General Considerations

• *Idea:* Our goal is to find a systematic way of calculating all virial coefficients. We will use the grand canonical ensemble description of a gas, because the mean values of thermodynamic quantities are essentially the same and the formalism, which relates properties of systems which different numbers of particles, provides a useful tool for calculations.

• *Setup:* We can write the classical grand canonical partition function as

$$Z_{\rm g} = {\rm tr}\, {\rm e}^{-\beta(H-\mu N)} = \sum_{N=0}^{\infty} Z_N\, z^N\ ,$$

where $z := {\rm e}^{\beta\mu}$ is the fugacity, we are using the convention $Z_0 = 1$, and

$$Z_N = {\rm tr}_N\, {\rm e}^{-\beta H_N} = \frac{1}{N!\, h^{3N}} \int {\rm d}^3r_1 ... \,{\rm d}^3r_N\, {\rm d}^3p_1 ... \,{\rm d}^3p_N\, {\rm e}^{-\beta H_N} = \frac{1}{N!\, \lambda^{3N}} \int {\rm d}^3r_1 ... \,{\rm d}^3r_N\, {\rm e}^{-\beta\, \Sigma_{i<j} v_{ij}}\ ,$$

with $\lambda = h/\sqrt{2\pi m k_{\rm B}T}$, is the N-particle canonical partition function, and $v_{ij} \equiv v(y_{ij})$, $\vec y_{ij} = \vec r_i - \vec r_j$.

• *Cluster expansion:* If we define, as before, $f_{ij} := {\rm e}^{-\beta v_{ij}} - 1$, then

$$Z_N = \frac{1}{N!\, \lambda^{3N}} \int {\rm d}^3r_1 ... \,{\rm d}^3r_N \prod_{i<j} (1+f_{ij})\ .$$

The product in the integrand can be expanded as

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

Each term in the right-hand side can be seen as a graph on N vertices, one for each particle, with each f_{ij} factor providing an edge; notice that no two vertices can be connected by more than one edge. Every graph of this type appears exactly once in the sum, with unconnected vertices in each graph contributing just $\int {\rm d}^3r = V$ to the term they are in, so

$$Z_N = \frac{1}{N!\, \lambda^{3N}} \left\{ V^N + V^{N-2} \sum_{i<j} \int {\rm d}^3r_i\, {\rm d}^3r_j\, f_{ij} + (\text{one term for each graph with more than one edge}) \right\},$$

and we need a way of classifying and evaluating the contributions of all graphs. It is convenient to consider sets of l connected vertices, "l-clusters", two of which are considered distinct if their topology and/or vertex labels are different. If we identify each l-cluster with the corresponding product of f_{ij}s, and define

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

[for example, there is one 1-cluster for every vertex (trivially), one 2-cluster for any two vertices (also trivially), four 3-clusters on any three vertices, many (more than 36) 4-clusters on any four vertices, ...] then

$$Z_{\rm g} = \sum_{N=1}^{\infty} \sum_{\{m_l\}}^{*} \prod_l \frac{z^{m_l l}}{m_l!} \Big(\frac{b_l V}{\lambda^3}\Big)^{m_l} = \sum_{\{m_l\}} \prod_l \frac{1}{m_l!} \Big(\frac{b_l V z^l}{\lambda^3}\Big)^{m_l} = \prod_{l=1}^{\infty} \sum_{m_l=0}^{\infty} \frac{1}{m_l!} \Big(\frac{b_l V z^l}{\lambda^3}\Big)^{m_l} = \exp\Big\{ \frac{V}{\lambda^3} \sum_{l=1}^{\infty} b_l\, z^l \Big\}\ ,$$

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

Thermodynamics

• *Grand potential:* From the general definition, $\Omega = -k_{\rm B}T \ln Z_{\rm g} = -k_{\rm B}T\, (V/\lambda^3) \sum_l b_l\, z^l$.

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

$$p = -\frac{k_{\rm B}T}{\lambda^3} \sum_l b_l\, z^l \quad \text{and} \quad \rho = \frac{\bar N}{V} = \frac{1}{\lambda^3} \sum_l l\, b_l\, z^l\ , \qquad \text{so} \qquad p = k_{\rm B}T \sum_{l=1}^{\infty} a_l\, \lambda^{3l-3}\, \rho^l \quad (a_2 = -b_2\ , ...)\ .$$

Relevant Sections: [Phys 731]; Chandler; Halley; Reif; Schwabl.