9 February 2001

ELSEVIER

Chemical Physics Letters 334 (2001) 337–342

CHEMICAL PHYSICS LETTERS

www.elsevier.nl/locate/cplett

Further investigation on the validity of Stokes–Einstein behaviour at the molecular level

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Received 30 May 2000; in final form 15 September 2000

Abstract

Stokes–Einstein behaviour at the molecular level is investigated by simulating water at different temperatures and by simulating 'water' models with different mass distributions. When combining Stokes' law for the viscosity with Einstein's formula for the diffusivity, an expression for the product of these quantities is obtained, which shows that the product of diffusivity and viscosity should be independent of the mass distribution and positively proportional to the temperature. Using both, equilibrium and non-equilibrium simulation techniques to compute the viscosity slight deviation from Stokes–Einstein behaviour was found for the 'water' models and temperatures investigated. Non-equilibrium simulation seems to yield systematically lower values for the viscosity than the equilibrium simulation.

1. Introduction

Stokes' law,

$$\eta = \frac{m\gamma}{3\pi d}, \tag{1}$$

expresses the shear viscosity η of a liquid in terms of the mass m, the friction coefficient γ and the diameter d of the particles of the liquid. The friction coefficient γ is related to the diffusion coefficient D of the particles through Einstein's expression

$$D = \frac{k_B T}{m\gamma}, \tag{2}$$

where k_B is Boltzmann's constant and T is the temperature. Combining Eqs. (1) and (2) one obtains the relation

$$D\eta = \frac{k_B T}{3\pi d}, \tag{3}$$

which characterises Stokes–Einstein behaviour of a liquid. Relation (1) is obtained by solving the equations of motion for the translational flow of a fluid around a rigid sphere of diameter d assuming so-called stick boundary conditions. In a previous Letter [1], it was investigated if non-atomic liquids consisting of small molecules obey Eq. (3), i.e., show Stokes–Einstein behaviour. This was done by simulating 'water' molecules with different mass and different mass distributions. Thus the diffusion constant and the viscosity of the liquid were changed without changing the intermolecular interaction or the molecular geometry.

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0009-2614/01/$ - see front matter
PII: S0009-2614(00)01290-2

When interpreting the results of the various simulations in [1], it was overlooked that scaling of the total mass of a system by a factor λ at constant temperature is equivalent to a scaling of the time dimension by a factor $\lambda^{1/2}$. The kinetic energy is related to the mass and the time by

$$E_{\text{kin}} = \frac{m}{2}\left(\frac{\mathrm{d}}{\mathrm{d}t}r\right)^2, \tag{4}$$

where m is the mass, t the time and r the distance. So, scaling the mass by a factor of λ, scales the time by a factor of $\lambda^{1/2}$ at constant kinetic energy. The viscosity should then scale by a factor of $\lambda^{1/2}$, the diffusion constant by a factor of $\lambda^{-1/2}$ and their product should be independent of λ. When scaling all masses equally, the same system is simulated, only on a different time scale. In [1] a thermostat was used to keep the kinetic energy at the equivalent of 300 K in all simulations. So, the product $D\eta$ should have been the same for those simulations that only differed in total mass. Since this product was not the same in [1] for the simulations of the different models with the same mass distribution but different total masses, we wish to examine here the reason for this discrepancy. Secondly, the occurrence of Stokes–Einstein behaviour, Eq. (3), at the molecular level is further investigated by simulating at different temperatures.

One reason for the dependence of the product $D\eta$ on the total mass as observed in [1] might be that all models were simulated for the same time period: 1000 ps. If one considers the scaling, the simple point charge water model with $\lambda = 100$ (SPC_{100}) for example, has therefore only been simulated for the equivalent of 100 ps, which is not sufficient to accurately determine the viscosity from fluctuations of the pressure tensor. The viscosity was calculated using the Einstein relation for the mean-square change as a function of time of the off-diagonal elements of the pressure tensor, which involves a linear least-squares fit of a chosen time period. In [1] this fitting necessary to calculate the viscosity has been done over the same time span (5–10 ps) for all models, which is effectively much shorter for the larger masses if one considers scaling. Another reason for the dependence of the product $D\eta$ on the total mass as observed in [1] might be that the same time step of 2 fs was used for all the models. So, SPC_{100} was simulated with a time step that would correspond to only 0.2 fs when scaled back to the mass of SPC. This much more accurate integration might lead to a more exact value for the viscosity. To examine these possibilities we have extended the simulations of SPC_{100} and SPC_{10} to the period corresponding to 1000 ps for SPC, and in addition we have simulated SPC using reduced time steps of 1 and 0.2 fs for 1000 ps. Because of the scaling, the simulations of SPC_{100} and of SPC at the reduced time step of 0.2 fs should yield the same results.

For a liquid displaying Stokes–Einstein behaviour, the product of $D\eta$ should be proportional to the temperature T and independent of the mass distribution in the molecule. To further check the validity of Eq. (3) for liquids consisting of small molecules, we performed simulations at higher temperatures and with 'water' molecules with different mass distributions.

Since the value of the shear viscosity as obtained from equilibrium MD simulation converges very slowly, the shear viscosities were also computed using a non-equilibrium MD simulation technique [2].

2. Method

Five different models were simulated, which only differed in their total mass or mass distribution. The model masses are summarised in Table 1. All other model parameters, such as charge distribution, Lennard-Jones parameters and molecular geometry are taken from the SPC water model [3]. The simulations of SPC_{10} and SPC_{100} are continuations of those reported in the first Letter [1] on the validity of Stokes' law to the period corresponding to 1000 ps for SPC, which is 3212.278 ps for SPC_{10} and 10 000.0 ps for SPC_{100}. Two simulations of SPC with reduced step sizes of 1 and 0.2 fs were performed for 1000 ps. Three simulations to investigate the influence of the temperature were performed, one at 330 K, one at 360 K and another at 390 K. In order to pursue converged values for the viscosity, these simulations covered 10 000 ps. Finally, two models with a mass distribution different from that of SPC were

Table 1
The mass distribution of the different 'water' models[a]

Model	SPC	SPC_{10}	SPC_{100}	EQ	CPS
m_{H_2O} (u)	18.0154	180.154	1801.54	18.0154	18.0154
m_O (u)	15.9994	159.994	1599.94	6.0154	2.0154
m_H (u)	1.008	10.08	100.8	6.0000	8.0000

[a] The total mass and mass distribution of the different 'water' models that have been simulated. SPC, SPC_{10} and SPC_{100} have the same mass distribution, but a different total mass. SPC, EQ and CPS have the same total mass, but a different mass distribution. EQ has the same mass distribution as the models of the EQ-series in [1], but is scaled to the same total mass as SPC to avoid scaling of the time. m denotes the atomic or molecular mass.

simulated. In one of those, named EQ, all atoms have (nearly) equal mass, in the other, named CPS, the H-atoms are much heavier than the O-atom. We note that the EQ model does not correspond exactly to one of the models of the EQ-series in the previous Letter [1]. None of those EQ-models had a total mass equal to that of SPC, so extending their simulations further would have involved scaling. The simulations of the models with different mass distributions were also run for 10 000 ps. To be able to compare the results of the SPC simulation at 300 K with the simulations at higher temperatures and the simulations of EQ and CPS, the SPC simulation was also extended to 10 000 ps. In all simulations 512 molecules were simulated in a cubic periodic box. In the simulations at 300 K, the box size was set to 15.625 nm^3 as in [1]. In the simulations at elevated temperatures, 100 ps equilibration at constant pressure was performed, where the pressure was kept at 0.06102 kJ mol^{-1} nm^3 by a Berendsen manostat [4]. The compressibility was set to 2.092 mol nm^3 kJ^{-1} and the pressure-bath coupling time to 0.5 ps. The box size averages in the second 50 ps of this equilibration period were used as the box sizes for the following constant volume simulations. The box sizes are summarised in Table 3. In all simulations the temperature was kept constant by a Berendsen thermostat [4] using a temperature-bath coupling time of 0.1 ps. The procedure SHAKE [5] was used to constrain the bonds and H–H distance with a tolerance of 0.0001. A single cut-off radius of 0.9 nm for the intermolecular interactions was used and no reaction-field force was calculated. At the beginning of each simulation the system was equilibrated for 50 ps at constant volume.

The shear viscosity η and the diffusion constant D were calculated as described in [1,6]. To calculate the viscosity, the fitting to the square of the integral of the elements of the pressure tensor was again performed between 5 and 10 ps for the models with a total mass equal to that of SPC. For the heavier models this time span was scaled according to their mass, so it was 15.9–31.8 ps for SPC_{10} and 50–100 ps for SPC_{100}. The error σ_D in the diffusion constant D was calculated from the diffusion constants D_α in the three ($\alpha = x, y, z$) dimensions via

$$\sigma_D = \sqrt{\langle D_\alpha^2 \rangle_{\alpha=x,y,z} - \langle D_\alpha \rangle_{\alpha=x,y,z}^2}. \tag{5}$$

The error σ_η in the viscosity η was calculated in the same way using the three off-diagonal elements of the pressure tensor. The error in the product $D\eta$, $\sigma_{D\eta}$, was calculated as

$$\sigma_{D\eta} = \left(\frac{\sigma_D}{D} + \frac{\sigma_\eta}{\eta} \right) D\eta. \tag{6}$$

The shear viscosities η were, alternatively, calculated using non-equilibrium MD simulations [2]. The computational procedure largely follows the one described in [7]. All atoms were accelerated in the x-direction. The magnitude of the acceleration a_x depends on the z-coordinate of the atom,

$$a_x = A \cos\left(2\pi z L_z^{-1}\right), \tag{7}$$

where L_z is the length of the rectangular computational box in the z-direction. Non-equilibrium MD simulations using Eq. (7) were carried out for boxes three times the size of the equilibrium boxes at the corresponding temperatures with edge lengths $L_x = L_y = 1/3L_z$, using values of A chosen such that the maximum sheer rate was always

about $1/8$ ps^{-1}, which is slightly larger than the inverse correlation time of the liquid. The values of A for all temperatures are given in Table 3. The boxes contained 1536 molecules. All other simulation parameters are equal to those used in the equilibrium MD simulations.

3. Results and conclusions

Table 2 gives the results of the simulations of SPC and mass scaled SPC as considered in [1], but extended in length, and of the simulations produced with reduced time steps. The results for D and η now do scale with $\lambda^{-1/2}$ and $\lambda^{1/2}$ respectively, where λ is the scaling factor of the masses. The higher accuracy of integration in the simulations with a smaller time step does not affect the result for the viscosity. The result of the normal ($\Delta t = 2$ fs) SPC simulation lies between the (scaled) results of SPC_{100} and SPC with a time step of 0.2 fs, which both are simulated with a higher accuracy. Increasing the simulation length, on the other hand, did improve the result. The better sampling allows fitting over the right time span, e.g., 50–100 ps for SPC_{100}, which is not possible with the shorter simulations as there is insufficient statistics for this time span. If in the longer simulation the fitting is still performed to the shorter time span, the results will also be off, for instance for SPC_{100} the result for the viscosity is only 4.47×10^{-3} kg m^{-1}s^{-1} if the fitting is performed from 5 to 10 ps. So, the apparent discrepancy in [1] between the simulations that only differed in total mass, is due to the different simulation lengths and disappears when equally long simulations are compared.

The results for the simulations performed to further investigate Stokes–Einstein behaviour are summarised in Table 3. For all the models and temperatures the 1000 ps non-equilibrium MD simulations yield values for the viscosity that are systematically smaller than the values obtained from 10 000 ps equilibrium MD simulations. The discrepancy shrinks with temperature from 24% at 300 K to 8% at 390 K. In the limit of infinite sampling time and, in the non-equilibrium case in the limit of vanishingly small acceleration A, which keeps the system off equilibrium, both techniques should, however, yield the same viscosity values. For a finite acceleration A, one can intuitively understand that the viscosity for a system in a stationary off-equilibrium state will be lower than the viscosity determined from fluctuations of a system in equilibrium. Since each method yields comparable relative differences in viscosity between different models and between different temperatures, we shall consider the results of the two methods separately. We note that a similar discrepancy has been observed between equilibrium and non-equilibrium MD methodology to compute diffusivity [8]. Non-equilibrium MD yields a larger diffusivity than equilibrium MD [8].

Table 2
Equilibrium MD simulations of the different water models covering an equivalent (scaled) time period[a]

Model	SPC	SPC_{10}	SPC_{100}	SPC	SPC
Δt (fs)	2.0	2.0	2.0	1.0	0.2
t (ns)	1.0	3.162	10.0	1.0	1.0
t_{fit} (ps)	5.0–10.0	15.9–31.8	50.0–100.0	5.0–10.0	5.0–20.0
$\langle T \rangle$ (K)	300.4	300.5	300.2	301.7	302.1
$\langle D \rangle$ (10^{-9} m^2 s^{-1})	4.074	1.302	0.397	4.009	4.202
σ_D (10^{-9} m^2 s^{-1})	0.173	0.206	0.030	0.194	0.345
$\langle \eta \rangle$ (10^{-3} kg m^{-1} s^{-1})	0.635	1.968	6.610	0.524	0.580
σ_η (10^{-3} kg m^{-1} s^{-1})	0.051	0.142	0.694	0.043	0.067
$\langle D \rangle \langle \eta \rangle$ (10^{-12} kg m s^{-2})	2.558	2.562	2.622	2.100	2.435
$\sigma_{D\eta}$ (10^{-12} kg m s^{-2})	0.318	0.590	0.474	0.273	0.484

[a] The results for SPC (1000 ps) with a time step of 2 fs were taken from [1]. The simulations of SPC_{10} and SPC_{100} have been extended to the length that corresponds to 1000 ps for SPC. Δt is the time step, t the simulation length, t_{fit} the time over which the fit is performed to calculate the viscosity, D is the diffusion coefficient, η the viscosity and σ_x the error in the quantity x as calculated using Eqs. (5) and (6).

Table 3
MD simulations of liquid 'water' models to investigate Stokes–Einstein behaviour at the molecular level[a]

Model	CPS	EQ	SPC	SPC	SPC	SPC
T_{bath} (K)	300	300	300	330	360	390
Equilibrium MD						
$\langle T\rangle$ (K)	300.6	301.1	300.4	330.6	360.7	390.8
V (nm^3)	15.625	15.625	15.625	16.060	16.620	17.233
$\langle D\rangle$ (10^{-9} m^2 s^{-1})	3.102	3.227	4.058	6.287	8.829	12.518
σ_D (10^{-9} m^2 s^{-1})	0.043	0.011	0.138	0.667	0.335	0.855
$\langle\eta\rangle$ (10^{-3} kg m^{-1} s^{-1})	0.697	0.683	0.582	0.371	0.258	0.178
σ_η (10^{-3} kg m^{-1} s^{-1})	0.012	0.033	0.006	0.015	0.009	0.009
$\langle D\rangle\langle\eta\rangle$ (10^{-12} kg m s^{-2})	2.161	2.204	2.363	2.332	2.274	2.224
$\sigma_{D\eta}$ (10^{-12} kg m s^{-2})	0.066	0.114	0.106	0.343	0.163	0.260
$\langle D\rangle\langle\eta\rangle T^{-1}$ (10^{-15} kg m s^{-2} K^{-1})	7.20	7.35	7.88	7.07	6.32	5.70
Non-equilibrium MD						
A (nm ps^{-2})	0.0375	0.0375	0.0375	0.2	0.14	0.1
$\langle T\rangle$ (K)	301.9	302.6	302.6	332.7	362.9	393.0
$\langle\eta\rangle$ (10^{-3} kg m^{-1} s^{-1})	0.525	0.527	0.425	0.306	0.231	0.164
$\langle D\rangle\langle\eta\rangle$ (10^{-12} kg m s^{-2})	1.628	1.701	1.724	1.923	2.041	2.057
$\langle D\rangle\langle\eta\rangle T^{-1}$ (10^{-15} kg m s^{-2} K^{-1})	5.43	5.67	5.75	5.83	5.67	5.27

[a] The equilibrium simulations have been performed for 10 000 ps with a time step of 2 fs, and the fitting in the calculation of η was performed between 5 and 10 ps. T_{bath} is the bath temperature, $\langle T\rangle$ the average temperature during the simulations, and V the volume of the box. The other symbols are explained in the caption of Table 2. The non-equilibrium MD results for the viscosity were obtained from 1000 ps MD simulations based on Eq. (7) using the given acceleration amplitudes A.

The results for diffusion and viscosity change considerably when going from SPC to EQ but only slightly when going from EQ to CPS. Feenstra et al. [7] also found a large difference between SPC and a model corresponding to EQ. However, contrary to our results, they found a slightly smaller diffusion constant for their model with all atoms of equal mass than for their model with heavy H-atoms. This small difference in D is probably not significant, since the simulations in [7] only covered 100 ps lengths. In general, Feenstra et al. [7] reported values of D that are similar to ours, and values for the viscosity, which were calculated using non-equilibrium simulations, similar to our non-equilibrium results. Brown and Clarke [9] simulated a liquid of rigid tri-atomic molecules without Coulomb interactions and with van der Waals interactions that are rather dissimilar to those of SPC water, and also investigated different mass distributions for their tri-atomic model. They obtained the lowest value of the viscosity for their 'B'-model, which has a normal water distribution of the masses and the highest value for their 'A'-model where all masses are equal. For their 'C'-model they calculated a viscosity closer to their 'B'-model than to their 'A'-model which does not agree with our or Feenstra et al.'s [7] results. For the diffusion constant of their 'C'-model they get a markedly lower value than for models 'A' and 'B', whereas in our study as well as in Feenstra et al.'s [7] the differences in the diffusion constant are not that large. Since the Brown and Clarke models are rather different from ours, the difference in the dependence of D and η on the mass distribution comes to no surprise. In the SPC water model, charge or hydrogen bonding interactions are dominant, thereby restricting the rotation of the molecules very much, which in turn will lessen the effect of modification of the molecular mass distribution, when compared to the Brown and Clark models which only contain van der Waals interactions.

In simulations at higher temperatures (right-hand side in Table 3) the product of diffusion and viscosity shows different behaviours for the equilibrium and the non-equilibrium simulations. For the equilibrium simulations, it becomes smaller with increasing temperature, it is decreasing from 2.363×10^{-12} kg m s^{-2} at 300 K to 2.224×10^{-12} kg m s^{-2} at 390 K, whereas for the non-

equilibrium simulations it increases from 1.724×10^{-12} kg m s^{-2} at 300 K to 2.057×10^{-12} kg m s^{-2} at 390 K. In both cases, the product $D\eta T^{-1}$ decreases for higher temperatures. The value obtained by averaging over the four temperatures is 6.74×10^{-15} kg m s^{-2} K^{-1} for the equilibrium simulations and 5.63×10^{-15} kg m s^{-2} K^{-1} for the non-equilibrium simulations which lead to atom diameters through Eq. (3) of 0.22 and 0.26 nm, respectively.

When investigating the mass distribution from SPC to EQ to CPS, the product $D_\eta T^{-1}$ becomes smaller, -0.7×10^{-15} kg m s^{-2} K^{-1} in the equilibrium simulation and -0.3×10^{-15} kg m s^{-2} K^{-1} in the non-equilibrium simulations. When raising the temperature from 300 to 390 K, the product $D_\eta T^{-1}$ also becomes smaller, -2.2×10^{-15} kg m s^{-2}K^{-1} in the equilibrium simulations and -0.5×10^{-15} kg m s^{-2} K^{-1} in the non-equilibrium simulations. Both tests, the simulations of models with a different mass distribution, as well as the simulations at higher temperatures, give results that slightly deviate from the simple relation between D, η, d and T as embodied in the Stokes–Einstein relation (3). The equilibrium method, the oldest and most used one, yields larger deviations than the non-equilibrium one. It would be of interest to further investigate the observed systematic deviation between the results of the equilibrium and non-equilibrium techniques with respect to other (electric, thermal conductance) transport coefficients as a function of the system and simulation parameters (system size, box shape, temperature, size of non-equilibrium driving force, etc.).

References

[1] R. Walser, A.E. Mark, W.F. van Gunsteren, Chem. Phys. Lett. 303 (1999) 583.
[2] H.J.C. Berendsen, in: LM. Meyer, V. Pontikis (Eds.), Computer Simulations in Materials Science, Kluwer Academic Publishers, Dordrecht, 1991. pp. 139–155.
[3] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, J. Hermans, in: B. Pullman (Ed.), Intermolecular Forces, Reidel, Dordrecht, 1981. pp. 331–342.
[4] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, J. Chem. Phys. 81 (1984) 3684.
[5] J.-P. Ryckaert, G. Ciccotti, H.J.C. Berendsen, J. Comp. Chem. 23 (1977) 327.
[6] I.G. Tironi, W.F. van Gunsteren, Mol. Phys. 83 (1994) 381.
[7] K.A. Feenstra, B. Hess, H.J.C. Berendsen, J. Comp. Chem. 20 (1999) 786.
[8] F. Müller-Plathe, S.C. Rogers, W.F. van Gunsteren, J. Chem. Phys. 98 (1993) 9895.
[9] D. Brown, J.H.R. Clarke, J. Chem. Phys. 86 (1987) 6446.