S9.D. Virial Coefficients for Quantum Gases

Quantum effects:

1. Diffraction effects if $\lambda_T \approx$ particle size
2. Statistics (or exchange effects) if $\lambda_T \approx$ distance between particles

The quantum grand partition function is defined as [c.f.(9.13)]

$$Z_\mu(T, V) = \sum_{N=0}^{\infty} \text{Tr} \exp\left[-\beta\left(\hat{H}^N - \mu \hat{N} \right) \right]$$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta\mu N} z^N}{N!} \text{Tr}\, \hat{W}_N(\beta) \tag{9.100}$$

where

$$\hat{W}_N(\beta) = \frac{N!}{z^N} \exp\left(-\beta \hat{H}^N \right) \qquad z = \lambda_T^{-3} \tag{9.101}$$

Reminder: $\hat{K}^N$ & $\hat{V}^N$ do not commute so that Tr $\hat{W}_N(\beta)$ is the closest quantum analog to the configuration integral $Q_N(V, T)$.

Note that the trace over an N-particle operator is given by

$$\text{Tr}\, \hat{O}_N = \frac{1}{N!} \sum_{\alpha_1 \ldots, \alpha_N} \left\langle \alpha_1 \ldots \alpha_N \mid \hat{O}_N \mid \alpha_1 \ldots \alpha_N \right\rangle \tag{9.101a}$$

where $\{ \mid \alpha_1 \ldots \alpha_N \rangle \}$ is a complete set of orthonormal N-particle states. Since $\hat{O}_N$ is symmetric in the particle labels, all $N!$ permutations among the quantum numbers $\alpha_1 \ldots \alpha_N$ correspond to the same state; hence the $1/N!$ factor in (9.101a). Reichl used the notation $\text{Tr}_N\, \hat{O}_N$ to emphasize this.

The quantum cumulant expansion is [c.f.(9.14)]

$$Z_\mu(T, V) = \exp\left[\sum_{N=1}^{\infty} \frac{e^{\beta\mu N} z^N}{N!} \text{Tr}\, \hat{U}_N(\beta) \right] \tag{9.102}$$

Since Tr $\hat{O}$ is a number, we can write down immediately the analog of (9.16-8):

$$\text{Tr}\, \hat{U}_1 = \text{Tr}\, \hat{W}_1 \tag{9.103}$$

$$\text{Tr}\, \hat{U}_2 = \text{Tr}\, \hat{W}_2 - \left(Tr\, \hat{W}_1 \right)^2 \tag{9.104}$$

$$\text{Tr}\, \hat{U}_3 = \text{Tr}\, \hat{W}_3 - 3\, \text{Tr}\, \hat{W}_1\, \text{Tr}\, \hat{W}_2 + 2\left(Tr\, \hat{W}_1 \right)^3 \tag{9.105}$$

As in (9.15),

$$\Omega(V, T, \mu) = -k_B T \ln Z_\mu(T, V)$$

$$= -k_B T \sum_{N=1}^{\infty} \frac{e^{\beta\mu N} z^N}{N!} \text{Tr}\, \hat{U}_N(\beta) \tag{9.106}$$

so that [c.f.(9.42)]

$$\frac{\langle N \rangle}{V} = -\frac{1}{V} \left(\frac{\partial \Omega}{\partial \mu} \right)_{T V} = \sum_{N=0}^{\infty} N z^N e^{\beta\mu N} b_N(T, V) \tag{9.107}$$

where [c.f.(9.39)]

$$b_N(T, V) = \frac{1}{N!\, V} \text{Tr}\, \hat{U}_N(\beta) \tag{9.108}$$

The virial expansion of the equation of state is the same as the classical case [see (9.43)]

$$\frac{P V}{\langle N \rangle k_B T} = \sum_{j=1}^{\infty} \mathcal{B}_j(T) \left(\frac{\langle N \rangle}{V} \right)^{j-1} \tag{9.109}$$

where the quantum virial coefficients $\mathcal{B}_j$ are related to the quantum b_N by the same equations (9.45-8) given for their classical counterparts.

See Ex.9.4-5 for the calculation of $\mathcal{B}_2$.

Combining (9.46) & (9.108), we have

$$\mathcal{B}_2(T) = -b_2(T) = -\frac{1}{2!\,V}\,\mathrm{Tr}\,\hat{U}_2(\beta)$$

$$= -\frac{1}{2!\,V}\left\{\mathrm{Tr}\,\hat{W}_2 - \left(\mathrm{Tr}\,\hat{W}_1\right)^2\right\} \qquad (9.110)$$

For the Hamiltonian (9.1),

$$\hat{W}_1(\beta) = \frac{1}{z}\exp\left(-\beta\,\hat{T}\right) \qquad \hat{W}_2(\beta) = \frac{2}{z^2}\exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2 + \hat{\mathcal{V}}_{12}\right)\right] \qquad (9.110a)$$

where $\hat{\mathcal{V}}_{12} = \hat{\mathcal{V}}_2\,(\boldsymbol{q}_{12}, s_1, s_2)$ is now possibly dependent on the spin $\boldsymbol{s}_j$ of the particles.

Setting

$$\hat{\boldsymbol{p}} = \frac{1}{2}\left(\hat{\boldsymbol{p}}_2 - \hat{\boldsymbol{p}}_1\right) = \text{relative momentum} \qquad \hat{\boldsymbol{P}} = \hat{\boldsymbol{p}}_2 + \hat{\boldsymbol{p}}_1 = \text{total momentum}$$

we have

$$\hat{\boldsymbol{p}}^2 = \frac{1}{4}\left(\hat{\boldsymbol{p}}_2^2 + \hat{\boldsymbol{p}}_1^2 - 2\,\hat{\boldsymbol{p}}_2\cdot\hat{\boldsymbol{p}}_1\right) \qquad \hat{\boldsymbol{P}}^2 = \hat{\boldsymbol{p}}_2^2 + \hat{\boldsymbol{p}}_1^2 + 2\,\hat{\boldsymbol{p}}_2\cdot\hat{\boldsymbol{p}}_1$$

$$\rightarrow \qquad \hat{T}_1 + \hat{T}_2 = \frac{1}{2\,m}\left(\hat{\boldsymbol{p}}_1^2 + \hat{\boldsymbol{p}}_2^2\right)$$

$$= \frac{1}{4\,m}\left(\hat{\boldsymbol{P}}^2 + 4\,\hat{\boldsymbol{p}}^2\right)$$

$$= \hat{T}_{\rm cm} + \hat{T}_{\rm rel}$$

where

$$\hat{T}_{\rm cm} = \frac{1}{4\,m}\hat{\boldsymbol{P}}^2 = \frac{1}{2\,M}\hat{\boldsymbol{P}}^2 \qquad M = 2\,m = \text{total mass}$$

$$\hat{T}_{\rm rel} = \frac{1}{m}\hat{\boldsymbol{p}}^2 = \frac{1}{2\,\mu}\hat{\boldsymbol{p}}^2 \qquad \text{Reduced mass } \mu \text{ is given by } \frac{1}{\mu} = \frac{2}{m}$$

The superscript 0 will be used to denote values for the non-interacting gas, e.g.,

$$\mathcal{B}_2^0(T) = \mathcal{B}_2(T)\Big|_{\mathcal{V}=0}$$

Since

$$\mathrm{Tr}\,\hat{W}_1 = \mathrm{Tr}\,\hat{W}_1^0$$

we have

$$\Delta\,\mathcal{B}_2(T) = \mathcal{B}_2(T) - \mathcal{B}_2^0(T)$$

$$= -\frac{1}{2!\,V}\left\{\mathrm{Tr}\,\hat{W}_2 - \mathrm{Tr}\,\hat{W}_2^0\right\}$$

$$= -\frac{1}{V z^2}\left\{\mathrm{Tr}\,e^{-\beta\left(\hat{T}_{\rm cm} + \hat{T}_{\rm rel} + \hat{\mathcal{V}}\right)} - \mathrm{Tr}\,e^{-\beta\left(\hat{T}_{\rm cm} + \hat{T}_{\rm rel}\right)}\right\}$$

$$= -\frac{1}{V z^2}\left\{\mathrm{Tr}\,e^{-\beta\,\hat{T}_{\rm cm}}\left[e^{-\beta\left(\hat{T}_{\rm rel} + \hat{\mathcal{V}}_2\right)} - e^{-\beta\,\hat{T}_{\rm rel}}\right]\right\} \qquad (9.111)$$

where we've used the fact that $\hat{T}_{\rm cm}$ commutes with both $\hat{T}_{\rm rel}$ & $\hat{\mathcal{V}}_2$.

For bosons, the N-particle states must be symmetrized.

For a gas of spin-0 bosons, the symmetrized 2-particle orthonormal complete states are

$$| \boldsymbol{k}, \boldsymbol{k}' \rangle_+ = \frac{1}{\sqrt{2}} \Big(| \boldsymbol{k}, \boldsymbol{k}' \rangle + | \boldsymbol{k}', \boldsymbol{k} \rangle \Big) \tag{9.112}$$

where $| \boldsymbol{k}, \boldsymbol{k}' \rangle$ means particle 1 & 2 are in states $| \boldsymbol{k} \rangle$ & $| \boldsymbol{k}' \rangle$, respectively.

(9.111) thus becomes

$$\Delta \mathcal{B}_2^{\text{BE}}(T) = -\frac{1}{V z^2} \frac{1}{2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} {}_+\Big\langle \boldsymbol{k}, \boldsymbol{k}' \Big| e^{-\beta \hat{T}_{\text{cm}}} \Big[e^{-\beta \left(\hat{T}_{\text{rel}} + \hat{\mathcal{V}}_2 \right)} - e^{-\beta \hat{T}_{\text{rel}}} \Big] \Big| \boldsymbol{k}, \boldsymbol{k}' \Big\rangle_+ \tag{9.113}$$

where the superscript BE stands for Bose-Einstein statistics.

Consider next a gas of spin-$\frac{1}{2}$ fermions. The natural basis for the spin states of N such particles is $\{ | s_{1z}, ..., s_{Nz} \rangle \}$, where $s_{jz} = \pm \frac{1}{2}$ or $\uparrow \downarrow$ is the z-component of the spin of the j^{th} particle.

For a 2-fermion cluster, the basis consists of 4 spin states

$$| \uparrow \uparrow \rangle, \qquad | \uparrow \downarrow \rangle, \qquad | \downarrow \uparrow \rangle, \qquad \text{and} \qquad | \downarrow \downarrow \rangle \tag{9.113a}$$

For processes which conserve angular momentum, it is more convenient to switch to the basis $\{ | S, S_z \rangle \}$, where $\hat{\boldsymbol{S}} = \sum_{j=1}^{N} \hat{\boldsymbol{s}}_j$ is the total spin and $S_z = -S, -S+1, ..., S$ its z-component.

For a 2-fermion cluster, $S = 1$ or 0 so that the basis consists of 4 spin states

$$| 1, 1 \rangle, \qquad | 1, 0 \rangle, \qquad | 1, -1 \rangle, \qquad \text{and} \qquad | 0, 0 \rangle \tag{9.113b}$$

The relation between these two bases can be found using $S_z = \sum_j s_{jz}$ and the raising and lowering operators $S_\pm = S_x \pm i S_y$ & $s_{j\pm} = s_{jx} \pm i s_{jy}$. The results are listed in tables of Clebsch-Gordan coefficients that can be found in most text book on quantum mechanics.

For the 2-fermion cluster, the basis consists of 4 spin states

$$\begin{aligned} | 0, 0 \rangle &= \frac{1}{\sqrt{2}} \Big(| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle \Big) \\ | 1, 1 \rangle &= | \uparrow \uparrow \rangle \\ | 1, 0 \rangle &= \frac{1}{\sqrt{2}} \Big(| \uparrow \downarrow \rangle + | \downarrow \uparrow \rangle \Big) \\ | 1, -1 \rangle &= | \downarrow \downarrow \rangle \end{aligned} \tag{9.113c}$$

Noting that $| 0, 0 \rangle$ is anti-symmetric under particle exchange, while $| 1, S_z \rangle$ are symmetric, we can write the ant-symmetrized 2-fermion basis states as

$$\begin{aligned} | \boldsymbol{k}, \boldsymbol{k}'; 0, 0 \rangle_a &= \frac{1}{2} \Big(| \boldsymbol{k}, \boldsymbol{k}' \rangle + | \boldsymbol{k}', \boldsymbol{k} \rangle \Big) \Big(| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle \Big) \\ | \boldsymbol{k}, \boldsymbol{k}'; 1, 1 \rangle_a &= \frac{1}{\sqrt{2}} \Big(| \boldsymbol{k}, \boldsymbol{k}' \rangle - | \boldsymbol{k}', \boldsymbol{k} \rangle \Big) | \uparrow \uparrow \rangle \\ | \boldsymbol{k}, \boldsymbol{k}'; 0, 0 \rangle_a &= \frac{1}{2} \Big(| \boldsymbol{k}, \boldsymbol{k}' \rangle - | \boldsymbol{k}', \boldsymbol{k} \rangle \Big) \Big(| \uparrow \downarrow \rangle + | \downarrow \uparrow \rangle \Big) \\ | \boldsymbol{k}, \boldsymbol{k}'; 1, -1 \rangle_a &= \frac{1}{\sqrt{2}} \Big(| \boldsymbol{k}, \boldsymbol{k}' \rangle - | \boldsymbol{k}', \boldsymbol{k} \rangle \Big) | \downarrow \downarrow \rangle \end{aligned} \tag{9.114}$$

The fermionic version of (9.113) is therefore

$$\Delta \mathcal{B}_2^{\text{FD}}(T) = -\frac{1}{V z^2} \frac{1}{2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \sum_{S, S_z} {}_a\Big\langle \boldsymbol{k}, \boldsymbol{k}'; S, S_z \Big| e^{-\beta \hat{T}_{\text{cm}}} \Big[e^{-\beta \left(\hat{T}_{\text{rel}} + \hat{\mathcal{V}}_2 \right)} - e^{-\beta \hat{T}_{\text{rel}}} \Big] \Big| \boldsymbol{k}, \boldsymbol{k}'; S, S_z \Big\rangle_a$$

(9.115)

where the superscript FD stands for Fermi-Dirac statistics.

For spin-independent operators, the sums over spin can be performed separately, giving

$$\sum_{S, S_z} {}_a\left\langle \alpha ; S, S_z \mid \hat{O} \mid \alpha ; S, S_z \right\rangle_a$$
$$= \sum_{S_z=-1}^{1} \left\langle \alpha_- ; 1, S_z \mid \hat{O} \mid \alpha_- ; 1, S_z \right\rangle + \sum_{S_z=0}^{0} \left\langle \alpha_+ ; 0, S_z \mid \hat{O} \mid \alpha_+ ; 0, S_z \right\rangle$$
$$= 3 \left\langle \alpha_- \mid \hat{O} \mid \alpha_- \right\rangle + \left\langle \alpha_+ \mid \hat{O} \mid \alpha_+ \right\rangle$$

where $\alpha_\pm$ is the $\begin{pmatrix} \text{symmetric} \\ \text{anti-symmetric} \end{pmatrix}$ part of α.

Generalizing (9.112) to

$$\mid \boldsymbol{k}, \boldsymbol{k}' \rangle_\pm = \frac{1}{\sqrt{2}} \left(\mid \boldsymbol{k}, \boldsymbol{k}' \rangle \pm \mid \boldsymbol{k}', \boldsymbol{k} \rangle \right) \tag{9.117}$$

(9.115) becomes, for spin-independent interactions, $\hat{\mathcal{V}}_2 = \mathcal{V}_2(\hat{\boldsymbol{q}})$,

$$\Delta \mathcal{B}_2^{\text{FD}}(T) = -\frac{1}{V z^2} \frac{1}{2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \left[3 \; {}_-\left\langle \boldsymbol{k}, \boldsymbol{k}' \right| e^{-\beta \hat{T}_{\text{cm}}} \left[e^{-\beta\left(\hat{T}_{\text{rel}} + \hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\text{rel}}} \right] \left| \boldsymbol{k}, \boldsymbol{k}' \right\rangle_- + {}_+\left\langle \boldsymbol{k}, \boldsymbol{k}' \right| e^{-\beta \hat{T}_{\text{cm}}} \left[e^{-\beta\left(\hat{T}_{\text{rel}} + \hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\text{rel}}} \right] \left| \boldsymbol{k}, \boldsymbol{k}' \right\rangle_+ \right] \tag{9.116}$$

Setting

$$\hat{\boldsymbol{p}} = \hbar \hat{\boldsymbol{\kappa}} = \frac{1}{2} \hbar \left(\hat{\boldsymbol{k}}_2 - \hat{\boldsymbol{k}}_1 \right) \qquad \hat{\boldsymbol{P}} = \hbar \hat{\boldsymbol{K}} = \hbar \left(\hat{\boldsymbol{k}}_2 + \hat{\boldsymbol{k}}_1 \right)$$

$$\rightarrow \qquad \hat{\boldsymbol{k}}_1 = \frac{1}{2} \hat{\boldsymbol{K}} - \hat{\boldsymbol{\kappa}} \qquad \hat{\boldsymbol{k}}_2 = \frac{1}{2} \hat{\boldsymbol{K}} + \hat{\boldsymbol{\kappa}}$$

Thus, in switching to the basis $\mid \boldsymbol{K}, \boldsymbol{\kappa} \rangle$, we set

$$\mid \boldsymbol{k}, \boldsymbol{k}' \rangle = \mid \boldsymbol{K}, \boldsymbol{\kappa} \rangle \qquad \mid \boldsymbol{k}', \boldsymbol{k} \rangle = \mid \boldsymbol{K}, -\boldsymbol{\kappa} \rangle$$

so that

$$\hat{\boldsymbol{k}}_1 \mid \boldsymbol{k}, \boldsymbol{k}' \rangle = \boldsymbol{k} \mid \boldsymbol{k}, \boldsymbol{k}' \rangle = \left(\frac{1}{2} \hat{\boldsymbol{K}} - \hat{\boldsymbol{\kappa}} \right) \mid \boldsymbol{K}, \boldsymbol{\kappa} \rangle = \left(\frac{1}{2} \boldsymbol{K} - \boldsymbol{\kappa} \right) \mid \boldsymbol{K}, \boldsymbol{\kappa} \rangle$$

$$\hat{\boldsymbol{k}}_2 \mid \boldsymbol{k}, \boldsymbol{k}' \rangle = \boldsymbol{k}' \mid \boldsymbol{k}, \boldsymbol{k}' \rangle = \left(\frac{1}{2} \hat{\boldsymbol{K}} + \hat{\boldsymbol{\kappa}} \right) \mid \boldsymbol{K}, \boldsymbol{\kappa} \rangle = \left(\frac{1}{2} \boldsymbol{K} + \boldsymbol{\kappa} \right) \mid \boldsymbol{K}, \boldsymbol{\kappa} \rangle$$

$$\hat{\boldsymbol{k}}_1 \mid \boldsymbol{k}', \boldsymbol{k} \rangle = \boldsymbol{k}' \mid \boldsymbol{k}', \boldsymbol{k} \rangle = \left(\frac{1}{2} \hat{\boldsymbol{K}} - \hat{\boldsymbol{\kappa}} \right) \mid \boldsymbol{K}, -\boldsymbol{\kappa} \rangle = \left(\frac{1}{2} \boldsymbol{K} + \boldsymbol{\kappa} \right) \mid \boldsymbol{K}, -\boldsymbol{\kappa} \rangle$$

$$\hat{\boldsymbol{k}}_2 \mid \boldsymbol{k}', \boldsymbol{k} \rangle = \boldsymbol{k} \mid \boldsymbol{k}', \boldsymbol{k} \rangle = \left(\frac{1}{2} \hat{\boldsymbol{K}} + \hat{\boldsymbol{\kappa}} \right) \mid \boldsymbol{K}, -\boldsymbol{\kappa} \rangle = \left(\frac{1}{2} \boldsymbol{K} - \boldsymbol{\kappa} \right) \mid \boldsymbol{K}, -\boldsymbol{\kappa} \rangle$$

$$\rightarrow \qquad \boldsymbol{k} = \frac{1}{2} \boldsymbol{K} - \boldsymbol{\kappa} \qquad \boldsymbol{k}' = \frac{1}{2} \boldsymbol{K} + \boldsymbol{\kappa}$$

as expected.

(9.117) thus becomes

$$\mid \boldsymbol{k}, \boldsymbol{k}' \rangle_\pm = \frac{1}{\sqrt{2}} \left(\mid \boldsymbol{K}, \boldsymbol{\kappa} \rangle \pm \mid \boldsymbol{K}, -\boldsymbol{\kappa} \rangle \right) \tag{9.118}$$

Using

$$e^{-\beta \hat{T}_{\text{cm}}} \left| \boldsymbol{K}, \pm \boldsymbol{\kappa} \right\rangle = e^{-\beta \hbar^2 K^2 / 4 m} \left| \boldsymbol{K}, \pm \boldsymbol{\kappa} \right\rangle$$

we can write the matrix element in (9.113) as

$$ {}_{+}\left\langle \boldsymbol{k}, \boldsymbol{k}' \right| e^{-\beta \hat{T}_{\mathrm{cm}}} \left[e^{-\beta\left(\hat{T}_{\mathrm{rel}}+\hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\mathrm{rel}}} \right] \left| \boldsymbol{k}, \boldsymbol{k}' \right\rangle_{+} $$

$$ = \frac{1}{2}\Big(\langle \boldsymbol{K}, \boldsymbol{\kappa} | + \langle \boldsymbol{K}, -\boldsymbol{\kappa} | \Big) e^{-\beta \hat{T}_{\mathrm{cm}}} \left[e^{-\beta\left(\hat{T}_{\mathrm{rel}}+\hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\mathrm{rel}}} \right] \Big(| \boldsymbol{K}, \boldsymbol{\kappa} \rangle + | \boldsymbol{K}, -\boldsymbol{\kappa} \rangle \Big) $$

$$ = \frac{1}{2} \left\langle \boldsymbol{K} \right| e^{-\beta \hat{T}_{\mathrm{cm}}} \left| \boldsymbol{K} \right\rangle \Big(\langle \boldsymbol{\kappa} | + \langle -\boldsymbol{\kappa} | \Big) \left[e^{-\beta\left(\hat{T}_{\mathrm{rel}}+\hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\mathrm{rel}}} \right] \Big(| \boldsymbol{\kappa} \rangle + | -\boldsymbol{\kappa} \rangle \Big) $$

$$ = e^{-\beta \hbar^2 K^2/4m} \; {}_{+}\left\langle \boldsymbol{\kappa} \right| \left[e^{-\beta\left(\hat{T}_{\mathrm{rel}}+\hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\mathrm{rel}}} \right] \left| \boldsymbol{\kappa} \right\rangle_{+} $$

where

$$ | \boldsymbol{\kappa} \rangle_{\pm} = \frac{1}{\sqrt{2}} \Big(| \boldsymbol{\kappa} \rangle \pm | -\boldsymbol{\kappa} \rangle \Big) $$

Using

$$ \begin{aligned} \sum_{\boldsymbol{K}} e^{-\beta \hbar^2 K^2/4m} &= \frac{V}{(2\pi)^3} \int d\boldsymbol{K}\, e^{-\beta \hbar^2 K^2/4m} \\ &= \frac{4\pi V}{(2\pi)^3} \int_0^\infty dK\, K^2\, e^{-\beta \hbar^2 K^2/4m} \\ &= 2\sqrt{2}\; V z \end{aligned} $$

and

$$ \sum_{\boldsymbol{k},\boldsymbol{k}'} = \sum_{\boldsymbol{K},\boldsymbol{\kappa}} $$

(9.113) becomes

$$ \Delta \mathcal{B}_2^{\mathrm{BE}}(T) = -\frac{\sqrt{2}}{z} \sum_{\boldsymbol{\kappa}} {}_{+}\left\langle \boldsymbol{\kappa} \right| \left[e^{-\beta\left(\hat{T}_{\mathrm{rel}}+\hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\mathrm{rel}}} \right] \left| \boldsymbol{\kappa} \right\rangle_{+} \tag{9.119} $$

Similarly, (9.116) becomes

$$ \begin{aligned} \Delta \mathcal{B}_2^{\mathrm{FD}}(T) = -\frac{\sqrt{2}}{z} \sum_{\boldsymbol{\kappa}} \Big\{ & 3\; {}_{-}\left\langle \boldsymbol{\kappa} \right| \left[e^{-\beta\left(\hat{T}_{\mathrm{rel}}+\hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\mathrm{rel}}} \right] \left| \boldsymbol{\kappa} \right\rangle_{-} \\ & + {}_{+}\left\langle \boldsymbol{\kappa} \right| \left[e^{-\beta\left(\hat{T}_{\mathrm{rel}}+\hat{\mathcal{V}}_2\right)} - e^{-\beta \hat{T}_{\mathrm{rel}}} \right] \left| \boldsymbol{\kappa} \right\rangle_{+} \Big\} \end{aligned} \tag{9.120} $$

Let

$$ \hat{\boldsymbol{q}} \,|\, \boldsymbol{r} \rangle = \boldsymbol{r} \,|\, \boldsymbol{r} \rangle $$

$$ \hat{H}_{\mathrm{rel}} = \hat{T}_{\mathrm{rel}} + \hat{\mathcal{V}}_2 = \frac{1}{m} \hat{\boldsymbol{p}}^2 + \mathcal{V}_2(\hat{\boldsymbol{q}}) = \frac{1}{2\mu} \hat{\boldsymbol{p}}^2 + \mathcal{V}_2(\hat{\boldsymbol{q}}) $$

then

$$ \hat{H}_{\mathrm{rel}} \,|\, E_{\boldsymbol{n}} \rangle = E_{\boldsymbol{n}} \,|\, E_{\boldsymbol{n}} \rangle $$

$$ \rightarrow \qquad -\frac{\hbar^2}{m} \nabla^2 \psi_{\boldsymbol{n}}(\boldsymbol{r}) + \mathcal{V}_2(\boldsymbol{r})\, \psi_{\boldsymbol{n}}(\boldsymbol{r}) = E_{\boldsymbol{n}}\, \psi_{\boldsymbol{n}}(\boldsymbol{r}) \qquad\qquad \psi_{\boldsymbol{n}}(\boldsymbol{r}) = \langle \boldsymbol{r} \,|\, E_{\boldsymbol{n}} \rangle \tag{9.121} $$

Note that $\boldsymbol{n}$ represents the complete set of quantum numbers necessary to specify the eigenstate.

The eigenstates $| E_{\boldsymbol{n}} \rangle$ are orthonormal & complete:

$$ \langle E_{\boldsymbol{m}} \,|\, E_{\boldsymbol{n}} \rangle = \delta_{\boldsymbol{m}\boldsymbol{n}} \qquad\qquad \sum_{\boldsymbol{n}} | E_{\boldsymbol{n}} \rangle \langle E_{\boldsymbol{n}} | = I \tag{9.121a} $$

Reminder: for $\mathcal{V}_2$ attractive and finite-ranged, $E_{\boldsymbol{n}}$ contains both discrete ($E < 0$) and continuous ($E > 0$) parts.

Similarly

$$\hat{T}_{\text{rel}} \mid E_{\boldsymbol{k}}^0 \rangle = (\hat{H}_{\text{rel}})_{\mathcal{V}_2=0} \mid E_{\boldsymbol{k}}^0 \rangle = E_{\boldsymbol{k}}^0 \mid E_{\boldsymbol{k}}^0 \rangle \tag{9.121b}$$

$$\to \quad -\frac{\hbar^2}{m} \nabla^2 \psi_{\boldsymbol{k}}^0(\boldsymbol{r}) = E_{\boldsymbol{k}}^0 \psi_{\boldsymbol{k}}^0(\boldsymbol{r}) \qquad \psi_{\boldsymbol{k}}^0(\boldsymbol{r}) = \langle \boldsymbol{r} \mid E_{\boldsymbol{k}}^0 \rangle$$

$$\langle E_{\boldsymbol{k}}^0 \mid E_{\boldsymbol{k'}}^0 \rangle = \delta_{\boldsymbol{k}\boldsymbol{k'}} \qquad \sum_{\boldsymbol{k}} \mid E_{\boldsymbol{k}}^0 \rangle \langle E_{\boldsymbol{k}}^0 \mid = I$$

Note: as a kinetic energy, $E_{\boldsymbol{k}}^0 \geq 0$.

In the r-representation, (9.119) becomes

$$\Delta \mathcal{B}_2^{\text{BE}}(T) = -\frac{\sqrt{2}}{z} \int d\boldsymbol{r} \; {}_{+}\langle \boldsymbol{r} \mid \left(e^{-\beta \hat{H}_{\text{rel}}} - e^{-\beta \hat{T}_{\text{rel}}} \right) \mid \boldsymbol{r} \rangle_{+}$$

where

$$\mid \boldsymbol{r} \rangle_{\pm} = \frac{1}{\sqrt{2}} \left(\mid \boldsymbol{r} \rangle \pm \mid -\boldsymbol{r} \rangle \right) \tag{9.121c}$$

With the help of (9.121a), we have

$$\Delta \mathcal{B}_2^{\text{BE}}(T) = -\frac{\sqrt{2}}{z} \int d\boldsymbol{r} \Big[\sum_{\boldsymbol{m},\boldsymbol{n}} {}_{+}\langle \boldsymbol{r} \mid E_{\boldsymbol{m}} \rangle \langle E_{\boldsymbol{m}} \mid e^{-\beta \hat{H}_{\text{rel}}} \mid E_{\boldsymbol{n}} \rangle \langle E_{\boldsymbol{n}} \mid \boldsymbol{r} \rangle_{+}$$

$$\sum_{\boldsymbol{k},\boldsymbol{k'}} - {}_{+}\langle \boldsymbol{r} \mid E_{\boldsymbol{k}}^0 \rangle \langle E_{\boldsymbol{k}}^0 \mid e^{-\beta \hat{T}_{\text{rel}}} \mid E_{\boldsymbol{k'}}^0 \rangle \langle E_{\boldsymbol{k'}}^0 \mid \boldsymbol{r} \rangle_{+} \Big]$$

$$= -\frac{\sqrt{2}}{z} \int d\boldsymbol{r} \left(\sum_{\boldsymbol{m},\boldsymbol{n}} \psi_{\boldsymbol{m}}^{(+)}(\boldsymbol{r}) \, e^{-\beta E_{\boldsymbol{m}}} \delta_{\boldsymbol{m}\boldsymbol{n}} \, \psi_{\boldsymbol{n}}^{(+)*}(\boldsymbol{r}) - \sum_{\boldsymbol{k},\boldsymbol{k'}} \psi_{\boldsymbol{k}}^{0\,(+)}(\boldsymbol{r}) \, e^{-\beta E_{\boldsymbol{k}}^0} \delta_{\boldsymbol{k}\boldsymbol{k'}} \, \psi_{\boldsymbol{k'}}^{0\,(+)*}(\boldsymbol{r}) \right)$$

$$= -\frac{\sqrt{2}}{z} \int d\boldsymbol{r} \left(\sum_{\boldsymbol{n}} \left| \psi_{\boldsymbol{n}}^{(+)}(\boldsymbol{r}) \right|^2 e^{-\beta E_{\boldsymbol{n}}} - \sum_{\boldsymbol{k}} \left| \psi_{\boldsymbol{k}}^{0\,(+)} \right|^2 e^{-\beta E_{\boldsymbol{k}}^0} \right) \tag{9.122}$$

where

$$\psi_{\boldsymbol{n}}^{(\pm)}(\boldsymbol{r}) = {}_{\pm}\langle \boldsymbol{r} \mid E_{\boldsymbol{n}} \rangle \qquad \psi_{\boldsymbol{k}}^{0\,(\pm)}(\boldsymbol{r}) = {}_{\pm}\langle \boldsymbol{r} \mid E_{\boldsymbol{k}}^0 \rangle$$

Similarly, (9.120) becomes

$$\Delta \mathcal{B}_2^{\text{FD}}(T) = -\frac{\sqrt{2}}{z} \int d\boldsymbol{r} \Big\{ 3 \left(\sum_{\boldsymbol{n}} \left| \psi_{\boldsymbol{n}}^{(-)}(\boldsymbol{r}) \right|^2 e^{-\beta E_{\boldsymbol{n}}} - \sum_{\boldsymbol{k}} \left| \psi_{\boldsymbol{k}}^{0\,(-)} \right|^2 e^{-\beta E_{\boldsymbol{k}}^0} \right) \tag{9.123}$$

$$+ \sum_{\boldsymbol{n}} \left| \psi_{\boldsymbol{n}}^{(+)}(\boldsymbol{r}) \right|^2 e^{-\beta E_{\boldsymbol{n}}} - \sum_{\boldsymbol{k}} \left| \psi_{\boldsymbol{k}}^{0\,(+)} \right|^2 e^{-\beta E_{\boldsymbol{k}}^0} \Big\}$$

For $\mathcal{V}_2$ a central potential, $\mathcal{V}_2(\boldsymbol{r}) = \mathcal{V}_2(r)$, we have [see any QM textbook]

$$\psi_{\boldsymbol{n}}(\boldsymbol{r}) = \psi_{n l m}(\boldsymbol{r}) = R_{n l}(r) \, Y_{l m}(\theta, \phi) \tag{9.124}$$

where $Y_{l m}$ are the spherical harmonics with

$$l = 0, 1, \ldots, n-1 \qquad m = -l, \ldots, l$$

and orthonormality

$$\int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \, Y_{l m}^*(\theta, \phi) \, Y_{l' m'}(\theta, \phi) = \delta_{l l'} \, \delta_{m m'} \tag{9.129}$$

$R_{n l}$ satisfies the radial Schrodinger equations

$$-\frac{\hbar^2}{m} \frac{1}{r} \frac{d^2}{d r^2} (r R_{n l}) + \frac{l(l+1)\hbar^2}{m r} R_{n l} + \mathcal{V}_2 R_{n l} = E_{n l} R_{n l} \quad \text{for} \qquad E_{n l} \leq 0 \tag{9.125}$$

and

$$-\frac{\hbar^2}{m}\frac{1}{r}\frac{d^2}{d r^2}(r R_{k l}) + \frac{l(l+1)\hbar^2}{m r} R_{k l} + \mathcal{V}_2 R_{k l} = E_k R_{k l} \quad \text{for} \qquad E_k = \frac{\hbar^2 k^2}{m} \geq 0 \quad (9.125a)$$

In general, $E_{n l}$ represents bound states with a discrete spectrum, while E_k represents scattering states with a continuous spectrum. For convenience, we shall assume $R_{n l}$ & $E_{n l}$ include both cases.

If $\mathcal{V}_2$ is repulsive, there are no bound states and only (9.125a) is required. But if $\mathcal{V}_2$ is attractive, both (9.125) & (9.125a) are needed.

We shall assume orthonormality

$$\int_0^\infty d r\, r^2 R_{n l}^*(r) R_{n' l'}(r) = \delta_{n n'} \delta_{l l'} \qquad (9.125a)$$

$$\int_0^\infty d r\, r^2 R_{k l}^*(r) R_{k' l'}(r) = \frac{1}{\rho_l(k)} \delta(k-k') \delta_{l l'} \qquad (9.125b)$$

where $\rho_l(k)$ is the density of state satisfying

$$\sum_k = \int d k\, \rho_l(k) \to \qquad \sum_k \delta_{k k'} = \int d k\, \rho_l(k)\, \delta_{k k'} = \int d k\, \delta(k-k') = 1$$

so that

$$\int d \boldsymbol{r}\, \psi_{n l m}^*(\boldsymbol{r}) \psi_{n' l' m'}(\boldsymbol{r}) = \delta_{n n'} \delta_{l l'} \delta_{m m'} \qquad (9.125c)$$

$$\int d \boldsymbol{r}\, \psi_{k l m}^*(\boldsymbol{r}) \psi_{k' l' m'}(\boldsymbol{r}) = \frac{1}{\rho_l(k)} \delta(k-k') \delta_{l l'} \delta_{m m'} \qquad (9.125d)$$

Note that

$$E_{\boldsymbol{n}} = E_{n l m} = E_{n l}$$

is $(2 l + 1)$-fold degenerated and we have assumed that $\rho_l(k)$ is independent of m.

Now,

$$\boldsymbol{r} = (r, \theta, \phi) \qquad \to \qquad -\boldsymbol{r} = (r, \pi-\theta, \pi+\phi)$$

By definition,

$$Y_{l m}(\theta, \phi) = C_{l m} P_l^m(\cos\theta)\, e^{i m \phi}$$

$$P_l^m(x) = c_{l m} \left(1-x^2\right)^{m/2} \frac{d^{l+m}}{d x^{l+m}} \left(x^2-1\right)^l$$

where $C_{l m}$ & $c_{l m}$ are normalization constants. Using

$$\cos(\pi-\theta) = -\cos\theta \qquad e^{i m \pi} = (-)^m$$

we have

$$P_l^m(-x) = (-)^{l+m} P_l^m(x)$$

$$Y_{l m}(\pi-\theta, \pi+\phi) = (-)^l Y_{l m}(\theta, \phi)$$

(9.124) then gives

$$\psi_{n l m}(-\boldsymbol{r}) = (-)^l R_{n l}(r) Y_{l m}(\theta, \phi) \qquad (9.126a)$$

so that

$$\psi_{n l m}^{(\pm)}(\boldsymbol{r}) = \frac{1}{\sqrt{2}} \left\{ \psi_{n l m}(\boldsymbol{r}) \pm \psi_{n l m}(-\boldsymbol{r}) \right\}$$

$$= \frac{1}{\sqrt{2}} \left[1 \pm (-)^l \right] R_{n l}(r) Y_{l m}(\theta, \phi)$$

$$= \frac{1}{\sqrt{2}} \left[1 \pm (-)^l \right] \psi_{n\,l\,m}(\boldsymbol{r}) \tag{9.126b}$$

Similarly,

$$\psi^{(\pm)}_{k\,l\,m}(\boldsymbol{r}) = \frac{1}{\sqrt{2}} \left[1 \pm (-)^l \right] \psi_{k\,l\,m}(\boldsymbol{r}) \tag{9.126c}$$

For the bound states, the sums in (9.122-3) have the form

$$\int d\boldsymbol{r} \sum_{\boldsymbol{n}} \left| \psi^{(\pm)}_{\boldsymbol{n}}(\boldsymbol{r}) \right|^2 e^{-\beta E_{\boldsymbol{n}}}$$

$$= \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} \frac{1}{2} \left[1 \pm (-)^l \right]^2 \int d\boldsymbol{r} \left| \psi_{n\,l\,m}(\boldsymbol{r}) \right|^2 e^{-\beta E_{n\,l}}$$

$$= \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} \frac{1}{2} \left[1 \pm (-)^l \right]^2 e^{-\beta E_{n\,l}} \qquad \text{[(9.125b) used.]}$$

$$= \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \frac{2\,l+1}{2} \left[1 \pm (-)^l \right]^2 e^{-\beta E_{n\,l}}$$

$$= \sum_{n=1}^{\infty} \begin{pmatrix} \sum_{l=\text{even}}^{n-1} \\ \sum_{l=\text{odd}}^{n-1} \end{pmatrix} 2\,(2\,l+1)\, e^{-\beta E_{n\,l}}$$

$$= 2 \sum_{n=1}^{\infty} \sum_{l=0}^{l_M} \begin{pmatrix} (4\,l+1)\, e^{-\beta E_{n,2l}} \\ (4\,l+3)\, e^{-\beta E_{n,2l+1}} \end{pmatrix} \qquad \text{with} \qquad \begin{pmatrix} 2\,l_M < n \\ 2\,l_M + 1 < n \end{pmatrix}$$

$$= 2 \sum_{l=0}^{\infty} \begin{pmatrix} (4\,l+1) \sum_{n=2l+1}^{\infty} e^{-\beta E_{n,2l}} \\ (4\,l+3) \sum_{n=2l+2}^{\infty} e^{-\beta E_{n,2l+1}} \end{pmatrix} \tag{9.127a}$$

For the scattering states,

$$\int d\boldsymbol{r} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \int_0^{\infty} d\,k\, \rho_l(k) \left| \psi^{(\pm)}_{k\,l\,m}(\boldsymbol{r}) \right|^2 e^{-\beta E_k}$$

$$= \sum_{l=0}^{\infty} \frac{2\,l+1}{2} \left[1 \pm (-)^l \right]^2 \int_0^{\infty} d\,k\, \rho_l(k)\, e^{-\beta E_k}$$

$$= \begin{pmatrix} \sum_{l=0}^{\infty} 2\,(4\,l+1) \int_0^{\infty} d\,k\, \rho_{2l}(k)\, e^{-\beta E_k} \\ \sum_{l=0}^{\infty} 2\,(4\,l+3) \int_0^{\infty} d\,k\, \rho_{2l+1}(k)\, e^{-\beta E_k} \end{pmatrix} \tag{9.127b}$$

For $\hat{T}_{\text{rel}} = (\hat{H}_{\text{rel}})_{\mathcal{V}_2=0}$, only scattering states exist and we have

$$\psi^0_{\boldsymbol{n}}(\boldsymbol{r}) = \psi^0_{k\,l\,m}(\boldsymbol{r}) = R^0_{n\,l}(r)\, Y_{l\,m}(\theta, \phi)$$

with

$$-\frac{\hbar^2}{m} \frac{1}{r} \frac{d^2}{d\,r^2} \left(r\, R^0_{k\,l} \right) + \frac{l\,(l+1)\,\hbar^2}{m\,r} R^0_{k\,l} = E_k\, R^0_{k\,l} \tag{9.127c}$$

The analog of (9.127b) is

$$\int d\boldsymbol{r} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \int_0^{\infty} d\,k\, \rho^0_l(k) \left| \psi^{0\,(\pm)}_{k\,l\,m}(\boldsymbol{r}) \right|^2 e^{-\beta E_k}$$

$$= \begin{pmatrix} \sum_{l=0}^{\infty} 2\,(4\,l+1) \int_0^{\infty} d\,k \rho^0_{2\,l}(k)\, e^{-\beta E_k} \\ \sum_{l=0}^{\infty} 2\,(4\,l+3) \int_0^{\infty} d\,k \rho^0_{2\,l+1}(k)\, e^{-\beta E_k} \end{pmatrix} \tag{9.127d}$$

(9.122) thus becomes

$$\Delta\,\mathcal{B}_2^{\rm BE}(T) = -\frac{2\sqrt{2}}{z} \sum_{l=0}^{\infty} (4\,l+1) \left(\sum_{n=2\,l+1}^{\infty} e^{-\beta E_{n,2\,l}} + \int_0^{\infty} d\,k \left[\rho_{2\,l}(k) - \rho^0_{2\,l}(k)\right] e^{-\beta E_k} \right) \tag{9.130}$$

Similarly, (9.123) becomes

$$\Delta\,\mathcal{B}_2^{\rm FD}(T) = -\frac{2\sqrt{2}}{z} \sum_{l=0}^{\infty} \left\{ 3\,(4\,l+3) \left(\sum_{n=2\,l+2}^{\infty} e^{-\beta E_{n,2\,l+1}} + \int_0^{\infty} d\,k \left[\rho_{2\,l+1}(k) - \rho^0_{2\,l+1}(k)\right] e^{-\beta E_k} \right) + (4\,l+1) \left(\sum_{n=2\,l+1}^{\infty} e^{-\beta E_{n,2\,l}} + \int_0^{\infty} d\,k \left[\rho_{2\,l}(k) - \rho^0_{2\,l}(k)\right] e^{-\beta E_k} \right) \right\} \tag{9.131}$$

Now, $R^0_{k\,l}(r)$ is just the radial part of a plane wave in spherical coordinates. Therefore

$$R^0_{k\,l}(r) = C_{k\,l}\, j_l(k\,r) \qquad \text{where} \qquad E_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2\,\mu} = \frac{\hbar^2 k^2}{m}$$

$C_{k\,l}$ is a normalization constant and j_l is the spherical Bessel function. Note that $R^0_{k\,l}(r)$ does not contain the other solution to (9.127c), namely, the spherical Neumann function n_l, because n_l is singular at $r = 0$.

Let $\mathcal{V}_2$ be an interaction of finite range R. Then

$$R_{k\,l}(r) = A_{k\,l}\, j_l(k\,r) + B_{k\,l}\, n_l(k\,r) \qquad \text{for} \qquad r > R \quad \& \quad E_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{m} \ge 0$$

Note that n_l is required here for completeness since $r \neq 0$.

The constants $A_{k\,l}$ & $B_{k\,l}$ can be written as

$$A_{k\,l} = C_{k\,l} \cos\delta_{k\,l} \qquad\qquad B_{k\,l} = C_{k\,l} \sin\delta_{k\,l}$$

so that

$$R_{k\,l}(r) = C_{k\,l}\left[\cos\delta_{k\,l}\, j_l(k\,r) + \sin\delta_{k\,l}\, n_l(k\,r)\right] \tag{9.132}$$

Using

$$\lim_{x\to\infty} j_l(x) = \frac{1}{x}\sin\left(x - l\,\frac{\pi}{2}\right) \qquad\qquad \lim_{x\to\infty} n_l(x) = -\frac{1}{x}\cos\left(x - l\,\frac{\pi}{2}\right)$$

(9.132) gives

$$R_{k\,l}(r) \xrightarrow[r\to\infty]{} \frac{C_{k\,l}}{k\,r}\left[\cos\delta_{k\,l}\sin\left(k\,r - l\,\frac{\pi}{2}\right) - \sin\delta_{k\,l}\cos\left(k\,r - l\,\frac{\pi}{2}\right)\right]$$
$$= \frac{C_{k\,l}}{k\,r}\sin\left(k\,r - l\,\frac{\pi}{2} - \delta_{k\,l}\right) \qquad r\to\infty \tag{9.133}$$

Comparing with

$$R^0_{k\,l}(r) \xrightarrow[r\to\infty]{} \frac{C_{k\,l}}{k\,r}\sin\left(k\,r - l\,\frac{\pi}{2}\right) \tag{9.133a}$$

we see that $\delta_{k\,l}$ is just the phase shift caused by $\mathcal{V}_2$.

To find the density of states $\rho(k)$, we discretize the spectrum by introducing the boundary condition

$$R_{k\,l}(r_M) = R^0_{k\,l}(r_M) = 0$$

where $r_M \gg R$ is assumed to be large enough for both (9.133) & (9.133a) to hold for $r = r_M$. Hence,

$$\text{for } R_{kl},\; k\,r_M - l\,\frac{\pi}{2} - \delta_{kl} = n\,\pi \qquad\qquad n = \text{integer}$$

$$\text{for } R^0_{kl},\; k\,r_M - l\,\frac{\pi}{2} = n\,\pi$$

Since a state is added if $\Delta n = 1$, the density of states is given by

$$1 = \rho(k)\,\Delta k\Big|_{\Delta n=1}$$

$$\to \qquad \rho(k) = \frac{1}{\Delta k}\Big|_{\Delta n=1} = \frac{\Delta n}{\Delta k}$$

For R_{kl}, $\quad r_M\,\Delta k - \Delta\,\delta_{kl} = \pi\,\Delta n \;\to\; \rho_l(k) = \frac{1}{\pi}\left(r_M - \frac{\Delta\,\delta_{kl}}{\Delta k}\right)$

For R^0_{kl}, $\quad r_M\,\Delta k = \pi\,\Delta n \;\to\; \rho^0_l(k) = \frac{r_M}{\pi}$

(9.130-1) thus become

$$\Delta\,\mathcal{B}_2^{\text{BE}}(T) = -\frac{2\sqrt{2}}{z}\sum_{l=0}^{\infty}(4\,l+1)\left(\sum_{n=2\,l+1}^{\infty} e^{-\beta E_{n,2l}} - \int_0^\infty \frac{d\,k}{\pi}\,\frac{d\,\delta_{2l}(k)}{d\,k}\,e^{-\beta E_k}\right) \tag{9.137}$$

and

$$\Delta\,\mathcal{B}_2^{\text{FD}}(T) = -\frac{2\sqrt{2}}{z}\sum_{l=0}^{\infty}\left\{3\,(4\,l+3)\left(\sum_{n=2\,l+2}^{\infty} e^{-\beta E_{n,2l+1}} - \int_0^\infty \frac{d\,k}{\pi}\,\frac{d\,\delta_{2l+1}(k)}{d\,k}\,e^{-\beta E_k}\right) + (4\,l+1)\left(\sum_{n=2\,l+1}^{\infty} e^{-\beta E_{n,2l}} - \int_0^\infty \frac{d\,k}{\pi}\,\frac{d\,\delta_{2l}(k)}{d\,k}\,e^{-\beta E_k}\right)\right\} \tag{9.138}$$

Ex. 9.4

Compute the 2nd virial coefficient $\mathcal{B}_2^0(T)$ for an ideal Fermi-Dirac gas of spin $\frac{1}{2}$ particles.

Answer

Combining (9.46) & (9.108), we have

$$\mathcal{B}_2(T) = -\tilde{b}_2(T) = \lim_{V\to\infty}\frac{-1}{2!\,V}\,\text{Tr}\,\hat{U}_2(\beta)$$

$$= \lim_{V\to\infty}\frac{-1}{2!\,V}\left\{\text{Tr}\,\hat{W}_2 - \left(\text{Tr}\,\hat{W}_1\right)^2\right\} \tag{1}$$

From (9.101), we get, for free particles,

$$\hat{W}_1(\beta) = \frac{1}{z}\exp\left(-\beta\,\hat{T}\right) \qquad\qquad \hat{W}_2(\beta) = \frac{2}{z^2}\exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \tag{1a}$$

where

$$\hat{T}_j = \frac{1}{2\,m}\,\hat{\mathbf{p}}_j^2$$

is the kinetic energy operator of the j^{th} particle.

The trace of $\hat{T}$ can be easily calculated in the momentum basis. For spin $\frac{1}{2}$ particles,

$$
\begin{aligned}
\operatorname{Tr} \hat{W}_1 &= \frac{1}{z} \operatorname{Tr} \exp\left(-\beta \hat{T}\right) \\
&= \frac{1}{z} \sum_{\boldsymbol{k}} \sum_{s=\pm 1} \left\langle \boldsymbol{k}, s \,\middle|\, \exp\left(-\beta \hat{T}\right) \,\middle|\, \boldsymbol{k}, s \right\rangle \\
&= \frac{2}{z} \sum_{\boldsymbol{k}} \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) \\
&= \frac{2V}{z (2\pi)^3} 4\pi \int_0^\infty dk\, k^2 \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) \\
&= 2V
\end{aligned}
$$

For fermions, the N-particle states must be anti-symmetrized. Thus, for $N = 2$,

$$
|\, \boldsymbol{k}, s; \boldsymbol{k}', s' \rangle_a = \frac{1}{\sqrt{2}} \left(|\, \boldsymbol{k}, s; \boldsymbol{k}', s' \rangle - |\, \boldsymbol{k}', s'; \boldsymbol{k}, s \rangle \right)
$$

where $|\, \boldsymbol{k}, s; \boldsymbol{k}', s' \rangle$ means particle 1 & 2 are in states $|\, \boldsymbol{k}, s \rangle$ & $|\, \boldsymbol{k}', s' \rangle$, respectively.

Thus,

$$
\begin{aligned}
\operatorname{Tr} \hat{W}_2 &= \frac{2}{z^2} \operatorname{Tr} \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \\
&= \frac{1}{z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \sum_{s, s'=\pm 1} {}_a\left\langle \boldsymbol{k}, s; \boldsymbol{k}', s' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, s; \boldsymbol{k}', s' \right\rangle_a \\
&= \frac{1}{2z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \sum_{s, s'=\pm 1} \left\{ \left\langle \boldsymbol{k}, s; \boldsymbol{k}', s' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, s; \boldsymbol{k}', s' \right\rangle \right. \\
&\qquad - \left\langle \boldsymbol{k}, s; \boldsymbol{k}', s' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}', s'; \boldsymbol{k}, s \right\rangle \\
&\qquad - \left\langle \boldsymbol{k}', s'; \boldsymbol{k}, s \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, s; \boldsymbol{k}', s' \right\rangle \\
&\qquad \left. + \left\langle \boldsymbol{k}', s'; \boldsymbol{k}, s \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}', s'; \boldsymbol{k}, s \right\rangle \right\} \\
&= \frac{1}{z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \sum_{s, s'=\pm 1} \left\{ \left\langle \boldsymbol{k}, s; \boldsymbol{k}', s' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, s; \boldsymbol{k}', s' \right\rangle \right. \\
&\qquad \left. - \left\langle \boldsymbol{k}, s; \boldsymbol{k}', s' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}', s'; \boldsymbol{k}, s \right\rangle \right\} \qquad \text{(3a)} \\
&= \frac{1}{z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \sum_{s, s'=\pm 1} \left[\left\langle \boldsymbol{k}, s \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k}, s \right\rangle \left\langle \boldsymbol{k}', s' \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k}', s' \right\rangle \right. \\
&\qquad \left. - \left\langle \boldsymbol{k}, s \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k}', s' \right\rangle \left\langle \boldsymbol{k}', s' \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k}, s \right\rangle \right] \\
&= \frac{1}{z^2} \left[2 \sum_{\boldsymbol{k}} \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) 2 \sum_{\boldsymbol{k}'} \exp\left(-\frac{\beta \hbar^2 k'^2}{2m}\right) - 2 \sum_{\boldsymbol{k}} \exp\left(-\frac{\beta \hbar^2 k^2}{m}\right) \right] \\
&= 4V^2 - \frac{4}{z^2} \sum_{\boldsymbol{k}} \exp\left(-\frac{\beta \hbar^2 k^2}{m}\right) \\
&= 4V^2 - \frac{V}{\sqrt{2}\, z} \qquad \text{(3b)}
\end{aligned}
$$

(1) thus becomes

$$
\mathcal{B}_2(T) = \frac{1}{2\sqrt{2}\, z} = \frac{\lambda_T^3}{2\sqrt{2}} \qquad \text{(4)}
$$

(4) gives the effects of the (Fermi-Dirac) statistics. Since it is positive, it increases the pressure of the gas [see (9.43)].

Ex. 9.5

Compute the 2nd virial coefficient $\mathcal{B}_2^0(T)$ for a dilute gas of hard sphere spin-0 bosons at low temperature.

Answer

For hard spheres of core radius a (or sphere radius $a/2$),

$$R_{nl}(r) = 0 \qquad \forall\; r \le a$$

(9.132) gives

$$0 = C_{kl}\left[\cos\delta_{kl}\; j_l(k a) + \sin\delta_{kl}\; n_l(k a)\right]$$

$$\rightarrow \qquad \tan\delta_{kl} = -\frac{j_l(k a)}{n_l(k a)} \qquad (1)$$

At low temperatures, $k a \ll 1$, and we have [see Arfken]

$$j_l(x) \approx \frac{2^l\, l!}{(2l+1)!}\, x^l \qquad\qquad n_l(k a) \approx -\frac{(2l)!}{2^l\, l!}\, x^{-l-1} = -(2l-1)!!\, x^{-l-1}$$

$$\rightarrow \qquad \tan\delta_{kl} \approx \frac{2^l\, l!}{(2l+1)!\,(2l-1)!!}\,(k a)^{2l+1}$$

$$= \frac{(2l)!}{(2l+1)!\,[\,(2l-1)!!\,]^2}\,(k a)^{2l+1}$$

$$= \frac{1}{(2l+1)\;[\,(2l-1)!!\,]^2}\,(k a)^{2l+1} \qquad (2)$$

Thus, the $l = 0$ term dominants, giving

$$\tan\delta_{k0} \approx k a \qquad \rightarrow \qquad \delta_{k0} \approx k a$$

$$\therefore \qquad \frac{d\,\delta_0(k)}{d k} = a$$

Hard sphere potential is repulsive so that there are no bound states. Hence, (9.137) becomes

$$\Delta\mathcal{B}_2(T) \approx \frac{2\sqrt{2}}{z}\int_0^\infty \frac{d k}{\pi}\, a\, e^{-\beta E_k} \qquad\qquad E_k = \frac{\hbar k^2}{m}$$

$$= \frac{2a}{z^{2/3}} \qquad (3)$$

$$\rightarrow \qquad \mathcal{B}_2(T) \approx \mathcal{B}_2^0(T) + \frac{2a}{z^{2/3}} \qquad (3a)$$

$\mathcal{B}_2^0(T)$ can be calculated as follows [cf. Ex.9.4]

$$\mathcal{B}_2^0(T) = \lim_{V\to\infty} \frac{-1}{2!\,V}\left\{\mathrm{Tr}\,\hat{W}_2 - \left(\mathrm{Tr}\,\hat{W}_1\right)^2\right\}$$

$$\mathrm{Tr}\,\hat{W}_1 = \frac{1}{z}\,\mathrm{Tr}\exp\left(-\beta\,\hat{T}\right)$$

$$= \frac{1}{z}\sum_{\boldsymbol{k}}\left\langle \boldsymbol{k}\,\middle|\,\exp\left(-\beta\,\hat{T}\right)\middle|\,\boldsymbol{k}\right\rangle$$

$$= \frac{1}{z}\sum_{\boldsymbol{k}}\exp\left(-\frac{\beta\,\hbar^2 k^2}{2m}\right)$$

$$= \frac{V}{z(2\pi)^3} 4\pi \int_0^\infty dk\, k^2 \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right)$$
$$= V$$

For bosons, the N-particle states must be symmetrized. Thus, for $N = 2$,

$$|\, \boldsymbol{k}, \boldsymbol{k}' \rangle_s = \frac{1}{\sqrt{2}} \left(|\, \boldsymbol{k}, \boldsymbol{k}' \rangle + |\, \boldsymbol{k}', \boldsymbol{k} \rangle \right)$$

where $|\, \boldsymbol{k}, \boldsymbol{k}' \rangle$ means particle 1 & 2 are in states $|\, \boldsymbol{k} \rangle$ & $|\, \boldsymbol{k}' \rangle$, respectively.

Thus,

$$\mathrm{Tr}\, \hat{W}_2 = \frac{2}{z^2} \mathrm{Tr} \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right]$$
$$= \frac{1}{z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} {}_s\left\langle \boldsymbol{k}, \boldsymbol{k}' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, \boldsymbol{k}' \right\rangle_s$$
$$= \frac{1}{2z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \left\{ \left\langle \boldsymbol{k}, \boldsymbol{k}' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, \boldsymbol{k}' \right\rangle \right.$$
$$+ \left\langle \boldsymbol{k}, \boldsymbol{k}' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}', \boldsymbol{k} \right\rangle$$
$$+ \left\langle \boldsymbol{k}', \boldsymbol{k} \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, \boldsymbol{k}' \right\rangle$$
$$\left. + \left\langle \boldsymbol{k}', \boldsymbol{k} \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}', \boldsymbol{k} \right\rangle \right\}$$
$$= \frac{1}{z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \left\{ \left\langle \boldsymbol{k}, \boldsymbol{k}' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}, \boldsymbol{k}' \right\rangle \right.$$
$$\left. + \left\langle \boldsymbol{k}, \boldsymbol{k}' \,\middle|\, \exp\left[-\beta\left(\hat{T}_1 + \hat{T}_2\right)\right] \,\middle|\, \boldsymbol{k}', \boldsymbol{k} \right\rangle \right\}$$
$$= \frac{1}{z^2} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \left[\left\langle \boldsymbol{k} \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k} \right\rangle \left\langle \boldsymbol{k}' \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k}' \right\rangle \right.$$
$$\left. + \left\langle \boldsymbol{k} \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k}' \right\rangle \left\langle \boldsymbol{k}' \,\middle|\, e^{-\beta \hat{T}} \,\middle|\, \boldsymbol{k} \right\rangle \right]$$
$$= \frac{1}{z^2} \left[\sum_{\boldsymbol{k}} \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right) \sum_{\boldsymbol{k}'} \exp\left(-\frac{\beta\hbar^2 k'^2}{2m}\right) + \sum_{\boldsymbol{k}} \exp\left(-\frac{\beta\hbar^2 k^2}{m}\right) \right]$$
$$= V^2 + \frac{1}{z^2} \sum_{\boldsymbol{k}} \exp\left(-\frac{\beta\hbar^2 k^2}{m}\right)$$
$$= V^2 + \frac{V}{2\sqrt{2}\, z}$$

$$\therefore \qquad \mathcal{B}_2^0(T) = -\frac{1}{2^{5/2} z}$$

(3a) thus becomes

$$\mathcal{B}_2(T) \approx -\frac{1}{2^{5/2} z} + \frac{2a}{z^{2/3}} \qquad (4)$$

The 1st term on the R.H.S. of (4) is due to (Bose-Einstein) statistics. Since it's negative, it lowers $\mathcal{B}_2(T)$ and hence the pressure [see (9.43)].

The 2nd term is due to the hard-core potential. Since it's positive, it raises $\mathcal{B}_2(T)$ and hence the pressure.

Code

```
(* Tr W1 *)
```

$$2\frac{V}{z\,(2\,\pi)^3}\,4\,\pi\int_0^{\infty}k^2\,\text{Exp}[-a\,k^2]\,dk\;/.\;\left\{a\to\beta\,\hbar^2/(2\,m),\;z\to\left(2\,\pi\,\hbar\sqrt{\frac{\beta}{2\,\pi\,m}}\right)^{-3}\right\}\;//\;\text{PowerExpand}$$

$$\text{ConditionalExpression}\left[2\,V,\;\text{Re}\left[\frac{\beta\,\hbar^2}{m}\right]>0\right]$$

$$2\frac{V}{z\,(2\,\pi)^3}\,4\,\pi\int_0^{\infty}k^2\,\text{Exp}[-a\,k^2]\,dk\;/.\;\left\{a\to\beta\,\hbar^2/m,\;z\to\left(2\,\pi\,\hbar\sqrt{\frac{\beta}{2\,\pi\,m}}\right)^{-3}\right\}\;//\;\text{PowerExpand}$$

$$\text{ConditionalExpression}\left[\frac{V}{\sqrt{2}},\;\text{Re}\left[\frac{\beta\,\hbar^2}{m}\right]>0\right]$$

$$\frac{V}{z\,(2\,\pi)^3}\,4\,\pi\int_0^{\infty}k^2\,\text{Exp}[-a\,k^2]\,dk\;/.\;\left\{a\to\beta\,\hbar^2/(4\,m),\;z\to\left(2\,\pi\,\hbar\sqrt{\frac{\beta}{2\,\pi\,m}}\right)^{-3}\right\}\;//\;\text{PowerExpand}$$

$$\text{ConditionalExpression}\left[2\sqrt{2}\,V,\;\text{Re}\left[\frac{\beta\,\hbar^2}{m}\right]>0\right]$$

$$\frac{2\sqrt{2}}{z\,\pi}\,a\int_0^{\infty}\text{Exp}[-b\,k^2]\,dk\;/.\;\left\{b\to\beta\,\hbar^2/m,\;z\to\left(2\,\pi\,\hbar\sqrt{\frac{\beta}{2\,\pi\,m}}\right)^{-3}\right\}\;//\;\text{PowerExpand}$$

$$\text{ConditionalExpression}\left[\frac{4\,a\,\pi\,\beta\,\hbar^2}{m},\;\text{Re}\left[\frac{\beta\,\hbar^2}{m}\right]>0\right]$$

In[6]:=

$$\frac{2\sqrt{2}}{z\,\pi}\,a\int_0^{\infty}\text{Exp}[-b\,k^2]\,dk\;//.\;\left\{b\to\beta\,\hbar^2/m,\;\beta\to2\,\pi\,m\,z^{-2/3}\left(\frac{1}{2\,\pi\,\hbar}\right)^2\right\}\;//\;\text{PowerExpand}$$

Out[6]=

$$\text{ConditionalExpression}\left[\frac{2\,a}{z^{2/3}},\;\frac{\text{Re}\left[\frac{1}{z^{2/3}}\right]}{\pi}>0\right]$$