J. Non-ideal Classical Gas: Canonical Ensemble

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

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

treated in ideal gas

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

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

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

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

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

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

What are we aiming at?

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

Classical ideal gas: $pV = NkT$

$$\Rightarrow \frac{p}{kT} = \frac{N}{V} = n$$

n ← # particles per unit volume OR number density

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

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

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

virial expansion

second/third virial coefficients [corrections/deviations from ideal gas behavior]

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

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

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

Remarks:

Chemists often consider one mole

$$\frac{p}{kT} = \frac{N_A}{v} + B_2(T)\left(\frac{N_A}{v}\right)^2 + \cdots \qquad \begin{cases} N_A = \text{Avogadro's number} \\ v = \text{molar volume} \end{cases}$$

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

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

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.

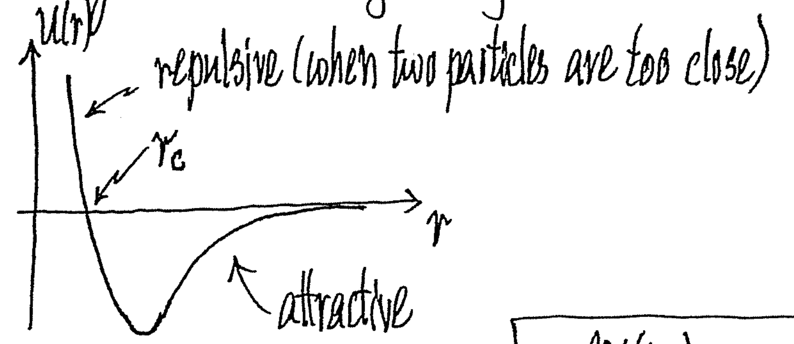
$$W = \frac{1}{2}\sum_{\substack{i \\ (i\neq j)}}\sum_{j} u(|\vec{r}_i - \vec{r}_j|) \equiv \frac{1}{2}\sum_{\substack{i \\ (i\neq j)}}\sum_{j} u(r_{ij}) = \sum_{\substack{\text{all pairs} \\ \text{of } ij}} u(r_{ij})$$

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

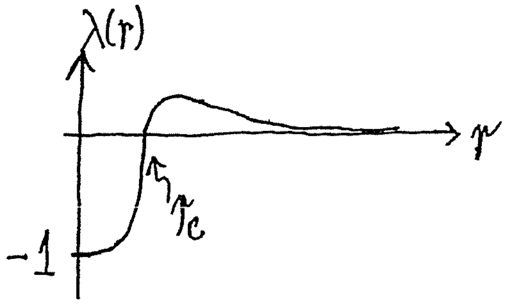
$$= \frac{1}{V^N}\int d^3x_1 \cdots d^3x_N \prod_{(\text{pairs})} e^{-\beta u(r_{ij})}$$

over $\underbrace{\text{all distinct pairs}}_{\frac{N(N-1)}{2} \text{ of them}}$ of i,j (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 $r \leq r_c$

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

Key features of λ_{ij}

As $e^{-\beta U(r_{ij})} = 1 + \lambda_{ij}$,

$$Z_{conf.} = \frac{1}{V^N}\int d^3x_1 \cdots d^3x_N \overbrace{\prod_{(pairs)} (1+\lambda_{ij})}^{\frac{N(N-1)}{2} \text{ terms in product}}$$

$$= \frac{1}{V^N}\int d^3x_1\cdots d^3x_N \Big(1 + \underbrace{\sum_{(pairs)}\lambda_{ij}}_{\text{one } \lambda \text{ term}} + \underbrace{\sum \lambda_{ij}\lambda_{kl}}_{\text{product of two } \lambda\text{'s}} + \cdots \Big) \quad \boxed{\text{still exact}}$$

three λ's, four λ's, etc.

No λ, ideal gas term → zeroth order approximation (ignore interaction)

one λ term → first-order approximation

keep terms of different order ← cluster expansion

Consider terms $\lambda_{ij}\lambda_{kl}$

$\lambda_{12}\lambda_{23}$ ≠0 when particles 1, 2, 3 are simultaneously close to each other (triple collision)

$\lambda_{12}\lambda_{34}$ ≠0 in simultaneous collisions of 1 with 2 AND 3 with 4

both are unlikely to occur when density $n = \frac{N}{V}$ is not too high

∴ neglect terms of $\lambda_{ij}\lambda_{kl}$ and higher order

Thus,

$$\boxed{Z_{conf.} \approx \frac{1}{V^N}\int d^3x_1\cdots d^3x_N \Big(1 + \underbrace{\sum_{(pairs)}\lambda_{ij}}_{\text{first correction term to ideal gas}}\Big)}$$

lowest order approximation

$$\therefore\ Z_{conf.} = 1 + \frac{1}{V^N}\int d^3x_1\cdots d^3x_N \sum_{(pairs)}\lambda_{ij}$$

$$= 1 + \frac{1}{V^N}\frac{N(N-1)}{2}\int d^3x_1\cdots d^3x_N\, \lambda_{12}$$

∵ there are $\frac{N(N-1)}{2}$ identical integrals

$$= 1 + \frac{1}{V^N}\frac{N(N-1)}{2}\cdot V^{N-2}\int d^3x_1\, d^3x_2\, \lambda_{12}$$

$$= 1 + \frac{N(N-1)}{2V^2}\int d^3x_1\, d^3x_2 \left(e^{-\beta U(r_{12})} - 1\right)$$

$\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}$ (CM)

$\vec{r} = \vec{r}_1 - \vec{r}_2$ (relative)

$$= 1 + \frac{N(N-1)}{2V^2}\underbrace{\int d^3R}_{V}\int d^3r \left(e^{-\beta U(r)} - 1\right)$$

$$= 1 + \frac{N(N-1)}{2V}\cdot\int d^3r \left(e^{-\beta U(r)} - 1\right)$$

$N \gg 1$, $n = \frac{N}{V}$

$$\approx 1 + \frac{Nn}{2} I_2(\beta) \quad \text{where} \quad \boxed{\begin{aligned} I_2(\beta) &\equiv \int d^3r\, \lambda(r) \\ &= \int d^3r \left(e^{-\beta U(r)} - 1\right) \\ &= 4\pi\int_0^\infty dr\, r^2 \left(e^{-\beta U(r)} - 1\right)\end{aligned}}$$

$$\therefore\ Z_{conf.} = \left(1 + \frac{n}{2}I_2(\beta) + \cdots\right)^N$$

The point is: If we can evaluate $I_2(\beta)$, then we have (an approximate form of) $Z_{conf.}$

Retaining λ_{ij} only, the calculation reduces to that of a single integral $I_2(\beta)$, which involves the detailed form of $U(r)$.

Let's say we have I_2. Since $Z_{\text{non-ideal}} = Z_{\text{ideal}} \cdot Z_{\text{conf.}}$,

$$F_{\text{non-ideal}} = -kT\ln Z_{\text{non-ideal}} = -kT\ln Z_{\text{ideal}} - NkT\ln\left(1+\frac{n}{2}I_2\right)$$

$$\cong -kT\ln Z_{\text{ideal}} - kT\,\frac{N}{2}\,\frac{N}{V}\,I_2$$

$$= F_{\text{ideal}} - NkT\,\frac{N}{2V}\,I_2$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \underset{\substack{\uparrow \\ \text{ideal gas term}}}{\frac{NkT}{V}} - \frac{N^2kT}{2V^2}I_2 = \frac{NkT}{V} - \frac{kT}{2}\left(\frac{N}{V}\right)^2 I_2$$

$$\Rightarrow \frac{p}{kT} = n - n^2\frac{I_2}{2} = n + \underbrace{B_2(T)}_{\uparrow\ \text{virial coefficient (second)}}n^2$$

$$\therefore \boxed{B_2(T) = -\frac{1}{2}I_2 = -2\pi\int_0^\infty dr\, r^2\left(e^{-\beta U(r)}-1\right)}^{\dagger} \quad (*)$$

$\therefore$ Evaluate $I_2 \Rightarrow B_2(T) \Rightarrow$ <u>leading correction term to ideal gas law</u>

Up to here, the formalism is general and works for any reasonable $U(r)$.

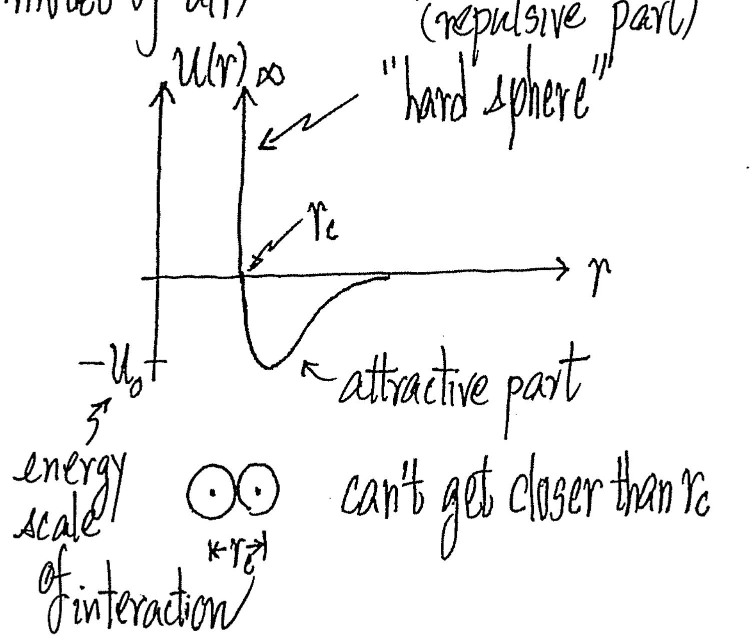
- (*) is the key result/idea

[†] The expression of $B_2(T)$ gives it the units of $(\text{length})^3$, e.g. cm^3. Data tables give the second virial coefficient in units of $\text{cm}^3\cdot\text{mol}^{-1}$. That value is $N_A \cdot B_2(T) = \overline{B}_2(T)$.

<u>The Van der Waals Equation of state</u>

- To proceed, we need a simple model of $U(r)$

$$U(r) = \begin{cases} \infty, & r < r_c \\ -U_0\,\underbrace{f\!\left(\frac{r}{r_c}\right)}_{\text{some nice function}}, & r \geq r_c \end{cases}$$



$$\lambda(r) = e^{-\beta U(r)} - 1$$

$$= \begin{cases} -1, & r < r_c \\ e^{\beta U_0 f\left(\frac{r}{r_c}\right)} - 1, & r \geq r_c \end{cases}$$

$$B_2(T) = -2\pi\int_0^\infty dr\, r^2\,\lambda(r)$$

$$= 2\pi\int_0^{r_c} dr\, r^2 - 2\pi\int_{r_c}^\infty dr\, r^2\left(e^{\beta U_0 f\left(\frac{r}{r_c}\right)} - 1\right)$$

assume temperature is high enough so that $\beta U_0 f\left(\frac{r}{r_c}\right) \ll 1$

$$\approx \frac{2\pi r_c^3}{3} - 2\pi\int_{r_c}^\infty dr\, r^2\,\beta U_0 f\left(\frac{r}{r_c}\right)$$

$$= \underbrace{4\cdot\frac{4\pi}{3}\left(\frac{r_c}{2}\right)^3}_{\substack{\uparrow \\ \text{relates to \underline{volume of hard spheres}} \\ \text{(or short-range strong repulsive part of } U(r))}} - \frac{2\pi U_0}{kT}\underbrace{\int_{r_c}^\infty dr\, r^2 f\left(\frac{r}{r_c}\right)}_{\substack{\leftarrow \text{ assume it converges} \\ \uparrow\ \text{relates to long-range \underline{weak attractive part} of } U}}$$

$$\equiv b' - \frac{a'}{kT}$$

Key result/concept

- While the derivation is itself interesting, it is more important to understand what the result says.
- $$\frac{p}{kT} = n + \underbrace{B_2(T)\, n^2 + \dots}_{\text{non-ideal gas behavior}}$$

$B_2(T)$ is related to inter-particle interaction

$B_2(T)$ is the lowest-order correction to ideal gas behavior

$B_2(T)$ is found to have two terms:

$$B_2(T) = \underbrace{b'}_{\text{positive}} - \underbrace{\frac{a'}{kT}}_{\text{negative}}$$

(Note: Opposite signs)

positive: related to volume of hard sphere and thus the short-range repulsive part in $U(r)$

"Repulsion leads to +ve contribution to $B_2(T)$"

negative: related to the longer-range attractive part in $U(r)$

"Attraction leads to -ve contribution to $B_2(T)$"

So we have finally

$$\frac{p}{kT} = n + \left(b' - \frac{a'}{kT}\right)n^2 = n(1+b'n) - \frac{a'}{kT}n^2$$

But $n = \frac{N}{V} = \frac{N}{N_A}\cdot\frac{N_A}{V} = N_A\cdot\frac{1}{N_A\left(\frac{V}{N}\right)} = \frac{N_A}{v}$, where $v =$ molar volume $= N_A\cdot\left(\frac{V}{N}\right)$

$$\therefore \frac{p}{kT} = \frac{N_A}{v}\left(1 + b'\frac{N_A}{v}\right) - \frac{a'}{kT}\frac{N_A^2}{v^2}$$

$$= \frac{N_A}{v}\left(1 + \frac{b}{v}\right) - \frac{a}{kTv^2} \qquad \text{where } \begin{cases} b \equiv N_A b' \\ a \equiv N_A^2 a' \end{cases}$$

$$\Rightarrow \left(p + \frac{a}{v^2}\right)\frac{1}{kT} = \frac{N_A}{v}\left(1 + \frac{b}{v}\right)$$

Note: $N_A k \equiv R$

$$\Rightarrow \left(p + \frac{a}{v^2}\right) = \frac{RT}{v}\left(1 + \frac{b}{v}\right) \approx \frac{RT}{v}\frac{1}{\left(1 - \frac{b}{v}\right)} = \frac{RT}{v-b}$$

Finally, we have $\boxed{\left(p + \frac{a}{v^2}\right)(v-b) = RT}$

which is the Van der Waals equation of state!

Notes: $a = a' N_A^2$ is related to long-range weak attractive part of $U(r)$

$b = b' N_A$ is related to short-range strong repulsive part of $U(r)$

- Van der Waals equation could lead to phase transitions

⇒ If we want to study phase transitions, we need to include interactions between particles!

Further Developments (Remarks)

- One could go back to

$$Z_{\text{conf.}} = \frac{1}{V^N}\int d^3x_1\cdots d^3x_N\left(\underset{\substack{\uparrow\\ \text{ideal}\\ \text{gas}}}{1} + \underbrace{\sum_{(\text{pairs})}\lambda_{ij}}_{\text{gives } B_2(T)} + \underbrace{\sum\lambda_{ij}\lambda_{kl} + \cdots}_{\text{give } B_3(T),\, B_4(T),\, \cdots}\right)$$

and work out the higher-order corrections.

This had led to a systematic treatment called "cluster expansions" and a diagrammatic description of terms of different orders.

[See Pathria, "Statistical Mechanics" Ch. 9] (Optional)

- The inclusion of interaction is also the starting point of liquid state physics.