Interacting Particles

1. *Debye–Hückel theory and Ring Diagrams:* The virial expansion gives the gas pressure as an *analytic* expansion in the density $n = N/V$. Long range interactions can result in *non-analytic* corrections to the ideal gas equation of state. A classic example is the Coulomb interaction in plasmas, whose treatment by Debye–Hückel theory is equivalent to summing all the *ring diagrams* in a cumulant expansion.

For simplicity consider a gas of N electrons moving in a uniform background of positive charge density Ne/V to ensure overall charge neutrality. The Coulomb interaction takes the form

$$\mathcal{U}_Q = \sum_{i<j} \mathcal{V}(\vec{q}_i - \vec{q}_j)\,, \quad \text{with} \quad \mathcal{V}(\vec{q}\,) = \frac{e^2}{4\pi|\vec{q}\,|} - c\,.$$

The constant c results from the background and ensures that the first order correction vanishes, i.e. $\int d^3\vec{q}\,\mathcal{V}(\vec{q}\,) = 0$. The Fourier transform of $\mathcal{V}(\vec{q}\,)$ is singular at the origin, and takes the form

$$\tilde{\mathcal{V}}(\vec{\omega}\,) = \begin{cases} e^2/\omega^2 & \text{for } \vec{\omega} \neq 0 \\ 0 & \text{for } \vec{\omega} = 0 \end{cases}\,.$$

(a) In the cumulant expansion for $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$, we shall retain only the diagrams forming a ring; which are proportional to

$$R_\ell = \int \frac{d^3\vec{q}_1}{V} \cdots \frac{d^3\vec{q}_\ell}{V}\, \mathcal{V}(\vec{q}_1 - \vec{q}_2)\mathcal{V}(\vec{q}_2 - \vec{q}_3)\cdots\mathcal{V}(\vec{q}_\ell - \vec{q}_1).$$

Use properties of Fourier transforms to show that

$$R_\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3\vec{\omega}}{(2\pi)^3}\, \tilde{\mathcal{V}}(\vec{\omega})^\ell.$$

(b) Show that the number of ring graphs generated in $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$ is

$$S_\ell = \frac{N!}{(N-\ell)!} \times \frac{(\ell-1)!}{2} \approx \frac{(\ell-1)!}{2} N^\ell\,.$$

(c) Show that the contribution of the ring diagrams can be summed as

$$\begin{aligned}\ln Z_{\text{rings}} &= \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{(-\beta)^\ell}{\ell!} S_\ell R_\ell \\ &\approx \ln Z_0 + \frac{V}{2}\int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\left(\frac{\kappa}{\omega}\right)^2 - \ln\left(1 + \frac{\kappa^2}{\omega^2}\right)\right],\end{aligned}$$

where $\kappa = \sqrt{\beta e^2 N/V}$ is the inverse Debye screening length.
(*Hint:* Use $\ln(1+x) = -\sum_{\ell=1}^{\infty}(-x)^\ell/\ell$.)

(d) The integral in part (c) can be simplified by changing variables to $x = \kappa/\omega$, and performing integration by parts. Show that the final result is

$$\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{12\pi}\kappa^3 \quad .$$

(e) Calculate the correction to pressure from the above ring diagrams.

(f) We can introduce an effective potential $\overline{V}(\vec{q}-\vec{q}\,')$ between two particles by integrating over the coordinates of all the other particles. This is equivalent to an expectation value that can be calculated perturbatively in a cumulant expansion. If we include only the loop-less diagrams (the analog of the rings) between the particles, we have

$$\overline{V}(\vec{q}-\vec{q}\,') = V(\vec{q}-\vec{q}\,') + \sum_{\ell=1}^{\infty}(-\beta N)^\ell \int \frac{d^3\vec{q}_1}{V}\cdots\frac{d^3\vec{q}_\ell}{V}\,\mathcal{V}(\vec{q}-\vec{q}_1)\mathcal{V}(\vec{q}_1-\vec{q}_2)\cdots\mathcal{V}(\vec{q}_\ell-\vec{q}\,').$$

Show that this sum leads to the screened Coulomb interaction $\overline{V}(\vec{q}) = \exp(-\kappa|\vec{q}\,|)/(4\pi|\vec{q}\,|)$.

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2. *Virial Coefficients:* Consider a gas of particles in d-dimensional space interacting through a pair-wise central potential, $\mathcal{V}(r)$, where

$$\mathcal{V}(r) = \begin{cases} +\infty & \text{for } 0 < r < a, \\ -\varepsilon & \text{for } a < r < b, \\ 0 & \text{for } b < r < \infty. \end{cases}$$

(a) Calculate the second virial coefficient $B_2(T)$, and comment on its high and low temperature behaviors.

(b) Calculate the first correction to isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_{T,N} .$$

(c) In the high temperature limit, reorganize the equation of state into the van der Waals form, and identify the van der Waals parameters.

(d) **(Optional)** For $b = a$ (a hard sphere), and $d = 1$, calculate the third virial coefficient $B_3(T)$.

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Suggested Reading: Landau & Lifshitz, chapter 7; Huang, chapter 10; Balescu, chapter 6.