Quantum Ideal Gases at Low Density §5.3

From $\Omega = -pV$ (G-D), $z = e^{\mu/k_B T}$

$$p(T,z) = \mp k_B T \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) \log\left(1 \mp z e^{-\varepsilon/k_B T}\right) \quad (5.33)$$

$$= k_B T \sum_{j=1}^{\infty} \frac{1}{j} C_j(T) z^j$$

$$n(T,z) = \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) \frac{1}{z^{-1} e^{\varepsilon/k_B T} \mp 1} \quad (5.31)$$

$$\equiv \sum_{j=1}^{\infty} C_j(T) z^j$$

where

$$C_j(T) = (\pm)^{j-1} \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) e^{-j\varepsilon/k_B T} \quad (5.32)$$

What we want:

$$n(z) \xrightarrow[\text{invert}]{} z(n) \xrightarrow[\text{substitute}]{} p(z(n),T) = p(n,T)$$

Virial eqn of state:

$$p(T,n) = nk_BT\left(1 + B_2(T)n + B_3(T)n^2 + \dots\right)$$

$B_j(T) = j^{th}$ virial coefficient

$$[B_j(T)] = V^{j-1}$$

Skip a bit...

$$B_1 = 1 \ , \quad B_2 = -\frac{C_2}{2C_1^2} \ , \quad B_3 = \frac{C_2^2}{C_1^4} - \frac{2C_3}{3C_1^3}$$

Also for classical systems:

vdW gas : $\left(p + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_BT$

$$p = \frac{nk_BT}{1-bn} - an^2$$

$$= nk_BT + (bk_BT - a)n^2 + k_BTb^2n^3 + \dots$$

i.e. $B_1 = 1$, $B_2 = (bk_BT - a)$, $B_3 = b^2$, $B_4 = b^3$, ...

Ballistic: $\varepsilon(k) = \frac{\hbar^2 k^2}{2m} \Rightarrow$

$$C_j(T) = (\pm)^{j-1} g_d \lambda_T^{-d} j^{-d/2}$$

$$C_1 = g_d \lambda_T^{-d}, \quad C_2 = \pm g_d \lambda_T^{-d} 2^{-d/2}, \ \ldots$$

$$B_2 = -\frac{C_2}{2C_1^2} = \mp 2^{-\left(\frac{d}{2}+1\right)} g_d^{-1} \lambda_T^{d}$$

Quantum Virial Expansion of Eqn of State

Want $p = p(T,n)$ e.g. $p = n k_B T$; $n = \frac{N}{V}$

$$\left.\begin{aligned} n(T,z) &= \sum_{j=1}^{\infty} C_j(T) z^j \\ p(T,z) &= k_B T \sum_{j=1}^{\infty} \frac{1}{j} C_j(T) z^j \end{aligned}\right\} \rightarrow p(T, z(T,n)) = p(T,n)$$

$$C_j(T) = (\pm)^{j-1} \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) \, e^{-j\varepsilon/k_B T}$$

$$g(\varepsilon) = \frac{1}{V} \sum_{\alpha} \delta(\varepsilon - \varepsilon_\alpha)$$

Virial eqn of state: $p = n k_B T \cdot \left(1 + B_2(T) n + B_3(T) n^2 + \ldots\right)$

$$B_1 = 1 \ , \quad B_2(T) = -\frac{C_2(T)}{2C_1^2(T)} \ , \quad B_3(T) = \frac{C_2^2(T)}{C_1^4(T)} - \frac{2C_3(T)}{3C_1^3(T)}$$

In d-dim^s, with $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} \Rightarrow g(\varepsilon) = (5.28)$
$\propto \varepsilon^{\frac{1}{2}d-1}$

$$C_j(T) = (\pm 1)^{j-1} g_d \lambda_T^{-d} \cdot j^{-d/2}$$

$$B_j^{FD}(T) = (-1)^{j-1} B_j^{BE}(T)$$

Photon Statistics

Photons are bosons with $\mu = 0$ and $g_d = 2$ (in $d=3$).
Why is $\mu = 0$? Because photons are not conserved.
So minimizing $F(T,V,N)$ w.r.t $N \Rightarrow \left.\frac{\partial F}{\partial N}\right|_{T,V} = \mu = 0$

$$dF = -SdT - pdV + \mu dN$$

Photon number occupancy : $n(\varepsilon) = \frac{1}{e^{\beta\varepsilon} - 1}$

$\uparrow$ $z^{-1} = e^{-\beta\mu}$ if $\mu \neq 0$

Thermodynamics :

$$\Omega(T,V) = Vk_BT \int_{-\infty}^{\infty} d\varepsilon \ g(\varepsilon) \log\left[1 - e^{-\frac{\varepsilon}{k_BT}}\right]$$

Photon dispersion : $\varepsilon(\vec{k}) = \hbar c |\vec{k}| = c|\vec{p}|$; $p = \hbar k$

DOS :

$$g(\varepsilon) = \frac{C_d}{(\hbar c)^d} \varepsilon^{d-1} \Theta(\varepsilon)$$

$$C_d = \frac{2 g_d \pi^{d/2}}{\Gamma(d/2)} \ ; \quad d=3 : C_d = 8\pi$$