Non-Ideal Gases. 2: Two Examples, and Cluster Expansion

• *Idea:* Apply the general formalism developed in Part B to the calculation of the second virial coefficient $B_2(T)$ for two examples of approximate, phenomenological forms of the interparticle potential $\phi(r_{ij})$.

C. Application: Potential with Hard-Core Term

• *Setup:* For a classical gas,

$$Z_N = \frac{1}{N!\,h^{3N}} \int \mathrm{d}^{3N}p \int \mathrm{d}^{3N}r\, \mathrm{e}^{-\beta\,[\Sigma_i\, p_i^2/2m + U(\mathbf{r})]} = \frac{1}{\lambda_T^{3N} N!} \int \mathrm{d}^{3N}r\, \mathrm{e}^{-\beta\, \Sigma_{i<j}\phi_{ij}} \;.$$

• *Second virial coefficient:* From the general result, classically we find (recall that $Z_1 = V/\lambda_T^3$),

$$Z_2 = \frac{V}{2\lambda_T^6} \int \mathrm{d}^3r\, \mathrm{e}^{-\beta\phi(r)}\;, \qquad \text{and} \qquad B_2 = -(Z_2 - \tfrac12\, Z_1^2)\, \frac{V}{Z_1^2} = -\tfrac12 \int \mathrm{d}^3r\, f(r)\;,$$

where the Mayer function $f(r) := \mathrm{e}^{-\beta\phi(r)} - 1$, contrary to $\phi(r)$, is well behaved as $r \to 0$. Notice that the cluster expansion generalizes this last expression to give all B_n.

• *Qualitative behavior of $B(T)$:* To proceed, we need to know something about $v(r)$. Let's assume that

$$\phi(r) = \phi_{\rm hc}(r) + \phi_{\rm lr}(r)$$

is well approximated by a sum of an infinite potential wall ("hard core") at $r = r_0$, and a weakly attractive potential for $r > r_0$ ($\star$ plot). Then

$$f(r) = \begin{cases} -1 & \text{for } r < r_0 \\ -w(r)/k_{\rm B}T & \text{for } r > r_0 \end{cases}$$

$$B(T) \approx -\tfrac12 \left[-\frac{4\pi}{3}\, r_0^3 + 4\pi \int_0^\infty \mathrm{d}r\, r^2\, \frac{w(r)}{k_{\rm B}T} \right] = \frac{b}{N} - \frac{a}{N^2 k_{\rm B}T}\;,$$

where $b = (2\pi/3)\, r_0^3 N$ is proportional to the molecular volume, and $a = 2\pi \int_0^\infty \mathrm{d}r\, r^2\, w(r) N^2$ arises from the attractive part of the potential. This tells us that at high temperatures the first term dominates and $B(T)$ is a positive constant, an added pressure coming from the fact that particles have a smaller available volume. At low temperatures, the second term dominates and $B(T)$ is negative, with an increasing magnitude as T decreases. The $B(T)$ we obtained is of the same form as the second virial coefficient for the van der Waals gas (in the form in which a and b are intensive parameters).

D. Application: The Lennard-Jones Potential

• *Idea:* Use for $\phi(r)$ the phenomenological Lennard-Jones potential, an expression that approximates well the measured potential for some gases,

$$\phi_{\rm LJ}(r) = 4\epsilon \Big[\Big(\frac{\sigma}{r}\Big)^{12} - \Big(\frac{\sigma}{r}\Big)^{6} \Big]\;.$$

• *Second virial coefficient:* Introducing dimensionless variables $r^* := r/\sigma$ and $T^* := k_{\rm B}T/\epsilon$, the general expression for B_2 in terms of $\phi(r)$ gives

$$B = -\tfrac12 \int \mathrm{d}^3r\, \big(\mathrm{e}^{-\beta\phi(r)} - 1\big) = \frac{2\pi}{3}\, \sigma^3\, \frac{4}{T^*} \int \mathrm{d}r^*\, r^{*2} \Big(\frac{12}{r^{*12}} - \frac{6}{r^{*6}} \Big)\, \mathrm{e}^{-4(r^{*-12} - r^{*-6})/T^*}$$

$$= \frac{2\pi}{3}\, \sigma^3 \Big(\frac{1.73}{T^{*1/4}} - \frac{2.56}{T^{*3/4}} - \frac{0.87}{T^{*5/4}} - ... \Big)\;,$$

where we have integrated by parts in the second step.

E. Classical Cluster Expansion for the Partition Function

• *Setup:* We will follow the classical theory developed by J E Mayer and collaborators starting in 1937. Using the potential $\phi(r)$ define the 2-particle Mayer function $f_{ij} = f(r_{ij}) := \mathrm{e}^{-\beta\phi(r_{ij})} - 1$. Then

$$Z_N = \frac{1}{N!\,\lambda_T^{3N}} \int \mathrm{d}^3r_1 ... \, \mathrm{d}^3r_N \prod\nolimits_{i<j} (1+f_{ij})\ .$$

(Notice that for an ideal system $f(r_{ij}) = 0$, and $\lim_{r\to 0} f_{ij}(r) = -1$.) The integrand can be expanded as

$$\prod_{i<j}(1+f_{ij}) = 1 + \sum_{i<j} f_{ij} + \sum_{(i<j)\neq(k<l)} f_{ij} f_{kl} + ... + (\text{product of all } \tbinom{N}{2} \text{ factors } f_{ij})\ .$$

We can represent each term in the right-hand side as a graph on N vertices, one for each particle, with one edge for each f_{ij} factor (no two vertices are connected by more than one edge). Every graph appears exactly once in the sum, and unconnected vertices in each graph contribute $\int \mathrm{d}^3r = V$ to the term they are in, so

$$Z_N = \frac{1}{N!\,\lambda_T^{3N}} \Big\{ V^N + V^{N-2} \sum\nolimits_{i<j} \int \mathrm{d}^3r_i\, \mathrm{d}^3r_j\, f_{ij} + \Big(\begin{matrix} \text{one term for each graph} \\ \text{with more than one edge} \end{matrix} \Big) \Big\},$$

and we need a way of classifying and evaluating the contributions of all graphs.

• *Clusters:* An "l-cluster" is a set of l connected vertices; two clusters are considered distinct if their topology and/or vertex labels differ. We identify each l-cluster with the corresponding product of f_{ij}s and define

$$b_l = \frac{1}{\lambda_T^{3l-3}\, l!\, V} \int \mathrm{d}^3r_1 ... \, \mathrm{d}^3r_l \,(\text{sum of all distinct } l\text{-clusters})\ .$$

For example, there is one (trivial) 1-cluster for every vertex, one 2-cluster for any two vertices (also trivially),

$$b_1 = \frac{1}{V} \int \mathrm{d}^3r = 1\ , \qquad b_2 = \frac{1}{2\,\lambda_T^3\, V} \binom{N}{2} \int \mathrm{d}^3r_1\, \mathrm{d}^3r_2\ f(r_{12})\ ,$$

four 3-clusters on any three vertices, many (more than 36) 4-clusters on any four vertices, and so on. Then

$$Z_\mathrm{g} = \sum_{N=0}^{\infty} Z_N\, z^N = \sum_{N=0}^{\infty} \sum_{\{m_l\}}^{*} \prod_l \frac{z^{m_l l}}{m_l!} \Big(\frac{b_l V}{\lambda_T^3}\Big)^{m_l} = \sum_{\{m_l\}} \prod_l \frac{1}{m_l!} \Big(\frac{b_l V z^l}{\lambda_T^3}\Big)^{m_l}$$

$$= \prod_{l=1}^{\infty} \sum_{m_l=0}^{\infty} \frac{1}{m_l!} \Big(\frac{b_l V z^l}{\lambda_T^3}\Big)^{m_l} = \exp\Big\{ \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} b_l\, z^l \Big\}\ ,$$

where m_l is the number of distinct l-clusters in each term, and the $*$ in the first summation stands for the condition $\sum_{l=1}^N l\, m_l = N$.

Thermodynamics

• *Grand potential:* Again from the general expression for Ω in a grand canonical ensemble, we get

$$\Omega = -k_\mathrm{B} T \ln Z_\mathrm{g} = -k_\mathrm{B} T\, \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} b_l\, z^l\ .$$

• *Equation of state:* From the general relations $p = -\Omega/V$ and $\bar{N} = -\partial\Omega/\partial\mu|_{T,V}$ we get

$$p = \frac{k_\mathrm{B} T}{\lambda_T^3} \sum_{l=1}^{\infty} b_l\, z^l \quad \text{and} \quad \rho = \frac{\bar N}{V} = \frac{1}{\lambda_T^3} \sum_{l=1}^{\infty} l\, b_l\, z^l\ ,$$

so, after eliminating z,

$$p = k_\mathrm{B} T \sum_{l=1}^{\infty} a_l\, \lambda_T^{3l-3}\, \rho^l = k_\mathrm{B} T\, (a_1 \rho + a_2\, \lambda_T^3 \rho^2 + ...)\ ,$$

with coefficients a_l that can be calculated; for example, $a_1 = 1$, $a_2 = -b_2$ (so $B_2 = -b_2\, \lambda_T^3$), etc.

Reading

• *References:* Not covered in Kennett's book; Pathria & Beale, Ch 10; Halley, Ch 6; Mattis & Swendsen, §§ 4.5–4.8; Plischke & Bergersen, § 5.1; Reichl, § 6.3; Reif, §§ 10.3–10.5; Schwabl, §§ 5.3–5.4.