

On the validity of Stokes' law at the molecular level

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Abstract

In order to investigate the dependence of the viscosity on the mass of the molecules in a liquid, and thus check the validity of Stokes' law for molecules, several molecular dynamics simulations of 'water' molecules with different mass and different molecular mass distributions were performed. The viscosity is shown to be sensitive to the mass but less sensitive to the mass distribution. The product of diffusion coefficient and viscosity, which according to Stokes' law should be independent of the mass, varies. We may therefore conclude that Stokes' law is not valid for small molecules. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

More than 150 years ago, Stokes [1] proposed the drag or frictional force \mathbf{f} for a sphere of diameter d moving with constant velocity \mathbf{v} in a fluid of shear viscosity η is given by,

$$\mathbf{f} = -3\pi\eta d\mathbf{v}. \quad (1)$$

This result is obtained by solving the equations of motion for the translational flow of fluid around a rigid sphere assuming so-called stick boundary conditions. Using slip boundary conditions the drag force is smaller: the factor 3 in (1) is replaced by a factor 2 [2]. When using Langevin's formalism [3], the drag or frictional force exerted on a particle with mass m moving with velocity \mathbf{v} through a viscous medium

$$\mathbf{f} = -m\gamma\mathbf{v} \quad (2)$$

is expressed in terms of the friction coefficient γ .

The friction coefficient is related to the diffusion coefficient D of the particle through Einstein's expression [4–6],

$$D = \frac{k_B T}{m\gamma}, \quad (3)$$

where k_B is Boltzmann's constant and T the temperature, which is related to the mean square velocity $\langle \mathbf{v}^2 \rangle$ through equipartition

$$\frac{1}{2}m\langle \mathbf{v}^2 \rangle = \frac{3}{2}k_B T. \quad (4)$$

Combining Eqs. (1)–(3) we arrive at another form of Stokes' law,

$$D\eta = \frac{k_B T}{3\pi d}, \quad (5)$$

which implies that for spherical particles of the same size at constant temperature the product of diffusion constant and shear viscosity is fixed. Thus, this product is independent of the mass of the particle.

Although Stokes' law is derived from purely macroscopic considerations, and the Einstein expression (3) is based on the assumption of Brownian

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motion, Eq. (5) describes the experimental data for atomic liquids well [6,7]. Stokes' law is also often used to obtain values for the friction coefficient γ from experimental data for a molecular solvent, such as water [8], which are required in stochastic dynamics simulations of a solute based on the Langevin equation [9,10].

Here we present results of molecular dynamics (MD) simulations of liquid water which show that Stokes' law (5) is not satisfied at the molecular level. By changing the masses of the water molecules, the diffusion constant and shear viscosity of the liquid can be changed, but their product should remain constant if Stokes' law (5) would apply.

When changing the masses of the atoms in a molecular system dynamic properties change. Thermodynamic equilibrium properties remain unaffected, since the configurational part of the statistical-mechanical partition function is independent of the atomic masses. This is true as long as no intramolecular constraints are applied in the case of flexible molecules [11]. This result has been used to lengthen the integration time step in MD simulation by increasing the masses of the hydrogen atoms by about a factor 10 to a value comparable to that of the other atoms in the molecule [12–14]. By this trick statistical sampling is enhanced at the expense of a correct simulation of dynamical properties. The results presented here for liquid water show the extent to which the dynamic properties of liquid water are distorted by varying the mass and its distribution within a water molecule.

The shear viscosity of liquid water as a function of the mass of the water molecule is also of interest because the function of a protein in solution depends on its structure, which is unique for each particular protein, and on its dynamical properties. The latter is influenced by the viscosity of the solvent, i.e. water. In order to determine the dependence of relaxation processes in proteins on the solvent viscosity, one must change the viscosity of the solvent without changing its interaction with the protein. Experimentally, a change of viscosity at constant temperature and pressure can only be brought about by changing the molecular composition of the solvent [15,16]. This, however, also implies a modification of the protein-solvent interaction. In a computer simulation the solvent viscosity can be changed by altering the

atomic masses of the solvent molecules, thereby keeping the protein-solvent interaction constant.

The viscosity and diffusivity of a liquid can be calculated straightforwardly using equilibrium or non-equilibrium MD simulation [17,18] or analytical theories [19,20]. The latter studies address the transition to non-Stokes-Einstein behaviour when liquid water is supercooled. Brown and Clarke [21] studied the dependence of the viscosity and diffusivity of tri-atomic model liquids on the distribution of a fixed molecular mass over the three atoms. They found Stokes' law (5) to be violated for the different mass distributions, but concluded that it is not easy to find a consistent explanation for the statistically significant differences between the values of expression (5) for the four mass distributions used in their study.

2. Method

A total of seven MD simulations, which only differed in the masses of the hydrogen and oxygen atoms, were carried out (Table 1). The water model used was the simple point charge (SPC) model [22]. Two other models with the same mass distribution as the SPC molecule, SPC₁₀ and SPC₁₀₀, were obtained by multiplying the masses of the atoms in the SPC model with a factor of 10 and 100, respectively, resulting in total masses of 180.154 u and 1801.54 u. Models with different molecular mass distributions were obtained by taking the mass of the oxygen atom equal to the mass of the hydrogen. In model EQ₁ all atom masses were set to 1 u, in EQ₁₀ to 10 u and in EQ₁₀₀ to 100 u. In the D2O model the mass of the oxygen atom was taken the same as in the SPC model, but the masses of the hydrogens were increased to 2.014 u. All the other parameters, such as charge distribution, Lennard-Jones parameters and molecular geometry, were as in the SPC model.

All simulations were performed with a system of 512 molecules in a cubic periodic box. The geometry of the rigid water molecules was maintained using the SHAKE algorithm [23] with a tolerance of 10^{-4} . To keep the system at a constant temperature of 300 K, a Berendsen thermostat [24] was applied using a coupling time of 0.1 ps. The systems were first equilibrated for 50 ps at a constant pressure of 1 atm. A Berendsen manostat [24] was used with a compressibility of $2.092 \times 10^{-3} \text{ (kJ mol}^{-1} \text{ nm}^{-3})^{-1}$

Table 1

Masses and thermodynamic properties for the seven water simulations averaged over 50 ps

Model	SPC	SPC ₁₀	SPC ₁₀₀	D ₂ O	EQ ₁	EQ ₁₀	EQ ₁₀₀
$m_{\text{H}_2\text{O}}$ (u)	18.0154	180.154	1801.54	20.0274	3.0	30.0	300.0
m_{O} (u)	15.9994	159.994	1599.94	15.9994	1.0	10.0	100.0
m_{H} (u)	1.008	10.08	100.8	2.014	1.0	10.0	100.0
ρ (g/cm ³)	0.980	9.799	97.995	1.089	0.163	1.632	16.318
T (K)	299.69	299.95	300.19	300.29	300.18	300.97	300.37
E_{pot} (kJ/mol)	-41.87	-41.93	-41.85	-41.87	-41.70	-41.84	-41.84
E_{kin} (kJ/mol)	7.48	7.49	7.48	7.47	7.48	7.50	7.48

The models are defined in the text. m , atomic or molecular mass; ρ , density of the simulated system; T , temperature; E_{pot} , E_{kin} : average potential and kinetic energy per water molecule, respectively.

and a coupling time of 0.5 ps. The next 50 ps were used to calculate the average box lengths. The mean box length averaged over the seven model simulations, was 2.5 nm. In none of the simulations did the box length differ by more than 0.003 nm from this average. The systems were equilibrated for a further 50 ps at constant volume and the next 1000 ps were used for analysis. All simulations were performed with the GROMOS96TM package [25], with a cut-off distance of 0.9 nm, a time step of 2 fs and at a temperature of 300 K.

The shear viscosity η , diffusion constant D and rotational correlation times τ_l were calculated as described by Tironi and van Gunsteren [26]. For calculating the viscosity the Einstein relation was used. The off-diagonal elements $P_{\alpha\beta}$ of the pressure tensor were saved every 2 fs. The time integral of these, $\Delta P_{\alpha\beta}$, was calculated every 0.1 ps. Because

of poor statistics at long simulation times, the viscosity was calculated from the resulting curve between 5 and 10 ps [27]. Using the three independent off-diagonal components of the pressure tensor a mean value $\langle\eta\rangle$ and a standard deviation σ_η were calculated. The diffusion coefficients were obtained from the slope of the mean square center of mass displacement as a function of time over 50 ps. The rotational correlation times were obtained by fitting to the linear part in a logarithmic plot of the dipolar rotational correlation function.

3. Results and conclusions

Table 1 presents the models together with the simulation results for the thermodynamic properties. As required, all thermodynamic properties tested re-

Table 2

Masses and dynamic properties for the seven water simulations calculated over 1000 ps (η) or 50 ps (D and τ_l)

Model	SPC	SPC ₁₀	SPC ₁₀₀	D ₂ O	EQ ₁	EQ ₁₀	EQ ₁₀₀
$m_{\text{H}_2\text{O}}$ (u)	18.015	180.154	1801.54	20.027	3.0	30.0	300.0
η_{xy} (cp)	0.693	1.660	4.042	0.784	0.215	0.662	1.999
η_{xz} (cp)	0.569	1.690	3.991	0.717	0.348	0.948	1.939
η_{yz} (cp)	0.642	1.636	3.945	0.583	0.307	0.871	2.821
$\langle\eta\rangle$ (cp)	0.635	1.662	3.993	0.695	0.290	0.827	2.253
σ_η (cp)	0.051	0.022	0.040	0.084	0.056	0.121	0.402
D (10 ⁻³ nm ² ps ⁻¹)	4.07	1.30	0.47	3.36	8.17	2.72	0.78
$D\eta$ (kJ/mol nm)	1.56	1.30	1.13	1.41	1.43	1.36	1.06
τ_1 (ps)	3.4	11.0	28.7	4.4	1.4	6.7	19.8
τ_2 (ps)	1.6	5.0	12.3	2.4	0.8	4.3	9.7
τ_1/τ_2	2.2	2.2	2.3	1.8	1.8	1.6	2.0

η , shear viscosity (σ_η , standard deviation); D , translational diffusion constant; τ_l , dipolar rotational correlation time for the l th order Legendre polynomial. Experimental values are: $\eta(\text{H}_2\text{O}) = 0.891$ cp at 298 K [28]; $\eta(\text{D}_2\text{O}) = 1.059$ cp at 298 K [29]; $D(\text{H}_2\text{O}) = 2.23 \times 10^{-3}$ nm² ps⁻¹ at 298 K [30]; $D(\text{D}_2\text{O}) = 2.27 \times 10^{-3}$ nm² ps⁻¹ at 298 K [31]; $\tau_1(\text{H}_2\text{O}) = 2.1$ ps at 303 K [32]; $\tau_1(\text{D}_2\text{O}) = 2.5$ ps at 303 K [32]. See also caption of Table 1.

main unaffected by the change of the molecular mass, except of course the density.

The dynamical properties, given in Table 2, on the other hand, change with mass. The viscosity increases with increasing mass, though less than one would expect from the experimental increase in viscosity between water and heavy water. As expected, the diffusion constant decreases with increasing mass and the viscosity increases. The product of viscosity and diffusion constant, which according to Eq. (5) should be independent of mass is not. This shows that Stokes' law is not valid for molecules. The product of viscosity and diffusion coefficient is not correlated with the molecular mass, but it is correlated for those models with the same mass distribution. The rotational correlation times increase with increasing mass. The increase is similar for τ_1 and τ_2 , as the ratio of τ_1/τ_2 is approximately 2 for all seven models.

When using equal masses for hydrogen and oxygen in a water molecule in order to lengthen the time step in a MD simulation, the dynamical properties of liquid water are significantly modified; the viscosity changes by about 50% and the translational and rotational diffusion by about 100%.

If one wishes to study the dependence of protein relaxation processes on solvent viscosity, the latter can be varied by changing the molecular mass; a change in mass by a factor 10 results in a change in viscosity of a factor 2.5.

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