OrthoBoXY

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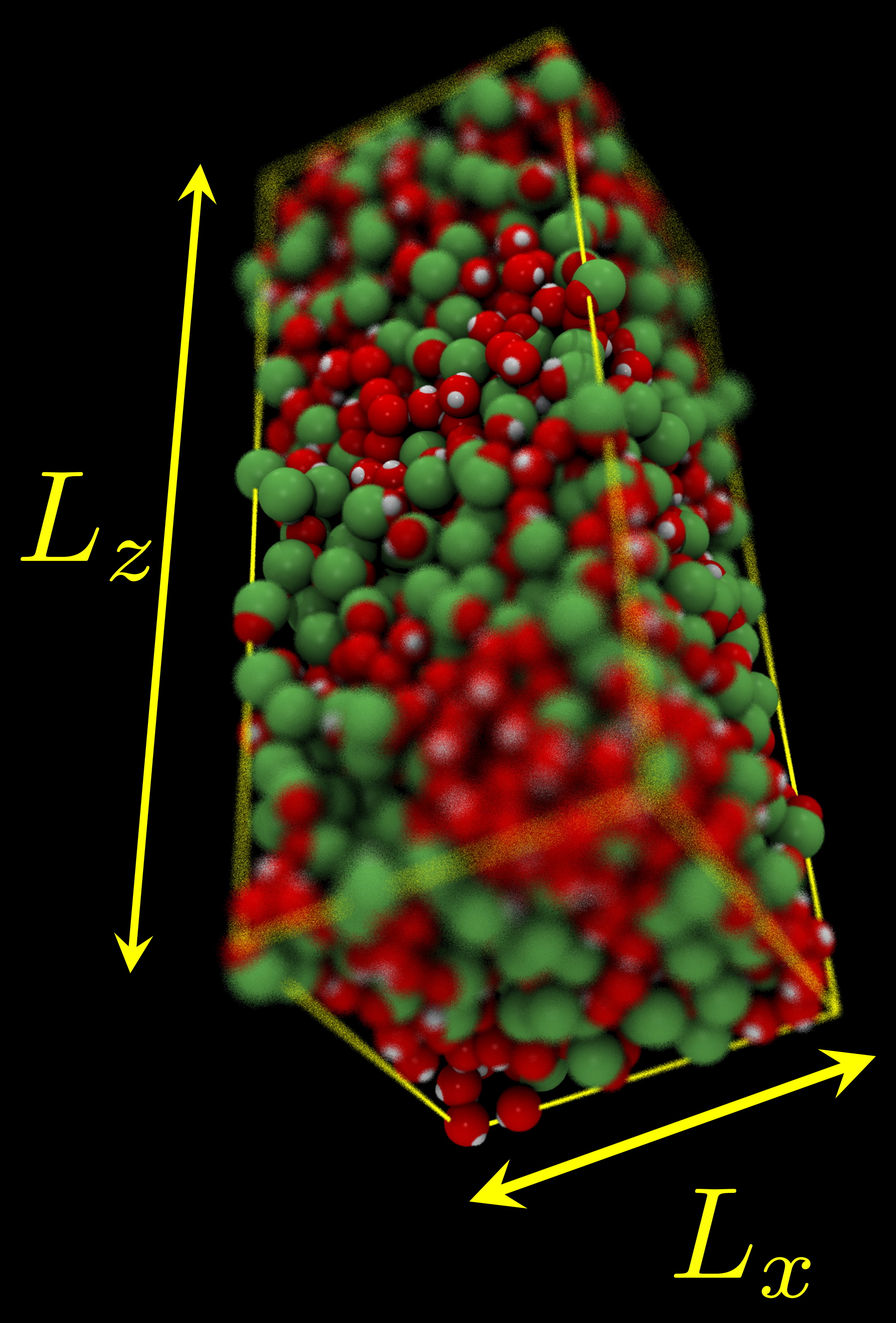
$$\frac{L_z}{L_x} = \frac{L_z}{L_y} = 2.7933596\ldots$$

github.com/Paschek-Lab/OrthoBoXY

$$D_0 = \frac{1}{2}\left(D_x + D_y\right)$$

$$\eta = \frac{k_{\mathrm{B}}T \cdot 8.17112}{6\pi L_z (D_0 - D_z)}$$

"Ubi materia, ibi geometria"
Johannes Keppler



Hydrodynamic Model

$$\mathbf{D}_{\mathrm{PBC}} = D_0\mathbf{1} + k_{\mathrm{B}}T \lim_{r\to 0}\left[\mathbf{T}_{\mathrm{PBC}}(\mathbf{r}) - \mathbf{T}_0(\mathbf{r})\right]$$

$$D_0 = D_{\mathrm{PBC},ii} + \frac{k_{\mathrm{B}}T\zeta_{ii}}{6\pi\eta L_i}$$

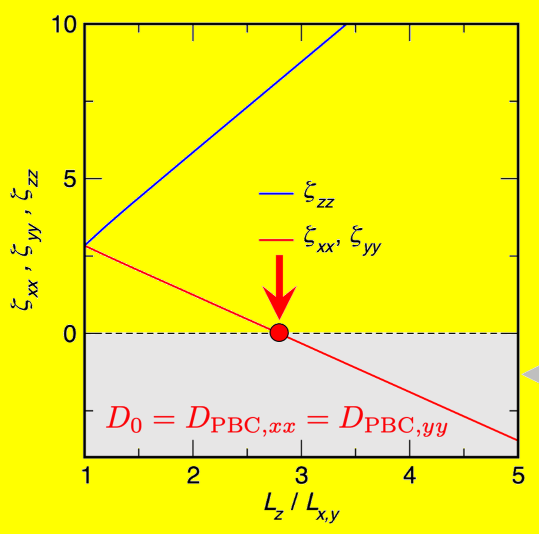
$$\begin{aligned}\zeta_{ii} \quad = \quad & -\frac{3}{2}\,L_i \cdot \Bigg\{ \frac{1}{2}\Bigg[\sum_{\mathbf{n}\neq 0}\frac{\mathrm{erfc}(\alpha\, n)}{n} \\ & + \frac{n_i^2}{n^2}\left(\frac{\mathrm{erfc}(\alpha\, n)}{n} + \frac{2\alpha}{\sqrt{\pi}}e^{-\alpha^2 n^2}\right)\Bigg] \\ & + \frac{\pi}{V}\Bigg[\sum_{\mathbf{k}\neq 0}\frac{4\,e^{-k^2/(4\alpha^2)}}{k^2} \\ & - \frac{k_i^2}{\alpha^2 k^2}e^{-k^2/(4\alpha^2)}\left(1 + \frac{4\alpha^2}{k^2}\right)\Bigg] \\ & - \frac{\pi}{\alpha^2 V} - \frac{\alpha}{\sqrt{\pi}}\Bigg\}\end{aligned}$$

"Magic" Box-Dimensions

$$L_z/L_x = L_z/L_y = 2.7933596497\ldots$$

$$\zeta_{xx} = \zeta_{yy} = 0$$

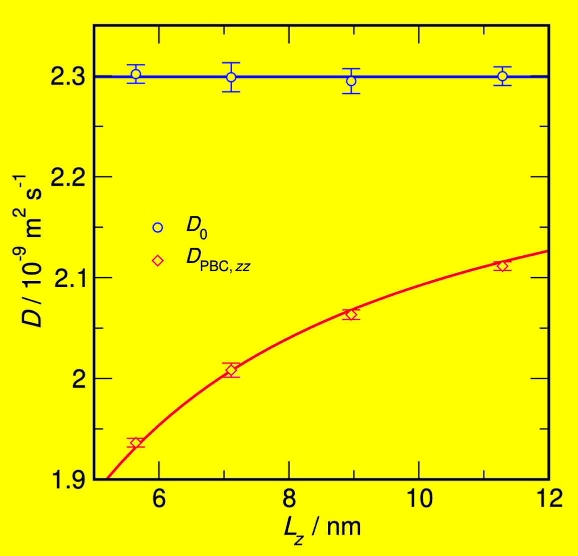
$$\zeta_{zz} = 8.1711245653$$



$\zeta_{xx} = \zeta_{yy} = 0$

$$D_0 = D_{\mathrm{PBC},ii} + \frac{k_{\mathrm{B}}T\zeta_{ii}}{6\pi\eta L_i}$$

- Values of Madelung-like constants depend only on the box-shape
- Data obtained from simulations using orthorhombic boxes can be used to determine both the system-size independent self-diffusion coefficient D_0 and the viscosity η



TIP4P/2005 Water

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N	L_x, L_y (nm)	L_z (nm)	D_0 (10^{-9} m^2 s^{-1})	$D_{\mathrm{PBC},zz}$ (10^{-9} m^2 s^{-1})	η (mPa s)
		NVT			
768	2.02050	5.64398	2.267 ± 0.039	1.922 ± 0.020	0.916 ± 0.116
1536	2.54566	7.11097	2.283 ± 0.027	1.989 ± 0.010	0.853 ± 0.084
3072	3.20734	8.95925	2.270 ± 0.021	2.066 ± 0.011	0.975 ± 0.113
6144	4.04100	11.28796	2.289 ± 0.019	2.104 ± 0.008	0.854 ± 0.095
		NPT			
3072	3.20734 ± 7.7 × 10^{-5}	8.95924 ± 2.2 × 10^{-4}	2.290 ± 0.030	2.065 ± 0.010	0.884 ± 0.124

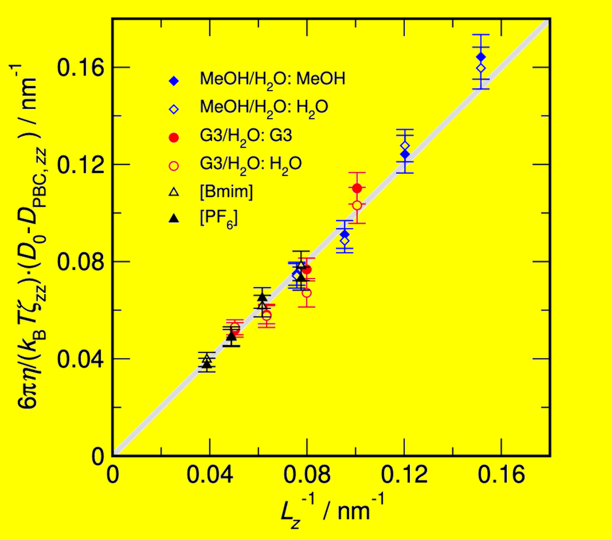
[a]Simulations were performed at a temperature of T = 298 K and a density of ρ = 0.9972 g cm^{-3} (NVT) or a pressure of P = 1 bar (NPT) with N indicating the number of water molecules and L_x, L_y, and L_z representing the box lengths of the orthorhombic unit cell. The direction-dependent self-diffusion coefficients, $D_{\mathrm{PBC},ii}$, are determined from the slope of the center-of-mass mean square displacement of the water molecules. The true self-diffusion coefficient D_0 is determined according to eq 5, and the shear viscosity η is determined according to eq 6. The errors indicate a range of ±1σ.

Various Liquids/Liquid Mixtures/Ionic Liquds

https://doi.org/10.1021/acs.jcpb.4c07540

system	T (K)	comp.	D_0 (10^{-9} m^2 s^{-1})	η (mPa·s)	R_{hyd} (nm)	α_{SE}
TIP4P/2005 water	298		2.2994 ± 0.0053	0.860 ± 0.018	0.110	0.149
dimethyl ether	303		12.285 ± 0.021	0.1400 ± 0.0040	0.129	0.201
methanol	298		3.0434 ± 0.0089	0.435 ± 0.012	0.165	0.112
triglyme	303		0.7064 ± 0.0018	1.750 ± 0.061	0.180	0.199
methanol/water (1:1)	298	MeOH	1.8968 ± 0.0052	0.910 ± 0.019	0.126	
		H_2O	1.8509 ± 0.0048		0.130	
triglyme/water (1:1)	303	G3	0.3896 ± 0.0010	3.070 ± 0.073	0.186	
		H_2O	0.5185 ± 0.0010		0.139	
[BMim][PF_6]	350	[BMim]	0.060848 ± 0.000096	34.29 ± 0.87	0.123	
		[PF_6]	0.048962 ± 0.000091		0.153	

[a]Values given represent weighted averages taking into account the computed uncertainties.[74] Here, T is the simulation temperature, D_0 is the true self-diffusion coefficient, and η is the viscosity. The $R_{\mathrm{hyd}} = k_{\mathrm{B}}T/(6\pi\eta D_0)$ denotes the computed hydrodynamic radii according to the Stokes–Einstein relation applying "stick" boundary conditions.[51] The dimensionless "Stokes–Einstein parameter" α_{SE}, as defined be eq 28, characterizes the validity of the Stokes-Einstein relation. It is, however, only defined for pure liquids.



A Simpler Way to Compute True Self-Diffusion Coefficients and Viscosities from Molecular Simulation

Recently, an analytical expression for the system size dependence and direction-dependence of self-diffusion coefficients for liquids, liquid mixtures and ionic liquids due to hydrodynamic interactions in periodic systems has been derived for molecular dynamics (MD) simulations using orthorhombic unit cells. Based on this description, we show that for systems with "magic" box length ratios of $L_z/L_x = L_z/L_y = 2.7933596497$ the computed self-diffusion coefficients D_x and D_y in the x- and y-direction become system-size independent and thus represent the *true* self-diffusion coefficient $D_0 = (D_x + D_y)/2$. Moreover, by using this particular box geometry, the viscosity can be determined with a high degree of accuracy from the difference of components of the diffusion coefficients in x-, y-, and z-directions using the simple expression $\eta = k_B T\times 8.1711245653/[3\pi L_z(D_x+D_y-2D_z)]$, where k_B denotes Boltzmann's constant and T represents the temperature. MD simulations of TIP4P/2005 water for various system sizes using both orthorhombic and cubic box geometries are used to test the approach. Our simulations show that the OrthoBoXY method provides accurate self-diffusion and viscosity data even for system sizes as small as 96 water molecules, thus making it an ideal candidate to determine viscosities and true self-diffusion coefficients from computationally expensive calculations such as *ab initio* molecular dynamics simulations.