Thermotools memo

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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,

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

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,

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

The second order correction becomes,

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

Here we have used the following definitions,

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

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

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

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

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

μ is molecular mass.

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

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

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,

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

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,

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

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,

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

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

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

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

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

$$F^{\mathrm{c}}_{T} = -\frac{F^{\mathrm{c}}}{T} + \mathrm{k_c}\frac{n^2}{V}\frac{1}{T}\left[D_T\frac{\Lambda^{\mathrm{Q_1}}}{\sigma^2} + DD_T\frac{\Lambda^{\mathrm{Q_2}}}{\sigma^4}\right], \tag{34}$$

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

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

$$\begin{aligned} F^{\mathrm{c}}_{TT} =& -2\frac{F^{\mathrm{c}}}{T^2} - 2\mathrm{k_c}\frac{n^2}{V}\frac{1}{T^2}\left[D_T\frac{\Lambda^{\mathrm{Q_1}}}{\sigma^2} + DD_T\frac{\Lambda^{\mathrm{Q_2}}}{\sigma^4}\right] \\ &+ \mathrm{k_c}\frac{n^2}{V}\frac{1}{T}\left[D_{TT}\frac{\Lambda^{\mathrm{Q_1}}}{\sigma^2} + \left(D_T^2 + DD_{TT}\right)\frac{\Lambda^{\mathrm{Q_2}}}{\sigma^4}\right]. \end{aligned} \tag{37}$$

4 The Helmholtz free energy shift correction

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

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

$$\begin{aligned} \Delta A_{\mathrm{c-cs}} &= 2\pi N\rho \int_0^{r_{\mathrm{c}}} g(r)\, \delta\phi_{\mathrm{cs}}(r)\, r^2 dr \\ &= 2\pi N\rho\phi(r_{\mathrm{c}}) \int_0^{r_{\mathrm{c}}} g(r)\, r^2 dr \end{aligned} \tag{39, 40}$$

Johnson et al. used that $2\pi\rho\int_0^{r_{\mathrm{c}}} g(r)\, r^2 dr$ 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,

$$\begin{aligned} \Delta A_{\mathrm{c-cs}} &= \frac{2}{3}\pi N\rho\phi(r_{\mathrm{c}})\, r_{\mathrm{c}}^3 \\ &= \frac{2}{3}\pi N\rho\mathcal{C}\epsilon\sigma^3\left[\Lambda_{\mathrm{s}} + D\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q_1}}}{\sigma^2} + \frac{D^2}{2}\frac{\Lambda_{\mathrm{s}}^{\mathrm{Q_2}}}{\sigma^4}\right] \end{aligned} \tag{41, 42}$$

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

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

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

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 potential 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,

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

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

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

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

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

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

$$F^{\mathrm{cs}}_{Tn} = 2\frac{F^{\mathrm{cs}}_{T}}{n}, \tag{54}$$

$$F^{\mathrm{cs}}_{TV} = -\frac{F^{\mathrm{cs}}_{T}}{V}, \tag{55}$$

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

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.