

# Supporting Information: Finite-size Effects of Binary Mutual Diffusion Coefficients from Molecular Dynamics

Seyed Hossein Jamali,<sup>†</sup> Ludger Wolff,<sup>‡</sup> Tim M. Becker,<sup>†</sup> André Bardow,<sup>‡</sup> Thijs  
J. H. Vlugt,<sup>†</sup> and Othonas A. Moulτος<sup>\*,†</sup>

<sup>†</sup>*Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical,  
Maritime and Materials Engineering, Delft University of Technology, Leeghwaterstraat 39,  
2628CB Delft, The Netherlands*

<sup>‡</sup>*Institute of Technical Thermodynamics, RWTH Aachen University, 52056 Aachen,  
Germany*

E-mail: o.moultos@tudelft.nl

## S1 Introduction

In this Supporting Information, the following information is provided: (a) the force field parameters, both for Lennard-Jones (LJ) and molecular mixtures; (b) system-size dependency of shear viscosity for all studied LJ systems; and (c) a detailed description of all MD simulation results for different system sizes, available as a ZIP file.

## S2 Force field parameters

Two types of systems are considered in this study: (1) LJ systems, and (2) molecular systems. The definitions of the force fields are listed below.

### S2.1 Lennard-Jones systems

The Lennard-Jones (LJ) interaction potential defined between two spherical particles is:

$$U_{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (\text{S1})$$

where  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the Lennard-Jones parameters and  $r_{ij}$  is the distance between two particles. To limit the range of the LJ interaction potential, we use a truncated and shifted Lennard-Jones potential:

$$U_{\text{LJ, truncated and shifted}}(r_{ij}) = \begin{cases} U_{\text{LJ}}(r_{ij}) - U_{\text{LJ}}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases} \quad (\text{S2})$$

For simulations of LJ systems, the cutoff radius  $r_c$  is  $4.0\sigma$ . For the interaction between unlike particles, the Lorentz-Berthelot mixing rules with an adjustable parameter ( $k_{ij}$ ) are used to include non-ideality:<sup>1</sup>

$$\begin{aligned} \epsilon_{ij} &= (1 - k_{ij}) \sqrt{\epsilon_{ii} \cdot \epsilon_{jj}} \\ \sigma_{ij} &= \frac{\sigma_{ii} + \sigma_{jj}}{2} \end{aligned} \quad (\text{S3})$$

### S2.2 Molecular systems

Molecules consist of several atoms connected together with bonds. Schematic representations of all molecules studied here (methanol, water, ethanol, acetone, methylamine, carbon tetrachloride) are shown in Figure S1. Each (pseudo-)atom is an interaction site, interacting

with the other interaction sites in the same molecule or other molecules. The force field consists of nonbonded intermolecular and bonded intramolecular interactions:

$$U = U_{\text{nonbonded}} + U_{\text{bonded}} = [U_{\text{LJ}} + U_{\text{electrostatic}}] + [U_{\text{bond}} + U_{\text{angle}} + U_{\text{torsion}}] \quad (\text{S4})$$

The nonbonded interactions are due to the LJ and electrostatic interactions between the atoms of different molecules or atoms of the same molecule separated by at least three bonds. The LJ potential is identical to what is defined in Equation (S1), however, a truncated Lennard-Jones potential at a cutoff radius of 10 Å with analytic tail corrections for energy and pressure is used:<sup>1</sup>

$$U_{\text{LJ,truncated}}(r_{ij}) = \begin{cases} U_{\text{LJ}}(r_{ij}) & r \leq r_c \\ 0 & r > r_c \end{cases} \quad (\text{S5})$$

Electrostatic interactions are computed from Coulomb’s law:

$$U_{\text{electrostatic}} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (\text{S6})$$

where  $q_i$  and  $q_j$  are the partial atomic charges on each atom.  $\epsilon_0$  is the permittivity of free space. The particle-particle particle-mesh (PPPM) method with a relative precision of  $10^{-6}$  is used to handle the long-range electrostatic interactions.<sup>1</sup> All nonbonded force field parameters needed for Equations (S5) and (S6) are listed in Table S1. The LJ interactions between unlike atoms are considered via the Lorentz-Berthelot mixing rules (Equation (S3) with  $k_{ij} = 0$ ).

The bonded interactions within a molecule consist of bond stretching, bond-angle bending, and dihedral angle torsion. Quadratic potentials for bond stretching and bond-angle bending are used:

$$U_{\text{bond}}(r) = K_b(r - r_0)^2 \quad (\text{S7})$$

$$U_{\text{angle}}(\theta) = K_\theta(\theta - \theta_0)^2 \quad (\text{S8})$$

where  $K_b$  and  $K_\theta$  are the force constants and  $r_0$  and  $\theta_0$  are the equilibrium bond length and angle, respectively. These force field parameters are reported in Tables S2 and S3 for bond stretching and bond-angle bending, respectively. For most of the studied molecules, bonds are considered to be rigid. The rigidity of bonds (and angles for water molecules) is taken into account with the SHAKE algorithm.<sup>1-3</sup>

In this study, only ethanol has a dihedral angle. The dihedral angle ( $\phi$ ) potential is taken from the TraPPE force field:<sup>4</sup>

$$U_{\text{torsion}}(\phi)/k_B/[K] = 0.0 + 209.82 [1 + \cos(\phi)] - 29.17 [1 - \cos(2\phi)] + 187.93 [1 + \cos(3\phi)] \quad (\text{S9})$$

### S3 System-size dependency of the shear viscosity

The studies by Yeh and Hummer<sup>5</sup> and Moulton et al.<sup>6</sup> revealed that the shear viscosity does not depend on the system size. Figure S2 shows a comparison of the shear viscosity for two different system sizes (500 and 4000 LJ particles), for all LJ systems considered. In all cases, the viscosity computed with 500 LJ particles equals the viscosity with 4000 LJ particles. In agreement with prior studies,<sup>5,6</sup> our results show that viscosity has no finite-size effects.

### S4 Simulation results

A ZIP file containing the processed results of all MD simulations is provided as a part of the Supporting Information. All computed properties for the simulated system sizes are listed in comma-separated values (csv) files. The description of each column along with the corresponding units is provided in Tables S4 and S5 for LJ and molecular systems, respectively. The results for the LJ systems are in dimensionless units. The extrapolated values to the thermodynamic limit are listed in “`Particles_Inifinite_Extrapolated.csv`” file and

the finite-size corrected thermodynamic factors can be found in the file “`thermodynamic_factor.csv`”.

Table S1: Nonbonded force field parameters for molecules used in this study. A schematic representation of these molecules is shown in Figure S1.

Molecule	pseudo-atom	$\sigma$ / [ $\text{\AA}$ ]	$\epsilon/k_B$ / [K]	$q_i$ / [e]
methanol <sup>4</sup>	CH <sub>3</sub>	3.75	98.0	0.265
	O	3.02	93.0	-0.700
	H	0.0	0.0	0.435
water <sup>7</sup>	O	3.166	78.175	-0.8476
	H	0.0	0.0	0.4238
ethanol <sup>4</sup>	CH <sub>3</sub>	3.75	98.0	0.000
	CH <sub>2</sub>	3.95	46.0	0.265
	O	3.02	93.0	-0.700
	H	0.0	0.0	0.435
acetone <sup>8</sup>	CH <sub>3</sub>	3.75	98.0	0.000
	C	3.82	40.0	0.424
	O	3.05	79.0	-0.424
methylamine <sup>9</sup>	CH <sub>3</sub>	3.75	98.0	0.180
	N	3.34	111.0	-0.892
	H	0.0	0.0	0.356
carbon tetrachloride <sup>10</sup>	C	3.41	50.39	-0.1616
	Cl	3.45	143.63	0.0404

Table S2: Bond stretching parameters of the molecules used in this study. A schematic representation of these molecules is shown in Figure S1. Bonds are kept rigid via the SHAKE algorithm.<sup>1</sup>

Molecule	bond	$K_b$ / [K/Å <sup>2</sup> ]	$r_0$ / [Å]
methanol <sup>4</sup>	CH <sub>3</sub> - O	rigid	1.430
	O - H	rigid	0.945
water <sup>7</sup>	O - H	rigid	1.000
ethanol <sup>4</sup>	CH <sub>3</sub> - CH <sub>2</sub>	156000 <sup>11</sup>	1.540
	CH <sub>2</sub> - O	rigid	1.430
	O - H	rigid	0.945
acetone <sup>8</sup>	CH <sub>3</sub> - C	rigid	1.520
	C - O	rigid	1.229
methylamine <sup>9</sup>	CH <sub>3</sub> - N	rigid	1.448
	N - H	rigid	1.010
carbon tetrachloride <sup>10</sup>	C - Cl	158500	1.766

Table S3: Bond-angle bending parameters of the molecules used in this study. A schematic representation of these molecules is shown in Figure S1. The water molecule is kept rigid via the SHAKE algorithm.<sup>1</sup>

Molecule	angle	$K_\theta / [\text{K}/\text{\AA}^2]$	$\theta_0 / [^\circ]$
methanol <sup>4</sup>	CH <sub>3</sub> - O - H	27700	108.5
water <sup>7</sup>	H - O - H	rigid	109.47
ethanol <sup>4</sup>	CH <sub>3</sub> - CH <sub>2</sub> - O	25200	109.5
	CH <sub>2</sub> - O - H	27700	108.5
acetone <sup>8</sup>	CH <sub>3</sub> - C - CH <sub>3</sub>	31250	117.2
	CH <sub>3</sub> - C - O	31250	121.4
methylamine <sup>9</sup>	CH <sub>3</sub> - N - H	31250	112.9
	H - N - H	21955	106.4
carbon tetrachloride <sup>10</sup>	Cl - C - Cl	37500	109.5

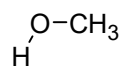


Table S4: Description for each column of the text files containing the simulation results of the Lennard-Jones mixtures. The equations shown in the description column refer to the equations in the main text.

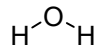
Column(s)	Name	Units	Description
1	X_1	[-]	Molefraction of species 1 in the mixture
2	Particle_1	[-]	Number of particles of species 1
3	epsilon_1	[ $\epsilon$ ]	LJ energy parameter for species 1 ( $\epsilon_1 = \epsilon = 1.0$ )
4	sigma_1	[ $\sigma$ ]	LJ size parameter for species 1 ( $\sigma_1 = \sigma = 1.0$ )
5	mass_1	[m]	Mass of species 1 ( $m_1 = m = 1.0$ )
6	Particle_2	[-]	Number of particles of species 2
7	epsilon_2	[ $\epsilon$ ]	LJ parameter for species 2
8	sigma_2	[ $\sigma$ ]	LJ parameter for species 2
9	mass_2	[m]	Mass of species 2
10	k_12	[-]	Adjustable parameter for the Lorez-Berthelot mixing rules
11	BoxLength	[ $\sigma$ ]	Length of the simulation box
12 - 15	Dself_i, 95%	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Self-diffusion coefficients (Eq. 1) and their 95% confidence intervals
16 - 21	Onsager_ij, 95%	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Onsager coefficients (Eq. 4) and their 95% confidence intervals
22 - 23	Viscosity, 95%	[ $\sigma^2 \cdot (m \cdot \epsilon)^{-1/2}$ ]	Shear viscosity of the system (Eq. 3) and its 95% confidence intervals
24 - 25	DDarken, 95%	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Darken equation diffusion coefficient computed from the self-diffusivities (Eq. 10) and its 95% confidence intervals
26 - 27	DMaxwellStefan, 95%	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Maxwell-Stefan (MS) diffusion coefficient computed from Onsager coefficients (Eq. 8) and its 95% confidence intervals
28	DYehHummer	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Yeh and Hummer correction to the Darken equation/self-diffusivities (Eq. 2)
29	DYehHummerMS	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Maxwell-Stefan Yeh and Hummer (MSYH) correction to the MS diffusion coefficient (Eq. 17)
30	DDarkenInfinite	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Corrected Darken equation with the YH correction (Eq. 2)
31	DMaxwellStefanInfinite	[ $\sigma \cdot \epsilon^{1/2} \cdot m^{-1/2}$ ]	Corrected MS diffusion coefficient with the MSYH correction (Eq. 17)

Table S5: Description for each column of the text files containing the simulation results of the molecular system. The equations shown in the description column refer to the equations in the main text.

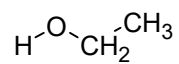
Column(s)	Name	Units	Description
1	X_1	[-]	Molefraction of the first species (methanol)
2 - 3	Component_i	[-]	Name of the species
4 - 5	Molecule_i	[-]	Number of molecules of the species
6	BoxLength	[m]	Side length of the simulation box
7 - 10	Dself_i, 95%	[m <sup>2</sup> ·s <sup>-1</sup> ]	Self-diffusion coefficients (Eq. 1) and their 95% confidence intervals
11 - 16	Onsager_ij, 95%	[m <sup>2</sup> ·s <sup>-1</sup> ]	Onsager coefficients (Eq. 4) and their 95% confidence intervals
17 - 18	Viscosity, 95%	[Pa·s]	Shear viscosity of the system (Eq. 3) and its 95% confidence intervals
19 - 20	DDarken, 95%	[m <sup>2</sup> ·s <sup>-1</sup> ]	Darken diffusion coefficient computed from the self-diffusivities (Eq. 10) and its 95% confidence intervals
21 - 22	DMaxwellStefan, 95%	[m <sup>2</sup> ·s <sup>-1</sup> ]	Maxwell-Stefan (MS) diffusion coefficient computed from Onsager coefficients (Eq. 8) and its 95% confidence intervals
23	DYehHummer	[m <sup>2</sup> ·s <sup>-1</sup> ]	Yeh and Hummer correction to the Darken equation/self-diffusivities (Eq. 2)
24	DYehHummerMS	[m <sup>2</sup> ·s <sup>-1</sup> ]	Maxwell-Stefan Yeh and Hummer (MSYH) correction to the MS diffusion coefficient (Eq. 17)
25	DDarkenInfinite	[m <sup>2</sup> ·s <sup>-1</sup> ]	Corrected Darken equation with the YH correction (Eq. 2)
26	DMaxwellStefanInfinite	[m <sup>2</sup> ·s <sup>-1</sup> ]	Corrected MS diffusion coefficient with the MSYH correction (Eq. 17)



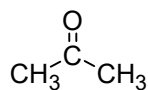
methanol



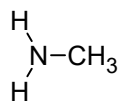
water



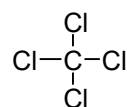
ethanol



acetone



methylamine



carbon tetrachloride

Figure S1: Schematic representation of the molecules used in this study. The bonded and nonbonded interaction parameters are listed in Tables S1 to S3.

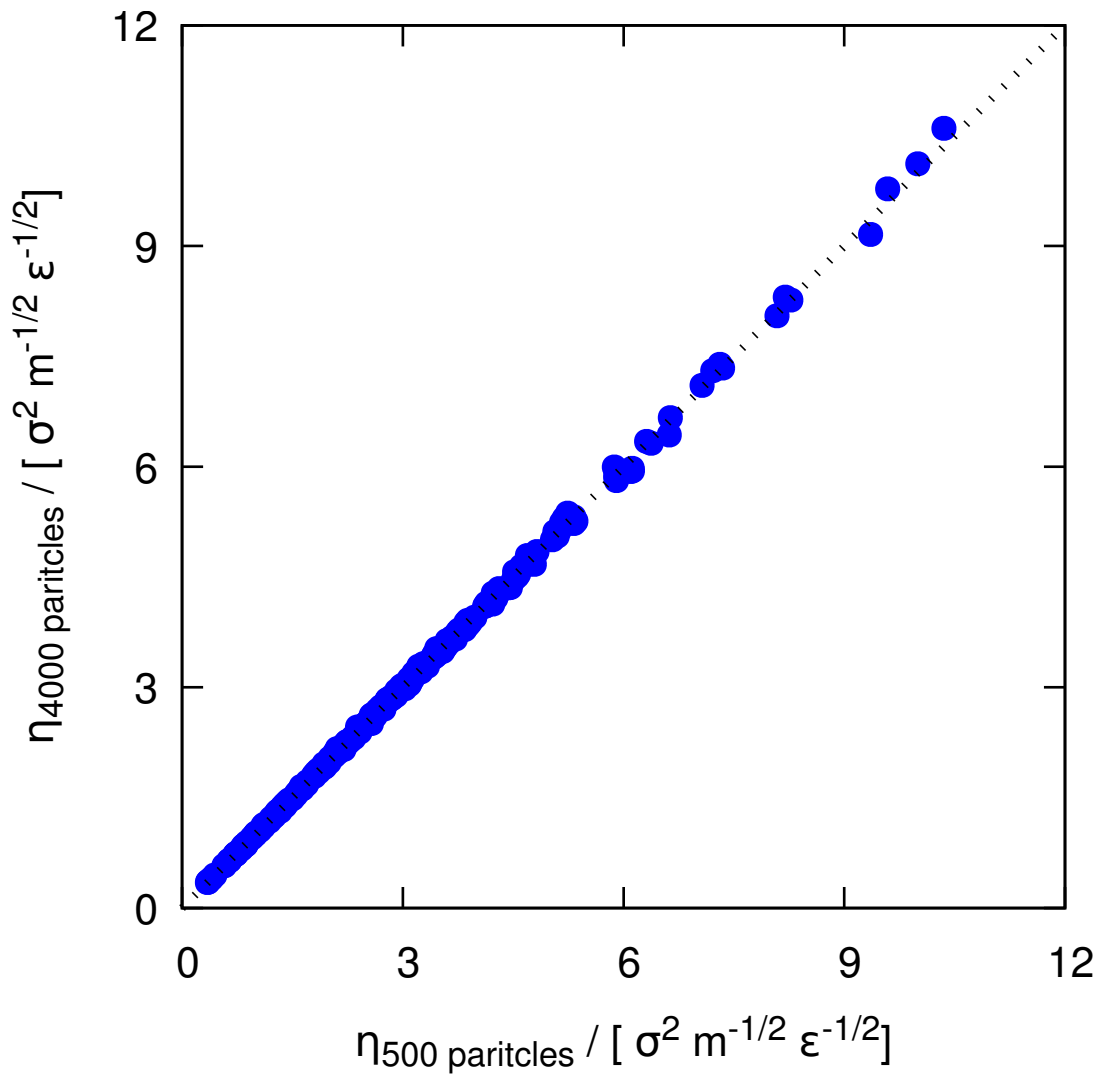


Figure S2: Comparison between the shear viscosity of the studied LJ systems for two system sizes of 500 and 4000 particles, computed from equilibrium Molecular Dynamics simulations. The dashed line indicates perfect agreement between the two system sizes.

## References

- (1) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*, 2nd ed.; Oxford University Press: Croydon, 2017.
- (2) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic Press: London, 2002.
- (3) Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. Numerical Integration of the Cartesian Equations of Motion of a System with Constraints: Molecular Dynamics of n-Alkanes. *J. Comput. Phys.* **1977**, *23*, 327–341.
- (4) Chen, B.; Potoff, J. J.; Siepmann, J. I. Monte Carlo Calculations for Alcohols and Their Mixtures with Alkanes. Transferable Potentials for Phase Equilibria. 5. United-Atom Description of Primary, Secondary, and Tertiary Alcohols. *J. Phys. Chem. B* **2001**, *105*, 3093–3104.
- (5) Yeh, I.-C.; Hummer, G. System-Size Dependence of Diffusion Coefficients and Viscosities from Molecular Dynamics Simulations with Periodic Boundary Conditions. *J. Phys. Chem. B* **2004**, *108*, 15873–15879.
- (6) Moulτος, O. A.; Zhang, Y.; Tsimpanogiannis, I. N.; Economou, I. G.; Maginn, E. J. System-Size Corrections for Self-Diffusion Coefficients Calculated from Molecular Dynamics Simulations: The Case of CO<sub>2</sub>, n-alkanes, and Poly(Ethylene Glycol) Dimethyl Ethers. *J. Chem. Phys.* **2016**, *145*, 074109.
- (7) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.
- (8) Stubbs, J. M.; Potoff, J. J.; Siepmann, J. I. Transferable Potentials for Phase Equilibria. 6. United-Atom Description for Ethers, Glycols, Ketones, and Aldehydes. *J. Phys. Chem. B* **2004**, *108*, 17596–17605.

- (9) Wick, C. D.; Stubbs, J. M.; Rai, N.; Siepmann, J. I. Transferable Potentials for Phase Equilibria. 7. Primary, Secondary, and Tertiary Amines, Nitroalkanes and Nitrobenzene, Nitriles, Amides, Pyridine, and Pyrimidine. *J. Phys. Chem. B* **2005**, *109*, 18974–18982.
- (10) Tummala, N. R.; Striolo, A. Hydrogen-Bond Dynamics for Water Confined in Carbon Tetrachloride-Acetone Mixtures. *J. Phys. Chem. B* **2008**, *112*, 10675–10683.
- (11) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.