

# Supplementary information

## **Behavior of rarified steam at very high temperature**

An orientation-averaged interaction potential approach towards its  
accurate description

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APPENDIX S1: Orientation-average  $\langle \phi_{12}^n(r) \rangle_\omega$  for simple dipole-dipole interactions

According to the definition of  $\langle \phi_{12}^n(\mathbf{r}, \boldsymbol{\omega}) \rangle_\omega$ , *i.e.*,

$$\langle \phi_{12}^n(r) \rangle_\omega = \int \phi_{12}^n(\mathbf{r}, \boldsymbol{\omega}) d\omega_1 d\omega_{12} / \int d\omega_1 d\omega_{12} \quad \text{S1-1}$$

the substitution of Eqn. (18) into S1-1 reads,

$$\langle \phi_{12}^n(r) \rangle_\omega = (8\pi)^{-1} \int (\mu_1^n \mu_2^n \mathcal{F}^n(\boldsymbol{\omega}_{12}) / r_{12}^{3n}) d\boldsymbol{\omega}_{12} \quad \text{S1-2}$$

where the prefactor  $(8\pi)^{-1}$  in S1-2 is simply  $(\int d\boldsymbol{\omega}_{12})^{-1} = (\int_1^{-1} d\cos\theta_1 \int_1^{-1} d\cos\theta_2 \int_0^{2\pi} d\varphi_{12})^{-1}$ , while the reminding term involves integrals of the form  $\int \mathcal{F}^n(\boldsymbol{\omega}_{12}) d\boldsymbol{\omega}_{12}$  with  $n = (1, 2, \dots)$ . In particular,

$$\begin{aligned} \int \mathcal{F}(\boldsymbol{\omega}_{12}) d\boldsymbol{\omega}_{12} &= \int (\sin\theta_1 \sin\theta_2 \cos\varphi_{12} - 2\cos\theta_1 \cos\theta_2) d\boldsymbol{\omega}_{12} \\ &= \int_1^{-1} d\cos\theta_1 \int_1^{-1} d\cos\theta_2 \int_0^0 d\sin\varphi_{12} - \\ &\quad 2 \int_0^0 d\sin\theta_1 \int_0^0 d\sin\theta_2 \int_0^{2\pi} d\varphi_{12} \end{aligned} \quad \text{S1-3}$$

and,

$$\begin{aligned} \int \mathcal{F}^2(\boldsymbol{\omega}_{12}) d\boldsymbol{\omega}_{12} &= \int (\sin\theta_1 \sin\theta_2 \cos\varphi_{12} - 2\cos\theta_1 \cos\theta_2)^2 d\boldsymbol{\omega}_{12} \\ &= \mathcal{I}_a + \mathcal{I}_b + \mathcal{I}_c \end{aligned} \quad \text{S1-4}$$

where,

$$\begin{aligned} \mathcal{I}_a &= \int \sin^2\theta_1 \sin^2\theta_2 \cos^2\varphi_{12} d\boldsymbol{\omega}_{12} \\ &= \int_0^\pi \sin^3\theta_1 d\theta_1 \int_0^\pi \sin^3\theta_2 d\theta_2 \int_0^{2\pi} \cos^2\varphi_{12} d\varphi_{12} = (4/3)^2 \pi \end{aligned} \quad \text{S1-5}$$

$$\begin{aligned} \mathcal{I}_b &= -4 \int \sin\theta_1 \cos\theta_1 \sin\theta_2 \cos\theta_2 \cos\varphi_{12} d\boldsymbol{\omega}_{12} \\ &= -4 \int_0^\pi \sin^2\theta_1 \cos\theta_1 d\theta_1 \int_0^\pi \sin^2\theta_2 \cos\theta_2 d\theta_2 \int_0^{2\pi} \cos\varphi_{12} d\varphi_{12} = 0 \end{aligned} \quad \text{S1-6}$$

$$\begin{aligned}
\mathcal{I}_c &= 4 \int \cos^2 \theta_1 \sin \theta_1 \cos^2 \theta_2 \sin \theta_2 \cos^2 \varphi_{12} d\omega_{12} \\
&= 4 \int_0^\pi \cos^2 \theta_1 \sin \theta_1 d\theta_1 \int_0^\pi \cos^2 \theta_2 \sin \theta_2 d\theta_2 \int_0^{2\pi} d\varphi_{12} \\
&= 4(2/3)^2 2\pi
\end{aligned} \tag{S1-7}$$

so that,

$$\int \mathcal{F}^2(\omega_{12}) d\omega_{12} = 16\pi/3 \tag{S1-8}$$

Likewise, by the same analysis,  $\int \mathcal{F}^m(\omega_{12}) d\omega_{12} = 0$  with  $m = 2n + 1$  as an outcome of the odd nature of the  $\mathcal{F}(\omega_{12})$  function for the dipole-dipole interactions. However,

$$\begin{aligned}
\int \mathcal{F}^4(\omega_{12}) d\omega_{12} &= \int (\sin \theta_1 \sin \theta_2 \cos \varphi_{12} - 2 \cos \theta_1 \cos \theta_2)^4 d\omega_{12} \\
&= \mathcal{I}_a + \mathcal{I}_b + \mathcal{I}_c + \mathcal{I}_d + \mathcal{I}_e
\end{aligned} \tag{S1-9}$$

where

$$\begin{aligned}
\mathcal{I}_a &= \int \sin^4 \theta_1 \sin^4 \theta_2 \cos^4 \varphi_{12} d\omega_{12} \\
&= \int_0^\pi \sin^5 \theta_1 d\theta_1 \int_0^\pi \sin^5 \theta_2 d\theta_2 \int_0^{2\pi} \cos^4 \varphi_{12} d\varphi_{12} = (16/15)^2 (3\pi/4)
\end{aligned} \tag{S1-10}$$

$$\begin{aligned}
\mathcal{I}_b &= -8 \int \sin^3 \theta_1 \cos \theta_1 \sin^3 \theta_2 \cos \theta_2 \cos^3 \varphi_{12} d\omega_{12} \\
&= -8 \int_0^\pi \sin^4 \theta_1 \cos \theta_1 d\theta_1 \int_0^\pi \sin^4 \theta_2 \cos \theta_2 d\theta_2 \int_0^{2\pi} \cos^3 \varphi_{12} d\varphi_{12} = 0
\end{aligned} \tag{S1-11}$$

$$\begin{aligned}
\mathcal{I}_c &= 24 \int \cos^2 \theta_1 \sin^2 \theta_1 \cos^2 \theta_2 \sin^2 \theta_2 \cos^2 \varphi_{12} d\omega_{12} \\
&= 24 \int_0^\pi \cos^2 \theta_1 \sin^3 \theta_1 d\theta_1 \int_0^\pi \cos^2 \theta_2 \sin^3 \theta_2 d\theta_2 \int_0^{2\pi} \cos^2 \varphi_{12} d\varphi_{12} \\
&= 24(4/15)^2 \pi
\end{aligned} \tag{S1-12}$$

$$\begin{aligned}
\mathcal{I}_d &= -32 \int \sin \theta_1 \cos^3 \theta_1 \sin \theta_2 \cos^3 \theta_2 \cos \varphi_{12} d\omega_{12} \\
&= -32 \int_0^\pi \sin^2 \theta_1 \cos^3 \theta_1 d\theta_1 \int_0^\pi \sin^2 \theta_2 \cos^3 \theta_2 d\theta_2 \int_0^{2\pi} \cos \varphi_{12} d\varphi_{12} \\
&= 0
\end{aligned} \tag{S1-13}$$

$$\begin{aligned}
\mathcal{I}_e &= 16 \int \cos^4 \theta_1 \cos^4 \theta_2 d\omega_{12} \\
&= 16 \int_0^\pi \sin \theta_1 \cos^4 \theta_1 d\theta_1 \int_0^\pi \sin \theta_2 \cos^4 \theta_2 d\theta_2 \int_0^{2\pi} d\phi_{12} \\
&= 32(2/5)^2 \pi
\end{aligned} \tag{S1-14}$$

Therefore, from S1-1 and the resulting integrals S1-2 to S1-14 we have that,

$$\left\langle [\phi_{12}^{\mu\mu}]^2(r) \right\rangle_\omega = (2\mu_1^2 \mu_2^2 / 3r_{12}^6) \tag{S1-15}$$

$$\begin{aligned}
\left\langle [\phi_{12}^{\mu\mu}]^4(r) \right\rangle_\omega &= (216\mu_1^4 \mu_2^4 / 225r_{12}^{12}) \\
&= (24\mu_1^4 \mu_2^4 / 25r_{12}^{12})
\end{aligned} \tag{S1-16}$$

and consequently, the second-order orientation-averaged dipole-dipole interaction potentials, Eqns. (16)-(17) become,

$$\Phi_{12}(r) = -(\beta/3)\mu_1^2 \mu_2^2 / r_{12}^6 - (7\beta^3/450)\mu_1^4 \mu_2^4 / r_{12}^{12} + \dots \tag{19}$$

$$\left\langle \phi_{12}(r) \right\rangle_\omega^{canon} = -(2\beta/3)\mu_1^2 \mu_2^2 / r_{12}^6 - (14\beta^3/225)\mu_1^4 \mu_2^4 / r_{12}^{12} + \dots \tag{20}$$

Likewise, for the permanent dipole-induced dipole interaction potential, *i.e.*,

$$\begin{aligned}
\phi_{12}^{\mu\alpha}(r_1, r_2, \omega_1, \omega_2) &= -\left\{ \alpha_1 \left[ (\boldsymbol{\mu}_2 \cdot \boldsymbol{\mu}_2) + 3(\boldsymbol{\mu}_2 \cdot \hat{r}_{12})^2 \right] + \right. \\
&\quad \left. \alpha_2 \left[ (\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_1) + 3(\boldsymbol{\mu}_1 \cdot \hat{r}_{12})^2 \right] \right\} / 2r_{12}^6
\end{aligned} \tag{S1-17}$$

where  $(\boldsymbol{\mu}_i \cdot \hat{r}_{12}) = \mu_i \cos \theta_i$ , *i.e.*,  $\mu_i \equiv |\boldsymbol{\mu}_i|$  and  $\hat{r}_{12} = \mathbf{r}_{12}/r_{12}$ , *i.e.*, S1-17 becomes Eqn. (21). By substitution of S1-17 into S1-1 we have that,

$$\left\langle [\phi_{12}^{\mu\alpha}]^n(r) \right\rangle_\omega = (8\pi)^{-1} \int (\alpha_1 \mu_2^2 \mathcal{F}_2(\omega_{12}) + \alpha_2 \mu_1^2 \mathcal{F}_1(\omega_{12}))^n / (-2r_{12}^6)^n d\omega_{12} \tag{S1-18}$$

with  $\mathcal{F}_i(\omega_{12}) = 3\cos^2 \theta_i + 1$ . Therefore,

$$\begin{aligned}
\int \mathcal{F}_1(\omega_{12}) d\omega_{12} &= \int (3\cos^2 \theta_1 + 1) d\omega_{12} \\
&= \int_0^\pi (3\cos^2 \theta_1 + 1) \sin \theta_1 d\theta_1 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^{2\pi} d\varphi_{12} \\
&= -16\pi
\end{aligned} \tag{S1-19}$$

$$\begin{aligned}
\int \mathcal{F}_1^2(\omega_{12}) d\omega_{12} &= \int (3\cos^2 \theta_1 + 1)^2 d\omega_{12} \\
&= \int_0^\pi (3\cos^2 \theta_1 + 1)^2 \sin \theta_1 d\theta_1 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^{2\pi} d\varphi_{12} \\
&= -4(48/5)\pi
\end{aligned} \tag{S1-20}$$

$$\begin{aligned}
\int \mathcal{F}_1(\omega_{12}) \mathcal{F}_2(\omega_{12}) d\omega_{12} &= \int (3\cos^2 \theta_1 + 1)(3\cos^2 \theta_2 + 1) d\omega_{12} \\
&= \int_0^\pi (3\cos^2 \theta_1 + 1) \sin \theta_1 d\theta_1 \times \\
&\quad \int_0^\pi (3\cos^2 \theta_2 + 1) \sin \theta_2 d\theta_2 \int_0^{2\pi} d\varphi_{12} \\
&= 2(48/5)^2 \pi
\end{aligned} \tag{S1-21}$$

and consequently,

$$\langle \phi_{12}^{\mu\alpha}(r) \rangle_\omega = -(\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2) / r_{12}^6 \tag{S1-22}$$

and,

$$\langle [\phi_{12}^{\mu\alpha}]^2(r) \rangle_\omega = -[30\alpha_1^2 \mu_2^4 - 288\alpha_1 \mu_2^2 \alpha_2 \mu_1^2 + 30\alpha_2^2 \mu_1^4] / 25r_{12}^{12} \tag{S1-23}$$

However, for the combined potential  $\phi_{12}(\mathbf{r}_1, \mathbf{r}_2, \omega_1, \omega_2) = \phi_{12}^{\mu\mu}(\mathbf{r}_1, \mathbf{r}_2, \omega_1, \omega_2) + \phi_{12}^{\mu\alpha}(\mathbf{r}_1, \mathbf{r}_2, \omega_1, \omega_2)$ , *i.e.*,

$$\begin{aligned}
\phi_{12}(\mathbf{r}_1, \mathbf{r}_2, \omega_1, \omega_2) &= (\mu_1 \mu_2 / r_{12}^3) (\sin \theta_1 \sin \theta_2 \cos \varphi_{12} - 2 \cos \theta_1 \cos \theta_2) - \\
&\quad [\alpha_1 \mu_2^2 (3\cos^2 \theta_2 + 1) + \alpha_2 \mu_1^2 (3\cos^2 \theta_1 + 1)] / 2r_{12}^6
\end{aligned} \tag{S1-24}$$

the averaged quantities  $\langle \phi_{12}^2(r) \rangle_\omega$  and  $\langle \phi_{12}^2(r) \rangle_\omega$  will in principle contain contributions from cross dipole-dipole and dipole-induced dipole interactions. In fact,

$$\langle \phi_{12}^2(r) \rangle_\omega = -(\mu_1 \mu_2 / 2r_{12}^9) \int \mathcal{F}(\omega_{12}) [\alpha_1 \mu_2^2 \mathcal{G}_2(\omega_{12}) + \alpha_2 \mu_1^2 \mathcal{G}_1(\omega_{12})] d\omega_{12} \tag{S1-25}$$

where  $\mathcal{F}(\omega_{12}) = (\sin\theta_1 \sin\theta_2 \cos\varphi_{12} - 2\cos\theta_1 \cos\theta_2)$  and  $\mathcal{G}_i(\omega_{12}) = (3\cos^2\theta_i + 1)$  so that,

$$\begin{aligned} \int \mathcal{F}(\omega_{12})\mathcal{G}_1(\omega_{12})d\omega_{12} &= \int (\sin\theta_1 \sin\theta_2 \cos\varphi_{12} - 2\cos\theta_1 \cos\theta_2)(3\cos^2\theta_2 + 1)d\omega_{12} \\ &= \int_0^\pi \sin^2\theta_1 d\theta_1 \int_0^\pi d\sin\varphi_{12} \int_0^\pi (3\cos^2\theta_2 + 1)\sin^2\theta_2 d\theta_2 - \\ &\quad 2 \int_1^{-1} \cos\theta_1 d\cos\theta_1 \int_1^{-1} (3\cos^2\theta_2 + 1)d\cos\theta_2 \int_0^{2\pi} d\varphi_{12} \\ &= 0 \end{aligned} \quad \text{S1-26}$$

Similarly,  $\int \mathcal{F}(\omega_{12})\mathcal{G}_2(\omega_{12})d\omega_{12} = 0$ , *i.e.*, there are no contributions from the cross dipole-dipole and dipole-induced dipole interactions to the first-order canonical and free-energy orientation-averaged potentials, *i.e.*,  $\langle \phi_{12}^{\mu\mu}(r)\phi_{12}^{\mu\alpha}(r) \rangle_\omega = 0$ .

Consequently, by substituting S1-15, S1-16, S1-22, S1-23 into Eqns. (13) and (15) we obtain the following orientation-averaged approximated up to the second non-vanishing contribution in the series expansion for a fluid described in terms of dipole-dipole plus dipole-induced dipole interactions,

$$\begin{aligned} \Phi_{12}(r) &= -[\alpha_1\mu_2^2 + \alpha_2\mu_1^2 + \beta\mu_1^2\mu_2^2/3]/r_{12}^6 - (\beta/25)[\beta^2\mu_1^4\mu_2^4 + \\ &\quad (144\alpha_1\mu_2^2\alpha_2\mu_1^2 - 15\alpha_1^2\mu_2^4 - 15\alpha_2^2\mu_1^4)]/r_{12}^{12} \end{aligned} \quad (23)$$

and,

$$\begin{aligned} \langle \phi_{12}(r) \rangle_\omega^{canon} &= -[\alpha_1\mu_2^2 + \alpha_2\mu_1^2 + 2\beta\mu_1^2\mu_2^2/3]/r_{12}^6 - (4\beta/25)[\beta^2\mu_1^4\mu_2^4 + \\ &\quad (144\alpha_1\mu_2^2\alpha_2\mu_1^2 - 15\alpha_1^2\mu_2^4 - 15\alpha_2^2\mu_1^4)]/r_{12}^{12} \end{aligned} \quad (24)$$

We note here that Cook and Rawlinson [1] derived earlier the first two terms of the free-energy orientation-averaged potential for simple dipole-dipole interactions, *i.e.*, the counterpart of Eqn. (23) for  $\alpha_i = 0$  and  $\mu_1 = \mu_2$ , their Eqn. 7.2 that reads,

$$E_d^*(r, T) = -\beta\mu^4/3r^6 + (7\beta^3\mu^8/450)/r^{12} + \dots$$

which becomes also identical to Eqn. (19) above.

## APPENDIX S2: Computation of the second virial coefficient of a polar polarizable model fluid

We start with the definition of the second virial coefficient for an anisotropic molecular fluid, *i.e.*,

$$\begin{aligned} B_{12}(T) &= -(N_A/2\Omega^2) \int \left( e^{-\beta\phi_{12}(r_{12}, \omega_1, \omega_2)} - 1 \right) d\mathbf{r}_{12} d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2 \\ &= -(N_A/2) \int_{\omega} \left\langle e^{-\beta\phi_{12}(r_{12}, \omega_1, \omega_2)} - 1 \right\rangle_{\omega} d\mathbf{r}_{12} \end{aligned} \quad \text{S2-1}$$

with  $\Omega \equiv \int d\boldsymbol{\omega}$  so that,

$$\left\langle e^{-\beta\phi_{12}(r_{12}, \omega_1, \omega_2)} - 1 \right\rangle_{\omega} = \Omega^{-2} \int \left( e^{-\beta\phi_{12}(r_{12}, \omega_1, \omega_2)} - 1 \right) d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2 \quad \text{S2-2}$$

From a computational viewpoint, the calculation of S2-1 requires the estimation of the canonical orientation average of the Boltzmann factor in S2-2, *i.e.*, the radial dependent integrand in S2-1, which can be efficiently carried out by Monte Carlo integration over the orientational phase space at evenly distributed pair distances  $r_{12}$  in the  $[r_{\min} \leq r_{12} \rightarrow \infty]$  range. For all practical purposes, the orientation averages are calculated only within the finite range  $[r_{\min} \leq r_{12} \leq r_{\max}]$ , where the  $r_{\min}$  is the minimum distance at which  $\left\langle e^{-\beta\phi_{12}(r_{12}, \omega_1, \omega_2)} \right\rangle_{\omega} \rightarrow 0$ , while  $r_{\max}$  is chosen as the distance where  $\left\langle e^{-\beta\phi_{12}(r_{12}, \omega_1, \omega_2)} \right\rangle_{\omega}$  can be represented accurately by the previously derived orientation-averaged potentials for polar-polarizable models, *e.g.*, Eqn. (25) in the main text. Consequently, the contributions to the virial coefficient in the  $[r_{\max} \leq r_{12} \rightarrow \infty]$  range are calculated analytically from S2-1 as follows,

$$\begin{aligned} B_{12}(T)_{LR}^{vdW} &= (2\pi\mathfrak{R}N_A/kT) \int_{r_{\max}}^{\infty} r^2 (\sigma/r)^6 dr \\ &= -(2\pi\mathfrak{R}N_A\sigma^6/3kTr_{\max}^3) \end{aligned} \quad \text{S2-3}$$

for the van der Waals interactions, where  $\mathfrak{R} = 4\epsilon$  with  $\sigma = 2^{-1/6} r_{\min}^{LJ}$  for Lennard-Jones and  $\mathfrak{R} = \epsilon\gamma/(\gamma - 6)$  with  $\sigma = r_{\min}^{Exp-6}$  for the exponential-6 potentials, respectively. Similarly, after invoking the first term of Eqn. (23) we have that,

$$\begin{aligned}
B_{12}(T)_{LR}^{\mu d} &= (2\pi N_A/kT) \int_{r_{\max}}^{\infty} r^2 (2\alpha\mu^2 + \beta\mu^4/3) dr / r^6 \\
&= -\left(2\pi\mu^4 N_A/9k^2 T^2 r_{\max}^3\right) - \left(4\pi\mu^2 \alpha N_A/3kT r_{\max}^3\right)
\end{aligned}
\tag{S2-4}$$

for the dipole-dipole interactions. In Figure S2-1 we illustrate the radial behavior of the actual integrand S2-2 and that for the corresponding first non-vanishing terms from its perturbation expansion for a polarizable dipolar model at  $T = 298K$ . This comparison shows clearly that, for the representative polarizable Stockmayer model fluid characterized by  $\varepsilon/k = 78K$ ,  $\sigma = 3.16\text{\AA}$ ,  $\mu = 1.85D$ , and  $\alpha = 1.44\text{\AA}^3$ , the contributions from the permanent dipole-induced dipole interactions to the integrand S2-2 converge faster, than those from the permanent dipole-permanent dipole interactions, to the corresponding orientation-averaged potentials, *i.e.*,

$$\left\langle e^{-\beta\phi_{12}^{\mu\alpha}(r_{12},\omega_1,\omega_2)} - 1 \right\rangle_{\omega} \rightarrow \left\langle -\beta\phi_{12}^{\mu\alpha} \left( r_{12} \gtrsim 4.5\text{\AA} \right) \right\rangle_{\omega}
\tag{S2-5}$$

$$\left\langle e^{-\beta\phi_{12}^{\mu\mu}(r_{12},\omega_1,\omega_2)} - 1 \right\rangle_{\omega} \rightarrow \left\langle -\beta\phi_{12}^{\mu\mu} \left( r_{12} \gtrsim 5.5\text{\AA} \right) \right\rangle_{\omega}
\tag{S2-6}$$

Now, for the actual computation of the orientational average  $\left\langle e^{-\beta\phi_{12}(r_{12},\omega_1,\omega_2)} \right\rangle_{\omega}$ , *i.e.*, within the finite range  $[r_{\min} \leq r_{12} \leq r_{\max}]$  at  $\sim 10^3$  equidistant locations, we carry out a Monte Carlo integration through the evaluation of the Mayer function at each fixed pair distance for  $\sim 10^5$  randomly chosen molecular orientations according to the quaternion-based uniform random rotation algorithm proposed by Shoemake. [2] The calculations are also complemented by a simple analysis of the uncertainties of the Monte Carlo evaluation according to Lepage's approach. [3] For all practical purposes, we have used  $r_{\min}(T) \leq 2\text{\AA}$  resulting in  $\left\langle e^{-\beta\phi_{12}(r_{12},\omega_1,\omega_2)} \right\rangle_{\omega} \lll 10^{-30}$ , and  $r_{\max} = 10\text{\AA}$  that translated in  $B_{GCPM}(298K)$  with uncertainties smaller than 0.3 % according to the sampling discussed above. Note however that we must be careful with the calculations at higher temperatures, *i.e.*,  $T \geq 1000K$ . In fact, for  $T = 3000K$  we need to set  $r_{\min}(3000) \leq 1.65\text{\AA}$  in order to have  $\left\langle e^{-\beta\phi_{12}(r_{12},\omega_1,\omega_2)} \right\rangle_{\omega} \lll 10^{-10}$ .

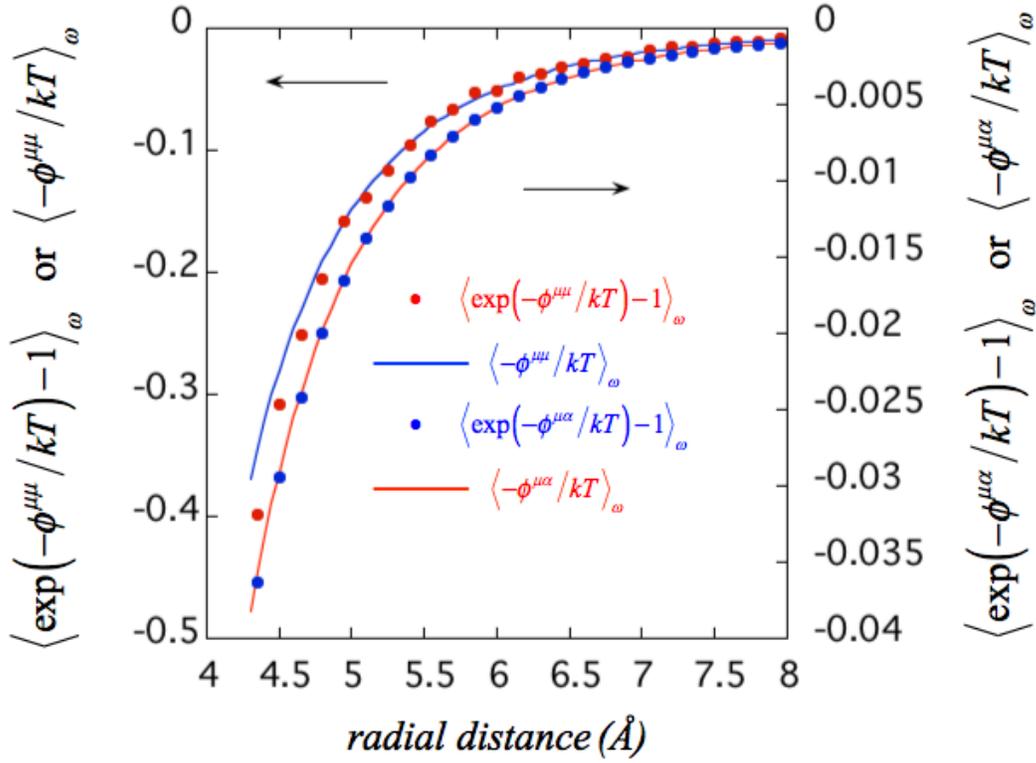


Figure S2-1: Comparison of the radial dependence of the orientational average for the second virial coefficient integrand given by S2-2 and the corresponding first non-vanishing perturbation expansion, *i.e.*, first term in Eqn. (25), for polarizable dipolar molecules with  $\mu = 1.855D$  and  $\alpha = 1.444\text{\AA}^3$  at  $T = 300K$ .

### APPENDIX S3: Temperature dependence of relevant collision integrals of, and molecular simulation-based, self-diffusion coefficient of rarified steam

The perturbation-based Chapman-Enskog [4] solution of Boltzmann's kinetic equation provides a route to the computation of transport properties of gases in terms of so-called reduced (by the hard sphere counterpart) collision integrals, *i.e.*,  $\Omega^{(l,s)*} \equiv \Omega_{gas}^{(l,s)} / \Omega_{hard\ sphere}^{(l,s)} = \Omega_{gas}^{(l,s)} / \pi\sigma^2$ , where  $\sigma$  is the size parameter,

$$\Omega^{(l,s)*} = \left(2/(s+1)!T^{*(s+2)}\right) \int_0^\infty e^{-(g^2/T^*)} g^{(2s+3)} Q^{l*} dg \quad S3-1$$

an expression that denotes the average over the Boltzmann distribution of the collision cross section,

$$Q^l = 2\pi \int_0^{\infty} (1 - \cos^l(\chi)) b db \quad \text{S3-2}$$

as a function of the angle of deflection  $\chi$  (*i.e.*, the angle between the asymptotes defined between the initial and the final direction of motion),

$$\chi = \pi - 2b \int_{r_o}^{\infty} (1 - b^2/r^2 - 2\phi(r)/\mu g^2)^{-0.5} r^{-2} dr \quad \text{S3-3}$$

with the impact parameter  $b$ , the distance of closest approach  $r_o$  given by the root of  $(1 - b^2/r_o^2 - 2\phi(r_o)/\mu g^2) = 0$ , the reduced mass  $\mu$ , the relative velocity  $g$ , and the pair interaction potential  $\phi(r)$ . Note that, from S3-1 follows immediately that,

$$\begin{aligned} d\Omega^{(l,s)*}/dT^* &= \left[ -2(s+2)/(s+1)! T^{*(s+3)} \right] \int_0^{\infty} e^{-(g^2/T^*)} g^{(2s+3)} Q^{l*} dg + \\ &\quad \left[ 2/(s+1)! T^{*(s+4)} \right] \int_0^{\infty} e^{-(g^2/T^*)} g^{(2s+5)} Q^{l*} dg \\ &= (s+2) (\Omega^{(l,s+1)*} - \Omega^{(l,s)*}) / T^* \end{aligned} \quad \text{S3-4}$$

$$d^2\Omega^{(l,s)*}/dT^{*2} = (s+2)(s+1) (\Omega^{(l,s+2)*} - 2\Omega^{(l,s+1)*} + \Omega^{(l,s)*}) / T^{*2} \quad \text{S3-5}$$

$$\begin{aligned} d^3\Omega^{(l,s)*}/dT^{*3} &= [(s+4)!/s!(s+3)] (\Omega^{(l,s+3)*} - 3\Omega^{(l,s+2)*} + \\ &\quad 3\Omega^{(l,s+1)*} - \Omega^{(l,s)*}) / T^{*3} \end{aligned} \quad \text{S3-6}$$

$$\begin{aligned} d^4\Omega^{(l,s)*}/dT^{*4} &= [(s+5)!/s!(s+3)] (\Omega^{(l,s+4)*} - 4\Omega^{(l,s+3)*} + 6\Omega^{(l,s+2)*} - \\ &\quad 4\Omega^{(l,s+1)*} + \Omega^{(l,s)*}) / T^{*4} \end{aligned} \quad \text{S3-7}$$

$$\begin{aligned} d^5\Omega^{(l,s)*}/dT^{*5} &= [(s+6)!/s!(s+3)] (\Omega^{(l,s+5)*} - 5\Omega^{(l,s+4)*} + 10\Omega^{(l,s+3)*} - \\ &\quad 10\Omega^{(l,s+2)*} + 5\Omega^{(l,s+1)*} - \Omega^{(l,s)*}) / T^{*5} \end{aligned} \quad \text{S3-8}$$

$$d^6\Omega^{(l,s)*}/dT^{*6} = [(s+7)!/s!(s+3)](\Omega^{(l,s+6)*} - 6\Omega^{(l,s+5)*} + 15\Omega^{(l,s+4)*} - 20\Omega^{(l,s+3)*} + 15\Omega^{(l,s+2)*} - 6\Omega^{(l,s+1)*} + \Omega^{(l,s)*})/T^{*6} \quad \text{S3-9}$$

where  $(s+n)!/s! = (s)_n \equiv \Gamma(s+n+1)/\Gamma(s+1)$  is the so-called Pochhammer symbol. [5]

Thus, for a given pair interaction potential, the solution of Eqns. S3-1 to S3-3 will ultimately provide the low-density transport properties of the system represented by the interaction potential. Obviously, Eqns. S3-1 to S3-3 have no analytical solution, consequently, the accurate determination of collision integrals requires overcoming some computational complications stemming from the “bad-behaved” nature of the involved functions. [6] Recently Kim and Monroe [7] developed arbitrary-precision algorithms for the computation of the collision integrals of Lennard-Jones fluids and provided interpolation regressions accurate to at least four significant figures within the  $0.3 \leq T^* \leq 400$  range, *i.e.*,

$$\Omega^{(l,s)*}(T^*) = a^{(l,s)} + \sum_{i=1}^6 \left[ b_i^{(l,s)} (T^*)^{-i} + c_i^{(l,s)} (\ln T^*)^i \right] \quad \text{S3-10}$$

The derivatives S3-4 to S3-6 become handy in at least a couple of scenarios, *i.e.*, either as a means to estimate  $\Omega^{(l,s+n)*}$  with  $n = (1, \dots, m)$  from the already known  $\Omega^{(l,s+t)*}$  with  $t = (n-1, \dots, 0)$ , or in conjunction with the directly computed collision integrals  $\Omega^{(l,s)*}$  to assess the accuracy of regressed interpolation expressions such as that given by Eqn. S3-10. In fact, Mason [8] has used the recursive relation S3-4 (or Eqn. 35) to compute  $\Omega^{(1,7)*}$  for the Lennard-Jones fluid using the  $s$  – lower order collision integrals. However, we are not aware of the derivation or use of higher order temperature derivatives, *e.g.*, S3-5, for either the recursive computation of higher-order collision integrals, or for the assessment of accuracy of proposed interpolation functions.

As an illustration of either scenario in column 6 of Table S3-1 we present the coefficients of the interpolation Eqn. S3-10 for  $\Omega^{(2,3)*}$  according to Kim and Monroe [7] in comparison with the resulting coefficients after applying the recursive relation S3-4 (column 7 of Table S3-1). The reader can easily check that, despite the contrasting coefficients, the two representations provide essentially the same numerical outcome, a testament to the higher accuracy, than that of previous tabulations, [9] of the recent tabulation. [7]

Table S3-1: Regression coefficients for Eqn. S3-10 for some relevant collision integrals within the  $0.3 \leq T^* \leq 400$  range

	$\Omega^{(1,1)*}$	$\Omega^{(1,2)*}$	$\Omega^{(1,3)*}$	$\Omega^{(2,2)*}$	$\Omega^{(2,3)*}$	$\Omega^{(2,3)*}$ #
a <sub>1</sub>	-1.1036729	1.3555554	1.0677115	-0.92032979	2.5955799	-0.512074465
b <sub>1</sub>	2.6431984	-0.44668594	-0.1394539	2.3508044	-1.8569443	1.76310330
b <sub>2</sub>	0.0060432255	0.42734391	0.17696362	0.50110649	0.96985775	0.250553245
b <sub>3</sub>	-0.15158773	-0.16036459	-0.02625221	-0.47193769	-0.3988526	-0.117984422
b <sub>4</sub>	0.054237938	0.031461648	-0.004381414	0.15806367	0.090063692	0.006591796
b <sub>5</sub>	-0.009046868	-0.0032587575	0.00167521	-0.026367184	-0.010918991	0.00
100b <sub>6</sub>	0.061742007	0.013860257	-0.014382801	0.18120118	0.056646797	-0.09060059
c <sub>1</sub>	1.6690746	-0.47499422	-0.25258689	1.6330213	-1.4586197	1.28404552
c <sub>2</sub>	-0.69145890	0.14482036	0.059709197	-0.69795156	0.52947262	-0.577227270
c <sub>3</sub>	0.15502132	-0.032158368	-0.013332695	0.16096572	-0.11946363	0.13885628
c <sub>4</sub>	-0.020642189	0.0044357933	0.001961928	-0.022109440	0.016264589	-0.019980510
100c <sub>5</sub>	0.15402077	-0.034138118	-0.016063076	0.17031434	-0.12354315	0.1618093
1000c <sub>6</sub>	-0.049729535	0.011259742	0.005580455	0.056699986	0.0403663	-0.056699

# resulting coefficients from the condition described by Eqn. (40)

In contrast Figure S3-1, where we display the comparison between  $\Omega^{(1,3)*}$  according to the coefficients of column 4 of Table S3-1 and that resulting from Eqn. (41), indicates that even though the individual interpolating functions described by S3-6 are significantly more accurate than previous ones, the uncertainties embodied in the curvature of the functions, *i.e.*, represented by their temperature derivatives, introduce uncertainties that give rise to significant inaccuracies (up to 9% within the low reduced temperature regime in the illustrated case).

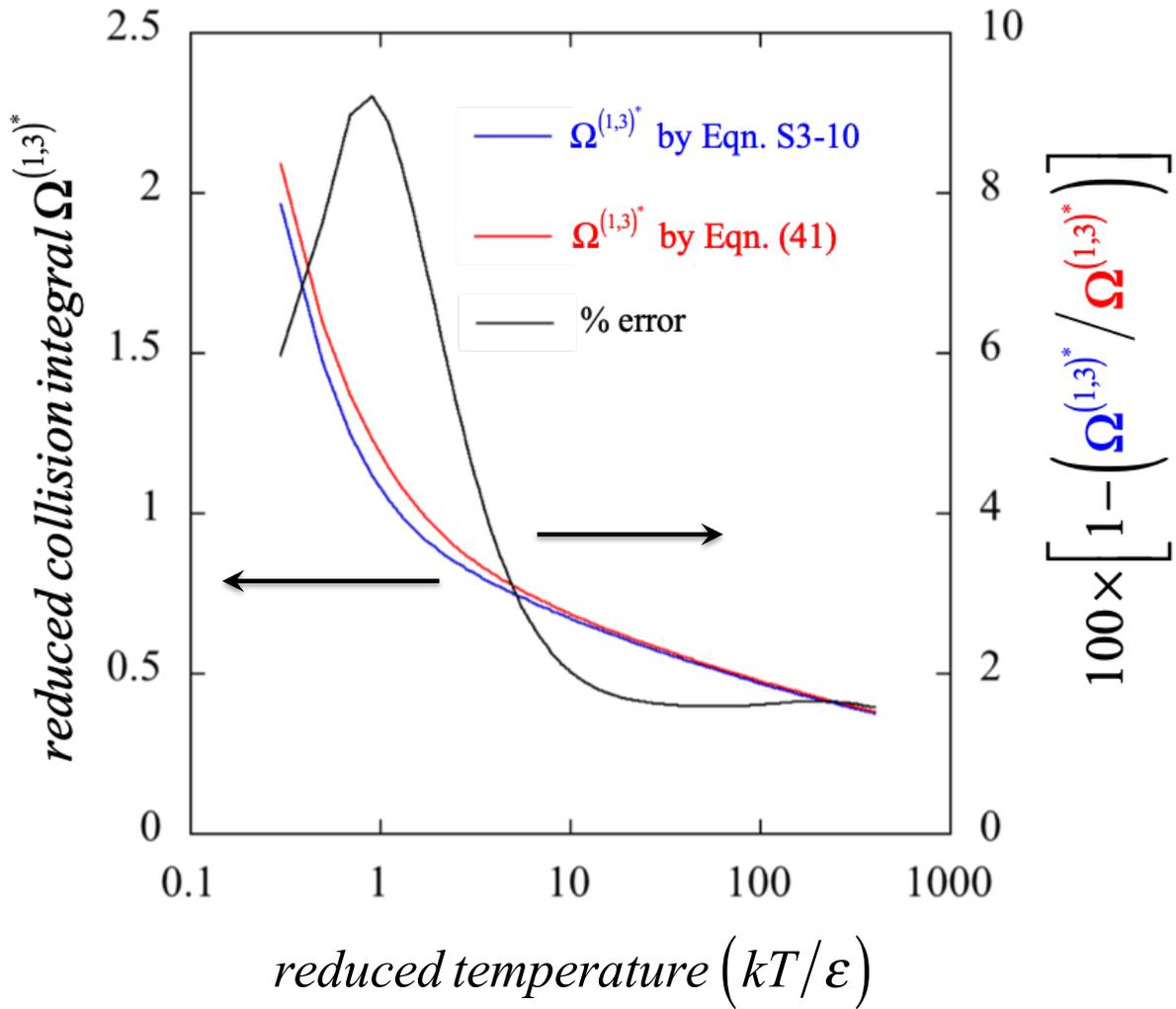


Figure S3-1: Comparison of the temperature dependence of the reduced collision integrals  $\Omega^{(1,3)*}$  according to the interpolation equation S3-10 [7] and the derived relation (41), including the resulting percent error.

As we have anticipated in the main manuscript, the accuracy of the resulting effective Lennard-Jones model in representing fluid properties depends strongly on the property type, *i.e.*, either thermodynamic or transport, used in the regression. This is the manifestation of the fact that these two types of quantities are governed by contrasting portions of the interaction potential: (a) the attractive portion (long radial distance) for the second virial coefficient and, (b) the repulsive portion (very short radial distance) for the collision integrals defining the transport properties. This feature becomes obvious when we compare the outcomes for the predicted

temperature dependences from the individual fits which shows up at the opposite sides of the temperature range, in contrast to the corresponding representations from simultaneous optimizations as clearly illustrated in Figure S3.2 for the zero-density shear viscosity, and Figure S3.3 for the second virial coefficient.

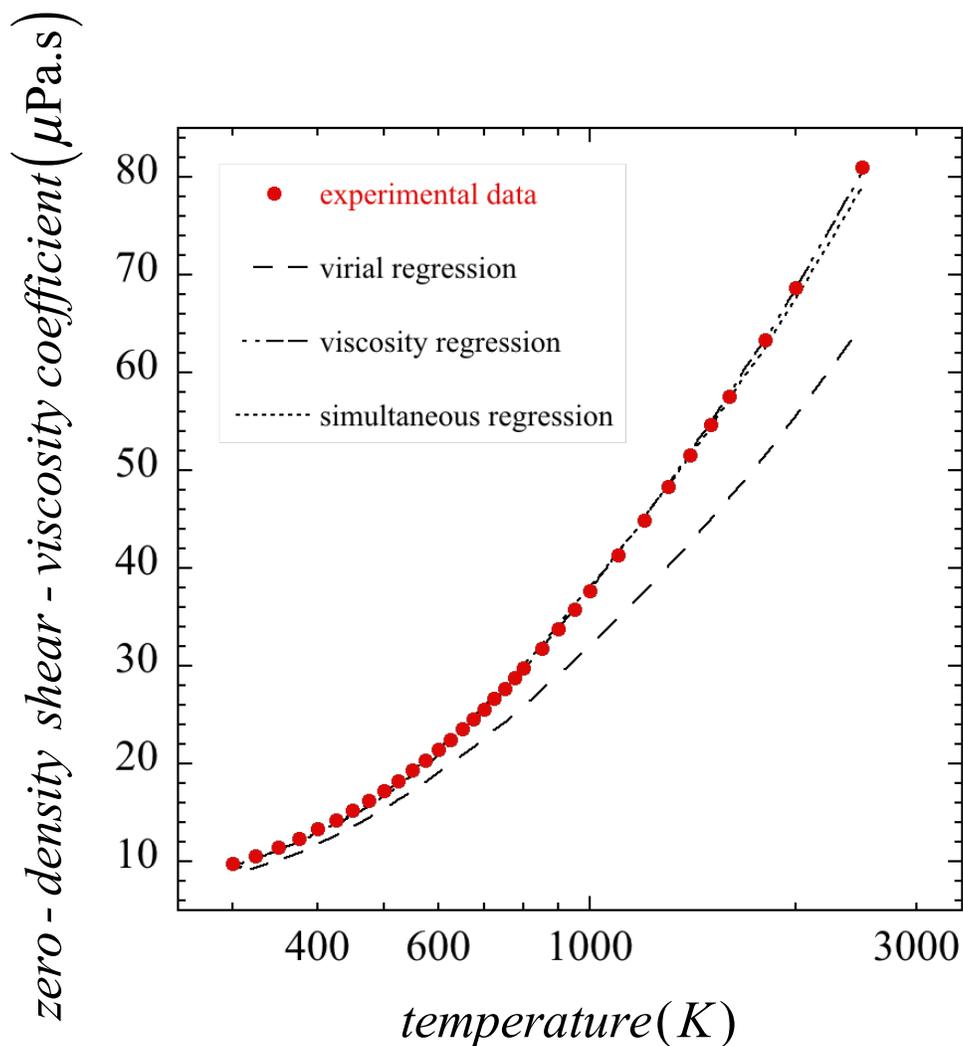


Figure S3-2: Comparison of the temperature dependence of the resulting the zero-density shear viscosity for the effective Lennard-Jones model according to the regression of the zero-density shear viscosity, [10]  $B(T)$  from the *ab initio* data, [11] and the simultaneous optimization of both properties.

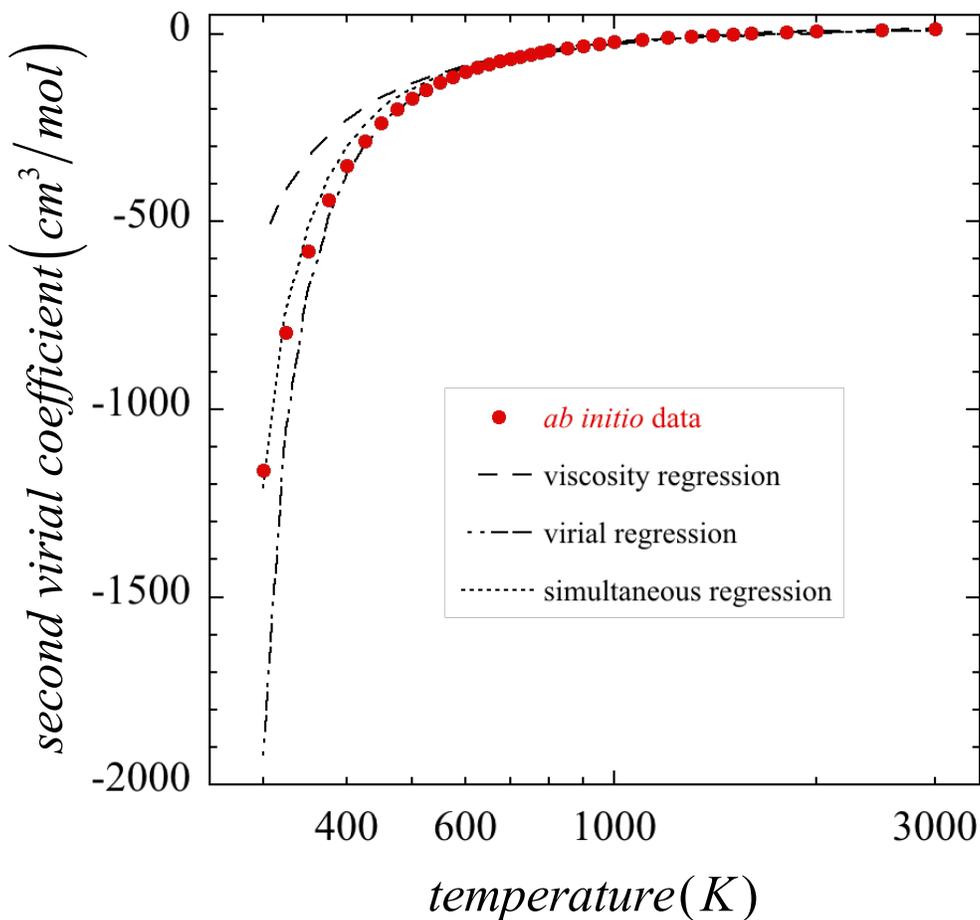


Figure S3-3: Comparison of the temperature dependence of the resulting 2<sup>nd</sup> virial coefficient for the effective Lennard-Jones model according to the regression of  $B(T)$  from the *ab initio* data, [11] the zero-density shear viscosity, [10] and the simultaneous optimization of both properties.

#### APPENDIX S4: Derivation of the low-density configurational integrals for a molecular fluid according to the isochoric-isothermal and isobaric-isothermal ensembles

The factorization of the classical canonical partition function, *i.e.*,  $Q = Q_{trans}Q_{rot}Q_{conf}$ , provides the following expressions for a rigid non-linear molecular fluid,

$$\begin{aligned}
Q_{transl} &= (2\pi kTm/h^2)^{3N} \\
Q_{rot} &= \pi^{N/2} (8\pi^2 kT I_x / h^2)^{N/2} (8\pi^2 kT I_y / h^2)^{N/2} (8\pi^2 kT I_z / h^2)^{N/2} \\
Q_{conf} &= \mathcal{Z} / \Omega^N N!
\end{aligned} \tag{S4-1}$$

where  $I_\alpha$  is the  $\alpha$ -axis principal moment of inertia,  $\Omega = \int d\omega$ ,  $\mathcal{Z} = \int e^{-\beta\mathcal{U}(\mathbf{r}^N \omega^N)} d\mathbf{r}^N d\omega^N$  is the canonical configurational integral, while the subscripts (*transl, rot, conf*) signify translation, rotational and configurational contributions, respectively. After invoking pairwise additivity for  $\mathcal{U}(\mathbf{r}^N \omega^N)$  we have that,

$$\mathcal{U}(\mathbf{r}^N \omega^N) = \sum_{i < j}^{N-1} \sum_j^N \phi_{ij}(r_{ij}, \omega_i, \omega_j) \tag{S4-2}$$

and thus,

$$\begin{aligned}
\exp[-\beta\mathcal{U}(\mathbf{r}^N \omega^N)] &= \exp\left[-\beta \sum_{i < j}^{N-1} \sum_j^N \phi_{ij}(r_{ij}, \omega_i, \omega_j)\right] \\
&= \prod_{1 \leq i < j \leq N} \exp[-\beta\phi_{ij}(r_{ij}, \omega_i, \omega_j)] \\
&= \prod_{i < j} (1 + \mathcal{F}_{ij})
\end{aligned} \tag{S4-3}$$

where  $\mathcal{F}_{ij} = \exp[-\beta\phi_{ij}(r_{ij}, \omega_i, \omega_j)] - 1$  denotes the Mayer function. [12]

Note that the product in the last line of S4-3 can be expanded into a summation as follows,

$$\prod_{i < j} (1 + \mathcal{F}_{ij}) = 1 + \sum_{1 \leq i < j \leq N} \mathcal{F}_{ij} + \sum_{i < j} \sum_{k < l} \mathcal{F}_{ij} \mathcal{F}_{kl} + \dots \tag{S4-4}$$

involving  $0.5N(N-1) \approx 0.5N^2$  identical terms in each single summation, therefore, according to E4 the configurational integral can be recast as follows,

$$\begin{aligned}
\mathcal{Z} &= \int d\mathbf{r}^N d\omega^N + \sum_{1 \leq i < j \leq N} \int \mathcal{F}_{ij} d\mathbf{r}^N d\omega^N + \sum_{i < j} \sum_{k < l} \int \mathcal{F}_{ij} \mathcal{F}_{kl} d\mathbf{r}^N d\omega^N + \dots \\
&= \Omega^N \left[ V^N + 0.5 N^2 V^{N-1} \left( \int \langle \mathcal{F}_{ij} \rangle_{\omega} d\mathbf{r}_{ij} + 0.5 N^2 V^{N-1} \int \langle \mathcal{F}_{ij} \mathcal{F}_{kl} \rangle_{\omega} d\mathbf{r}_{ij} + \dots \right) \right]
\end{aligned} \tag{S4-5}$$

For a low-density system we need to consider the first two terms of S4-5 since the second integral becomes negligible due to its quadratic density dependence, *i.e.*,

$$\begin{aligned}
\lim_{\substack{N, V \rightarrow \infty \\ N/V \rightarrow \text{small}}} \mathcal{Z}(NVT) &= \Omega^N \left[ V^N + 0.5 N^2 V^{N-1} \int \langle \mathcal{F}_{ij} \rangle_{\omega} d\mathbf{r}_{ij} \right] \\
&= \Omega^N V^N \left[ 1 + 2\pi N \rho \int \langle e^{-\phi_{12}(r, \omega)/kT} - 1 \rangle_{\omega} r^2 dr \right]
\end{aligned} \tag{S4-6}$$

and consequently, from E1 the low density canonical configurational partition function reads,

$$\lim_{\substack{N, V \rightarrow \infty \\ N/V \rightarrow \text{small}}} Q_{conf} = (V^N/N!) [1 - N\rho B(T)] \tag{S4-7}$$

so that the  $Q(NVT)/Q^{IG}(NVT) = (\mathcal{Z}/V^N)$  defines the residual Helmholtz free energy, *i.e.*,

$$F^{res}(NVT) = -kT \ln(\mathcal{Z}/V^N) \tag{S4-8}$$

Since  $P^{res}(\rho T) = P(\rho T) - P^{IG}(\rho T) = -[\partial F^{res}(\rho T)/\partial V]_{NT}$ , then,

$$\begin{aligned}
P^{res}(\rho T) &= kT \left[ \partial \ln(\mathcal{Z}/V^N) / \partial V \right]_{NT} \\
&= \rho^2 B(T)
\end{aligned} \tag{S4-9}$$

which provides the equation of state (EoS) for the low-density regime as,

$$P = kT \rho [1 + \rho B(T)] \tag{S4-10}$$

*i.e.*, the first-order density-truncated virial-EoS.

Now, for the isothermal-isobaric configurational contribution  $Q_{conf}(NPT)$  we have that,

$$Q_{conf}(NPT) = (C/N!) \int_0^{\infty} e^{-\beta PV} \mathcal{Z}(NVT) dV \tag{S4-11}$$

where  $\mathcal{Z}(NVT)$  is given by E5 and  $\mathcal{C}$  involves alternative forms, [13] a fact that does not alter the outcome of our analysis. Thus,

$$\begin{aligned} \lim_{\substack{N, V \rightarrow \infty \\ N/V \rightarrow \text{small}}} Q_{conf}(NPT) &= (\mathcal{C}/N!) \int_0^\infty e^{-\beta PV} V^N [1 - N\rho B(T)] dV \\ &= (\mathcal{C}/N!) \left[ N! / (\beta P)^{N+1} - N^2 B(N-1)! / (\beta P)^N \right] \\ &= (1 - N\beta PB) / (\beta P)^N \end{aligned} \quad \text{S4-12}$$

where we have mapped the above integral onto the one defining the gamma function, [14] *i.e.*,  $\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$ , and invoked the identity  $\Gamma(z) = (z-1)!$ .

From S4-12 and the relation  $\langle V \rangle_{NPT} = V = -kT (\partial \ln Q_{conf} / \partial P)_{TN}$ , where  $\langle \dots \rangle_{NPT}$  denotes an isobaric-isothermal ensemble average, we immediately have again the low-density equation of state,

$$V = kTN(P^{-1} + \beta B) \quad \text{S4-13}$$

resulting in  $P = kT\rho(1 + \beta PB)$ , *i.e.*, the first order pressure-truncated virial expansion. Note that both S4-10 and S4-13 truncated expressions are obviously describing the same low-density regime given by the compressibility factor  $z = P/\rho kT$ , *i.e.*, either  $z = 1 + \rho B$  from S4-10 or  $z = (1 - \rho B)^{-1}$  from S4-13, according to the first-order truncation of the series expansion  $(1-x)^{-1} \cong 1 + x + \dots$  for small  $x \equiv \rho B$ .

Moreover, by recalling the expression for the residual Gibbs free energy, *i.e.*,

$$\begin{aligned} G^{res}(NPT) &= -kT \ln [Q_{conf}(NPT) / Q_{conf}^{IG}(NPT)] \\ &= -kT \ln(1 - N\beta PB) \cong NPB \end{aligned} \quad \text{S4-14}$$

as well as its isobaric temperature derivatives,  $H^{res}(NTP) = -kT^2 [\partial \beta G^{res} / \partial T]_{NP}$ ,

$S^{res}(NTP) = -(\partial G^{res} / \partial T)_{NP}$ , and  $C_P^{res}(NPT) = (\partial H^{res} / \partial T)_{NP}$ , we get the following equations

from S4-12 and S4-14,

$$H^{res}(NTP) = NP(B - TB_T) \quad \text{S4-15}$$

$$S^{res}(NTP) = -NPB_T \quad \text{S4-16}$$

$$C_p^{res}(NPT) = -NPTB_{TT} \quad \text{S4-17}$$

where  $B_T \equiv dB/dT$  and  $B_{TT} = dB_T/dT$ .

## APPENDIX S5: Determination of the thermodynamic residual properties at fixed temperature and pressure from the IAPWS95 formulation

Here we present the thermodynamic relations that allow us to extract the isothermal-isobaric residual properties of steam from the IAPWS95-EoS. [15] For that purpose we point at Table 6.3 of Wagner and Pruss' publication where the relevant thermodynamic properties are written in dimensionless form as functions of the density and temperature. In particular we have that,

$$g(\rho, T)/RT = 1 + \phi^o + \phi^r + \delta\phi_\delta^r \quad \text{S5-1}$$

$$h(\rho, T)/RT = 1 + \tau(\phi_\tau^o + \phi_\tau^r) + \delta\phi_\delta^r \quad \text{S5-2}$$

$$s(\rho, T)/RT = \tau(\phi_\tau^o + \phi_\tau^r) - (\phi^o + \phi^r) \quad \text{S5-3}$$

$$f(\rho, T)/RT = \phi^o + \phi^r \quad \text{S5-4}$$

where  $\phi(\delta, \tau) \equiv f(\rho, T)/RT$  is the reduced Helmholtz free energy  $f(\rho, T)$ , the superscripts  $o$  and  $r$  denote ideal gas and residual components, respectively, while the subscripts  $\delta$  and  $\tau$  are the dimensionless state variables  $\delta = \rho/\rho_c$  and  $\tau = T_c/T$  in the notation of Wagner and Pruss [15], so that  $\phi_\alpha^\beta \equiv \partial\phi^\beta/\partial\alpha$  with  $\beta = o, r$  and  $\alpha = \delta, \tau$ . Thus, from S5-1 and S5-4 we have that the compressibility factor is given by,

$$z(\delta, \tau) = 1 + \delta\phi_\delta^r \quad \text{S5-5}$$

Now, we invoke the definition of the isochoric-isothermal residual quantity  $\mathcal{P}$ , *i.e.*,

$$\mathcal{P}^{res}(T, \rho) = \mathcal{P}(T, \rho) - \mathcal{P}^{IG}(T, \rho) \quad \text{S5-6}$$

so that, from S5-1 to S5-5 we immediately have that,

$$\begin{aligned} g^{res}(\delta, \tau) &= f^{res}(\delta, \tau) + RT[z(\delta, \tau) - 1] \\ &= RT[\phi^r + z(\delta, \tau) - 1] \end{aligned} \quad \text{S5-7}$$

$$s^{res}(\delta, \tau) = R(\tau\phi_\tau^r - \phi^r) \quad \text{S5-8}$$

$$h^{res}(\delta, \tau) = RT[\tau\phi_\tau^r + z(\delta, \tau) - 1] \quad \text{S5-9}$$

Moreover, from the relations between the isochoric-isothermal and the isobaric-isothermal residual thermodynamic quantities, [16] *i.e.*,

$$g^{res}(T, P) = g^{res}(T, \rho) - RT \ln z(T, \rho) \quad \text{S5-10}$$

$$s^{res}(T, P) = s^{res}(T, \rho) + R \ln z(T, \rho) \quad \text{S5-11}$$

$$h^{res}(T, P) = h^{res}(T, \rho) \quad \text{S5-12}$$

$$c_p^{res}(T, P) = \left( \partial h^{res} / \partial T \right)_p \quad \text{S5-13}$$

we immediately have that,

$$g^{res}(P, T) = RT[\phi^r + \delta\phi_\delta^r - \ln(1 + \delta\phi_\delta^r)] \quad \text{S5-14}$$

$$h^{res}(T, P) = RT(\tau\phi_\tau^r + \delta\phi_\delta^r) \quad \text{S5-15}$$

$$s^{res}(T, P) = R[\tau\phi_\tau^r - \phi^r + \ln(1 + \delta\phi_\delta^r)] \quad \text{S5-16}$$

$$c_p^{res}(T, P) = R\left[-1 - \tau^2\phi_{\tau\tau}^r + (1 + \delta\phi_\delta^r - \delta\tau\phi_{\delta\tau}^r)^2 / (1 + 2\delta\phi_\delta^r + \delta^2\phi_{\delta\delta}^r)\right] \quad \text{S5-17}$$

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