Interacting Particles

1. *Debye–Hückel theory and Ring Diagrams:* Consider a gas of N electrons moving in a uniform background of positive charge density Ne/V. The Coulomb interaction is

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

The constant c represents the attraction to the positively charged background, and satisfies $\int d^3\vec{q}\,\mathcal{V}(\vec{q}\,) = 0$, from the condition of overall neutrality. The Fourier transform of $\mathcal{V}(\vec{q}\,)$ is singular at the origin, and can be defined explicitly as

$$\tilde{\mathcal{V}}(\vec{\omega}) = \lim_{\varepsilon\to 0} \int d^3\vec{q}\,\mathcal{V}(\vec{q}\,) e^{i\vec{\omega}\cdot\vec{q} - \varepsilon q},$$

which is then given by

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

Proof: The result at $\vec{\omega} = 0$ follows immediately from the definition of c. For $\vec{\omega} \neq 0$,

$$\begin{aligned}
\tilde{\mathcal{V}}(\vec{\omega}) &= \lim_{\varepsilon\to 0} \int d^3\vec{q} \left(\frac{e^2}{4\pi q} - c\right) e^{i\vec{\omega}\cdot\vec{q} - \varepsilon q} = \lim_{\varepsilon\to 0} \int d^3\vec{q} \left(\frac{e^2}{4\pi q}\right) e^{i\vec{\omega}\cdot\vec{q} - \varepsilon q} \\
&= \lim_{\varepsilon\to 0} \left[2\pi \int_0^\pi \sin\theta d\theta \int_0^\infty q^2 dq \left(\frac{e^2}{4\pi q}\right) e^{i\omega q\cos\theta - \varepsilon q}\right] \\
&= -\frac{e^2}{2} \int_0^\infty \frac{e^{i\omega q - \varepsilon q} - e^{-i\omega q - \varepsilon q}}{i\omega} dq \\
&= \lim_{\varepsilon\to 0} \frac{e^2}{2i\omega} \left(\frac{1}{i\omega - \varepsilon} + \frac{1}{i\omega + \varepsilon}\right) = \lim_{\varepsilon\to 0} \left(\frac{e^2}{\omega^2 + \varepsilon^2}\right) = \frac{e^2}{\omega^2}.
\end{aligned}$$

(a) In the cumulant expansion for $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$, we retain only the diagrams forming a ring. The contribution of these diagrams to the partition function is

$$\begin{aligned}
R_\ell &= \int \frac{d^3\vec{q}_1}{V} \frac{d^3\vec{q}_2}{V} \cdots \frac{d^3\vec{q}_\ell}{V} \mathcal{V}(\vec{q}_1 - \vec{q}_2)\mathcal{V}(\vec{q}_2 - \vec{q}_3) \cdots \mathcal{V}(\vec{q}_\ell - \vec{q}_1) \\
&= \frac{1}{V^\ell} \int \cdots \int d^3\vec{x}_1 d^3\vec{x}_2 \cdots d^3\vec{x}_{\ell-1} d^3\vec{q}_\ell \mathcal{V}(\vec{x}_1)\mathcal{V}(\vec{x}_2) \cdots \mathcal{V}(\vec{x}_{\ell-1}) \mathcal{V}\left(-\sum_{i=1}^{\ell-1} \vec{x}_i\right),
\end{aligned}$$

where we introduced the new set of variables $\{\vec{x}_i \equiv \vec{q}_i - \vec{q}_{i+1}\}$, for $i = 1, 2, \cdots, \ell - 1$. Note that since the integrand is independent of $\vec{q}_\ell$,

$$R_\ell = \frac{1}{V^{\ell-1}} \int \cdots \int d^3\vec{x}_1 d^3\vec{x}_2 \cdots d^3\vec{x}_{\ell-1} \mathcal{V}(\vec{x}_1)\mathcal{V}(\vec{x}_2) \cdots \mathcal{V}\left(-\sum_{i=1}^{\ell-1} \vec{x}_i\right).$$

Using the inverse Fourier transform

$$\mathcal{V}(\vec{q}) = \frac{1}{(2\pi)^3} \int d^3\vec{\omega} \cdot \tilde{\mathcal{V}}(\vec{\omega}) e^{-i\vec{q}\cdot\vec{\omega}},$$

the integral becomes

$$R_\ell = \frac{1}{(2\pi)^{3\ell} V^{\ell-1}} \int \cdots \int d^3\vec{x}_1 \cdots d^3\vec{x}_{\ell-1} \tilde{\mathcal{V}}(\vec{\omega}_1) e^{-i\vec{\omega}_1\cdot\vec{x}_1} \tilde{\mathcal{V}}(\vec{\omega}_2) e^{-i\vec{\omega}_2\cdot\vec{x}_2}$$

$$\cdots \tilde{\mathcal{V}}(\vec{\omega}_\ell) \exp\left(-i \sum_{k=1}^{\ell-1} \vec{\omega}_\ell \cdot \vec{x}_k\right) d^3\vec{\omega}_1 \cdots d^3\vec{\omega}_\ell.$$

Since

$$\int \frac{d^3\vec{q}}{(2\pi)^3} e^{-i\vec{\omega}\cdot\vec{q}} = \delta^3(\vec{\omega}\,),$$

we have

$$R_\ell = \frac{1}{(2\pi)^3 V^{\ell-1}} \int \cdots \int \left(\prod_{k=1}^{\ell-1} \delta(\vec{\omega}_k - \vec{\omega}_\ell) \tilde{\mathcal{V}}(\vec{\omega}_k) d^3\vec{\omega}_k \right) d^3\vec{\omega}_\ell,$$

resulting finally in

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

(b) The number of rings graphs generated in $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$ is given by the product of the number of ways to choose ℓ electrons out of a total of N,

$$\frac{N!}{(N-\ell)!}.$$

multiplied by the number of ways to arrange the ℓ electrons in a ring

$$\frac{\ell!}{2\ell}.$$

The numerator is the number of ways of distributing the ℓ labels on the ℓ points of the ring. This overcounts by the number of equivalent arrangements that appear in the denominator. The factor of $1/2$ comes from the equivalence of clockwise and counterclockwise arrangements (reflection), and there are ℓ equivalent choices for the starting point of the ring (rotations). Hence

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

For $N \gg \ell$, we can approximate $N(N-1)\cdots(N-\ell+1) \approx N^\ell$, and

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

Another way to justify this result is by induction: A ring of length $\ell + 1$ can be created from a ring of ℓ links by inserting an additional point in between any of the existing ℓ nodes. Hence $S_{\ell+1} = S_\ell \times (N - \ell - 1) \times \ell$, leading to the above result, when starting with $S_2 = N(N-1)/2$.

(c) The contribution of the ring diagrams is summed as

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

where we have used $\ln(1+x) = -\sum_{\ell=1}^{\infty}(-x)^\ell/\ell$. Finally, substituting $\kappa = \sqrt{\beta e^2 N/V}$, leads to

$$\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{2} \int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\left(\frac{\kappa}{\omega}\right)^2 - \ln\left(1 + \frac{\kappa^2}{\omega^2}\right) \right].$$

(d) Changing variables to $x = \kappa/\omega$, and integrating the integrand by parts, gives

$$\begin{aligned}
\int_0^\infty \omega^2 d\omega \left[\left(\frac{\kappa}{\omega}\right)^2 - \ln\left(1 + \frac{\kappa^2}{\omega^2}\right) \right] &= \kappa^3 \int_0^\infty \frac{dx}{x^4} \left[x^2 - \ln(1+x^2)\right] \\
= \frac{\kappa^3}{3} \int_0^\infty \frac{dx}{x^3} \left[2x - \frac{2x}{1+x^2} \right] &= \frac{2\kappa^3}{3} \int_0^\infty \frac{dx}{1+x^2} = \frac{\pi\kappa^3}{3},
\end{aligned}$$

resulting in

$$\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{4\pi^2} \cdot \frac{\pi\kappa^3}{3} = \ln Z_0 + \frac{V}{12\pi}\kappa^3.$$

(e) The correction to the ideal gas pressure due to the Debye–Hückel approximation is

$$\begin{aligned}
P &= k_B T \left(\left. \frac{\partial \ln Z_{\text{rings}}}{\partial V} \right|_{T,N} \right) \\
&= P_0 + k_B T \frac{\partial}{\partial V} \left. \left(\frac{V\kappa^3}{12\pi} \right) \right|_{T,N} = P_0 - \frac{k_B T}{24\pi}\kappa^3 \\
&= P_0 - \frac{k_B T}{24\pi} \left(\frac{e^2 N}{k_B T V} \right)^{3/2}.
\end{aligned}$$

Note that the correction to the ideal gas behavior is non-analytic, and cannot be expressed by a virial series. This is due to the long range nature of the Coulomb interaction.

(f) Introducing the effective potential $\overline{\mathcal{V}}(\vec{q}-\vec{q}\,')$, and summing over the loop–less diagrams gives

$$\begin{aligned}\overline{\mathcal{V}}(\vec{q}-\vec{q}\,') &= \mathcal{V}(\vec{q}-\vec{q}\,') + \sum_{\ell=1}^{\infty}(-\beta N)^{\ell}\int\frac{d^3\vec{q}_1}{V}\cdots\frac{d^3\vec{q}_\ell}{V}\mathcal{V}(\vec{q}-\vec{q}_1)\mathcal{V}(\vec{q}_1-\vec{q}_2)\cdots\mathcal{V}(\vec{q}_\ell-\vec{q}\,')\\ &= \mathcal{V}(\vec{q}-\vec{q}\,') - \beta N\int\frac{d^3\vec{q}_1}{V}\mathcal{V}(\vec{q}-\vec{q}_1)\mathcal{V}(\vec{q}_1-\vec{q}\,')\\ &\quad + (\beta N)^2\int\frac{d^3\vec{q}_1}{V}\frac{d^3\vec{q}_2}{V}\mathcal{V}(\vec{q}-\vec{q}_1)\mathcal{V}(\vec{q}_1-\vec{q}_2)\mathcal{V}(\vec{q}_2-\vec{q}\,') - \cdots .\end{aligned}$$

Using the changes of notation

$$\begin{aligned}&\vec{x}_1\equiv\vec{q}, \quad \vec{x}_2\equiv\vec{q}\,', \quad \vec{x}_3\equiv\vec{q}_1, \quad \vec{x}_4\equiv\vec{q}_2, \quad \cdots \quad \vec{x}_\ell\equiv\vec{q}_\ell,\\ &\mathcal{V}_{12}\equiv\mathcal{V}(\vec{x}_1-\vec{x}_2), \qquad \text{and} \qquad n\equiv N/V,\end{aligned}$$

we can write

$$\overline{\mathcal{V}}_{12} = \mathcal{V}_{12} - \beta n\int d^3\vec{x}_3\mathcal{V}_{13}\mathcal{V}_{32} + (\beta n)^2\int d^3\vec{x}_3 d^3\vec{x}_4\mathcal{V}_{13}\mathcal{V}_{34}\mathcal{V}_{42} - \cdots .$$

Using the inverse Fourier transform (as in part (a)), and the notation $\vec{x}_{ij}\equiv\vec{x}_i-\vec{x}_j$,

$$\overline{\mathcal{V}}_{12} = \mathcal{V}_{12} - \beta n\int\frac{d^3\vec{x}_3}{(2\pi)^6}\tilde{\mathcal{V}}(\vec{\omega}_{13})\tilde{\mathcal{V}}(\vec{\omega}_{32})e^{-i(\vec{x}_{13}\cdot\vec{\omega}_{13}+\vec{x}_{32}\cdot\vec{\omega}_{32})}d^3\vec{\omega}_{13}d^3\vec{\omega}_{32} + \cdots ,$$

and employing the delta function, as in part (a)

$$\begin{aligned}\overline{\mathcal{V}}_{12} &= \mathcal{V}_{12} - \beta n\int\frac{d^3\vec{\omega}_{13}d^3\vec{\omega}_{32}}{(2\pi)^3}\delta^3\left(\vec{\omega}_{13}-\vec{\omega}_{32}\right)\tilde{\mathcal{V}}(\vec{\omega}_{13})\tilde{\mathcal{V}}(\vec{\omega}_{32})\exp[\vec{x}_1\cdot\vec{\omega}_{13}-\vec{x}_2\cdot\vec{\omega}_{32}] + \cdots\\ &= \mathcal{V}_{12} - \beta n\int\frac{d^3\vec{\omega}}{(2\pi)^3}\left[\tilde{\mathcal{V}}(\vec{\omega})\right]^2\exp[\vec{\omega}\cdot\vec{x}_{12}] + \cdots .\end{aligned}$$

Generalizing this result and dropping the subscript such that $\vec{x}\equiv\vec{x}_{12}$,

$$\overline{\mathcal{V}}_{12} = \mathcal{V}_{12} + \sum_{\ell=1}^{\infty}\frac{(-\beta n)^{\ell}}{(2\pi)^3}\int\left[\tilde{\mathcal{V}}(\vec{\omega})\right]^{\ell+1}e^{i\vec{x}\cdot\vec{\omega}}d^3\vec{\omega}.$$

Finally, including the Fourier transform of the direct potential (first term), gives

$$\begin{aligned}\overline{\mathcal{V}}_{12} &= \sum_{\ell=0}^{\infty}\int\frac{d^3\vec{\omega}}{(2\pi)^3}(-\beta n)^{\ell}\frac{e^{2\ell+2}}{\omega^{2\ell+2}}e^{i\vec{x}\cdot\vec{\omega}} = \sum_{\ell=0}^{\infty}\int\frac{d^3\vec{\omega}}{(2\pi)^3}\frac{(-1)^{\ell}e^2\kappa^{2\ell}}{\omega^{2\ell+2}}e^{ix\omega\cos\theta}\\ &= \int_0^{\infty}d\omega\sum_{\ell=0}^{\infty}\frac{(-1)^{\ell}e^2}{2\pi^2}\left(\frac{\kappa}{\omega}\right)^{2\ell}\int_{-1}^{1}e^{ix\omega\cos\theta}d\cos\theta\\ &= \int_0^{\infty}d\omega\frac{e^2}{2\pi^2}\frac{2\sin x\omega}{x\omega}\sum_{\ell=0}^{\infty}(-1)^{\ell}\left(\frac{\kappa}{\omega}\right)^{2\ell}.\end{aligned}$$

Setting $y \equiv \omega/\kappa$, gives

$$\overline{\mathcal{V}}_{12} = \frac{1}{2}\int_{-\infty}^{\infty} \frac{e^2}{2\pi^2}\kappa \frac{e^{ix\kappa y} - e^{-ix\kappa y}}{2ix\kappa y} \frac{-1}{y^2+1} dy.$$

Intergrating in the complex plane, via the residue theorem, gives

$$\overline{\mathcal{V}}_{12} = \frac{e^2}{4\pi^2}\left(\frac{e^{-\kappa x}}{2x} + \frac{e^{-\kappa x}}{2x}\right)\cdot \pi = \frac{e^2 e^{-\kappa x}}{4\pi x}.$$

Recalling our original notation, $x = |\vec{q} - \vec{q}\,'| \equiv |\vec{q}|$, we obtain the screened Coulomb potential

$$\overline{\mathcal{V}}(\vec{q}) = \frac{e^2}{4\pi}\frac{e^{-\kappa|\vec{q}|}}{|\vec{q}|}.$$

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

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

(a) The second virial coefficient is obtained from

$$B_2 \equiv -\frac{1}{2}\int d^d r_{12}\left\{\exp[-\beta\mathcal{V}(r_{12})] - 1\right\},$$

where $r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$, as

$$\begin{aligned} B_2 &= -\frac{1}{2}\left[\int_0^a d^d r_{12}(-1) + \int_a^b d^d r_{12}\left(e^{\beta\varepsilon} - 1\right)\right] \\ &= -\frac{1}{2}\left\{V_d(a)(-1) + [V_d(b) - V_d(a)]\cdot[\exp(\beta\varepsilon) - 1]\right\}, \end{aligned}$$

where

$$V_d(r) = \frac{S_d}{d} r^d = \frac{2\pi^{d/2}}{d\,(d/2-1)!}\, r^d,$$

is the volume of a d–dimensional sphere of radius r. Thus,

$$B_2(T) = \frac{1}{2}V_d(b) - \frac{1}{2}\exp(\beta\varepsilon)\left[V_d(b) - V_d(a)\right].$$

For high temperatures $\exp(\beta\varepsilon) \approx 1 + \beta\varepsilon$, and

$$B_2(T) \approx \frac{1}{2}V_d(a) - \frac{\beta\varepsilon}{2}\left[V_d(b) - V_d(a)\right].$$

At the highest temperatures, $\beta\varepsilon \ll 1$, the hard-core part of the potential is dominant, and

$$B_2(T) \approx \frac{1}{2}V_d(a).$$

For low temperatures $\beta \gg 1$, the attractive component takes over, and

$$\begin{aligned} B_2 &= -\frac{1}{2}\left\{V_d(a)(-1) + \left[V_d(b) - V_d(a)\right] \cdot \left[\exp(\beta\varepsilon) - 1\right]\right\} \\ &\approx -\frac{1}{2}\left[V_d(b) - V_d(a)\right]\exp(\beta\varepsilon), \end{aligned}$$

resulting in $B_2 < 0$.

(b) The isothermal compressibility is defined by

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

From the expansion

$$\frac{P}{k_B T} = \frac{N}{V} + \frac{N^2}{V^2}B_2,$$

for constant temperature and particle number, we get

$$\frac{1}{k_B T}dP = -\frac{N}{V^2}dV - 2B_2\frac{N^2}{V^3}dV.$$

Thus

$$\left.\frac{\partial V}{\partial P}\right|_{T,N} = -\frac{1}{k_B T}\frac{1}{N/V^2 + 2B_2 N^2/V^3} = -\frac{V^2}{N k_B T}\left(\frac{1}{1 + 2B_2 N/V}\right),$$

and

$$\kappa_T = \frac{V}{N k_B T}\left(\frac{1}{1 + 2B_2 N/V}\right) \approx \frac{V}{N k_B T}\left(1 - 2B_2\frac{N}{V}\right).$$

(c) Including the correction introduced by the second virial coefficient, the equation of state becomes

$$\frac{PV}{N k_B T} = 1 + \frac{N}{V}B_2(T).$$

Using the expression for B_2 in the high temperature limit,

$$\frac{PV}{N k_B T} = 1 + \frac{N}{2V}\left\{V_d(a) - \beta\varepsilon[V_d(b) - V_d(a)]\right\},$$

and

$$P+\frac{N^2}{2V^2}\varepsilon[V_d(b)-V_d(a)]=k_BT\frac{N}{V}\left(1+\frac{N}{2V}V_d(a)\right).$$

Using the variable $n=N/V$, and noting that for low concentrations

$$1+\frac{n}{2}V_d(a)\approx\left(1-\frac{n}{2}V_d(a)\right)^{-1}=V\left(V-\frac{N}{2}V_d(a)\right)^{-1},$$

the equation of state becomes

$$\left(P+\frac{n^2\varepsilon}{2}\left[V_d(b)-V_d(a)\right]\right)\cdot\left(V-\frac{N}{2}V_d(a)\right)=Nk_BT.$$

This can be recast in the usual van der Waals form

$$(P-an^2)\cdot(V-Nb)=Nk_BT,$$

with

$$a=\frac{\varepsilon}{2}\left[V_d(b)-V_d(a)\right],\qquad \text{and}\qquad b=\frac{1}{2}V_d(a).$$

(d) By definition, the third virial coefficient is

$$B_3=-\frac{1}{3}\int d^drd^dr'f(r)f(r')f(r-r'),$$

where, for a hard core gas

$$f(r)\equiv\exp\left(-\frac{\mathcal{V}(r)}{k_BT}\right)-1=\begin{cases}-1 & \text{for} \quad 0<r<a,\\ 0 & \text{for} \quad a<r<\infty\end{cases}.$$

In one–dimension, the only contributions come from $0<r$, and $r'<a$, where $f(r)=f(r')=-1$. Using the notations $|x|\equiv r$, $|y|\equiv r'$ (i.e. $-a<x$, and $y<a$),

$$B_3=-\frac{1}{3}\int_{-a}^{a}dx\int_{-a}^{a}dy\cdot f(x-y)=\frac{1}{3}\int\int_{-a<x,y<a,-a<x-y<a}(-1)=\frac{1}{3}\frac{6}{8}(2a)^2=a^2,$$

where the relevant integration area is plotted below.