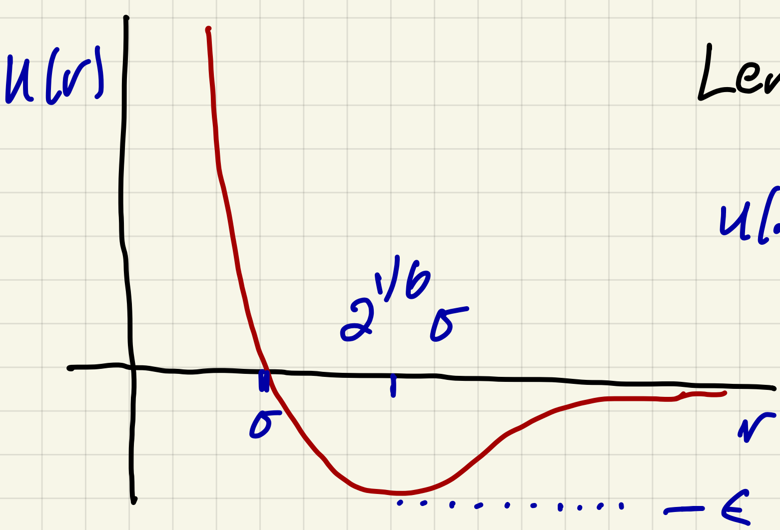
OCE : $Z(T,V,N) = \frac{1}{N!} \int \frac{d^d x_1 \, d^d p_1}{h^d} \cdots \int \frac{d^d x_N \, d^d p_N}{h^d} \, e^{-\beta \hat{H}}$

$$Z(T,V,N) = \lambda_T^{-dN} \, Q_N(T,V)$$

configuration integral

$$Q_N(T,V) = \frac{1}{N!} \int d^d x_1 \cdots \int d^d x_N \, e^{-\beta \sum_{n<n'} u(|\vec{x}_n - \vec{x}_{n'}|)}$$

For configurations $\{\vec{x}_n\}$ where one or more particles overlap, the integrand is very small:



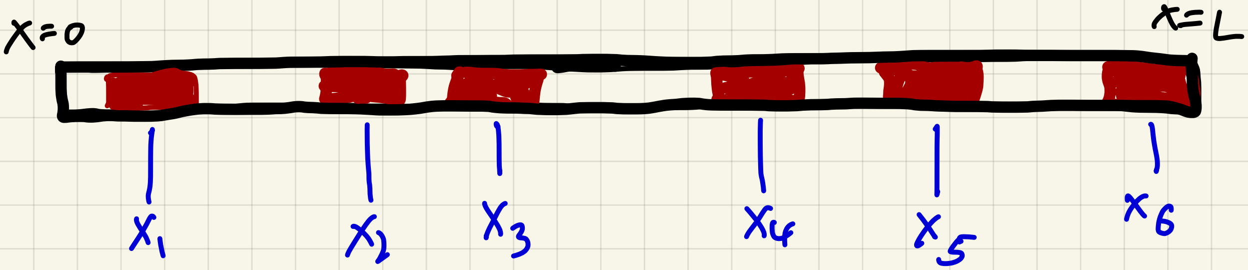
Lennard-Jones potential:

$$u(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\}$$

phenomenological short-ranged repulsion

attraction of induced dipoles

One-dimensional Tonks gas: hard rods of length a, with x_n the location of the center of the n^{th} rod:



Hamiltonian:

$$\hat{H} = \underbrace{\sum_{n=1}^{N} \frac{\vec{p}_n^{\,2}}{2m}}_{\text{kinetic}} + \underbrace{\sum_{m<n} u(|x_m - x_n|)}_{\text{2-body}} + \underbrace{\sum_{n=1}^{N} v(x_n)}_{\text{1-body}}$$

where

$$u(|x-x'|) = \begin{cases} 0 & \text{if } |x-x'| \geq a \\ \infty & \text{if } |x-x'| < a \end{cases}, \qquad v(x) = \begin{cases} \infty & \text{if } 0 \leq x < \frac{a}{2} \\ 0 & \text{if } \frac{a}{2} \leq x \leq L - \frac{a}{2} \\ \infty & \text{if } L - \frac{a}{2} < x \leq L \end{cases}$$

$$\chi(x_1, \dots, x_N) = e^{-\beta \sum_{m<n} u(|x_m - x_n|)} \cdot e^{-\beta \sum_n v(x_n)}$$

characteristic function $= \begin{cases} \infty & \text{if any overlaps between particles or between particles and edges} \\ 0 & \text{if not (allowed config)} \end{cases}$

Note that $\chi(x_1, \dots, x_N)$ independent of T, so $Q_N(T,L) = Q_N(L)$. Allowed configurations:

- $x_n > x_{n-1} + a$
- $x_n < L - \frac{1}{2}a - (N-n)a \equiv Y_n$

$Y_n = Y_{n-1} + a$

Thus, $Q_N(L) = \frac{1}{N!} \int_0^L dx_1 \cdots \int_0^L dx_N \, \chi(x_1, \dots, x_N) \Rightarrow$

$$= \int_0^L dx_1 \int_{x_1}^L dx_2 \dots \int_{x_{N-1}}^L dx_N \, \chi(x_1, \dots, x_N)$$

$$Q_N(L) = \int_{a/2}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \cdots \int_{x_{N-1}+a}^{Y_N} dx_N = \int_{a/2}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \cdots \int_{x_{N-2}+a}^{Y_{N-1}} dx_{N-1} \left(\overbrace{Y_N - a - x_{N-1}}^{Y_{N-1} - x_{N-1}}\right)$$

$$= \int_{a/2}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \cdots \int_{x_{N-3}+a}^{Y_{N-2}} dx_{N-2} \, \frac{1}{2}\left(Y_{N-2} - x_{N-2}\right)^2$$

$$= \dots = \frac{1}{N!}(L - Na)^N$$

Thus, $Z(T,L,N) = \frac{1}{N!}\left(\frac{L-Na}{\lambda_T}\right)^N$

$F(T,L,N) = -k_B T \log Z(T,L,N)$ = Helmholtz energy

$$F(T,V,N) = +k_BT\log N! - Nk_BT\log\left(\frac{L-Na}{\lambda_T}\right)$$

Stirling's approx: $\log N! = N\log N - N + \frac{1}{2}\log N + \mathcal{O}(N^0)$

$$\Rightarrow F(T,L,N) = -Nk_BT\log\left(\frac{L-Na}{N\lambda_T}\right) - Nk_BT$$

$$p = -\left.\frac{\partial F}{\partial L}\right|_{T,N} = \frac{Nk_BT}{L-Na} = \frac{nk_BT}{1-na}$$

So for $na \ll 1$ we recover the ideal gas law,

$p = nk_BT$. Note

$$p(1-na)L = nk_BTL \Rightarrow p\underbrace{(L-Na)}_{L_{eff}} = Nk_BT$$

$L_{eff} = L - Na$ subtracts the "excluded volume" Na