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Memo

Truncation corrections for equations of state

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1 Introduction

Johnson et al. [1, Eq. 17] derive an equation describing the approximate contribution form the truncated part of the interaction potential, in their case the Lennard-Jones fluid was considered. The derivation express the change in the Helmholtz free energy due to a change in potential as a functional differential,

$$\frac{\delta A}{\delta \phi} = \rho^2 g\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right), \tag{1}$$

where A is the Helmholtz free energy, ϕ is the potential acting between particles, $g\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right)$ is the pair correlation function, and $\boldsymbol{r}_i$ is the position vector of a molecule.

Johnson et al. [1, Eq. 17] defines the following reduced properties,

$$T^* = \frac{\mathrm{k_B} T}{\epsilon}, \tag{2}$$

$$\rho^* = \frac{N\sigma^3}{V}, \tag{3}$$

$$A^* = \frac{A}{N\epsilon}, \tag{4}$$

and they will also be used in this memo.

In the following we will derive the same properties for the quantum corrected Mie potential.

2 The potential

The Mie potential is expressed as follows,

$$\phi^{\mathrm{Mie}}\left(r\right) = \mathcal{C}\epsilon\left(\left(\frac{\sigma}{r}\right)^{\lambda_{\mathrm{r}}} - \left(\frac{\sigma}{r}\right)^{\lambda_{\mathrm{a}}}\right), \tag{5}$$

where,

$$\mathcal{C} = \frac{\lambda_{\mathrm{r}}}{\lambda_{\mathrm{r}} - \lambda_{\mathrm{a}}}\left(\frac{\lambda_{\mathrm{r}}}{\lambda_{\mathrm{a}}}\right)^{\frac{\lambda_{\mathrm{a}}}{\lambda_{\mathrm{r}}-\lambda_{\mathrm{a}}}}, \tag{6}$$

The quantum correction of the Mie potential to first order, using the Feynman Hibbs approach, take the following form,

$$\phi^{\mathrm{Q_1,Mie}}\left(r,T\right) =\mathcal{C}\epsilon D\frac{1}{r^2}\left(Q_1\left(\lambda_{\mathrm{r}}\right)\left(\frac{\sigma}{r}\right)^{\lambda_{\mathrm{r}}} - Q_1\left(\lambda_{\mathrm{a}}\right)\left(\frac{\sigma}{r}\right)^{\lambda_{\mathrm{a}}}\right). \tag{7}$$

The second order correction becomes,

$$\phi^{\mathrm{Q_2,Mie}}\left(r,T\right) =\mathcal{C}\epsilon\frac{D^2}{2}\frac{1}{r^4}\left(Q_2\left(\lambda_{\mathrm{r}}\right)\left(\frac{\sigma}{r}\right)^{\lambda_{\mathrm{r}}} - Q_2\left(\lambda_{\mathrm{a}}\right)\left(\frac{\sigma}{r}\right)^{\lambda_{\mathrm{a}}}\right). \tag{8}$$

Here we have used the following definitions,

$$D =\frac{\beta\hbar^2}{24\mu}, \tag{9}$$

$$\beta = \frac{1}{\mathrm{k_B}T}, \tag{10}$$

$$h = 2\pi\hbar, \tag{11}$$

$$Q_1\left(\lambda\right) =\lambda\left(\lambda-1\right), \tag{12}$$

$$Q_2\left(\lambda\right) = \left(\lambda+2\right)\left(\lambda+1\right)\lambda\left(\lambda-1\right). \tag{13}$$

μ is molecular mass.

The overall quantum corrected Mie potential then take the following form,

$$\phi\left(r,T\right) =\phi^{\mathrm{Mie}}\left(r\right) + \phi^{\mathrm{Q_1,Mie}}\left(r,T\right) + \phi^{\mathrm{Q_2,Mie}}\left(r,T\right). \tag{14}$$

In the following, for simplicity, we drop writing out the temperature dependence of the potential explicitly.

For the change in going from a cut potential, truncated at r_{c}, to a full quantum corrected potential, we get,

$$\delta\phi_{\mathrm{c}}\left(r\right) =\phi\left(r\right) - \phi_{\mathrm{c}}\left(r\right) = \begin{cases} 0 & \text{if } r \leq r_{\mathrm{c}} \\ \phi\left(r\right) & \text{if } r > r_{\mathrm{c}} \end{cases}. \tag{15}$$

Here ϕ_{c} is the potential cut at r_{c}.

For the change in going from a cut and shifted potential, truncated at r_c, to a full quantum corrected potential, we get,

$$\delta\phi_{\mathrm{cs}}(r) = \phi(r) - \phi_{\mathrm{cs}}(r) = \begin{cases} \phi(r_\mathrm{c}) & \text{if } r \leq r_\mathrm{c} \\ \phi(r) & \text{if } r > r_\mathrm{c} \end{cases}. \tag{16}$$

For the change in going from a cut to a cut and shifted potential, we get by combining equations 15 and 16,

$$\delta\phi_{\mathrm{c-cs}}(r) = \phi_\mathrm{c}(r) - \phi_{\mathrm{cs}}(r) = \begin{cases} \phi(r_\mathrm{c}) & \text{if } r \leq r_\mathrm{c} \\ 0 & \text{if } r > r_\mathrm{c} \end{cases}. \tag{17}$$

3 The Helmholtz free energy truncation correction

Using equations 1 and 15, the change in Helmholtz free energy due to truncation is,

$$\Delta A_\mathrm{c} = A - A_\mathrm{c} = 2\pi N\rho \int_0^\infty g(r)\,\delta\phi_\mathrm{c}(r)\,r^2 dr \tag{18}$$

$$= 2\pi N\rho \int_{r_\mathrm{c}}^\infty g(r)\,\phi(r)\,r^2 dr \tag{19}$$

Assuming, as Johnson et al., that $g(r) = 1$ for $r > r_\mathrm{c}$, the integration becomes simple. The Mie integral becomes,

$$\int_{r_\mathrm{c}}^\infty \phi^{\mathrm{Mie}}(r)\,r^2 dr = \mathcal{C}\epsilon\sigma^3 \left(\frac{1}{\lambda_\mathrm{r} - 3} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{r}-3)} - \frac{1}{\lambda_\mathrm{a} - 3} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{a}-3)} \right) \tag{20}$$

$$= \mathcal{C}\epsilon\sigma^3\Lambda \tag{21}$$

The integral for the first order quantum correction to the Mie potential becomes,

$$\int_{r_\mathrm{c}}^\infty \phi^{\mathrm{Q_1,Mie}}(r)\,r^2 dr = \mathcal{C}\epsilon\sigma D \left(\frac{Q_1(\lambda_\mathrm{r})}{\lambda_\mathrm{r} - 1} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{r}-1)} - \frac{Q_1(\lambda_\mathrm{a})}{\lambda_\mathrm{a} - 1} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{a}-1)} \right) \tag{22}$$

$$= \mathcal{C}\epsilon\sigma D \left(\lambda_\mathrm{r} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{r}-1)} - \lambda_\mathrm{a} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{a}-1)} \right) \tag{23}$$

$$= \mathcal{C}\epsilon\sigma D\Lambda^{\mathrm{Q_1}} \tag{24}$$

The integral for the second order quantum correction to the Mie potential becomes,

$$\int_{r_\mathrm{c}}^\infty \phi^{\mathrm{Q_2,Mie}}(r)\,r^2 dr = \mathcal{C}\epsilon\frac{1}{\sigma}\frac{D^2}{2} \left(\frac{Q_2(\lambda_\mathrm{r})}{\lambda_\mathrm{r} + 1} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{r}+1)} - \frac{Q_2(\lambda_\mathrm{a})}{\lambda_\mathrm{a} + 1} \left(\frac{\sigma}{r_\mathrm{c}}\right)^{(\lambda_\mathrm{a}+1)} \right) \tag{25}$$

$$= \mathcal{C}\epsilon\frac{1}{\sigma}\frac{D^2}{2}\Lambda^{\mathrm{Q_2}} \tag{26}$$

The reduced Helmholtz free energy change then becomes,

$$A^* - A^*_\mathrm{c} = 2\pi\rho^*\mathcal{C}\left[\Lambda + D\frac{\Lambda^{\mathrm{Q_1}}}{\sigma^2} + \frac{D^2}{2}\frac{\Lambda^{\mathrm{Q_2}}}{\sigma^4}\right] \tag{27}$$

3.1 The Helmholtz free energy truncation correction for Thermopack

$$F^{\mathrm{c}} = \frac{\Delta A_{\mathrm{c}}}{RT} = \frac{A - A_{\mathrm{c}}}{RT} = 2\pi \mathrm{N_A} \sigma^3 \mathcal{C} \left[\frac{\epsilon}{\mathrm{k_B}}\right] \frac{n^2}{V} \frac{1}{T} \left[\Lambda + D \frac{\Lambda^{\mathrm{Q}_1}}{\sigma^2} + \frac{D^2}{2} \frac{\Lambda^{\mathrm{Q}_2}}{\sigma^4}\right] \tag{28}$$

Introducing $\mathrm{k_c} = 2\pi \mathrm{N_A} \sigma^3 \mathcal{C} \left[\frac{\epsilon}{\mathrm{k_B}}\right]$, the differentials of F^{c} becomes,

$$F^{\mathrm{c}}_{n} = 2\frac{F^{\mathrm{c}}}{n}, \tag{29}$$

$$F^{\mathrm{c}}_{nn} = 2\frac{F^{\mathrm{c}}}{n^2}, \tag{30}$$

$$F^{\mathrm{c}}_{V} = -\frac{F^{\mathrm{c}}}{V}, \tag{31}$$

$$F^{\mathrm{c}}_{VV} = 2\frac{F^{\mathrm{c}}}{V^2}, \tag{32}$$

$$F^{\mathrm{c}}_{Vn} = -2\frac{F^{\mathrm{c}}}{Vn}, \tag{33}$$

$$F^{\mathrm{c}}_{T} = -\frac{F^{\mathrm{c}}}{T} + \mathrm{k_c} \frac{n^2}{V} \frac{1}{T} \left[D_T \frac{\Lambda^{\mathrm{Q}_1}}{\sigma^2} + D D_T \frac{\Lambda^{\mathrm{Q}_2}}{\sigma^4}\right], \tag{34}$$

$$F^{\mathrm{c}}_{Tn} = 2\frac{F^{\mathrm{c}}_{T}}{n}, \tag{35}$$

$$F^{\mathrm{c}}_{TV} = -\frac{F^{\mathrm{c}}_{T}}{V}, \tag{36}$$

$$\begin{aligned} F^{\mathrm{c}}_{TT} =& -2\frac{F^{\mathrm{c}}}{T^2} - 2\mathrm{k_c} \frac{n^2}{V} \frac{1}{T^2} \left[D_T \frac{\Lambda^{\mathrm{Q}_1}}{\sigma^2} + D D_T \frac{\Lambda^{\mathrm{Q}_2}}{\sigma^4}\right] \\ &+ \mathrm{k_c} \frac{n^2}{V} \frac{1}{T} \left[D_{TT} \frac{\Lambda^{\mathrm{Q}_1}}{\sigma^2} + \left(D_T^2 + D D_{TT}\right) \frac{\Lambda^{\mathrm{Q}_2}}{\sigma^4}\right]. \end{aligned} \tag{37}$$

4 The Helmholtz free energy shift correction

Using equations 1, 15 16, the change in Helmholtz free energy due to truncation is,

$$\Delta A_{\mathrm{cs}} = A - A_{\mathrm{c}} - A_{\mathrm{s}} = \Delta A_{\mathrm{c}} + \Delta A_{\mathrm{c-cs}} \tag{38}$$

$$\Delta A_{\mathrm{c-cs}} = 2\pi N \rho \int_0^{r_{\mathrm{c}}} g\left(r\right) \delta\phi_{\mathrm{cs}}\left(r\right) r^2 dr \tag{39}$$

$$= 2\pi N \rho \phi\left(r_{\mathrm{c}}\right) \int_0^{r_{\mathrm{c}}} g\left(r\right) r^2 dr \tag{40}$$

Johnson et al. noticed that $2\pi\rho \int_0^{r_{\mathrm{c}}} g\left(r\right) r^2 dr$ is just the number of pairs of atoms within the cutoff of a central atom. This can be approximate by the average number of pairs of atoms in the volume of a sphere of radius r_{c}.

The integration then becomes simple. And the quantum corrected Mie integral becomes,

$$\Delta A_{\mathrm{c-cs}} = \frac{2}{3}\pi N \rho \phi\left(r_{\mathrm{c}}\right) r_{\mathrm{c}}^{3} \tag{41}$$

$$= \frac{2}{3}\pi N \rho \mathcal{C} \epsilon \sigma^{3}\left[\Lambda_{\mathrm{s}} + D\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_1}}{\sigma^2} + \frac{D^2}{2}\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_2}}{\sigma^4}\right] \tag{42}$$

$$\Lambda_{\mathrm{s}} = \left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{(\lambda_{\mathrm{r}}-3)} - \left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{(\lambda_{\mathrm{a}}-3)} \tag{43}$$

$$\Lambda_{\mathrm{s}}^{\mathrm{Q}_1} = Q_1\left(\lambda_{\mathrm{r}}\right)\left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{(\lambda_{\mathrm{r}}-1)} - Q_1\left(\lambda_{\mathrm{a}}\right)\left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{(\lambda_{\mathrm{a}}-1)} \tag{44}$$

$$\Lambda_{\mathrm{s}}^{\mathrm{Q}_2} = Q_2\left(\lambda_{\mathrm{r}}\right)\left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{(\lambda_{\mathrm{r}}+1)} - Q_2\left(\lambda_{\mathrm{a}}\right)\left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{(\lambda_{\mathrm{a}}+1)} \tag{45}$$

In reduced variables this becomes,

$$\Delta A_{\mathrm{c-cs}}^{*} = \frac{2}{3}\pi \rho^{*} \mathcal{C}\left[\Lambda_{\mathrm{s}} + D\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_1}}{\sigma^2} + \frac{D^2}{2}\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_2}}{\sigma^4}\right]. \tag{46}$$

4.1 The Helmholtz free energy potentiala shift correction for Thermopack

$$F^{\mathrm{cs}} = \frac{\Delta A_{\mathrm{c-cs}}}{RT} = \frac{A_{\mathrm{c}} - A_{\mathrm{cs}}}{RT} = \frac{2}{3}\pi \mathrm{N_A}\sigma^3\mathcal{C}\left[\frac{\epsilon}{\mathrm{k_B}}\right]\frac{n^2}{V}\frac{1}{T}\left[\Lambda_{\mathrm{s}} + D\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_1}}{\sigma^2} + \frac{D^2}{2}\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_2}}{\sigma^4}\right] \tag{47}$$

Introducing $\mathrm{k_{cs}} = 2\pi\mathrm{N_A}\sigma^3\mathcal{C}/3 = \mathrm{k_c}/3\left[\frac{\epsilon}{\mathrm{k_B}}\right]$, the differentials of F^{cs} becomes,

$$F_n^{\mathrm{cs}} = 2\frac{F^{\mathrm{cs}}}{n}, \tag{48}$$

$$F_{nn}^{\mathrm{cs}} = 2\frac{F^{\mathrm{cs}}}{n^2}, \tag{49}$$

$$F_V^{\mathrm{cs}} = -\frac{F^{\mathrm{cs}}}{V}, \tag{50}$$

$$F_{VV}^{\mathrm{cs}} = 2\frac{F^{\mathrm{cs}}}{V^2}, \tag{51}$$

$$F_{Vn}^{\mathrm{cs}} = -2\frac{F^{\mathrm{cs}}}{Vn}, \tag{52}$$

$$F_T^{\mathrm{cs}} = -\frac{F^{\mathrm{cs}}}{T} + \mathrm{k_{cs}}\frac{n^2}{V}\frac{1}{T}\left[D_T\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_1}}{\sigma^2} + DD_T\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_2}}{\sigma^4}\right], \tag{53}$$

$$F_{Tn}^{\mathrm{cs}} = 2\frac{F_T^{\mathrm{cs}}}{n}, \tag{54}$$

$$F_{TV}^{\mathrm{cs}} = -\frac{F_T^{\mathrm{cs}}}{V}, \tag{55}$$

$$F_{TT}^{\mathrm{cs}} = -2\frac{F^{\mathrm{cs}}}{T^2} - 2\mathrm{k_{cs}}\frac{n^2}{V}\frac{1}{T^2}\left[D_T\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_1}}{\sigma^2} + DD_T\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_2}}{\sigma^4}\right] + \mathrm{k_{cs}}\frac{n^2}{V}\frac{1}{T}\left[D_{TT}\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_1}}{\sigma^2} + \left(D_T^2 + DD_{TT}\right)\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q}_2}}{\sigma^4}\right]. \tag{56}$$

References

[1] J Karl Johnson, John A Zollweg, and Keith E Gubbins. The Lennard-Jones equation of state revisited. *Molecular Physics*, 78(3):591–618, 1993.