

General Considerations

• *The system:* Consider a gas of N pointlike particles interacting with each other with short-range pairwise potential energies $v_{ij}(\mathbf{r}_i, \mathbf{r}_j)$, in a box of volume V in equilibrium at temperature T . The Hamiltonian is

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

• *Goal:* We want to find a systematic way of expressing deviations of the behavior of the gas from the ideal gas law. Since those deviations arise when particles spend enough time close to each other to feel the effect of the interparticle potentials v_{ij} , this will lead to a power series expansion in the density, of the form

$$p = k_B T \rho [1 + B_2(T) \rho + B_3(T) \rho^2 + \dots],$$

where $\rho = N/V$ and B_i is the i -th virial coefficient. At low densities, we only need to take the first few terms into account; in particular, we want to know how to estimate the first correction term, $B_2(T) = B(T)$.

• *Setup:* We can write down the classical grand canonical partition function $Z_g = \text{tr} e^{-\beta(H-\mu N)}$ as

$$Z_g = \sum_{N=0}^{\infty} Z_N z^N, \quad \text{with} \quad Z_N = \text{tr}_N e^{-\beta H_N} = \frac{1}{N! h^{3N}} \int d^3 r_1 \dots d^3 r_N \int d^3 p_1 \dots d^3 p_N e^{-\beta H_N},$$

where $z := e^{\beta\mu}$ is the fugacity, and we are using the convention $Z_0 = 1$. Notice also that $Z_1 = \zeta_{\text{free}} = V/\lambda^3$.

The Virial Expansion

• *Setup:* Start with the grand canonical partition function, not because we are really interested in a system in which the particle number may vary, but because it provides a useful tool to relate effects arising from interaction among subsets of the N particles.

• *Grand potential:* From the general relationship (using the expansion $\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \dots$),

$$\begin{aligned} \Omega &= -k_B T \ln Z_g = -k_B T \ln(1 + Z_1 z + Z_2 z^2 + \dots) \\ &= -k_B T (Z_1 z + Z_2 z^2 - \frac{1}{2} Z_1^2 z^2 + \dots) = -k_B T [Z_1 z + (Z_2 - \frac{1}{2} Z_1^2) z^2 + \dots]. \end{aligned}$$

• *Chemical potential:* Many expressions obtained from Z_g will contain z or μ . To replace that dependence with one on \bar{N} , which we can identify with the known N , we find the relationship between them. Start from

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

Solving this equation iteratively for z gives

$$z = \frac{\bar{N}}{Z_1} - \frac{2(Z_2 - Z_1^2/2)}{Z_1} \left(\frac{\bar{N}}{Z_1} \right)^2 + \dots$$

• *Virial coefficients:* Plugging z into Ω we get

$$\Omega = -k_B T \left[\bar{N} - (Z_2 - \frac{1}{2} Z_1^2) \frac{\bar{N}^2}{Z_1^2} + \dots \right],$$

and, using this expression in $\Omega = \bar{E} - TS - \mu N = pV$,

$$p = \frac{k_B T}{V} \left[\bar{N} - (Z_2 - \frac{1}{2} Z_1^2) \frac{\bar{N}^2}{Z_1^2} + \dots \right] = k_B T \rho [1 + B(T) \rho + \dots],$$

which means that the second virial coefficient, in classical and quantum theory, can be calculated from

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

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