J. Non-ideal Classical Gas: Canonical Ensemble

- Include $\mathcal{U}(r_{ij})$ into calculation of Z

$$H(\{x,p\}) = \underbrace{\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}}_{\substack{\text{K.E.} \\ \Uparrow \\ \text{treated in ideal gas}}} + \underbrace{\sum_{\text{all pairs of }(ij)} \mathcal{U}(r_{ij})}_{\substack{\text{sum of 2-body interactions} \\ \text{(potential energy term)}}} = K(\{p_i\}) + W(\{x_i\})$$

$$Z_{\text{non-ideal}} = \underbrace{\frac{1}{N!\,h^{3N}} \int d^3p_1 \cdots d^3p_N \, d^3x_1 \cdots d^3x_N}_{\text{sum over } N\text{-particle states}} \; \underbrace{e^{-\frac{\beta}{2m}(\vec{p}_1^{\,2}+\cdots+\vec{p}_N^{\,2})} e^{-\beta W(\{x_i\})}}_{e^{-\beta H(\{x,p\})}}$$

$$= \frac{1}{N!}\left(\frac{1}{h^3}\int d^3p \, e^{-\frac{\beta p^2}{2m}}\right)^N \int d^3x_1 \cdots d^3x_N \, e^{-\beta W(\{x_i\})}$$

$$= \underbrace{\frac{1}{N!}\left(\frac{V}{h^3}\int d^3p \, e^{-\frac{\beta p^2}{2m}}\right)^N}_{} \cdot \underbrace{\frac{1}{V^N}\int d^3x_1 \cdots d^3x_N \, e^{-\beta W(\{x_i\})}}_{}$$

$$= \underbrace{Z_{\text{ideal}}}_{\text{gives ideal gas behavior}} \cdot \underbrace{Z_{\text{configuration}}}_{\leftarrow \text{ beyond ideal gas behavior}}$$

$$\boxed{Z_{\text{conf.}} \equiv \frac{1}{V^N}\int d^3x_1 \cdots d^3x_N \, e^{-\beta W(\{x_i\})} = \text{configuration partition function}}$$

- Evaluate $Z_{\text{conf.}}$ (approximately)
- Non-interacting $\Rightarrow W=0 \Rightarrow Z_{\text{conf.}}=1 \Rightarrow$ Ideal gas behavior

What are we aiming at?

- Deviation from ideal gas behavior!
- How to describe deviation from ideal gas behavior?

Classical ideal gas: $pV = NkT$

$$\Rightarrow \frac{p}{kT} = \frac{N}{V} = n \;\leftarrow\; \substack{\#\text{ particles per unit volume} \\ \text{OR number density}}$$

$\uparrow$ goes like n^1 (first power of n)

[good when gas is dilute, thus n is small or $\frac{V}{N}$ is large[†]]

Non-ideal gas: Expect it to behave as

$$\frac{p}{kT} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \cdots$$

$$= n + B_2(T)\, n^2 + B_3(T)\, n^3 + \cdots$$

$\Uparrow$ virial expansion

$\uparrow$ second/third virial coefficients

$$\boxed{\text{Q: Can we obtain the virial coefficients by evaluating } Z_{\text{conf.}}\text{?}}$$

The ratio $\frac{pV}{NkT}$ is a quantity that can be obtained experimentally.

[†] $\frac{V}{N}$ is "large", compared with what?

Remarks:

Chemists often consider one mole

$$\frac{p}{kT} = \frac{N_A}{v} + B_2(T)\left(\frac{N_A}{v}\right)^2 + \cdots$$

N_A = Avogadro's number

v = molar volume

$$\Rightarrow \frac{pv}{N_A kT} = 1 + B_2(T)\frac{N_A}{v} + \cdots$$

$$\Rightarrow \frac{pv}{RT} = \underset{\text{ideal gas}}{1} + \underbrace{B_2(T)\frac{N_A}{v}}_{\text{correction to ideal gas behavior}} + \cdots \qquad (N_A k \equiv R) \quad (*)$$

In data tables and physical chemistry books, (*) is often rewritten as:

$$\frac{pv}{RT} = 1 + \frac{\overline{B}_2(T)}{v} + \frac{\overline{B}_3(T)}{v^2} + \cdots \qquad (**)$$

$\therefore$ $\overline{B_2}(T)$ in (**) is related to $B_2(T)$ in (*) by $\boxed{\overline{B}_2(T) = B_2(T) N_A}$

> In data tables, the second virial coefficients are given in units of $(\text{cm}^3 \cdot \text{mol}^{-1})$ for $\overline{B_2}(T)$.

Eq.(**) is an expansion in $\frac{1}{v}$. For dilute gas, v is large and $\frac{1}{v}$ is small.

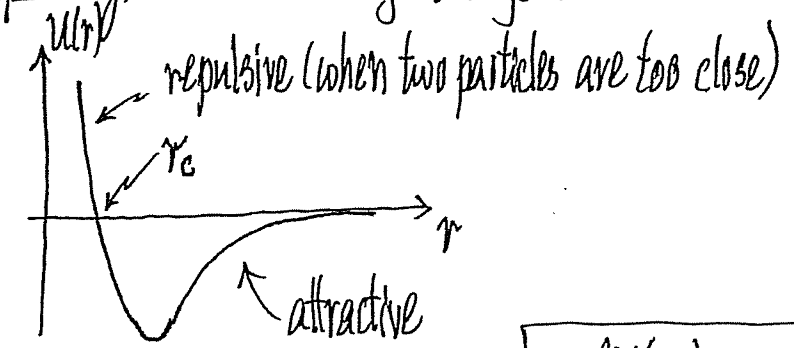
$$W = \frac{1}{2}\sum_i \sum_{j \, (i\neq j)} u(|\vec{r}_i - \vec{r}_j|) \equiv \frac{1}{2}\sum_i \sum_{j \, (i\neq j)} u(r_{ij}) = \sum_{\substack{\text{all pairs} \\ \text{of } ij}} u(r_{ij})$$

$$\therefore Z_{\text{conf.}} = \frac{1}{V^N}\int d^3x_1 \cdots d^3x_N \, e^{-\beta \sum_{(\text{pairs})} u(r_{ij})}$$

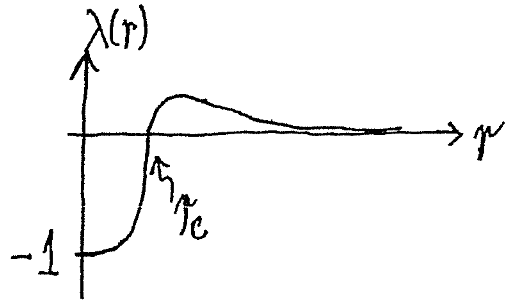
$$= \frac{1}{V^N}\int d^3x_1 \cdots d^3x_N \prod_{(\text{pairs})} e^{-\beta u(r_{ij})}$$

over $\underbrace{\text{all distinct pairs}}_{\frac{N(N-1)}{2} \text{ of them}}$ of ij (pairwise 2-body interaction)

Typically, $u(r)$ is of the form



It is convenient to introduce: $\boxed{e^{-\beta u(r_{ij})} - 1 \equiv \lambda_{ij} = \lambda(r_{ij})}$



- a nice function to handle (e.g. numerically)
- $\lambda(r)$ differs appreciably from zero only for $r \leq r_c$

$\Rightarrow$ $\boxed{\lambda_{ij} \approx 0 \text{ unless particles } i \text{ and } j \text{ are very close to each other (i.e., when they collide)}}$

Key features of λ_{ij}