SUPPLEMENTARY INFORMATION: A general model for thermodynamic properties of fluid mixtures based on Helmholtz energy formulations for the components. Virial expansion and reduction to van der Waals mixing rules.

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A Supplementary information for the virial equation of state

In virial expansion (6) of residual pressure p^{res}, we collect terms representing interactions between the same set of molecular kinds; in other words, we collect terms with the same set of powers of the molar concentrations. To represent a given set, we choose (cross) virial coefficient with indices forming a non-decreasing sequence. We express the number of occurrences using multinomial coefficient, Eq. (17). In this way we obtain a virial expansion which is formally more complex, although containing less terms than Eq. (6):

$$p^{\mathrm{res}} = RT\Bigg[\sum_{i=1}^{I} B_{ii}\rho_i^2 + 2\sum_{i=1}^{I-1}\sum_{j=i+1}^{I} B_{ij}\rho_i\rho_j + \sum_{i=1}^{I} C_{iii}\rho_i^3 + 3\sum_{i=1}^{I-1}\sum_{j=i+1}^{I}\left(C_{iij}\rho_i^2\rho_j + C_{ijj}\rho_i\rho_j^2\right) + 6\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I} C_{ijk}\rho_i\rho_j\rho_k$$

$$+\sum_{i=1}^{I} D_{iiii}\rho_i^4 + \sum_{i=1}^{I-1}\sum_{j=i+1}^{I}\left(4D_{iiij}\rho_i^3\rho_j + 6D_{iijj}\rho_i^2\rho_j^2 + 4D_{ijjj}\rho_i\rho_j^3\right)$$
$$+ 12\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I}\left(D_{iijk}\rho_i^2\rho_j\rho_k + D_{ijjk}\rho_i\rho_j^2\rho_k + D_{ijkk}\rho_i\rho_j\rho_k^2\right)$$
$$+ 24\sum_{i=1}^{I-3}\sum_{j=i+1}^{I-2}\sum_{k=j+1}^{I-1}\sum_{\ell=k+1}^{I} D_{ijk\ell}\rho_i\rho_j\rho_k\rho_\ell + \ldots\Bigg]. \quad \text{(SI.1)}$$

In a similar fashion we will treat virial expansion (26) of the residual reduced Helmholtz energy density α^{dr}. We collect terms with the same powers of concentrations, recall the fact that the cross-virial coefficients are invariant with respect to permutations of their indices, and use Eq. (17) for the number of occurrences of corresponding terms in Eq. (26):

$$\alpha^{\mathrm{dr}} = \sum_{i=1}^{I} B_{ii}\rho_i^2 + 2\sum_{i=1}^{I-1}\sum_{j=i+1}^{I} B_{ij}\rho_i\rho_j + \frac{1}{2}\sum_{i=1}^{I} C_{iii}\rho_i^3$$
$$+ \frac{3}{2}\sum_{i=1}^{I-1}\sum_{j=i+1}^{I}\left(C_{iij}\rho_i^2\rho_j + C_{ijj}\rho_i\rho_j^2\right) + 3\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I} C_{ijk}\rho_i\rho_j\rho_k$$
$$+ \frac{1}{3}\sum_{i=1}^{I} D_{iiii}\rho_i^4 + \sum_{i=1}^{I-1}\sum_{j=i+1}^{I}\left(\frac{4}{3}D_{iiij}\rho_i^3\rho_j + 2D_{iijj}\rho_i^2\rho_j^2 + \frac{4}{3}D_{ijjj}\rho_i\rho_j^3\right)$$
$$+ 4\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I}\left(D_{iijk}\rho_i^2\rho_j\rho_k + D_{ijjk}\rho_i\rho_j^2\rho_k + D_{ijkk}\rho_i\rho_j\rho_k^2\right)$$
$$+ 8\sum_{i=1}^{I-3}\sum_{j=i+1}^{I-2}\sum_{k=j+1}^{I-1}\sum_{\ell=k+1}^{I} D_{ijk\ell}\rho_i\rho_j\rho_k\rho_\ell + \ldots. \quad \text{(SI.2)}$$

B Supplementary information for cubic equations of state: composition dependence of the virial coefficients

We consider virial expansion of the Peng-Robinson equation of state (28) with mixing rules (29)

$$\bar{b}(\mathbf{x}) = \sum_{i=1}^{I} \bar{b}_i x_i\,, \quad (29)$$

and (31),

$$\mathcal{A}(T,\mathbf{x}) = \sum_{ij} \mathcal{A}_{ij}(T)\, x_i x_j\,. \quad (31)$$

The second, third, and fourth virial coefficients are given by expressions (34),

$$B = \bar{b} - \mathcal{A}\,, \tag{34a}$$

$$C = \bar{b}^2 + 2\bar{b}\mathcal{A}\,, \tag{34b}$$

$$D = \bar{b}^3 - 5\bar{b}^2\mathcal{A}\,. \tag{34c}$$

We will use mixing rules (29) and (31) in expressions (34a) through (34c). We then re-shape the resulting formulas in form of Eqs. (14), (15), and (16). This procedure will lead to expressions for B_{ij}, C_{ijk}, and $D_{ijk\ell}$, the (cross) second, third, and fourth virial coefficients.

The first term in Eq. (34a) is given as

$$\begin{aligned}\bar{b} = \sum_{i=1}^{I} \bar{b}_i x_i = \left(\sum_{i=1}^{I} \bar{b}_i x_i\right) \times \left(\sum_{j=1}^{I} x_j\right) = \sum_{i,j=1}^{I} \bar{b}_i x_i x_j = \sum_{i,j=1}^{I} \bar{b}_j x_i x_j \\ = \sum_{i,j=1}^{I} \tfrac{1}{2}(\bar{b}_i + \bar{b}_j)\, x_i x_j\,. \end{aligned} \tag{SI.3}$$

Here we used the following "trics". In the third expression, we multiplied by the sum of molar fractions, which is equal to unity. The fifth expression is obtained from the fourth expression by swapping indices i and j. The final expression is obtained as an arithmetic average of the fourth and fifth expressions. Since the fourth and fifth expressions are equal, also their average has the same value. By using result (34a) and Eq. (31) in Eq. (34a) we obtain

$$B = \sum_{i,j=1}^{I} \left[\tfrac{1}{2}(\bar{b}_i + \bar{b}_j) - \mathcal{A}_{ij}\right]\, x_i x_j\,, \tag{SI.4}$$

which, by comparison with (14), gives (cross) second virial coefficients (35).

We proceed to the third virial coefficient. The first term in Eq. (34b) can be treated as

$$\begin{aligned}\bar{b}^2 = \left(\sum_{i=1}^{I} \bar{b}_i x_i\right) \times \left(\sum_{j=1}^{I} \bar{b}_j x_j\right) \times \left(\sum_{k=1}^{I} x_k\right) \\ = \sum_{i,j,k=1}^{I} \bar{b}_i \bar{b}_j x_i x_j x_k = \sum_{i,j,k=1}^{I} \bar{b}_i \bar{b}_k x_i x_j x_k = \sum_{i,j,k=1}^{I} \bar{b}_j \bar{b}_k x_i x_j x_k \\ = \sum_{i,j,k=1}^{I} \tfrac{1}{3}\left(\bar{b}_i \bar{b}_j + \bar{b}_i \bar{b}_k + \bar{b}_j \bar{b}_k\right) x_i x_j x_k\,. \end{aligned} \tag{SI.5}$$

The product in the second term in Eq. (34b) is

$$\bar{b}\mathcal{A} = \left(\sum_{i=1}^{I} \bar{b}_i x_i\right) \times \left(\sum_{j,k=1}^{I} \mathcal{A}_{jk} x_j x_k\right)$$
$$= \sum_{i,j,k=1}^{I} \bar{b}_i \mathcal{A}_{jk} x_i x_j x_k = \sum_{i,j,k=1}^{I} \bar{b}_j \mathcal{A}_{ik} x_i x_j x_k = \sum_{i,j,k=1}^{I} \bar{b}_k \mathcal{A}_{ij} x_i x_j x_k$$
$$= \sum_{i,j,k=1}^{I} \tfrac{1}{3}\left(\bar{b}_i \mathcal{A}_{jk} + \bar{b}_j \mathcal{A}_{ik} + \bar{b}_k \mathcal{A}_{ij}\right) x_i x_j x_k \,. \quad \text{(SI.6)}$$

By using results (SI.5) and (SI.6) in Eq. (34b) we obtain

$$C = \sum_{i,j,k=1}^{I} \left[\tfrac{1}{3}\left(\bar{b}_i \bar{b}_j + \bar{b}_i \bar{b}_k + \bar{b}_j \bar{b}_k\right) + \tfrac{2}{3}\left(\bar{b}_i \mathcal{A}_{jk} + \bar{b}_j \mathcal{A}_{ik} + \bar{b}_k \mathcal{A}_{ij}\right)\right] x_i x_j x_k \,, \quad \text{(SI.7)}$$

which, by comparison with (15), gives (cross) third virial coefficients (36).

We proceed to the fourth virial coefficient. The first term in Eq. (34c) can be treated as

$$\bar{b}^3 = \left(\sum_{i=1}^{I} \bar{b}_i x_i\right) \times \left(\sum_{j=1}^{I} \bar{b}_j x_j\right) \times \left(\sum_{j=1}^{I} \bar{b}_k x_j\right) \times \left(\sum_{\ell=1}^{I} x_\ell\right)$$
$$= \sum_{i,j,k,\ell=1}^{I} \bar{b}_i \bar{b}_j \bar{b}_k x_i x_j x_k x_\ell = \sum_{i,j,k,\ell=1}^{I} \bar{b}_i \bar{b}_j \bar{b}_\ell x_i x_j x_k x_\ell$$
$$= \sum_{i,j,k,\ell=1}^{I} \bar{b}_i \bar{b}_k \bar{b}_\ell x_i x_j x_k x_\ell = \sum_{i,j,k,\ell=1}^{I} \bar{b}_j \bar{b}_k \bar{b}_\ell x_i x_j x_k x_\ell$$
$$= \sum_{i,j,k,\ell=1}^{I} \tfrac{1}{4}\left(\bar{b}_i \bar{b}_j \bar{b}_k + \bar{b}_i \bar{b}_j \bar{b}_\ell + \bar{b}_i \bar{b}_k \bar{b}_\ell + \bar{b}_j \bar{b}_k \bar{b}_\ell\right) x_i x_j x_k x_\ell \,. \quad \text{(SI.8)}$$

The product in the second term of Eq. (34c) can be treated as

$$\bar{b}^2\mathcal{A} = \left(\sum_{i=1}^{I} \bar{b}_i x_i\right) \times \left(\sum_{j=1}^{I} \bar{b}_j x_j\right) \times \left(\sum_{k,\ell=1}^{I} \mathcal{A}_{k\ell} x_k x_\ell\right)$$
$$= \sum_{i,j,k,\ell=1}^{I} \bar{b}_i \bar{b}_j \mathcal{A}_{k\ell} x_i x_j x_k x_\ell = \sum_{i,j,k,\ell=1}^{I} \bar{b}_i \bar{b}_k \mathcal{A}_{j\ell} x_i x_j x_k x_\ell$$
$$= \sum_{i,j,k,\ell=1}^{I} \bar{b}_i \bar{b}_\ell \mathcal{A}_{jk} x_i x_j x_k x_\ell = \sum_{i,j,k,\ell=1}^{I} \bar{b}_j \bar{b}_k \mathcal{A}_{i\ell} x_i x_j x_k x_\ell$$

$$= \sum_{i,j,k,\ell=1}^{I} \bar{b}_j \bar{b}_\ell \mathcal{A}_{ik} x_i x_j x_k x_\ell = \sum_{i,j,k,\ell=1}^{I} \bar{b}_k \bar{b}_\ell \mathcal{A}_{i\ell} x_i x_j x_k x_\ell$$

$$= \sum_{i,j,k,\ell=1}^{I} \tfrac{1}{6}\big(\bar{b}_i \bar{b}_j \mathcal{A}_{k\ell} + \bar{b}_i \bar{b}_k \mathcal{A}_{j\ell} + \bar{b}_i \bar{b}_\ell \mathcal{A}_{jk} + \bar{b}_j \bar{b}_k \mathcal{A}_{i\ell} + \bar{b}_j \bar{b}_\ell \mathcal{A}_{ik} + \bar{b}_k \bar{b}_\ell \mathcal{A}_{ij}\big)\, x_i x_j x_k x_\ell \,. \quad \text{(SI.9)}$$

By using results (SI.8) and (SI.9) in Eq. (34c) we obtain

$$D = \sum_{i,j,k,\ell=1}^{I} \Big[\tfrac{1}{4}\big(\bar{b}_i \bar{b}_j \bar{b}_k + \bar{b}_i \bar{b}_j \bar{b}_\ell + \bar{b}_i \bar{b}_k \bar{b}_\ell + \bar{b}_j \bar{b}_k \bar{b}_\ell\big) - \tfrac{5}{6}\big(\bar{b}_i \bar{b}_j \mathcal{A}_{k\ell} + \bar{b}_i \bar{b}_k \mathcal{A}_{j\ell} + \bar{b}_i \bar{b}_\ell \mathcal{A}_{jk} + \bar{b}_j \bar{b}_k \mathcal{A}_{i\ell} + \bar{b}_j \bar{b}_\ell \mathcal{A}_{ik} + \bar{b}_k \bar{b}_\ell \mathcal{A}_{ij}\big) \Big] \times x_i x_j x_k \,, \quad \text{(SI.10)}$$

which, by comparison with expression (16), gives (cross) fourth virial coefficients (37).

C Supplementary information for the corresponding states mixture model

In this section we describe the methods used to compute (cross) second virial coefficients for the corresponding states mixture model described in section 2.3 and we show additional results for system nitrogen-oxygen.

C.1 Computation of virial and cross-virial coefficients in a binary mixture based on derivatives with respect to molar concentrations $\boldsymbol{\rho_1}$ and $\boldsymbol{\rho_2}$.

The (cross) second virial coefficient is expressed as limit (56)

$$B_{ij}(x_1) = \frac{1}{2RT} \lim_{\rho \to 0} p_{ij}^{\mathrm{res}}(\rho, x_1) = \frac{1}{2RT} p_{ij}^{\mathrm{res}}(0, x_1) \,, \quad \text{(SI.11)}$$

where the right-most expression is a simplified notation for the zero-density limit of the derivative. We note that the (cross) virial coefficients in physical systems do not depend on composition; however, we explore here an artefact of the corresponding states-based mixture model. Here we compute the needed partial derivatives using central difference formulas. The numerical derivative of residual pressure can be generally expressed as

$$\frac{\partial^n p^{\mathrm{res}}(T, \boldsymbol{\rho})}{\partial \rho_1^{n_1} \partial \rho_2^{n_2}} \approx \frac{1}{w_{\mathbf{n}} \Delta \rho_1^{n_1} \cdot \Delta \rho_2^{n_2}} \sum_k v_{\mathbf{n}k} p^{\mathrm{res}}\left(T, \rho_{\mathbf{n}k}, \mathbf{x}_{\mathbf{n}k}\right) \,. \quad \text{(SI.12)}$$

The residual pressure is computed in nodal points

$$\boldsymbol{\rho}_{\mathbf{n}k} = \{\rho_{\mathbf{n}k1}, \rho_{\mathbf{n}k2}\}\,, \tag{SI.13}$$

with coordinates

$$\rho_{\mathbf{n}k1} = \rho_1 + u_{\mathbf{n}k1}\Delta\rho_1\,, \quad \rho_{\mathbf{n}k2} = \rho_2 + u_{\mathbf{n}k2}\Delta\rho_2\,, \tag{SI.14}$$

Matrix u, vector v, and scalar w are given in Table SI.1 for the three derivatives needed to compute the (cross) second virial coefficients in a binary mixture. Because the corresponding states mixture model is implemented as function of density ρ and molar fractions $\mathbf{x}$ rather then molar concentrations $\boldsymbol{\rho}$, an intermediate step is needed in which we compute molar density and molar fractions for nodal points (SI.14):

$$\rho_{\mathbf{n}k} = \rho_{\mathbf{n}k1} + \rho_{\mathbf{n}k2}\,, \tag{SI.15}$$

$$\mathbf{x}_{\mathbf{n}k} = \frac{\boldsymbol{\rho}_{\mathbf{n}k}}{\rho_{\mathbf{n}k}}\,. \tag{SI.16}$$

Numerical derivatives of residual pressure for the corresponding states mixture

	$\mathbf{n} = \{n_1, n_2\}$								
	$\{0,2\}$			$\{1,1\}$			$\{2,0\}$		
k	$u_{\mathbf{n}k1}$	$u_{\mathbf{n}k2}$	$v_{\mathbf{n}k}$	$u_{\mathbf{n}k1}$	$u_{\mathbf{n}k2}$	$v_{\mathbf{n}k}$	$u_{\mathbf{n}k1}$	$u_{\mathbf{n}k2}$	$v_{\mathbf{n}k}$
1	0	−1	1	−1	−1	1	−1	0	1
2	0	0	−2	−1	1	−1	0	0	−2
3	0	1	1	1	−1	−1	1	0	1
4	0	0	0	1	1	1	0	0	0
$w_{\mathbf{n}}$	1			4			1		

Table SI.1 Matrix u, vector v and scalar w needed for computation of numerical derivatives using formula (SI.12).

model cannot be expressed in the zero density limit, because their value is indefinite in this limit. Instead, we compute these derivatives for a series points with increasing density ρ at constant composition given by molar fraction x_1. The density range is chosen such that the computed values of numerical derivatives form a straight line as function of ρ and they can be extrapolated towards $\rho \to 0$, as illustrated in Fig. 1 (Left).

C.2 Computation of virial and cross virial coefficients in a binary mixture based on derivatives of the mixture virial coefficient B with respect to molar fraction x_1.

We first develop formulas for computation of virial and cross virial coefficients based on derivatives of the residual pressure, Eq. (10), for a binary mixture. These relations assume molar concentrations ρ_1 and ρ_2 as independent variables. Temperature is a constant parameter and, in this section, we leave it

out from the list of variables. We will express the derivatives with respect to ρ_i, $i = 1, 2$, in terms of derivatives with respect to molar density ρ and molar fraction x_1.

Using the chain rule, we obtain for the first derivative

$$\frac{\partial p^{\mathrm{res}}(\rho_1, \rho_2)}{\partial \rho_i} = \frac{\partial p^{\mathrm{res}}(\rho, x_1)}{\partial \rho} \cdot \frac{\partial \rho(\rho_1, \rho_2)}{\partial \rho_i} + \frac{\partial p^{\mathrm{res}}(\rho, x_1)}{\partial x_1} \cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_i} . \quad \text{(SI.17)}$$

Molar density ρ and molar fraction x_1 are related to molar concentrations as

$$\rho = \rho_1 + \rho_2 , \quad x_1 = \frac{\rho_1}{\rho_1 + \rho_2} . \quad \text{(SI.18a-b)}$$

From Eq. (SI.18a) we have

$$\frac{\partial \rho(\rho_1, \rho_2)}{\partial \rho_i} = 1 , \quad \text{(SI.19)}$$

so that Eq. (SI.17) simplifies to

$$\frac{\partial p^{\mathrm{res}}(\rho_1, \rho_2)}{\partial \rho_i} = \frac{\partial p^{\mathrm{res}}(\rho, x_1)}{\partial \rho} + \frac{\partial p^{\mathrm{res}}(\rho, x_1)}{\partial x_1} \cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_i} . \quad \text{(SI.20)}$$

We take a second derivative with respect to ρ_j, $j = 1, 2$, again using the chain rule:

$$\begin{aligned} \frac{\partial^2 p^{\mathrm{res}}(\rho_1, \rho_2)}{\partial \rho_i \partial \rho_j} &= \frac{\partial^2 p^{\mathrm{res}}(\rho, x_1)}{\partial \rho^2} \cdot \frac{\partial \rho(\rho_1, \rho_2)}{\partial \rho_j} + \frac{\partial^2 p^{\mathrm{res}}(\rho, x_1)}{\partial \rho \partial x_1} \cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_j} \\ &+ \frac{\partial^2 p^{\mathrm{res}}(\rho, x_1)}{\partial x_1 \partial \rho} \cdot \frac{\partial \rho(\rho_1, \rho_2)}{\partial \rho_j} \cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_i} + \frac{\partial^2 p^{\mathrm{res}}(\rho, x_1)}{\partial {x_1}^2} \cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_j} \\ &\cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_i} + \frac{\partial p^{\mathrm{res}}(\rho, x_1)}{\partial x_1} \cdot \frac{\partial^2 x_1(\rho_1, \rho_2)}{\partial \rho_i \partial \rho_j} . \end{aligned} \quad \text{(SI.21)}$$

With help of Eq. (SI.19), expression (SI.21) simplifies to

$$\begin{aligned} \frac{\partial^2 p^{\mathrm{res}}(\rho_1, \rho_2)}{\partial \rho_i \partial \rho_j} &= \frac{\partial^2 p^{\mathrm{res}}(\rho, x_1)}{\partial \rho^2} \\ &+ \frac{\partial^2 p^{\mathrm{res}}(\rho, x_1)}{\partial \rho \partial x_1} \left[\frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_i} + \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_j} \right] \\ &+ \frac{\partial^2 p^{\mathrm{res}}(\rho, x_1)}{\partial {x_1}^2} \cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_i} \cdot \frac{\partial x_1(\rho_1, \rho_2)}{\partial \rho_j} \\ &+ \frac{\partial p^{\mathrm{res}}(\rho, x_1)}{\partial x_1} \cdot \frac{\partial^2 x_1(\rho_1, \rho_2)}{\partial \rho_i \partial \rho_j} . \end{aligned} \quad \text{(SI.22)}$$

The derivatives of x_1 with respect to molar concentrations ρ_i are obtained based on Eq. (SI.18b) as

$$\frac{\partial x_1(\rho_1,\rho_2)}{\partial \rho_1} = \frac{\rho_2}{(\rho_1+\rho_2)^2}\,, \qquad \frac{\partial x_1(\rho_1,\rho_2)}{\partial \rho_2} = -\frac{\rho_1}{(\rho_1+\rho_2)^2}\,. \tag{SI.23}$$

Both expressions can be reduced to a single one with $i = 1, 2$:

$$\frac{\partial x_1(\rho_1,\rho_2)}{\partial \rho_i} = (-1)^{i+1}\frac{\rho_{3-i}}{(\rho_1+\rho_2)^2} = (-1)^{i+1}\frac{x_{3-i}}{\rho}\,. \tag{SI.24}$$

The second derivatives of molar fraction x_1 with respect to molar concentrations are obtained by deriving equations (SI.23),

$$\frac{\partial^2 x_1(\rho_1,\rho_2)}{\partial {\rho_1}^2} = -\frac{2\rho_2}{(\rho_1+\rho_2)^3}\,, \tag{SI.25}$$

$$\frac{\partial^2 x_1(\rho_1,\rho_2)}{\partial \rho_1 \partial \rho_2} = \frac{\rho_1-\rho_2}{(\rho_1+\rho_2)^3}\,, \tag{SI.26}$$

$$\frac{\partial^2 x_1(\rho_1,\rho_2)}{\partial {\rho_2}^2} = \frac{2\rho_1}{(\rho_1+\rho_2)^3}\,. \tag{SI.27}$$

Results (SI.25) to (SI.27) can be expressed by a single formula

$$\frac{\partial^2 x_1(\rho_i,\rho_j)}{\partial \rho_i \partial \rho_j} = \frac{(-1)^i\rho_{3-i} + (-1)^j\rho_{3-j}}{(\rho_1+\rho_2)^3} = \frac{(-1)^i x_{3-i} + (-1)^j x_{3-j}}{\rho^2}\,. \tag{SI.28}$$

We substitute results (SI.24) and (SI.28) into Eq. (SI.22) and obtain

$$\begin{aligned} p_{ij}^{\mathrm{res}} = \frac{\partial^2 p^{\mathrm{res}}(\rho_1,\rho_2)}{\partial\rho_i\partial\rho_j} = \frac{\partial^2 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho^2} - \left[(-1)^i x_{3-i} + (-1)^j x_{3-j}\right] \\ \times \frac{1}{\rho}\frac{\partial^2 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho\partial x_1} + (-1)^{i+j} x_{3-i}x_{3-j}\frac{1}{\rho^2}\frac{\partial^2 p^{\mathrm{res}}(\rho,x_1)}{\partial {x_1}^2} \\ + \left[(-1)^i x_{3-i} + (-1)^j x_{3-j}\right]\frac{1}{\rho^2}\frac{\partial p^{\mathrm{res}}(\rho,x_1)}{\partial x_1}\,. \end{aligned} \tag{SI.29}$$

We are interested in the zero-density limit of expression (SI.29). This expression contains terms inversely proportional to ρ and ρ^2. We need to investigate the limits of these terms. We will use the fact that the residual pressure is proportional to ρ^2 at constant composition. Using l'Hôpital's rule,

$$\lim_{\rho\to 0}\frac{1}{\rho}\frac{\partial^2 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho\partial x_1} = \lim_{\rho\to 0}\frac{\partial^3 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho^2\partial x_1} = p^{\mathrm{res}}_{\rho\rho x}(0,x_1)\,. \tag{SI.30}$$

The right-most expression is a simplified notation for the zero-density limit of the derivative. Because the second derivative of residual pressure with respect

to density is finite and it is a smooth function of molar fraction, result (SI.30) is a finite number. By using l'Hôpital's rule doubly we obtain

$$\lim_{\rho\to 0}\frac{1}{\rho^2}\frac{\partial p^{\mathrm{res}}(\rho,x_1)}{\partial x_1}=\lim_{\rho\to 0}\frac{1}{2\rho}\frac{\partial^2 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho\partial x_1}$$
$$=\frac{1}{2}\lim_{\rho\to 0}\frac{\partial^3 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho^2\partial x_1}=\frac{1}{2}p^{\mathrm{res}}_{\rho\rho x}(0,x_1)\,, \quad \text{(SI.31)}$$

and again using l'Hôpital's rule doubly we have

$$\lim_{\rho\to 0}\frac{1}{\rho^2}\frac{\partial^2 p^{\mathrm{res}}(\rho,x_1)}{\partial {x_1}^2}=\lim_{\rho\to 0}\frac{1}{2\rho}\frac{\partial^3 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho\partial x_1^2}=\lim_{\rho\to 0}\frac{1}{2}\frac{\partial^4 p^{\mathrm{res}}(\rho,x_1)}{\partial\rho^2\partial x_1^2}$$
$$=\frac{1}{2}p^{\mathrm{res}}_{\rho\rho xx}(0,x_1)\,. \quad \text{(SI.32)}$$

Zero-density limits (SI.31) and (SI.32) are also finite numbers. We express zero-density limit of the second derivative of residual pressure as given by Eq. (SI.29) with help of pre-computed limits of individual terms, Eqs. (SI.30) and (SI.32):

$$p^{\mathrm{res}}_{ij}(0,x_1)=\lim_{\rho\to 0}p^{\mathrm{res}}_{ij}(\rho,x_1)$$
$$=p^{\mathrm{res}}_{\rho\rho}(0,x_1)-\frac{1}{2}\left[(-1)^i x_{3-i}+(-1)^j x_{3-j}\right]$$
$$\times\, p^{\mathrm{res}}_{\rho\rho x}(0,x_1)+\frac{(-1)^{i+j}}{2}x_{3-i}x_{3-j}\,p^{\mathrm{res}}_{\rho\rho xx}(0,x_1)\,. \quad \text{(SI.33)}$$

We write Eq. (SI.33) separately for the individual cases:

$$p^{\mathrm{res}}_{11}(0,x_1)=p^{\mathrm{res}}_{\rho\rho}(0,x_1)+x_2 p^{\mathrm{res}}_{\rho\rho x}(0,x_1)+\frac{x_2^2}{2}\,p^{\mathrm{res}}_{\rho\rho xx}(0,x_1)\,, \quad \text{(SI.34)}$$

$$p^{\mathrm{res}}_{12}(0,x_1)=p^{\mathrm{res}}_{21}(0,x_1)$$
$$=p^{\mathrm{res}}_{\rho\rho}(0,x_1)+\frac{x_2-x_1}{2}p^{\mathrm{res}}_{\rho\rho x}(0,x_1)-\frac{x_1x_2}{2}\,p^{\mathrm{res}}_{\rho\rho xx}(0,x_1)\,, \quad \text{(SI.35)}$$

$$p^{\mathrm{res}}_{22}(0,x_1)=p^{\mathrm{res}}_{\rho\rho}(0,x_1)-x_1 p^{\mathrm{res}}_{\rho\rho x}(0,x_1)+\frac{x_1^2}{2}p^{\mathrm{res}}_{\rho\rho xx}(0,x_1)\,, \quad \text{(SI.36)}$$

With respect to Eqs. (13a) and (56) we can express Eqs. (SI.34) to (SI.36) in terms of the mixture virial coefficient $B(x_1)$ and its first and second derivatives

with respect to x_1, $B_x(x_1)$ and $B_{xx}(x_1)$, respectively:

$$B_{11}(x_1) = B(x_1) + x_2 B_x(x_1) + \frac{x_2^2}{2} B_{xx}(x_1)\,, \tag{57}$$

$$B_{12}(x_1) = B(x_1) + \frac{x_2 - x_1}{2} B_x(x_1) - \frac{x_1 x_2}{2} B_{xx}(x_1)\,, \tag{58}$$

$$B_{22}(x_1) = B(x_1) - x_1 B_x(x_1) + \frac{x_1^2}{2} B_{xx}(x_1)\,. \tag{59}$$

Formulas (57) to (59) appear to be most convenient way for evaluating (cross) virial coefficients for corresponding states mixture models, because the mixture virial coefficient $B(x_1)$ is an easily accessible result. Its first and second derivatives with respect to molar fraction x_1 can be computed numerically.

By substituting formulas (57) to (59) into the right-hand side of Eq. (18),

$$B(\mathbf{x}) = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}\,, \tag{18}$$

we can verify that this equation holds even for the more general (although not physical) case that B_{ij} depend on composition, as it is in case of the corresponding states mixture model.

As another test of formulas (57) to (59), let us consider the case when the mixture second virial coefficient obeys the proper composition dependence as given by Eq. (18) with composition-independent coefficients B_{ij}. We substitute $x_2 = 1 - x_1$ to obtain

$$B(x_1) = x_1^2 B_{11} + (2x_1 - 2x_1^2) B_{12} + (1 - 2x_1 + x_1^2) B_{22}\,. \tag{SI.37}$$

Derivatives B_x and B_{xx} are easily obtained as

$$B_x(x_1) = 2x_1 B_{11} + (2 - 4x_1) B_{12} + (-2 + 2x_1) B_{22}\,, \tag{SI.38}$$

$$B_{xx}(x_1) = 2B_{11} - 4B_{12} + 2B_{22}\,. \tag{SI.39}$$

When expressions (SI.37), (SI.38), and (SI.39), are substituted in formulas (57), (58), and (59), we recover, respectively, the (cross) virial coefficients B_{11}, B_{12}, and B_{22}.

C.3 Virial coefficients for nitrogen-oxygen mixture

In section 2.3.1 of the article, (cross) second virial coefficients for system nitrogen-water are presented. Figures SI.1, SI.2, and SI.3 show, respectively, the nitrogen-nitrogen, nitrogen-oxygen, and oxygen-oxygen virial coefficients. For both systems, the curves were computed with two methods: the numerical differentiation and extrapolation introduced in section C.1, and semi-analytical formulas developed in section C.2. Both methods agree mutually within the graphical resolution.

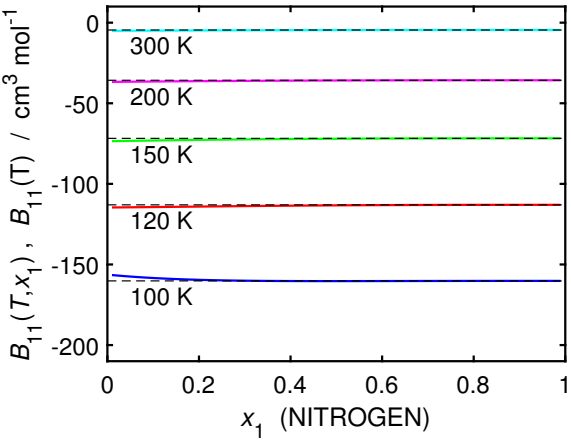

Fig. SI.1 Composition-dependent second virial coefficient of nitrogen B_{11} in the mixture with oxygen. (An artifact of mixture model [8, 9].) Isotherms $B_{11}(T, \mathbf{x})$ [9] (solid lines) and $B_{11}(T)$ [31] (dashed lines).

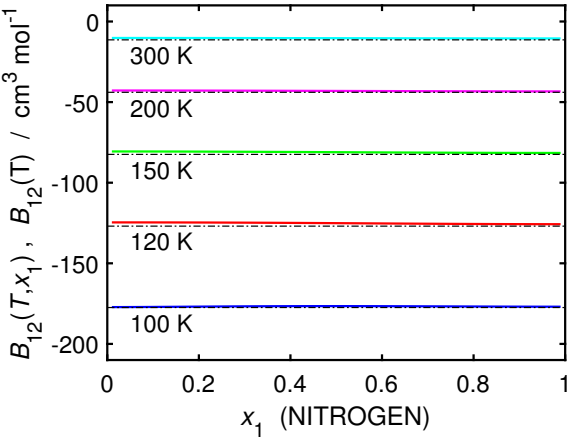

Fig. SI.2 Solid lines: composition-dependent cross second virial coefficient of nitrogen and oxygen $B_{12}(T, \mathbf{x})$ (An artifact of mixture model [8, 9].) Dashed lines: cross second virial coefficient of nitrogen and oxygen $B_{12}(T)$ [44]

D Supplementary information for the proposed mixture model

D.1 Virial expansion for the proposed mixture model

In this section we will treat expansion (116) of the proposed mixture model in a similar fashion as we treated virial expansion (SI.2). The comparison of the two results will serve for expressing the virial coefficients B_{ij}, C_{ijk}, and $D_{ijk\ell}$, in terms of coefficients $\hat{B}_{ij}$, $\hat{C}_{ijk}$, and $\hat{D}_{ijk\ell}$. For convenience we recall Eq. (116) here:

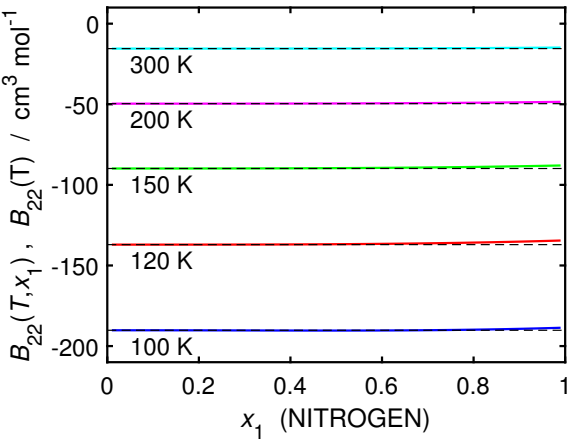

Fig. SI.3 Solid lines: composition dependent second virial coefficient of oxygen in mixture with nitrogen $B_{22}(T, \mathbf{x})$ (right). (An artifact of mixture model [8, 9].) Dashed lines: second virial coefficient for oxygen $B_{22}(T)$ [43].

$$\alpha^{\mathrm{dr}}(\theta,\boldsymbol{\rho}) = \sum_{i,j=1}^{I} \hat{B}_{ij}\rho_i\rho_j + \frac{1}{2}\sum_{i,j,k=1}^{I} \hat{C}_{ijk}\,\rho_i\rho_j\rho_k + \frac{1}{3}\sum_{i,j,k,\ell=1}^{I} \hat{D}_{ijk\ell}\,\rho_i\rho_j\rho_k\rho_\ell + \dots . \quad (116)$$

We note that coefficients $\hat{B}_{ij}$, $\hat{C}_{ijk}$, and $\hat{D}_{ijk\ell}$, are not fully invariant with respect to permutations of the indices (unlike the cross virial coefficients). Therefore, we first use all the permutations of indices in the sums:

$$\begin{aligned}
\alpha^{\mathrm{dr}}(\theta,\boldsymbol{\rho}) = {} & \sum_{i=1}^{I} \hat{B}_{ii}\rho_i^2 + \sum_{i=1}^{I-1}\sum_{j=i+1}^{I} \left(\hat{B}_{ij}+\hat{B}_{ji}\right)\rho_i\rho_j + \frac{1}{2}\sum_{i=1}^{I} \hat{C}_{iii}\,\rho_i^3 \\
& + \frac{1}{2}\sum_{i=1}^{I-1}\sum_{j=i+1}^{I} \left[\left(\hat{C}_{iij}+\hat{C}_{iji}+\hat{C}_{jii}\right)\rho_i^2\rho_j + \left(\hat{C}_{ijj}+\hat{C}_{jij}+\hat{C}_{jji}\right)\rho_i\rho_j^2\right] \\
& + \frac{1}{2}\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I} \left(\hat{C}_{ijk}+\hat{C}_{ikj}+\hat{C}_{jik}+\hat{C}_{jki}+\hat{C}_{kij}+\hat{C}_{kji}\right)\rho_i\rho_j\rho_k \\
& + \frac{1}{3}\sum_{i}^{I} \hat{D}_{iiii}\,\rho_i^4 + \frac{1}{3}\sum_{i=1}^{I-1}\sum_{j=i+1}^{I} \left[\left(\hat{D}_{iiij}+\hat{D}_{iiji}+\hat{D}_{ijii}+\hat{D}_{jiii}\right)\rho_i^3\rho_j \right. \\
& \left. + \left(\hat{D}_{iijj}+\hat{D}_{ijij}+\hat{D}_{ijji}+\hat{D}_{jiij}+\hat{D}_{jiji}+\hat{D}_{jjii}\right)\rho_i^2\rho_j^2 \right.
\end{aligned}$$

$$
\begin{aligned}
&+\left(\hat{D}_{ijjj}+\hat{D}_{jijj}+\hat{D}_{jjij}+\hat{D}_{jjji}\right)\rho_i\rho_j^3\Big] \\
&+\frac{1}{3}\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I}\Big[\Big(\hat{D}_{iijk}+\hat{D}_{iikj}+\hat{D}_{ijik}+\hat{D}_{ijki}+\hat{D}_{ikij}+\hat{D}_{ikji} \\
&+\hat{D}_{jiik}+\hat{D}_{jiki}+\hat{D}_{jkii}+\hat{D}_{kiij}+\hat{D}_{kiji}+\hat{D}_{kjii}\Big)\rho_i^2\rho_j\rho_k \\
&+\Big(\hat{D}_{ijjk}+\hat{D}_{ijkj}+\hat{D}_{ikjj}+\hat{D}_{jiik}+\hat{D}_{jikj}+\hat{D}_{jjik} \\
&+\hat{D}_{jjki}+\hat{D}_{jkij}+\hat{D}_{jkji}+\hat{D}_{kijj}+\hat{D}_{kjij}+\hat{D}_{kjji}\Big)\rho_i\rho_j^2\rho_k \\
&+\Big(\hat{D}_{ijkk}+\hat{D}_{ikjk}+\hat{D}_{ikkj}+\hat{D}_{jikk}+\hat{D}_{jkik}+\hat{D}_{jkki} \\
&+\hat{D}_{kijk}+\hat{D}_{kikj}+\hat{D}_{kjik}+\hat{D}_{kjki}+\hat{D}_{kkij}+\hat{D}_{kkji}\Big)\rho_i\rho_j\rho_k^2\Big] \\
&+\frac{1}{3}\sum_{i=1}^{I-3}\sum_{j=i+1}^{I-2}\sum_{k=j+1}^{I-1}\sum_{\ell=k+1}^{I}\Big(\hat{D}_{ijk\ell}+\hat{D}_{ij\ell k}+\hat{D}_{ikj\ell}+\hat{D}_{ik\ell k}+\hat{D}_{i\ell jk}+\hat{D}_{i\ell kj} \\
&+\hat{D}_{jik\ell}+\hat{D}_{ji\ell k}+\hat{D}_{jki\ell}+\hat{D}_{jk\ell i}+\hat{D}_{j\ell ik}+\hat{D}_{j\ell ki} \\
&+\hat{D}_{kij\ell}+\hat{D}_{ki\ell j}+\hat{D}_{kji\ell}+\hat{D}_{kj\ell i}+\hat{D}_{k\ell ij}+\hat{D}_{k\ell ji} \\
&+\hat{D}_{\ell ijk}+\hat{D}_{\ell ikj}+\hat{D}_{\ell jik}+\hat{D}_{\ell jki}+\hat{D}_{\ell kij}+\hat{D}_{\ell kji}\Big)\rho_i\rho_j\rho_k\rho_\ell+\ldots\,. \qquad \text{(SI.40)}
\end{aligned}
$$

Using symmetries (120), (121), and (122), we can replace repeated terms by multipliers. In this way, Eq. (SI.40) reduces to shape

$$
\begin{aligned}
\alpha^{\mathrm{dr}}(\theta,\boldsymbol{\rho}) &= \sum_{i=1}^{I}\hat{B}_{ii}\rho_i^2+2\sum_{i=1}^{I-1}\sum_{j=i+1}^{I}\hat{B}_{ij}\rho_i\rho_j+\frac{1}{2}\sum_{i=1}^{I}\hat{C}_{iii}\,\rho_i^3 \\
&+\frac{1}{2}\sum_{i=1}^{I-1}\sum_{j=i+1}^{I}\left[\left(\hat{C}_{iij}+2\hat{C}_{iji}\right)\rho_i^2\rho_j+\left(2\hat{C}_{ijj}+\hat{C}_{jji}\right)\rho_i\rho_j^2\right] \\
&+\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I}\left(\hat{C}_{ijk}+\hat{C}_{ikj}+\hat{C}_{jki}\right)\rho_i\rho_j\rho_k \\
&+\frac{1}{3}\sum_{i}^{I}\hat{D}_{iiii}\,\rho_i^4+\frac{1}{3}\sum_{i=1}^{I-1}\sum_{j=i+1}^{I}\Big[2\left(\hat{D}_{iiij}+\hat{D}_{ijii}\right)\rho_i^3\rho_j \\
&+\left(\hat{D}_{iijj}+4\hat{D}_{ijij}+\hat{D}_{jjii}\right)\rho_i^2\rho_j^2+2\left(\hat{D}_{ijjj}+\hat{D}_{jjij}\right)\rho_i\rho_j^3\Big] \\
&+\frac{2}{3}\sum_{i=1}^{I-2}\sum_{j=i+1}^{I-1}\sum_{k=j+1}^{I}\Big[\Big(\hat{D}_{iijk}+2\hat{D}_{ijik}+2\hat{D}_{ikij}+\hat{D}_{jkii}\Big)\rho_i^2\rho_j\rho_k
\end{aligned}
$$

$$+\left(2\hat{D}_{ijjk}+\hat{D}_{ikjj}+\hat{D}_{jjik}+2\hat{D}_{jkij}\right)\rho_i\rho_j^2\rho_k$$
$$+\left(\hat{D}_{ijkk}+2\hat{D}_{ikjk}+2\hat{D}_{jkik}+\hat{D}_{kkij}\right)\rho_i\rho_j\rho_k^2\Bigg]$$
$$+\frac{4}{3}\sum_{i=1}^{I-3}\sum_{j=i+1}^{I-2}\sum_{k=j+1}^{I-1}\sum_{\ell=k+1}^{I}\Big(\hat{D}_{ijk\ell}+\hat{D}_{ikj\ell}+\hat{D}_{i\ell jk}$$
$$+\hat{D}_{jki\ell}+\hat{D}_{j\ell ik}+\hat{D}_{k\ell ij}\Big)\rho_i\rho_j\rho_k\rho_\ell+\dots\,. \quad \text{(SI.41)}$$

D.2 Numerical test of the virial expansion for the proposed mixture model

Virial coefficients are obtained by comparing Eq. (SI.2) with expression (SI.41). This procedure results into formulas (123) to (129).

The virial expansion of formulation (75) was checked numerically in the following manner.

1. For a chosen number of components I we assumed dimensionless Helmholtz energy volumities of components and cross-components $\hat{\alpha}_{ij}^{\mathrm{vr}}$ in form of the fourth-order virial equation (103),

$$\hat{\alpha}_{ij}^{\mathrm{vr}}(\tau_{ij}+\Delta\tau_{ij},\delta_{ij})=\bar{B}_{ij}(\tau_{ij}+\Delta\tau_{ij})+\frac{1}{2}\bar{C}_{ij}(\tau_{ij}+\Delta\tau_{ij})\delta_{ij}$$
$$+\frac{1}{3}\bar{D}_{ij}(\tau_{ij}+\Delta\tau_{ij})\delta_{ij}^2\,. \quad \text{(SI.42)}$$

2. Reduced virial coefficients $\bar{B}_{ij}$, $\bar{C}_{ij}$, and $\bar{D}_{ij}$ for the components and cross-components were assumed as polynomial functions of the difference $\Delta\tau_{ij}$ of reduced reciprocal temperature from a reference value τ_{ij},

$$\bar{B}_{ij}(\tau_{ij}+\Delta\tau_{ij})=\bar{B}_{ij,0}+\bar{B}'_{ij,0}\Delta\tau_{ij}+\tfrac{1}{2}\bar{B}''_{ij,0}(\Delta\tau_{ij})^2\,, \quad \text{(SI.43)}$$

$$\bar{C}_{ij}(\tau_{ij}+\Delta\tau_{ij})=\bar{C}_{ij,0}+\bar{C}'_{ij,0}\Delta\tau_{ij}\,, \quad \text{(SI.44)}$$

$$\bar{D}_{ij}(\tau_{ij}+\Delta\tau_{ij})=\bar{D}_{ij,0}\,. \quad \text{(SI.45)}$$

Coefficients $\bar{B}_{ij,0}$, $\bar{B}'_{ij,0}$, $\bar{B}''_{ij,0}$,$\bar{C}_{ij,0}$,$\bar{C}'_{ij,0}$, $\bar{D}_{ij,0}$, and scaling volumes v_{ij} were generated as symmetric random matrices $I\times I$.

3. Quadratic density scaling function (100)

$$\mathcal{D}_{ij}(\boldsymbol{\rho})=\sum_{k=1}^{I}b_{ijk}\rho_k+\frac{1}{2}\sum_{k,\ell=1}^{I}b_{ijk\ell}\rho_k\rho_\ell \quad (100)$$

was substituted for δ_{ij} in Eq. (SI.42). Coefficients b_{ijk} and $b_{ijk\ell}$ for the density scaling function, and coefficients c_{ijk} and $c_{ijk\ell}$ for the temperature scaling function, were chosen as random numbers satisfying constraints (88), (89), (91), and (94).

4. The quadratic temperature scaling function (102)

$$\mathcal{T}_{ij}(\theta, \boldsymbol{\rho}) = T_{ij}\theta + \sum_{k=1}^{I} c_{ijk}\rho_k + \frac{1}{2}\sum_{k,\ell=1}^{I} c_{ijk\ell}\rho_k\rho_\ell \tag{102}$$

was substituted at place of $\tau_{ij} + \Delta\tau_{ij}$ in Eqs. (SI.43) through (SI.45). Coefficients c_{ijk} and $c_{ijk\ell}$ were chosen as random numbers satisfying constraints (88), (89), (91), and (93). We note that $T_{ij}\theta = \tau_{ij}$, so that technically expression

$$\sum_{k=1}^{I} c_{ijk}\rho_k + \frac{1}{2}\sum_{k,\ell=1}^{I} c_{ijk\ell}\rho_k\rho_\ell \tag{SI.46}$$

is substituted for $\Delta\tau_{ij}$ in Eqs. (SI.43) through (SI.45).
5. Using $\bar{B}_{ij}$, $\bar{C}_{ij}$, and $\bar{D}_{ij}$, resulting from the previous step, in Eq. (SI.42).
6. Using $\hat{\alpha}^{\mathrm{vr}}_{ij}$, resulting from the previous step, in Eq. (75),

$$\alpha^{\mathrm{dr}} = \sum_{i,j=1}^{I} \rho_i\rho_j v_{ij}\hat{\alpha}^{\mathrm{vr}}_{ij}\,. \tag{75}$$

In this way the test implementation of formulation (75) is completed.

The tested virial expansion of formulation (75) was constructed as follows. The zero-density limits of derivatives of the quadratic density and temperature scaling functions are

$$\mathcal{D}^{<}_{mn,p} = b_{mnp}\,, \quad \mathcal{D}^{<}_{mn,pq} = b_{mnpq}\,, \quad \mathcal{T}^{<}_{mn,p} = c_{mnp}\,, \quad \mathcal{T}^{<}_{mn,pq} = c_{mnpq}\,. \tag{SI.47}$$

Coefficients $\hat{B}_{mn}$, $\hat{C}_{mn}$, and $\hat{D}_{mn}$, were computed using, respectively, equations (117), (118), and (119). Consequently, the second, third, and fourth cross-virial coefficients could be evaluated using, respectively, Eqs. (124), (127), and (129). After that, we evaluated the residual reduced Helmholtz energy density $\alpha^{\mathrm{dr}}_{\mathrm{vir}}$ using virial expansion (26).

$$\alpha^{\mathrm{dr}}_{\mathrm{vir}} = \sum_{i,j=1}^{I} B_{ij}\rho_i\rho_j + \frac{1}{2}\sum_{i,j,k=1}^{I} C_{ijk}\rho_i\rho_j\rho_k + \frac{1}{3}\sum_{i,j,k,\ell=1}^{I} D_{ijk\ell}\rho_i\rho_j\rho_k\rho_\ell\,. \tag{26}$$

For numerical comparison, we chose a random vector of molar fractions $\mathbf{x}$ satisfying condition that the sum of molar fraction is unity. We chose a range of values of density ρ and constructed corresponding ranges for concentrations $\boldsymbol{\rho} = \rho\mathbf{x}$. For this "data set" we evaluated residual reduced Helmholtz density α^{dr}, Eq. (75), and its virial expansion $\alpha^{\mathrm{dr}}_{\mathrm{vir}}$, Eq. (26), were evaluated. We checked how the difference $\alpha^{\mathrm{dr}} - \alpha^{\mathrm{dr}}_{\mathrm{vir}}$ depends on density and we found that the main term in this deviation is proportional to ρ^5 as expected, because

series (26) is terminated after the fourth term. This was best seen by constructing a variable $\xi = \rho^n$, where n is an integer exponent, and plotting a numerical derivative $\mathrm{d}(\alpha^{\mathrm{dr}} - \alpha^{\mathrm{dr}}_{\mathrm{vir}})/\,\mathrm{d}\xi$ as a function of ρ. For $n = 5$, the obtained line extrapolates to a finite limit for $\rho \to 0$. For $n > 5$, it diverges, and for $n < 5$ it bends to zero.

E Reduced density of Helmholtz energy α^{d} as a thermodynamic potential

Molar Helmholtz energy a is defined based on molar internal energy u and molar entropy s as

$$a = u - Ts\,. \tag{SI.48}$$

Helmholtz energy can also be obtained via an Euler-type equation as

$$a = \sum_{i=1}^{I} \mu_i x_i - \frac{p}{\rho}\,, \tag{SI.49}$$

where μ_i is chemical potential of component i. A change of molar Helmholtz energy a can be expressed in terms of changes of temperature T, molar density ρ, and molar fractions x_i as

$$\mathrm{d}a = -s\,\mathrm{d}T + \frac{p}{\rho^2}\,\mathrm{d}\rho + \sum_{i=1}^{I} \mu_i\,\mathrm{d}x_i\,, \tag{SI.50}$$

where s stands for molar entropy. We defined the reduced Helmholtz energy density α^{d} by Eq. (23) as

$$\alpha^{\mathrm{d}} = \frac{a\rho}{RT}\,. \tag{23}$$

From Eq. (23) we find by differentiation

$$\mathrm{d}a = \frac{RT\,\mathrm{d}\alpha^{\mathrm{d}}}{\rho} + \frac{R\alpha^{\mathrm{d}}\,\mathrm{d}T}{\rho} - \frac{RT\,\mathrm{d}\rho}{\rho^2}\,. \tag{SI.51}$$

From Eq. (11) we can express molar fraction x_i in terms of concentration ρ_i and molar density ρ as

$$x_i = \frac{\rho_i}{\rho}\,. \tag{SI.52}$$

By differentiation we obtain

$$\mathrm{d}x_i = \frac{\mathrm{d}\rho_i - x_i\,\mathrm{d}\rho}{\rho}\,. \tag{SI.53}$$

We substitute expressions (SI.51) and (SI.53) into Eq. (SI.50) and obtain

$$\mathrm{d}\alpha^{\mathrm{d}} = \left(\frac{\rho T s}{R} + T\alpha^{\mathrm{d}}\right)\left(-\frac{\mathrm{d}T}{T^2}\right) + \frac{1}{RT}\left(\frac{p}{\rho} + \frac{RT\alpha^{\mathrm{d}}}{\rho} - \sum_{i=1}^{I}\mu_i x_i\right)\mathrm{d}\rho + \sum_{i=1}^{I}\frac{\mu_i}{RT}\,\mathrm{d}\rho_i\,. \quad \text{(SI.54)}$$

We note that the first term on the right-hand side can be related to internal energy through Eq. (SI.48). We also note that the second term on the right-hand side cancels on account of Eq. (SI.49). Consequently, we can simplify Eq. (SI.54) to

$$\mathrm{d}\alpha^{\mathrm{d}} = \frac{\rho u}{R}\left(-\frac{\mathrm{d}T}{T^2}\right) + \sum_{i=1}^{I}\frac{\mu_i}{RT}\,\mathrm{d}\rho_i\,. \quad \text{(SI.55)}$$

We further replace temperature T by reciprocal temperature θ,

$$\theta = \frac{1}{T}\,, \quad (24)$$

which allows to rewrite Eq. (SI.55) as

$$\mathrm{d}\alpha^{\mathrm{d}} = \frac{\rho u}{R}\,\mathrm{d}\theta + \sum_{i=1}^{I}\frac{\mu_i}{RT}\,\mathrm{d}\rho_i\,. \quad \text{(SI.56)}$$

Differentiation of function $\alpha^{\mathrm{d}}(\theta, \boldsymbol{\rho})$ gives

$$\mathrm{d}\alpha^{\mathrm{d}} = \alpha^{\mathrm{d}}_{\theta}\,\mathrm{d}\theta + \sum_{i=1}^{I}\alpha^{\mathrm{d}}_{i}\,\mathrm{d}\rho_i\,, \quad \text{(SI.57)}$$

where we introduce a notation for derivatives

$$\frac{\partial\alpha^{\mathrm{d}}(\theta,\boldsymbol{\rho})}{\partial\theta} \equiv \alpha^{\mathrm{d}}_{\theta}\,, \quad \frac{\partial\alpha^{\mathrm{d}}(\theta,\boldsymbol{\rho})}{\partial\rho_i} \equiv \alpha^{\mathrm{d}}_{i}\,. \quad \text{(SI.58)}$$

By comparison of Eqs. (SI.56) and (SI.57) we see

$$\alpha^{\mathrm{d}}_{\theta} = \frac{\rho u}{R}\,. \quad \text{(SI.59)}$$

This quantity can be called *reduced internal energy density*. Its unit is $\mathrm{K}\cdot\mathrm{mol}\cdot\mathrm{m}^{-3}$. Further we observe identity

$$\alpha^{\mathrm{d}}_{i} = \frac{\mu_i}{RT}\,. \quad \text{(SI.60)}$$

Dimensionless quantity α_i^{d} can be called *reduced chemical potential* of component i. Pressure can be obtained based on Eq. (SI.49) as

$$p = RT\left(\sum_{i=1}^{I}\alpha_i^{\mathrm{d}}\rho_i - \alpha^{\mathrm{d}}\right) . \tag{SI.61}$$

Molar entropy s can be obtained based on Eq. (SI.48) as

$$s = \frac{R}{\rho}\left(\theta\alpha_\theta^{\mathrm{d}} - \alpha^{\mathrm{d}}\right) . \tag{SI.62}$$