The Classical Approximation

• *Idea:* From general properties we expect the interparticle potential $v(y)$ to have, and using a suitable approximation, we can draw some conclusions on the general behavior of $B(T)$ in some range of temperatures.
• *Setup:* For a classical gas,

$$Z_N = \frac{1}{N!\,h^{3N}} \int \mathrm{d}^3p_1 ... \mathrm{d}^3p_N \int \mathrm{d}^3r_1 ... \mathrm{d}^3r_N\, \mathrm{e}^{-\beta\,[\Sigma_i\, p_i^2/2m + V(\mathbf{r}_1,...,\mathbf{r}_N)]}$$
$$= \frac{1}{\lambda^{3N} N!} \int \mathrm{d}^3r_1 ... \mathrm{d}^3r_N\, \mathrm{e}^{-\beta V(\mathbf{r}_1,...,\mathbf{r}_N)} = \frac{1}{\lambda^{3N} N!} \int \mathrm{d}^3r_1 ... \mathrm{d}^3r_N\, \mathrm{e}^{-\beta\,\Sigma_{i<j} v_{ij}} .$$

• *Second virial coefficient:* From the general expression for B_2, we find that classically (recall $Z_1 = V/\lambda^3$),

$$Z_2 = \frac{V}{2\lambda^6} \int \mathrm{d}^3y\, \mathrm{e}^{-v_{12}(y)/k_\mathrm{B}T} , \qquad \text{and} \qquad B_2 = -(Z_2 - \tfrac12\, Z_1^2)\, \frac{V}{Z_1^2} = -\tfrac12 \int \mathrm{d}^3y\, f_{12}(y) ,$$

where $f_{12}(y) := \mathrm{e}^{-v(y)/k_\mathrm{B}T} - 1$ is a function that, contrary to $v(y)$, is well-behaved as $y \to 0$. Notice that this last expression for B_2 is the one that will be generalized in the cluster expansion to give all B_n.
• *Qualitative behavior of $B(T)$:* To proceed, we need to know something about $v(y)$. Let's assume that it has an infinite potential wall $v_\mathrm{HC}(y)$ at $y = y_0$, and a weakly attractive form for $y > y_0$. Then (⋆ plot)

$$f(y) = \begin{cases} -1 & \text{for } |y| < y_0 \\ -v(y)/k_\mathrm{B}T & \text{for } y > y_0 \end{cases} , \qquad \text{and} \qquad B(T) \approx -\tfrac12 \left[-\frac{4\pi}{3}\, y_0^3 + 4\pi \int_0^\infty \mathrm{d}y\, y^2\, \frac{v(y)}{k_\mathrm{B}T} \right] = b - \frac{a}{k_\mathrm{B}T} ,$$

where b is proportional to the molecular volume, and a arises from the attractive part of the potential.

Application to the Lennard-Jones Potential

• *Idea:* Use the phenomenological expression, that approximates well the measured potential for some gases,

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

• *Second virial coefficient:* Substituting into the general expression, and defining $r^* := r/\sigma$, $T^* := k_\mathrm{B}T/\epsilon$,

$$B = -\tfrac12 \int \mathrm{d}^3y\, \big(\mathrm{e}^{-\beta v(y)} - 1\big) = \frac{2\pi}{3}\, \sigma^3\, \frac{4}{T^*} \int \mathrm{d}r^*\, r^{*2} \Big(\frac{12}{r^{*12}} - \frac{6}{r^{*6}} \Big)\, \mathrm{e}^{-4(r^{*-12} - r^{*-6})/T^*}$$
$$= \frac{2\pi}{3}\, \sigma^3 \Big(\frac{1.73}{T^{*1/4}} - \frac{2.56}{T^{*3/4}} - \frac{0.87}{T^{*5/4}} - ... \Big)$$

where we have integrated by parts in the second step.

Derivation of the van der Waals Equation of State

• *Idea:* We will apply a different kind of approximation, the mean-field approximation in which correlations between particles are ignored, and derive a common form for the equation of state for a dilute gas.
• *Setup:* Assume that the interparticle potential energy is of the form $v(y) = v_\mathrm{HC}(y) + w(y)$, where the hard-core term v_HC is infinite for $y < y_0$, and w is regular. We want to get the equation of state from

$$Z = \frac{1}{\lambda^{3N} N!} \int \mathrm{d}^3x_1 ... \mathrm{d}^3x_N\, \mathrm{e}^{-\beta\,\Sigma_{i<j} vij} .$$

• *Mean-field approximation:* The mean field felt by the j-th particle due to the remaining $N-1$ particles is

$$\textstyle\sum_{i\neq j} w(y_{ij}) \approx (N-1)\, \frac{1}{V} \int \mathrm{d}^3x\, w(x) = (N-1)\, \bar w , \qquad \text{so} \qquad \sum_{j,\, i<j} w(y_{ij}) \approx \frac12\, N^2\, \bar w ,$$

and, if we define the parameter a by $\bar w =: 2a/V$,

$$Z \approx \frac{1}{\lambda^{3N} N!} \int_{y_{ij} > y_0} \mathrm{d}^3r_1 ... \mathrm{d}^3r_N\, \mathrm{e}^{-\beta N^2 \bar w/2} \approx \frac{(V - V_0)^N}{\lambda^{3N} N!}\, \mathrm{e}^{N^2 a/V k_\mathrm{B}T} ,$$

where $V_0 = (N-1)\, b$, and $b := \frac43\, \pi y_0^3$ is the effective volume of each molecule.
• *Equation of state:* From the free energy is $F = -k_\mathrm{B}T \ln Z = -N k_\mathrm{B}T \ln(V - V_0)/\lambda^3 + k_\mathrm{B}T \ln N! - N^2 a/V$,

$$p = -\frac{\partial F}{\partial V}\Big|_{T,N} = \frac{N k_\mathrm{B}T}{V - V_0} + \frac{N^2 a}{V^2} , \qquad \text{or} \qquad p = \frac{k_\mathrm{B}T}{v - b} - \frac{a}{v^2} \qquad (v := V/N) .$$

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