Non-Ideal Gases. 1: Two General Approaches

• *The system:* Consider a gas whose pressure equation of state departs from $pV = Nk_{\mathrm{B}}T$ because its Hamiltonian includes pairwise interaction potential terms of the form $\phi_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \phi(|\mathbf{r}_i - \mathbf{r}_j|)$, where $\phi(r)$ has a strongly repulsive short-range behavior and a weakly attractive one for large values of r,

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + U(\mathbf{r}) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \sum_{i<j} \phi_{ij}(\mathbf{r}_i, \mathbf{r}_j) \, .$$

We will develop two general approaches to calculating approximate equations of state for this gas.

A. Mean-Field Derivation of the van der Waals Equation of State

• *Idea:* The mean-field approximation is a pretty crude one in which fluctuations and correlations between particles are ignored, but it allows us to take into account some qualitative features of non-ideal gases and to derive the equation of state for the van der Waals fluid, a commonly used model for a dilute gas.

• *Setup:* Assume that the interparticle potential energy can be thought of as the sum of two terms,

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

where the hard-core term ϕ_{hc} is infinite for $r < r_0$, and ϕ_{lr} is a regular (negative) function. This models potentials of the Lennard-Jones form, for example. The equation of state can be obtained from

$$Z_N = \frac{\zeta^N}{\lambda_T^{3N} N!} \int \mathrm{d}^{3N} r \, \mathrm{e}^{-\beta \Sigma_{i<j} \phi(r_{ij})} \, .$$

where ζ is any applicable part of the partition function that does not depend on r (for example, $\zeta = g_s$).

• *Mean field:* On average, the field felt by the j-th particle due to its interactions with the remaining ones is

$$\sum_{i \neq j} \phi_{\mathrm{lr}}(r_{ij}) \approx (N-1) \frac{1}{V} \int \mathrm{d}^3 r \, \phi_{\mathrm{lr}}(r) = (N-1) \, \bar{\phi}_{\mathrm{lr}} \, , \qquad \text{so} \qquad \sum_{j, \, i<j} \phi_{\mathrm{lr}}(r_{ij}) \approx \tfrac{1}{2} \, N^2 \, \bar{\phi}_{\mathrm{lr}} \, .$$

This means that the N-particle partition function can be approximated by (setting $\zeta = 1$ here)

$$Z_N \approx \frac{1}{\lambda_T^{3N} N!} \Big(\int_{r_{ij} > r_0} \mathrm{d}^{3N} r \Big) \mathrm{e}^{-\beta N^2 \bar{\phi}_{\mathrm{lr}}/2} \approx \frac{(V - Nb)^N}{\lambda_T^{3N} N!} \, \mathrm{e}^{\beta a N^2/V} \, ,$$

where the (positive) parameter a defined by $\bar{\phi}_{\mathrm{lr}} =: -2a/V$ summarizes the effect of the weakly attractive potential, and $b := \frac{4}{3}\pi r_0^3$ is the effective volume of each molecule.

• *Equation of state:* The Helmholtz free energy and the pressure are then obtained as usual,

$$F = -k_{\mathrm{B}}T \ln Z = -N k_{\mathrm{B}}T \ln \frac{V - Nb}{\lambda_T^3} + k_{\mathrm{B}}T \ln N! - \frac{aN^2}{V} \, , \qquad p = -\frac{\partial F}{\partial V}\Big|_{T,N} = \frac{N k_{\mathrm{B}}T}{V - Nb} - \frac{aN^2}{V^2} \, .$$

This is the van der Waals equation of state.

• *Mean energy:* Starting from this microscopic model and the partition function we can also find the remaining equations of state for thi non-ideal gas, such as the mean energy,

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z_N = -\frac{\partial}{\partial \beta} \ln \left[\frac{(V - Nb)^N}{\lambda_T^{3N} N!} \, \mathrm{e}^{\beta a N^2/V} \right] = \frac{\partial}{\partial \beta} \Big(3N \ln \lambda_T - \frac{\beta a N^2}{V} \Big) = \tfrac{3}{2} N \, k_{\mathrm{B}}T - \frac{aN^2}{V} \, ,$$

where we have used the fact that $\lambda_T = (h^2 \beta / 2\pi m)^{1/2}$. In Kennett's notation the thermal wavelength cn be replaced by $\lambda_T^{-3} =: n_{\mathrm{Q}}$, the quantum density. [⋆ Find the entropy S and chemical potential μ.]

B. Systematic Calculation of the Virial Coefficients

● *Idea:* One limitation of the mean-field approximation is that it does not indicate directly what steps one can take to improve upon it taking correlations into account. We will therefore develop a different procedure for systematically calculating the virial coefficients for a non-ideal gas.

● *Approach:* In weakly interacting gases we can think of the departures from ideal gas behavior as arising gradually, with increasing number density, from interactions among increasingly larger subsets of particles. We then start with the grand canonical partition function, which is a useful tool for relating effects arising from interactions among subsets of the N particles, even if we think of N as fixed.

● *Setup:* We can write down the classical grand canonical $Z_{\mathrm{g}} = \mathrm{tr}\, e^{-\beta(H-\mu N)}$ as

$$Z_{\mathrm{g}} = \sum_{N=0}^{\infty} Z_N\, z^N , \quad \text{with} \quad Z_N = \mathrm{tr}_N\, e^{-\beta H} = \frac{1}{N!\, h^{3N}} \int \mathrm{d}^{3N}r \int \mathrm{d}^{3N}p\, e^{-\beta H} = \frac{1}{N!\, \lambda_T^{3N}} \int \mathrm{d}^{3N}r\, e^{-\beta U(\mathbf{r})},$$

where $z := e^{\beta\mu}$ is the fugacity, and we are using the convention that $Z_0 = 1$. Notice that $Z_1 = V/\lambda_T^3$, so N/Z_1 equals the degeneracy discriminant or classicality parameter $\delta := \rho\,\lambda_T^3 = N/Z_1$ for the gas. Our first goal is to calculate the configuration integral in the expression for $Z_N(V,T)$ above.

● *Grand potential:* From the general expression for $\Omega = E - TS - \mu N$, and using $\ln(1+x) = x - \frac{1}{2}\,x^2 + \frac{1}{3}\,x^3 - ...$,

$$\Omega = -k_{\mathrm{B}}T \ln Z_{\mathrm{g}} = -k_{\mathrm{B}}T \ln(1 + Z_1 z + Z_2 z^2 + ...) = -k_{\mathrm{B}}T \left[Z_1 z + (Z_2 - \tfrac{1}{2} Z_1^2)\, z^2 + ... \right] .$$

● *Chemical potential:* Many expressions obtained from Z_{g} will contain z or μ. To replace that dependence with one on $\bar{N}$, identified with the known, fixed N, we find the relationship between z and $\bar{N}$. Start from

$$\bar{N} = -\frac{\partial\Omega}{\partial\mu}\bigg|_{T,V} = -\beta z\, \frac{\partial\Omega}{\partial z}\bigg|_{T,V} = Z_1 z + 2\,(Z_2 - \tfrac{1}{2} Z_1^2)\, z^2 + ...$$

Setting $\bar{N} = N$ and solving this equation iteratively for z (this works because $\delta = N/Z_1 = \rho\,\lambda_T^3 \ll 1$) gives

$$z = \frac{N}{Z_1} - \frac{2\,(Z_2 - Z_1^2/2)}{Z_1} \left(\frac{N}{Z_1}\right)^2 + ... , \qquad \text{and therefore} \qquad \Omega = -k_{\mathrm{B}}T \left[N - (Z_2 - \tfrac{1}{2} Z_1^2)\, \frac{N^2}{Z_1^2} + ... \right] .$$

● *Virial coefficients:* Calculating p as $-\partial\Omega/\partial V|_{T,\mu}$ is made complicated in this case by the dependence of Z_1 and (especially) Z_2 on V. However, using the fact that $\Omega = \bar{E} - TS - \mu N = -pV$, we find

$$p = -\frac{\Omega}{V} = \frac{k_{\mathrm{B}}T}{V} \left[N - (Z_2 - \tfrac{1}{2} Z_1^2)\, \frac{N^2}{Z_1^2} + ... \right] = k_{\mathrm{B}}T\rho\,[1 + B(T)\,\rho + ...] ,$$

which means that the second virial coefficient (both in the classical and in the quantum theory) is given by

$$B = -(Z_2 - \tfrac{1}{2} Z_1^2)\, \frac{V}{Z_1^2} .$$

Thus, for $B(T)$ one needs to take into account only the two-particle configuration integral, reflecting the fact that as the density grows the first corrections to the pressure will come from small sets of particles that are close enough to each other to feel the effects of $\phi(r)$. In order to calculate $B(T)$ in specific examples, therefore, the main task will be to find Z_2.

Reading

● *Kennett:* Section 4.6; *Pathria & Beale:* Chapter 10.

● *Other textbooks:* Halley, Ch 6; Mattis & Swendsen, §§ 4.7–4.8;
Plischke & Bergersen, § 5.1; Reif, §§ 10.3–10.5; Schwabl, § 5.4.