Supporting Information: A Generalized Form for Finite-size Corrections in Mutual Diffusion Coefficients of Multicomponent Mixtures Obtained from Equilibrium Molecular Dynamics Simulation

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S1 Simulation results

A Microsoft Excel file containing the processed results of all MD simulations is provided as a part of the Supporting Information. Results for transport properties (4 finite system sizes and extrapolated thermodynamic limit) and thermodynamic factors are provided in separate sheets of the file. The description of each column along with the corresponding units is provided in Tables S4 and S5 for LJ and molecular systems, respectively.

Table S1: Adjustable parameters (k_{ij}) to the Lorentz-Berthelot mixing rules (Equation (9)) for the LJ systems studied.[1]

adjustable parameter	Values
k_{12}	-0.6, -0.3, 0.05
k_{13}	-0.6, -0.3, 0.05
k_{23}	-0.6, -0.3, 0.0, 0.05

Table S2: Force field parameters for non-bonded interactions for the molecules used in this study.[2–4] A schematic representation of these molecules is shown in Figure S1.

Molecule	pseudo-atom	σ / [Å]	ϵ/k_B / [K]	q_i / [e]
chloroform[2]	C	3.80	37.74	-0.050
	Cl	3.47	150.94	-0.045
	H	-	-	0.185
acetone[3]	CH_3	3.910	80.9655	+0.062
	C	3.750	52.8673	+0.300
	O	2.960	105.7419	-0.424
methanol[4]	CH_3	3.775	104.17	+0.265
	O	3.07	85.55	-0.700
	H	-	-	+0.435

Table S3: Rigid bond lengths and angles of the molecules used in this study. A schematic representation of these molecules is shown in Figure S1.

Bond	Bond length / Å	Angle	Angle / [°]
C-Cl	1.771	CH_3-C-CH_3	116.30
C-H	1.085	CH_3-C=O	121.86
C=O	1.220	CH_3-O-H	108.50
CH_3-C	1.507	Cl-C-Cl	110.60
O-H	0.945	H-C-Cl	108.31
CH_3-O	1.430		

Table S4: Description for each column of the Microsoft excel files containing the simulation results of the molecular system provided as SI.

Column(s)	Name	Units	Description
1-3	X_i	[-]	Mole fractions of component 1, 2, and 3 in the mixture
4-6	Component_i	[-]	Names of component 1, 2, and 3 ($\epsilon_1 = \epsilon = 1.0$)
7-9	Molecule_i	[-]	Numbers of molecules of component 1, 2, and 3
10-12	Molar mass_i	$[\mathrm{g \cdot mol^{-1}}]$	Molar masses of component 1, 2, and 3 ($m_1 = m = 1.0$)
13	BoxLength	[m]	Length of the simulation box
14-19	Dself_i, 95%	$[\mathrm{m^2 \cdot s^{-1}}]$	Self-diffusion coefficients and their 95% confidence intervals
20-31	Onsager_ij, 95%	$[\mathrm{m^2 \cdot s^{-1}}]$	Onsager coefficients and their 95% confidence intervals
32-33	Viscosity, 95%	[Pa·s]	Shear viscosity of the system and its 95% confidence intervals
34-41	Delta_ij, 95%	$[\mathrm{m^2 \cdot s^{-1}}]$	Elements of matrix of phenomenological diffusion coefficient and their 95% confidence intervals
42-47	DMaxwellStefan_ij, 95%	$[\mathrm{m^2 \cdot s^{-1}}]$	Maxwell-Stefan (MS) diffusion coefficients and their 95% confidence intervals
48-55	DFick_ij, 95%	$[\mathrm{m^2 \cdot s^{-1}}]$	Fick diffusion coefficients and their 95% confidence intervals
56	DYehHummer	$[\mathrm{m^2 \cdot s^{-1}}]$	Yeh and Hummer correction
57-60	DeltaCorrection_ij	$[\mathrm{m^2 \cdot s^{-1}}]$	Finite-size corrections to elements of the matrix of phenomenological diffusion coefficient
61-64	Delta_ij_Inf, 95%	$[\mathrm{m^2 \cdot s^{-1}}]$	Corrected elements of the matrix of phenomenological diffusion coefficient
65-67	DMaxwellStefan_ij_Inf	$[\mathrm{m^2 \cdot s^{-1}}]$	Corrected MS diffusion coefficients
68-71	DFick_ij_Inf	$[\mathrm{m^2 \cdot s^{-1}}]$	Corrected Fick diffusion coefficients

Table S5: Description for each column of the Microsoft Excel file containing the simulation results of the Lennard-Jones (LJ) systems.

Column(s)	Name	Units	Description
1-3	X_i	[-]	Mole fraction of species 1, 2, and 3 in the mixture
4-6	Particle_i	[-]	Number of particles of species 1, 2, and 3
7-9	epsilon_i	$[\epsilon]$	LJ energy parameter for species 1, 2, and 3 ($\epsilon_1 = \epsilon = 1.0$)
10-12	sigma_i	$[\sigma]$	LJ size parameter for species 1, 2, and 3 ($\sigma_1 = \sigma = 1.0$)
13-15	mass_i	[m]	Mass of species 1, 2, and 3 ($m_1 = m = 1.0$)
16-18	k_ij	[-]	Adjustable parameter for the Lorenz-Berthelot mixing rules
19	BoxLength	$[\sigma]$	Length of the simulation box
20-25	Dself_i, 95%	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Self-diffusion coefficients and their 95% confidence intervals
26-37	Onsager_ij, 95%	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Onsager coefficients and their 95% confidence intervals
38-39	Viscosity, 95%	$[\sigma^2 \cdot (\mathrm{m} \cdot \epsilon)^{-1/2}]$	Shear viscosity of the system and its 95% confidence intervals
40-47	Delta_ij, 95%	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Elements of matrix of phenomenological diffusion coefficient and their 95% confidence intervals
48-53	DMaxwellStefan_ij, 95%	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Maxwell-Stefan (MS) diffusion coefficients and their 95% confidence intervals
54-61	DFick_ij, 95%	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Fick diffusion coefficients and their 95% confidence intervals
62	DYehHummer	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Yeh and Hummer correction
63-66	DeltaCorrection_ij	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Finite-size corrections to elements of the matrix of phenomenological diffusion coefficient
67-70	Delta_ij_Inf, 95%	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Corrected elements of the matrix of phenomenological diffusion coefficient
71-73	DMaxwellStefan_ij_Inf	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Corrected MS diffusion coefficients
74-77	DFick_ij_Inf	$[\sigma \cdot \epsilon^{1/2} \cdot \mathrm{m}^{-1/2}]$	Corrected Fick diffusion coefficients

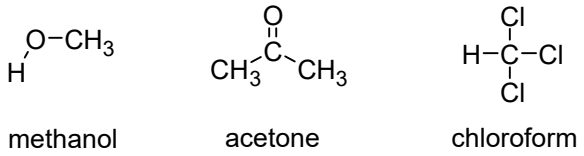

Figure S1: Schematic representation of the molecules used in this study. The intermolecular interaction parameters are listed in Table S2, and rigid bond lengths and angles are provided in Table S3. The united-atom approach is used for acetone.

References

(1) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*, 2nd ed.; Oxford University Press: Croydon, 2017.

(2) Tummala, N. R.; Striolo, A. Hydrogen-bond Dynamics for Water Confined in Carbon Tetrachloride-acetone Mixtures. *Journal of Physical Chemistry B* **2008**, *112*, 10675–10683.

(3) Gupta, R.; Chandra, A. Structural, Single-particle and Pair Dynamical Properties of Acetone-Chloroform Mixtures with Dissolved Solutes. *Chemical Physics* **2011**, *383*, 41–49.

(4) Jorgensen, W. L. Optimized Intermolecular Potential Functions for Liquid Alcohols. *The Journal of Physical Chemistry* **1986**, *90*, 1276–1284.