

Ideal Gas: $H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$

$$Z(T, V, N) = \frac{1}{N! h^{3N}} \int \prod_{i=1}^N d^3 q_i d^3 p_i e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}}$$

$$= \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N, \quad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

Each independent square term in Hamiltonian

Equipartition Theorem: average value $= \frac{1}{2} k_B T$

total Hamiltonian $H = \sum_{a=1}^M A_a q_a^2 + B_a p_a^2$

$$\begin{aligned} \langle A_a q_a^2 \rangle &= \frac{1}{Z} \int \prod_a d^3 q_a d^3 p_a A_a q_a^2 e^{-\beta (\sum_{a=1}^M A_a q_a^2 + B_a p_a^2)} \frac{\int dq_a A_a q_a^2 e^{-\beta A_a q_a^2}}{\int dq_a e^{-\beta A_a q_a^2}} \\ &= -\frac{\partial}{\partial \beta} \ln \left(\int dq_a e^{-\beta A_a q_a^2} \right) = -\frac{\partial}{\partial \beta} \left(\ln \sqrt{\frac{\pi}{\beta A_a}} \right) = \frac{1}{2\beta} = \frac{1}{2} k_B T \end{aligned}$$

for the same reason. $\langle B_a p_a^2 \rangle = \frac{1}{2} k_B T$

$$\Rightarrow E = \frac{1}{2} k_B T \cdot 3N = \frac{3}{2} N k_B T \Rightarrow \text{monatomic gas}$$

* Diatomic Gas  two masses attached via a spring

$$H = H_{\text{com}} + H_{\text{vib}} + H_{\text{rot}}$$

$$Z = Z_{\text{com}} \cdot Z_{\text{vib}} \cdot Z_{\text{rot}} \quad \begin{array}{l} \text{Only } Z_{\text{com}} \text{ depends on } V \\ \Rightarrow pV = N k_B T \end{array}$$

$$H_{\text{com}} \Rightarrow E_{\text{com}} = \frac{3}{2} k_B T$$

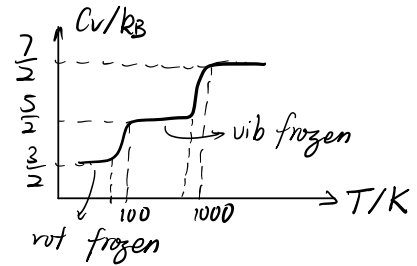
$$H_{\text{vib}} = \sum_{i=1}^N \frac{p_i^2}{2\mu} + \frac{1}{2} \mu \omega^2 q_i^2 \Rightarrow E_{\text{vib}} = 2 \cdot \frac{1}{2} k_B T = k_B T \quad \left(\begin{array}{l} \text{1 degree of} \\ \text{freedom, but} \\ \text{2} \cdot \frac{1}{2} k_B T \end{array} \right)$$

$$H_{\text{rot}} = \sum_{i=1}^N \frac{L_i^2}{2I} \Rightarrow E_{\text{rot}} = 2 \cdot \frac{1}{2} k_B T = k_B T$$

$$E = \frac{7}{2} N k_B T, \quad C_v = \frac{7}{2} k_B$$

Experiment Results (e.g. H_2)

successive freezing of vibrational & rotational modes



Quantum Effects at temp $\sim 10^3 K$

→ the energy gap is too big to activate by thermal fluctuation

a quantized vibrational & rotational mode

thermal excitations of these modes are suppressed at 'low' temp.

* Vibration $E_n = (n + \frac{1}{2})\hbar\omega$

partition function of a single molecule

$$Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta E_n} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$\ln Z_{vib} = -\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega})$$

$$\epsilon_{vib} = -\frac{\partial}{\partial \beta} \ln Z_{vib} = \frac{1}{2}\hbar\omega + \hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$C_{vib} = \frac{d\epsilon_{vib}}{dT} = -k_B T^2 \frac{d\epsilon_{vib}}{d\beta} = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

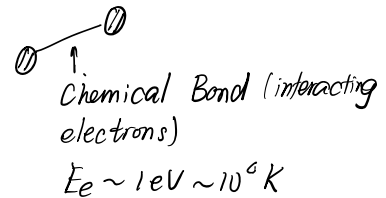
① high T limit ($\beta\hbar\omega \ll 1$) $\frac{\hbar\omega}{k_B T} = \frac{\Theta_{vib}}{T} \rightarrow$ characteristic temp

$$C_{vib} \approx k_B (\beta\hbar\omega)^2 \frac{1}{(\beta\hbar\omega)^2} = k_B$$

② low T limit ($\beta\hbar\omega \gg 1$)

$$C_{vib} \approx k_B (\beta\hbar\omega)^2 e^{-\beta\hbar\omega} \text{ suppressed!}$$

* Rotation



$$\epsilon_l = \frac{L^2}{2I} = \frac{\hbar^2}{2I} l(l+1) \quad \text{degree of degeneracy } g = 2l+1$$

$$Z_{\text{rot}} = \sum_{l=0}^{\infty} e^{-\beta \frac{\hbar^2}{2I} l(l+1)} \cdot (2l+1)$$

① high T limit $\beta \frac{\hbar^2}{2I} \ll 1, \frac{\hbar^2}{2Ik_B T} \equiv \frac{\Theta_{\text{rot}}}{T}, \Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$

denote $x = l(l+1), dx = (2l+1)dl$

$$\Rightarrow Z_{\text{rot}} = \sum_{l=0}^{\infty} e^{-\frac{\Theta_{\text{rot}}}{T} x} dx = \int_0^{+\infty} e^{-\frac{\Theta_{\text{rot}}}{T} x} dx = \frac{T}{\Theta_{\text{rot}}}$$

$$C_{\text{rot}} \approx k_B$$

② low T limit $\beta \frac{\hbar^2}{2I} \gg 1$

$$Z_{\text{rot}} \simeq 1 + 3e^{-\beta \frac{\hbar^2}{2I}}, \quad C_{\text{rot}} = 3k_B \left(\frac{2\Theta_{\text{rot}}}{T} \right)^2 e^{-\frac{2\Theta_{\text{rot}}}{T}}$$

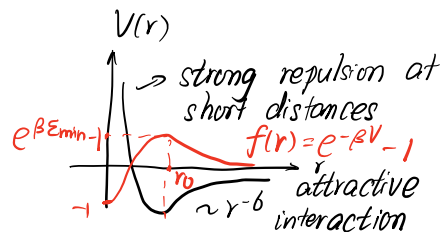
* Interacting gases

ideal gas: dilute limit $n \rightarrow 0$

Virial expansion (Correction to ideal gas)

$$\frac{P}{k_B T} = n + B_2 n^2 + B_3 n^3 + \dots$$

expansions in small parameter n



Goal: compute virial coefficient, $B_2 \Rightarrow$ van der Waals equ.

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i < j} V(r_{ij}), \quad r_{ij} = |\vec{r}_i - \vec{r}_j|$$

$$Z(T, V, N) = \int \frac{1}{N!} \frac{d^3 r_i d^3 p_i}{h^3} \exp \left[-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} - \beta \sum_{i < j} V(r_{ij}) \right]$$

$$= \frac{1}{N! \lambda_T^{3N}} \int \prod_{i=1}^N d^3 r_i e^{-\beta \sum_{i < j} V(r_{ij})} \quad \text{small?}$$

$$\rightarrow 1 - \beta \sum_{i < j} V(r_{ij}) + \frac{1}{2} \beta^2 \sum_{i < j} \sum_{k < l} V(r_{ij}) V(r_{kl}) - \dots$$

Define $f(r_{ij}) = e^{-\beta V(r_{ij})} - 1 \Rightarrow e^{-\beta V(r_{ij})} = 1 + f_{ij}$

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N! \lambda_T^{3N}} \int \prod_{i=1}^N d^3 r_i \prod_{\substack{j < k \\ \text{pairs}}}^{C_N^2} (1 + f_{jk}) \\ &= \frac{1}{N! \lambda_T^{3N}} \int \prod_{i=1}^N d^3 r_i \left(1 + \sum_{j < k} f_{jk} + \sum_{j < k} \sum_{l < m}^{2 C_N^2 \text{ terms}} f_{jk} f_{lm} + \dots \right) \end{aligned}$$

Diagrammatic Representation

(a) drawn N dots $\Rightarrow N$ particles;

(b) each $f_{jk} \Rightarrow$ draw a line connecting particle j & k
 e.g. $N=6$

$$\begin{array}{c} \textcircled{1} \quad \textcircled{2}-\textcircled{3} \\ \textcircled{4} \quad \textcircled{5}-\textcircled{6} \end{array} = \int d^3 r_1 \dots d^3 r_6 f_{23} f_{56} = \left(\int d^3 r_1 d^3 r_4 \right) \left(\int d^3 r_2 d^3 r_3 f_{23} \right) \left(\int d^3 r_5 d^3 r_6 f_{56} \right)$$

$$\begin{array}{c} \textcircled{1}-\textcircled{2} \quad \textcircled{3} \\ \textcircled{4} \quad \textcircled{5}-\textcircled{6} \end{array} = \int d^3 r_1 \dots d^3 r_6 f_{12} f_{56} \\ = \left(\int d^3 r_1 d^3 r_2 d^3 r_3 f_{12} f_{13} \right) \left(\int d^3 r_4 \right) \left(\int d^3 r_5 d^3 r_6 f_{56} \right)$$

\Rightarrow product of linked clusters of l -particles \rightarrow cluster expansion

Partition of N dots into l -clusters:

$$\# \text{ of } l\text{-cluster} = n_l, \quad \sum_l l n_l = N$$

value of l -cluster: b_l

e.g. $b_1 = \int d^3 r_1 = V$

$$b_2 = \textcircled{1}-\textcircled{2} = \int d^3 r_1 d^3 r_2 f_{12} \quad b_2 \sim V$$

is it proper to classify the clusters by the # of particles, not the topological shape? make different contribution

$$b_3 = \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \text{diagram 4}$$

$$= \int d^3r_1 d^3r_2 d^3r_3 (f_{12}f_{23} + f_{12}f_{13} + f_{13}f_{23} + f_{12}f_{13}f_{23})$$

$$\Xi(T, V, N) = \frac{1}{N! \lambda_T^{3N}} \left[\int \prod_{i=1}^N d^3r_i \prod_{j < k} (1 + f_{jk}) \right] \xrightarrow{\text{divide all the } N \text{ particles into } \sum n_l \text{ clusters. \# of } l\text{-clusters is } n_l}$$

$$= \frac{1}{N! \lambda_T^{3N}} \sum_{\{n_l\}} \prod_l \frac{1}{l!} (b_l)^{n_l} \cdot W(\{n_l\}) \xrightarrow{\int d^3r_1 d^3r_2 f_{12} = \int d^3r_3 d^3r_4 f_{34}} \text{\# of distinct diagrams w/ the same } \{n_l\}$$

$$W(\{n_l\}) = \frac{N!}{\prod_l (l!)^{n_l} n_l!}$$

permutation of l particles within a cluster permutation of distinct l -clusters

$$\Xi(T, V, N) = \frac{1}{N! \lambda_T^{3N}} \sum_{\{n_l\}} N! \prod_l \frac{(b_l)^{n_l}}{(l!)^{n_l} n_l!}$$

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{z}{\lambda_T^3} \right)^N \sum_{\{n_l\}} N! \prod_l \frac{(b_l)^{n_l}}{(l!)^{n_l} n_l!}$$

$$= \sum_{\{n_l=0\}}^{\infty} \left(\frac{z}{\lambda_T^3} \right)^N \prod_l \frac{(b_l)^{n_l}}{(l!)^{n_l} n_l!}$$

$$= \sum_{\{n_l=0\}}^{\infty} \prod_l \frac{(b_l)^{n_l}}{(l!)^{n_l} n_l!} \left(\frac{z^l}{\lambda_T^{3l}} \right)^{n_l} \quad (N = \sum_l n_l \cdot l)$$

$$= \prod_l \sum_{n_l=0}^{\infty} \frac{1}{n_l!} \left(\frac{b_l z^l}{\lambda_T^{3l} l!} \right)^{n_l} = \prod_l \exp \left(\frac{b_l z^l}{\lambda_T^{3l} l!} \right)$$

$$= \exp \left(\sum_{l=1}^{\infty} \frac{z^l}{\lambda_T^{3l}} \frac{b_l}{l!} \right)$$

$$\Rightarrow \ln \Xi = \sum_{l=1}^{\infty} \left(\frac{z}{\lambda_T^3} \right)^l \frac{b_l}{l!} \quad pV = k_B T \ln Q = \frac{1}{\beta} \sum_{l=1}^{\infty} \left(\frac{z}{\lambda_T^3} \right)^l \frac{b_l}{l!}$$

$$N = - \frac{\partial \ln \Xi}{\partial \alpha} = z \frac{\partial \ln \Xi}{\partial z} = \sum_{l=1}^{\infty} l \left(\frac{z}{\lambda_T^3} \right)^l \frac{b_l}{l!} \quad \text{denote } b_l = \bar{b}_l \cdot V$$

$$\left\{ \begin{array}{l} \frac{p}{k_B T} = \sum_{l=1}^{\infty} x^l \frac{\bar{b}_l}{l!} \\ n = \sum_{l=1}^{\infty} l x^l \frac{\bar{b}_l}{l!} \end{array} \right. \quad \frac{p}{k_B T} = \sum_{l=1}^{\infty} a_l n^l \Rightarrow \text{Virial Expansion}$$

Eliminate x (namely z) perturbatively, order by order in n

$$n = x b_1 + x^2 b_2 + \frac{x^3}{2} b_3$$

$$\frac{P}{k_B T} = \sum_{l=1}^{\infty} a_l \left(\sum_{m=1}^{\infty} m x^m \frac{b_m}{m!} \right)^l = \sum_{l=1}^{\infty} x^l \frac{b_l}{l!}$$

Compare the coefficients of x^l :

$$x^1: b_1 = a_1 b_1 \Rightarrow a_1 = b_1 = 1$$

$$x^2: \frac{b_2}{2} = a_1 b_2 + a_2 b_1^2 \Rightarrow a_2 = -\frac{b_2}{2}$$

$$x^3: \frac{b_3}{6} = \frac{a_1}{2} b_3 + 2 a_2 b_1 b_2 + a_3 b_1^3 \Rightarrow a_3 = b_2^2 - \frac{1}{3} b_3$$

$$B_1(T) = 1, B_2(T) = -\frac{b_2}{2} = -\frac{1}{2} \int d^3r [e^{-\beta V(r)} - 1]$$

$$B_3(T) = b_2^2 - \frac{1}{3} b_3 = -\frac{1}{3} \int d^3r_2 d^3r_3 f(r_{12}) f(r_{13}) f(r_{23})$$

* Van der Waals Equation

$$V(r) = \begin{cases} +\infty & r < r_0 \\ -u_0 \left(\frac{r_0}{r}\right)^6 & r > r_0 \end{cases}$$

$$B_2(T) = -\frac{1}{2} \int d^3r [e^{-\beta V(r)} - 1]$$

$$= -2\pi \int dr r^2 [e^{-\beta V(r)} - 1]$$

$$= -2\pi \int_0^{r_0} r^2 dr \cdot (-1) - 2\pi \int_{r_0}^{\infty} dr r^2 [e^{\beta u_0 \left(\frac{r_0}{r}\right)^6} - 1]$$

$$= \frac{2\pi}{3} r_0^3 - 2\pi \beta u_0 \int_{r_0}^{\infty} dr r^2 \cdot \left(\frac{r_0}{r}\right)^6$$

$$= \frac{2\pi}{3} r_0^3 (1 - \beta u_0)$$

$$B_2(T) = \frac{\Omega}{2} (1 - \beta u_0), \text{ where } \Omega = \frac{4\pi}{3} r_0^3, \text{ excluded volume}$$

$$\frac{P}{k_B T} = n + \frac{\Omega}{2} \left(1 - \frac{u_0}{k_B T}\right) n^2$$

$$\Rightarrow \frac{1}{k_B T} \left(p + \frac{\Omega}{2} u_0 \frac{1}{V^2} \right) = n + \frac{\Omega}{2} n^2 = n \left(1 + \frac{\Omega}{2V} \right) \approx \frac{1}{V - \frac{\Omega}{2}} \quad (\Omega \ll V)$$

$$\left(p + \frac{\Omega}{2} u_0 \frac{1}{V^2} \right) \left(V - \frac{\Omega}{2} \right) = k_B T$$

$$\frac{\Omega}{V} \sim 10^{-3}$$

$$\text{van der Waals: } \left(p + \frac{a}{V^2} \right) \left(V - \frac{b}{2} \right) = k_B T, \quad a = \frac{\Omega}{2} u_0, \quad b = \frac{\Omega}{2}$$