ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理 Chinese Physics B

Fractional Stokes-Einstein relation in TIP5P water at high temperatures

Gan Ren(任淦), Ge Sang(桑革)
Citation: Chin. Phys. B . 2018, 27(6): 066101. **doi:** 10.1088/1674-1056/27/6/066101

Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Ab initio molecular dynamics study on the local structures in $Ce_{70}Al_{30}$ and $La_{70}Al_{30}$ metallic glasses

F X Li(李福祥), J B Kong(孔吉波), M Z Li(李茂枝)
Chin. Phys. B . 2018, 27(5): 056102. **doi:** 10.1088/1674-1056/27/5/056102

Molecular dynamics simulations of cascade damage near the $Y_2Ti_2O_7$ nanocluster/ferrite interface in nanostructured ferritic alloys

Yi-Qiang Sun(孙祎强), Wen-Sheng Lai(赖文生)
Chin. Phys. B . 2017, 26(7): 076106. **doi:** 10.1088/1674-1056/26/7/076106

Diffusion and thermite reaction process of film-honeycomb Al/NiO nanothermite: Molecular dynamics simulations using ReaxFF reactive force field

Hua-Dong Zeng(曾华东), Zhi-Yang Zhu(祝志阳), Ji-Dong Zhang(张吉东), Xin-Lu Cheng(程新路)
Chin. Phys. B . 2017, 26(5): 056101. **doi:** 10.1088/1674-1056/26/5/056101

Thermodynamic and transport properties of spiro-(1,1')-bipyrrolidinium tetrafluoroborate and acetonitrile mixtures: A molecular dynamics study

Qing-Yin Zhang(张庆印), Peng Xie(谢鹏), Xin Wang(王欣), Xue-Wen Yu(于学文), Zhi-Qiang Shi(时志强), Shi-Huai Zhao(赵世怀)
Chin. Phys. B . 2016, 25(6): 066102. **doi:** 10.1088/1674-1056/25/6/066102

Finite temperature effect on mechanical properties of graphene sheets with various grain boundaries

Yong Ge(葛勇), Hong-Xiang Sun(孙宏祥), Yi-Jun Guan(管义钧), Gan-He Zeng(曾赣鹤)
Chin. Phys. B . 2016, 25(6): 066104. **doi:** 10.1088/1674-1056/25/6/066104

Fractional Stokes–Einstein relation in TIP5P water at high temperatures*

Gan Ren(任淦)† and Ge Sang(桑革)

Science and Technology on Surface Physics and Chemistry Laboratory, Jiangyou 621908, *China*

(Received 15 January 2018; revised manuscript received 22 March 2018; published online 10 May 2018)

Fractional Stokes–Einstein relation described by $D \sim (\tau/T)^{\xi}$ is observed in supercooled water, where D is the diffusion constant, τ the structural relaxation time, T the temperature, and the exponent $\xi \neq -1$. In this work, the Stokes–Einstein relation in TIP5P water is examined at high temperatures within 400 K–800 K. Our results indicate that the fractional Stokes–Einstein relation is explicitly existent in TIP5P water at high temperatures, demonstrated by the two usually adopted variants of the Stokes–Einstein relation, $D \sim \tau^{-1}$ and $D \sim T/\tau$, as well as by $D \sim T/\eta$, where η is the shear viscosity. Both $D \sim \tau^{-1}$ and $D \sim T/\tau$ are crossed at temperature $T_x = 510$ K. The $D \sim \tau^{-1}$ is in a fractional form as $D \sim \tau^{\xi}$ with $\xi = -2.09$ for $T \leq T_x$ and otherwise $\xi = -1.25$. The $D \sim T/\tau$ is valid with $\xi = -1.01$ for $T \leq T_x$ but in a fractional form for $T > T_x$. The Stokes–Einstein relation $D \sim T/\eta$ is satisfied below $T_x = 620$ K but in a fractional form above T_x. We propose that the breakdown of $D \sim T/\eta$ may result from the system entering into the super critical region, the fractional forms of $D \sim \tau^{-1}$ and $D \sim T/\tau$ are due to the disruption of the hydration shell and the local tetrahedral structure as well as the increase of the shear viscosity.

Keywords: Stokes–Einstein relation, TIP5P water, molecular dynamics, hydration shells

PACS: 61.20.Ja, 61.20.Gy **DOI:** 10.1088/1674-1056/27/6/066101

1. Introduction

Water is the most abundant liquid on earth. Although a water molecule is a simple compound composed of one oxygen atom and two hydrogen atoms, it exhibits many anomalies compared with simple liquids,[1] such as its density decreasing upon cooling below 4 °C, and volume fluctuation increasing with temperature decreasing if temperature $T < 46$ °C, but exhibits normal behavior when $T > 46$ °C. Apart from the anomalies in structure and thermodynamic properties, the breakdown of the Stokes–Einstein relation is observed in supercooled water.[2–4]

The Stokes–Einstein relation relates the diffusion constant to the frictional coefficient for a particle moving through a viscous fluid,[5] namely $D = k_{\mathrm{B}}T/C\eta a$, where D is the diffusion constant, k_{B} is the Boltzmann constant, T is the temperature, η is the shear viscosity, a is the effective hydrodynamic radius, and C is a constant determined by the boundary conditions.[6] The correctness of the Stokes–Einstein relation has been confirmed in many cases.[7–11] However, the Stokes–Einstein relation is observed to be invalid for liquids undergoing deep supercooling:[2,10–14] the increase rate of η can be much faster than the decrease rate of D in a deep supercooled regime. The effective hydrodynamic radius is usually considered to be a constant. The ratio $D\eta/T$ is almost a constant for $T > 1.5T_{\mathrm{g}}$ and otherwise not a constant if $T < 1.5T_{\mathrm{g}}$, where T_{g} is the glass transition temperature.[3,15]

It is difficult to accurately determine η in molecular dynamics (MD) simulations. The structural relaxation τ changes similarly to η when cooling and is usually adopted as a substitute for η.[5] Two variants of the Stokes–Einstein relation, $D \sim T/\tau$[2,3] and $D \sim \tau^{-1}$,[16,17] are usually adopted as substitutes to test the Stokes–Einstein relation. The dynamics of liquid experience a large change with a slight temperature decrease in a deep supercooling regime; the two variants give almost the same results. The $D \sim \tau^{-1}$ is based on the structural relaxation given by the self-intermediate scattering function, which can be described by $F_{\mathrm{s}}(k,t) = \mathrm{e}^{-k^2Dt}$ if the displacement of particle follows the Gaussian function. In simple liquids, $F_{\mathrm{s}}(k,t)$ relaxes exponentially as $F_{\mathrm{s}}(k,t) \sim \mathrm{e}^{-t/\tau}$; thereafter D is coupled with τ like $D \sim \tau^{-1}$. The same variant is also proposed in the mode coupling theory if the temperature is close to the glass phase transition point.[16] $D \sim T/\tau$ is based on the approximate relation $\eta = G_{\infty}\tau$,[2,3] where G_{∞} is the instantaneous shear modulus and is presumed to be constant.

Both $D \sim T/\tau$[2,3] and $D \sim \tau^{-1}$[16,17] are observed to be invalid in supercooled liquids; moreover, they are usually in a fractional form as $D \sim (T/\tau)^{\xi}$ and $D \sim \tau^{\xi}$, respectively. The variant $D \sim T/\tau$ was usually adopted to evaluate the Stokes–Einstein relation in supercooled water. Xu *et al.*[2] carried out experiments with confined water and performed MD simulations with TIP5P water and the Jagla model; they observed that the variant has a cross point while cooling from 400 K to 210 K. It takes a fractional form as $D \sim (\tau/T)^{\xi}$ with $\xi > -1$

*Project supported by the National Natural Science Foundation of China (Grant No. 2153200) and the China Postdoctoral Science Foundation (Grant No. 2016M602712).

†Corresponding author. E-mail: renganzyl@sina.com

© 2018 Chinese Physical Society and IOP Publishing Ltd

in supercooled state and $\xi \approx 1$ at high temperatures. Kumar *et al.*[3] evaluated the Stokes–Einstein relation in TIP5P and ST2 water with the same variant; they found that the breakdown of the Stokes–Einstein is related with the crossing of the Widom line. The Stokes–Einstein relation and the Stokes–Einstein–Debye relation were also observed to breakdown in ST2[18] and SPC/E water.[15] A similar fractional form is observed for both mobile and immobile ST2 water. It is proposed that the breakdown of the Stokes–Einstein relation is due to the dynamic heterogeneity that some water molecules relax faster and some relax slower.[19] Different relaxation components and relaxation decoupling have been observed in SPC/E water.[15] The dynamic heterogeneity is proposed to result from the structure change, after crossing the Widom line, water decomposes into the low density water and high density water.[2,3]

The Stokes–Einstein relation described by the variant breaks down in supercooled water; an interesting question is whether the same breakdown is also existent in water at high temperature away from the glass transition point. Shi *et al.*[5] performed simulations with Lenard-Jones-like liquids and coarse-graining ortho-terphenyl across a broad range of temperatures and densities, aiming to test the rationality of the two variants, $D \sim \tau^{-1}$ and $D \sim T/\tau$, by comparing with results given by $D \sim T/\eta$. They found that the results given by $D \sim \tau^{-1}$ and $D \sim T/\tau$ deviate from the results given by $D \sim T/\eta$ while cooling; although $D \sim T/\eta$ is still valid for some temperature regime, $D \sim \tau^{-1}$ and $D \sim T/\tau$ breakdown. The self-consistent generalized Langevin equation theory[20–22] has predicted the dynamic equivalence between soft-sphere liquid and hard sphere-liquid,[21] and both D and τ are functions of $P\sigma^3/T$ only, where P is the pressure of the system and σ is the effective rigid sphere diameter. P is usually a monotonic function of T; so similar breakdown of $D \sim \tau^{-1}$ and $D \sim T/\tau$ may be observed at high temperatures. Moreover, a water molecule is not existent as a bare molecule but is hydrated in liquid water. The hydrated structure and local tetrahedral structure are likely to be disrupted at high temperatures, and further leading to different increase rate D and decrease rate τ. Based on the facts, we propose that a similar fractional Stokes–Einstein relation may also be existent in water at high temperature. In this work, we perform MD simulation with TIP5P water with a constant density at temperatures within 400 K–800 K to examine our proposition; the two variants of the Stokes–Einstein relation, $D \sim \tau^{-1}$ and $D \sim T/\tau$, are evaluated, and the Stokes–Einstein relation given by $D \sim T/\eta$ is also evaluated.

2. Simulation methods

The configuration for the MD simulation is composed of 2048 TIP5P water molecules[23] with a constant density of 1 g/cm^3; the system displays a cross point from a normal Stokes–Einstein relation to a fractional form when cooling from 400 K to 210 K.[2] All our MD simulations were performed with the GROMACS package.[24,25] The periodic boundary conditions were applied in all three directions of the Cartesian space. The particle mesh Ewald algorithm[26] was employed to calculate the long-range electrostatic interactions with a cutoff of 1.0 nm in the real space. The van der Waals interactions were calculated directly with a truncated spherical cutoff of 1.0 nm. The temperature simulated in this work is uniformly distributed within 400 K–800 K in steps of 20 K. The system temperature was kept constant by the Nosé–Hoover thermostat.[27,28] The system was first equilibrated for 5 ns at each temperature, after which another NVE MD simulation was performed to sample data. The time step for all MD simulations was 1 fs and the configurations were sampled every 10 steps for data analysis.

3. Results and discussion

3.1. Diffusion and structural relaxation

To evaluate the variants of the Stokes–Einstein in TIP5P water, we first determine the diffusion constant and the structural relaxation time. The diffusion constant is calculated via its asymptotic relation with the mean square displacement (MSD)

$$D = \lim_{t\to\infty} \frac{\left\langle |r_i(t) - r_i(0)|^2 \right\rangle}{6t}, \tag{1}$$

where $r_i(t)$ is the position of i-th water molecule at time t, $\langle\ \rangle$ denotes the time average. The MSDs at different temperatures are shown in Fig. 1(a); each of all MSDs is a linear function of t. Figure 1(b) shows that D increases with temperature increasing.

The structural relaxation of water is described by the self-intermediate scattering function

$$F_s(k,t) = (1/N)\sum_j^N \left\langle e^{ik\cdot[r_j(t)-r_j(0)]} \right\rangle, \tag{2}$$

where N is the number of water molecules, k is usually chosen to be the first maximum of the static structure factor, and $k = 24.0\ \text{nm}^{-1}$ in this work. The structural relaxation time τ is determined by $F_s(k,\tau) = e^{-1}$. $F_s(k,t)$ and τ at different temperatures are plotted in Figs. 2(a) and 2(b), respectively. The system exhibits a faster relaxation at higher temperatures. The fitted τ decreases with temperature increasing. Comparing with the diffusion constant, it is shown that a molecule with a faster relaxation has a larger diffusion constant; however, the increase of D is about one time larger than the decrease of τ within 400 K–800 K, which is different from that observed in supercooled liquid, the increase of τ is much faster than the decrease of D in supercooled water while cooling.[2–4] The dynamic property usually follows an Arrhenius behavior as $D = D_0 \exp(-E_0/k_B T)$ or $\tau = \tau_0 \exp(E_0/k_B T)$ with a constant activation energy E_0. The logarithms of D and τ versus

$1/T$ are plotted in Fig. 3. All data for both D and τ are not fallen onto one line but can be well fitted by two Arrhenius laws with different values of E_0. A turning point is observed for each of D and τ, the turning temperature T_x is 490 K for D and 670 K for τ. The values of E_0 are different for $T > T_x$ and $T < T_x$; moreover, the values of E_0 are also different for D and τ. Water molecule diffuses with a smaller E_0 for $T > T_x$ but relaxes with a greater E_0. It is shown that neither of D and τ shows an Arrhenius law but two, which may display a cross point as the case in supercooled water. In the following we will evaluate the two variants of the Stokes–Einstein relation, i.e., $D \sim \tau^{-1}$ and $D \sim T/\tau$.

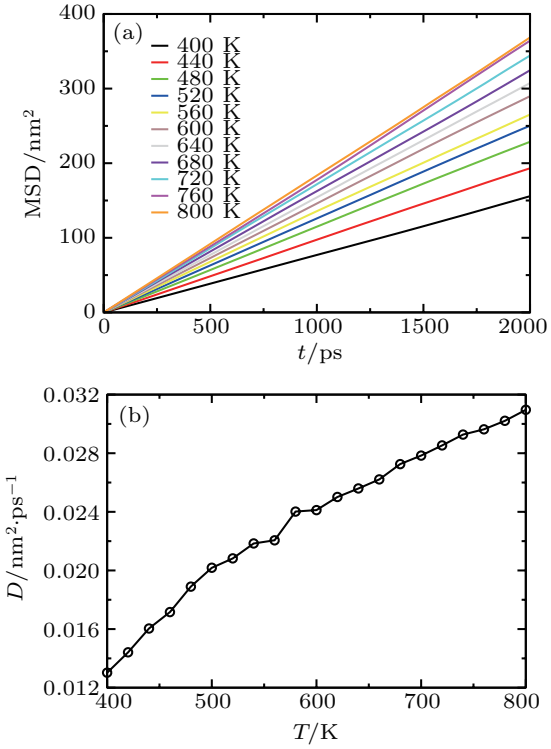


Fig. 1. (color online) (a) Plots of mean square displacement (MSD) versus time t at different temperatures; (b) plots of diffusion constant D versus temperature T.

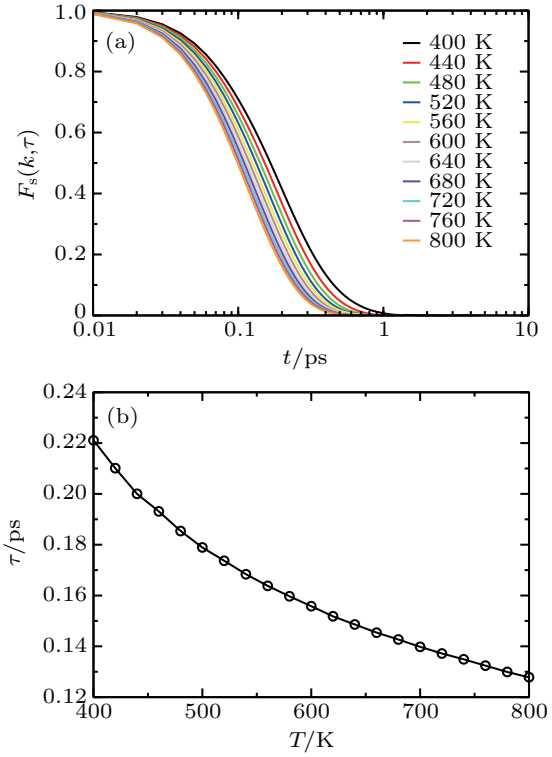


Fig. 2. (color online) (a) Plots of self-intermediate scattering function $F_s(k,t)$ versus t at different temperatures; (b) plots of structural relaxation time τ characterized by $F_s(k,\tau) = e^{-1}$ versus temperature T.

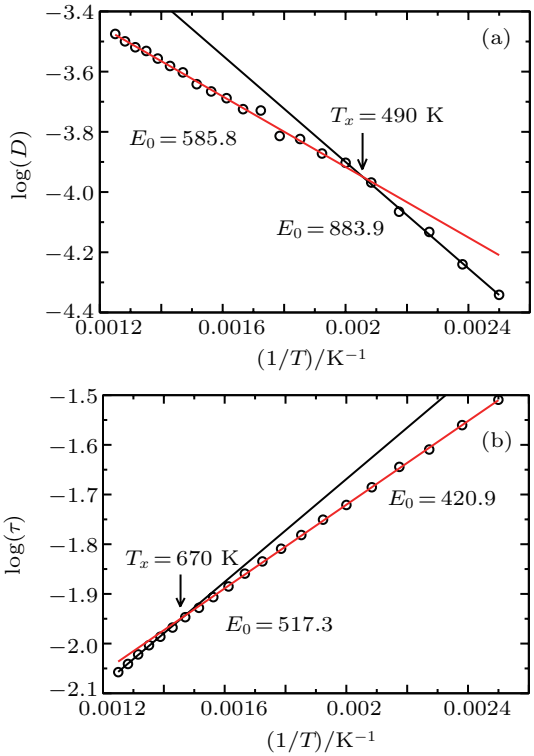


Fig. 3. (color online) Testing whether (a) diffusion constant D and (b) structural relaxation τ follow an Arrhenius law as $D = D_0 \exp(-E_0/k_B T)$ and $\tau = \tau_0 \exp(E_0/k_B T)$ respectively, with E_0 being the activation energy in unit of $k_B T$. The fitted exponent E is in the same color as the fitted solid line.

3.2. Variants of Stokes–Einstein relation

The two variants of the Stokes–Einstein relation, $D \sim \tau^{-1}$ and $D \sim T/\tau$, are evaluated by $D \sim \tau^{\xi}$ and $D \sim (\tau/T)^{\xi}$. The logarithms of τ and D are plotted in Fig. 4(a), and the logarithms of τ/T and D are plotted in Fig. 4(b). Both $D \sim \tau^{\xi}$ and $D \sim (\tau/T)^{\xi}$ are crossed at $T_x = 510$ K. For $D \sim \tau^{\xi}$, $\xi = -2.09$ when $T \leq T_x$ otherwise $\xi = -1.25$ for $T > T_x$. The value of ξ is not equal to -1 for all temperatures. The results suggest that the variant $D \sim \tau^{-1}$ takes two fractional forms and $D \sim \tau^{-1}$ is breakdown for all temperatures within 400 K–800 K, which is consistent with the data shown in Fig. 3 that both D and τ follow two Arrhenius laws with different values of E_0 within 300 K–800 K. For $D \sim (\tau/T)^{\xi}$, $\xi = -1.01$ for $T \leq T_x$ but $\xi = -0.51$ above T_x. The value of ξ is almost equal to -1 for $T \leq T_x$ but takes a fractional form if $T > T_x$. The results suggest that the Stokes–Einstein relation given by $D \sim T/\tau$ is valid below T_x but breakdown above T_x. Comparing with supercooled water, the fractional exponent $\xi = -0.77$ in TIP5P[2] and ST2[3] water for $D \sim (\tau/T)^{\xi}$, but $\xi = -0.51$

in this work. The exponent $\xi > -1$ in ionic liquids[16] for $D \sim \tau^{\xi}$, but $\xi < -1$ in this work. The differences are due to the different changes of D and τ at low or high temperatures. The D and τ dramatically change in the supercooling process: τ increases much faster than D decreases.[2–4] However, D increases faster than τ decreases at high temperature as demonstrated by comparing Fig. 1(b) and Fig. 2(b). Combining the results given by $D \sim \tau^{\xi}$ and $D \sim (\tau/T)^{\xi}$, it is shown that the fractional variants of the Stokes–Einstein relation are explicitly existent in TIP5P water at high temperatures within 400 K–800 K, analogous to that observed in supercooled water at a much lower temperature.

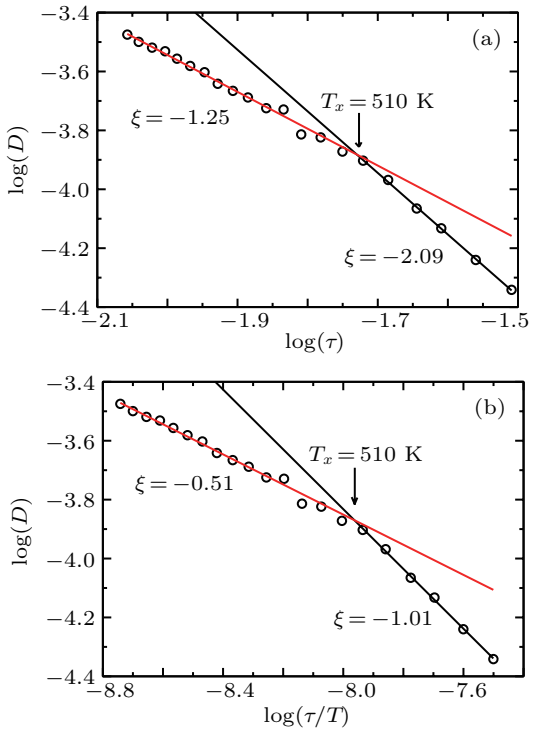


Fig. 4. (color online) Testing the two variants of the Stokes–Einstein relation, $D \sim \tau^{-1}$ and $D \sim T/\tau$: (a) $D \sim \tau^{-1}$; (b) $D \sim T/\tau$. The symbols are the calculated data, and solid lines are fitted by $D \sim \tau^{\xi}$ and $D \sim (\tau/T)^{\xi}$, respectively. The fitted exponent ξ is in the same color as the fitted solid line.

3.3. Shear viscosity and Stokes–Einstein relation

Each of $D \sim \tau^{-1}$ and $D \sim T/\tau$ takes a fractional form within 400 K–800 K. To make sure whether the Stokes–Einstein is really breakdown and also takes a fractional form, we evaluate the Stokes–Einstein relation by $D \sim T/\eta$. In this work, the method proposed by Hess is adopted to calculate the shear viscosity due to its reliability and fast convergence.[29] The method is a non-equilibrium method. An external force $a_x = A \cdot \cos(qz)$ is applied in the X direction, where A is the maximum of a_x, $q = 2\pi/l$, l is the simulation box size. The steady-state solution of the fluid equation is

$$u_x(z) = V(1 - \mathrm{e}^{-t/\tau})\cos(qz). \tag{3}$$

After reaching a non-equilibrium steady state, V can be determined from $u_x(z)$. The shear viscosity is

$$\eta = A\rho/Vq^2. \tag{4}$$

As the density ρ and q are the same for all simulations, thereafter $\eta \sim A/V$; we use the ratio A/V to evaluate the shear viscosity.

The force a_x needs choosing carefully to determine the shear viscosity: neither too large nor too small.[29] To obtain a correct shear viscosity, we determine the linear dependence regime for different temperatures. The schematic representation of the linear dependence regime between A and V at $T = 400$, 500, and 800 K is plotted in Fig. 5(a). The V is proportional to A when A is within 0.01 nm/ps^2–0.1 nm/ps^2 for $T = 400$, 500, and 800 K. To achieve good statistics, we choose $A = 0.01$, 0.02, 0.03, 0.04, and 0.05 nm/ps^2 to calculate the shear viscosity η at each temperature; and the temperature drift is smaller than 1 K. The calculated $\eta \sim A/V$ curve is plotted in Fig. 5(b). The shear viscosity η quickly decreases with temperature increasing for $T < 520$ K, and becomes almost a constant within 520 K–580 K, and then starts to slowly increase when $T \geq 600$ K.

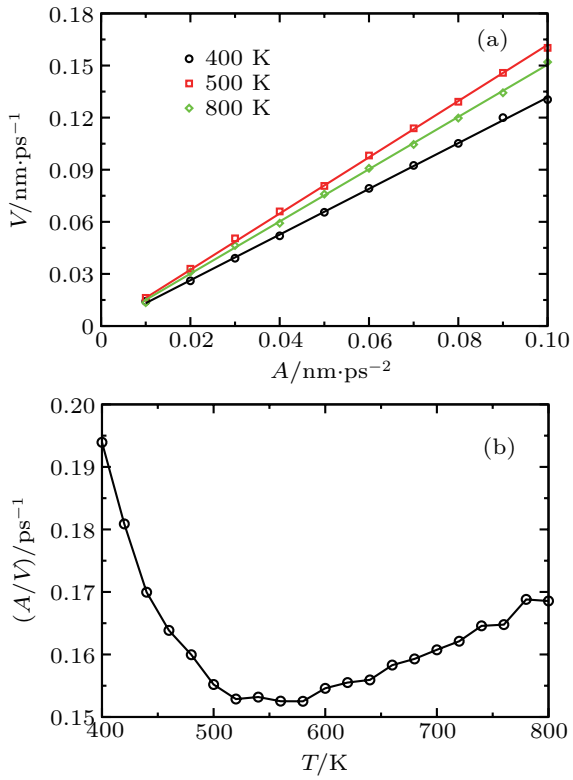


Fig. 5. (color online) (a) Plots of the linear dependence regime of V versus A at temperature $T = 400$, 500, and 800 K. The symbols represent simulation data and the solid lines are fitted by $A \sim V$; (b) curve of calculated shear viscosity $\eta \sim A/V$ versus temperature T.

Combining the diffusion constant with shear viscosity, the Stokes–Einstein relation $D \sim T/\eta$ is evaluated by $D \sim (T/\eta)^{\xi}$. The curves of the logarithm of D versus the logarithm of T/η are plotted in Fig. 6. As the simulated system

is at high temperature and in an equilibrium state, the Stokes–Einstein relation should be valid. To demonstrate the validity of $D \sim T/\eta$, we first fit the calculated data in Fig. 6 with $\xi = 1$. The data below $T_x = 620$ K fall on the line $D \sim T/\eta$, but deviate from the line while $T > T_x$. The data above T_x can be well fitted by $D \sim (T/\eta)^{\xi}$ with $\xi = 1.21$. The results suggest that the Stokes–Einstein relation given by $D \sim T/\eta$ holds true within 400 K–620 K and breaks down above T_x.

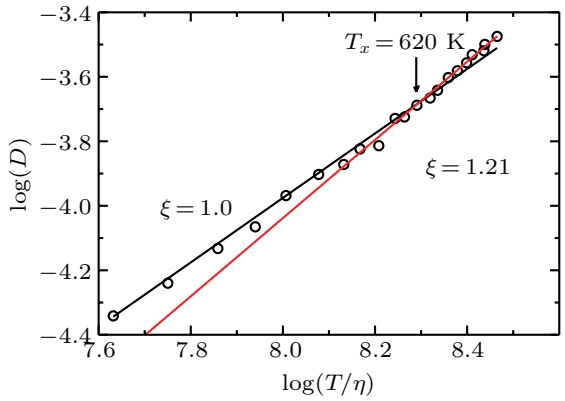


Fig. 6. (color online) Testing the Stokes–Einstein relation by $D \sim T/\eta$. The symbols represent the calculated data and solid lines are fitted by $D \sim (T/\eta)^{\xi}$.

A comparison between the results given by $D \sim \tau^{-1}$ and $D \sim T/\tau$ suggests that $D \sim T/\tau$ is a good variant of the Stokes–Einstein relation within 400 K–520 K but $D \sim \tau^{-1}$ is not for all temperatures. The values of cross point temperature T_x are different for $D \sim T/\eta$, $D \sim \tau^{-1}$ and $D \sim T/\tau$: $T_x = 620$ K for $D \sim T/\eta$, $T_x = 510$ K for $D \sim \tau^{-1}$ and $D \sim T/\tau$. The temperature $T_x = 510$ K is almost located at the temperature at which the shear viscosity gets its last decrease as shown in Fig. 5, and $T_x = 620$ K is almost located at the temperature at which the shear viscosity gets its later increase. The D decouples from η at a higher temperature than τ. Figure 5(b) shows that the changes of η are similar to the scenarios of liquids for $T < 520$ K; however, the changes are similar to the cases of gases when $T > 600$ K. The pressures under different temperatures are determined and are plotted in Fig. 7. It is an almost linear increase with temperature increasing and no jump is observed as temperature increases. No gas–liquid phase transition is observed around $T = 600$ K or 520 K. The experimentally determined critical temperature (T_c), pressure (P_c), and density (ρ_c) for water[30] are $T_c = 647.1$ K, $P_c = 22.1$ MPa, $\rho_c = 0.322$ g/cm^3; and the critical parameters for TIP5P water[31] are $T_c = 530$ K, $P_c = 10$ MPa, $\rho_c = 0.33$ g/cm^3. The cross point temperature $T_x = 510$ K is close to the critical temperature for TIP5P water. Moreover, the change of the shear viscosity is only similar to fluids for $T < 520$ K. So the system is probably located in the super critical region when $T > 520$ K and the breakdown of the Stokes–Einstein relation described by $D \sim T/\eta$ may be due to their entering into the super critical region. The shear viscosity and dynamics are determined by the structure; in the following, we will discuss the observed phenomena from structure including the hydration structure and local tetrahedral structure.

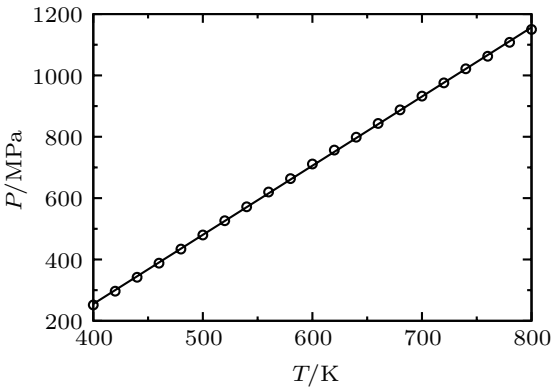


Fig. 7. Plot of pressure P versus temperature T.

3.4. Dynamic heterogeneity, hydration, and tetrahedral structure

The breakdown of the Stokes–Einstein relation is proposed to be due to the dynamic heterogeneity.[3,15] The dynamic heterogeneity is usually charaterized by the non-Gaussian parameter $\alpha_2(t) = 3\langle r^4(t)\rangle/5\langle r^2(t)\rangle^2 - 1$.[32] Figure 8 shows the time dependent α_2 curves for TIP5P water at different temperatures. We find that α_2 shows the similar changes to the cases in supercooled liquids.[32] The deviation from Gaussian decreases and water has a more homogenous dynamics with temperature increasing. An explicit difference is that the deviations are much smaller than those obseved in supercooled liquids at a much lower temperature.[32] The $D \sim \tau^{-1}$ is an exact result if the displacement of particle follows a Gaussian distribution. The deviation from the Gaussian distribution leads to the breakdown of $D \sim \tau^{-1}$. The large deviations and changes are obseved at lower temperatures than at higher temperatures as shown in Fig. 8, which is consistent with the result given by $D \sim \tau^{\xi}$ where the ξ at $T > T_x$ is greater than at $T < T_x$. However, $D \sim T/\tau$ is still valid within 400 K–520 K but is broken down above T_x =510 K; $D \sim T/\eta$ is broken down at $T_x = 620$ K. The results suggest that $D \sim T/\tau$ and $D \sim T/\eta$ are broken down when the dynamic heterogeneity is small, but is valid with a larger dynamic heterogeneity. They do not follow the proposition, which is attributed to the dynamic heterogeneity. The results are different from those in the case of supercooled water that the breakdown of the Stokes–Einstein relation happens at much lower temperatures with larger dynamic heterogeneity;[3,15] in this work, the Stokes–Einstein relation described by $D \sim T/\tau$ and $D \sim T/\eta$ are broken down at high temperatures with smaller dynamic heterogeneity.

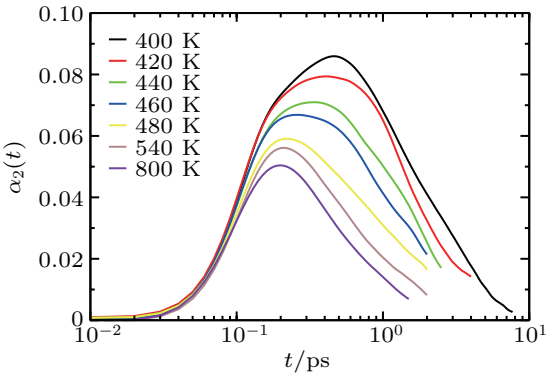


Fig. 8. (color online) Variations of non-Gaussian parameter α_2 with time t at different temperatures.

A water molecule is existent as a hydrated water molecule surrounded by the hydration shell. It is not free but moving partially or whole with the hydration shell. The hydration shell is significant for the dynamics of the center water molecule.[33] To obtain a picture of the hydration structure change with temperature, we calculate the radial distribution functions (RDFs) of water at different temperatures and plot the results in Fig. 9. Two peaks are displayed in all RDFs at different temperatures. The main peak presents larger changes than the second peak. The main peak of RDF decreases with temperature increasing but the second peak possesses a reverse trend. The hydration effect is mainly determined by the first hydration shell. The results suggest that less water molecules are distributed around the center water and the hydration effect decreases while heating.

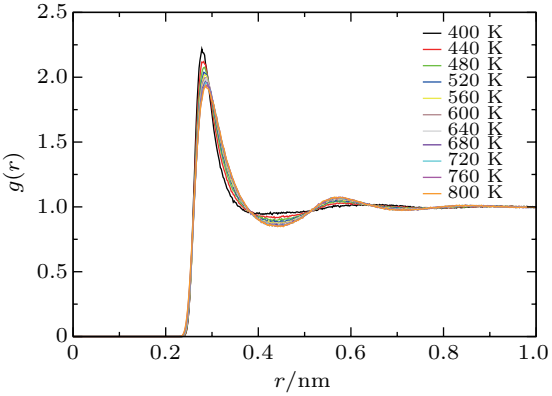


Fig. 9. (color online) Radial distribution functions $g(r)$ of water at different temperatures.

To characterize the dynamics of the hydration shell, we calculate the residence correlation function $(C(t))$[34] of the main hydration shell. $C(t)$ describes the lifetime of the water molecule in the main hydration shell. We choose the first minimum of the RDF as the size of the main hydration shell, namely 0.4 nm. $C(t)$ at different temperatures and lifetime τ_{H} is defined by $C(\tau_{\mathrm{H}}) = \mathrm{e}^{-1}$ and its time depedent values at different temperatures are plotted in Fig. 10. The $C(t)$ decays faster at a higher temperature than τ_{H} decreases with temperature increasing. The diffusion of water molecule needs to jump out of the hydration shell. The curves of logarithm of τ_{H} versus $1/T$ are plotted in Fig. 11 and similar changes to the diffusion versus temperature are observed. The turning point temperature and activation energy are in rough agreement with those in the diffusion as shown in Fig. 3(a). Combining the results given by RDF with $C(t)$, it is shown that the thermal random movement is likely to disrupt the hydration shell, and the hydration effect decreases while heating. The disruption of the hydration shell leads to less water in the hydration shell moving with the center water molecule; the center water molecule more easily jumps out of the hydration shell, and it has a smaller activation energy above the turning point temperature.

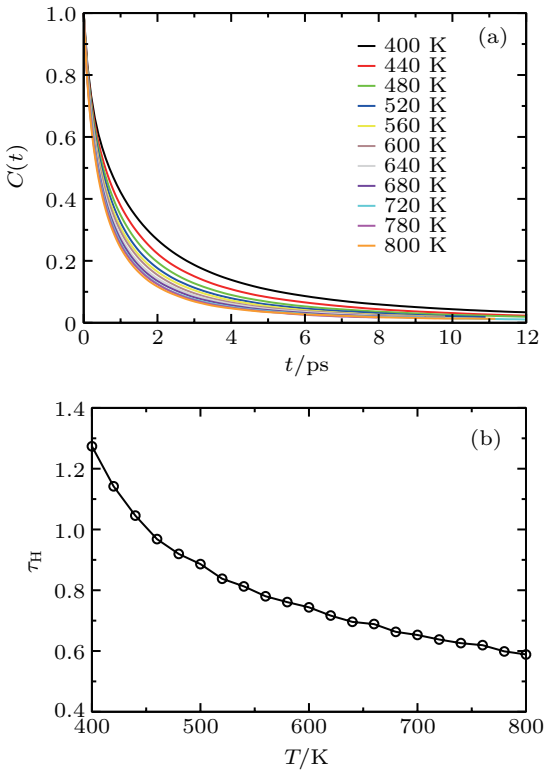


Fig. 10. (color online) (a) Variations of residence correlation function $C(t)$ with time for the main hydration shell at different temperatures; (b) curve of lifetime τ_{H} of hydration shell versus temperature T.

The structural relaxation relates to the fluctuation of the density. Water molecules are likely to form a local tetrahedral structure due to the hydrogen-bonding. To characterize the local structure, we adopt the local tetrahedral structural order parameter[2] defined as $Q_i = 1 - (3/8)\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\phi_{jk} + 1/3\right)$, where Q_i is the local tetrahedral order parameter for the i-th water molecule, ϕ_{jk} is the angle formed by the lines connecting the oxygen atom of the i-th water molecule with its four nearest neighbours j and k. We define the high density amorphous (HDA) molecule if $Q_i < 0.8$.[2] Figure 12 shows that the population of HDA firstly fast then slowly increases as temperature increases. The changes are almost saturated for $T > 600$ K. The local struc-

ture becomes denser. Moreover, due to the increase of the shear viscosity, it is more difficult for a water molecule to adjust its configuration and relax with a greater activation energy.

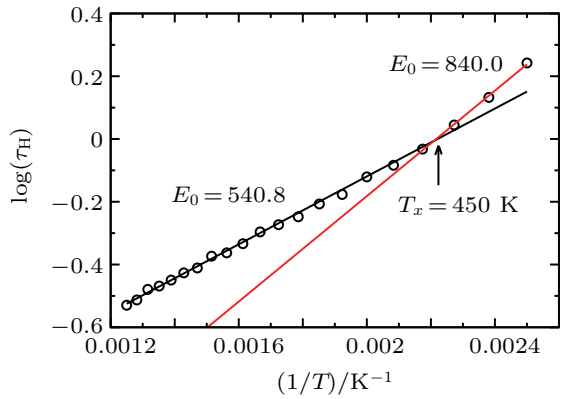


Fig. 11. (color online) Plots of logarithm of $\tau_{\rm H}$ versus $1/T$. The data are fitted by $\tau_{\rm H} = \tau_{\rm H0}\exp(E_0/k_{\rm B}T)$.

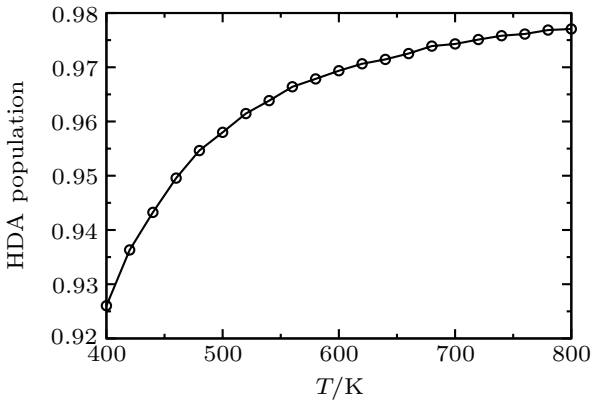


Fig. 12. Population of HDA versus temperature T.

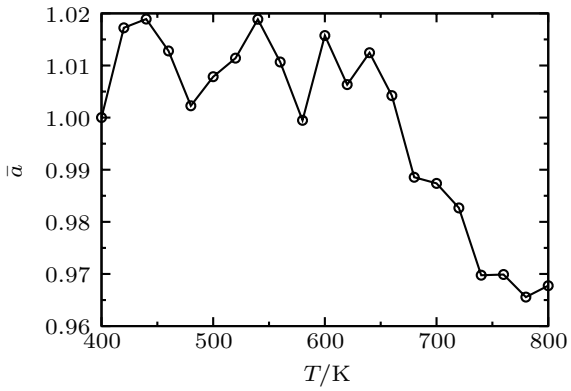


Fig. 13. Scaled effective hydrodynamic radius $\bar{a}$ versus temperature T.

Combining the results given by the hydration structure, HDA and viscosity, the disruption of hydration shell and the local tetrhedral structure as well as the increase of the shear viscosity lead to different increases of the diffusion and decreases of the relaxation, which further leads the variants of the Stokes–Einstein relation to break down. The breakdown of $D \sim T/\eta$ may result from the system entering into a super critical region while heating. As the hydration effect decreases and the system is located in the super critical region while heating, the effective hydrodynamic radius should not be a constant for all temperatures. The effective hydrodynamic radius is evaluated by $a \sim T/\eta D$ and the scaled effective hydrodynamic radius $\bar{a}$ versus temperature is plotted in Fig. 13. It is shown that $\bar{a}$ is flucuated around 1.01 for $T < 660$ K and almost a constant, but decreases with temperature increasing for $T > 660$ K. The fractional form of the Stokes–Einstein relation given by $D \sim T/\eta$ is a result of the change of the effective hydrodynamic radius as the system enters into the super critical region.

4. Conclusions

In this work, we have performed atomistic molecular dynamics simulations to explore the Stokes–Einstein relation of TIP5P water with a constant density at high temperatures in a range of 400 K–800 K. Our results indicate that the fractional Stokes–Einstein is also existent in TIP5P water at high temperatures within 400 K–800 K similar to the scenario in supercooled water. The two variants of the Stokes–Einstein relation, $D \sim \tau^{-1}$ and $D \sim T/\tau$, are crossed at temperature $T_x = 510$ K while heating; a similar cross point is observed at $T_x = 620$ K for the Stokes–Einstein relation evaluated by $D \sim T/\eta$. For $D \sim \tau^{-1}$, it takes a fractional form like $D \sim \tau^{\xi}$ for all temperatures with $\xi = -2.09$ when $T < T_x$ and -1.25 if $T > T_x$. For $D \sim T/\tau$, it takes a fractional form as $D \sim (\tau/T)^{\xi}$; ξ is -1.01 below T_x and -0.51 above T_x.$D \sim T/\eta$ is satisfied below $T_x = 620$ K but is existent in a fractional form as $D \sim (T/\eta)^{\xi}$ with $\xi = 1.21$ when $T > T_x$. Each of the three formulas takes a fractional form above a crossover temperature, which is similar to the scenario in supercooled water at low temperatures. Our results indicate that the fractional form of the Stokes–Einstein relation is explicitly existent in TIP5P water at high temperatures.

A comparison of the results given by $D \sim \tau^{-1}$ and $D \sim T/\tau$ with those obtained by the Stokes–Einstein relation given $D \sim T/\eta$ shows that $D \sim T/\tau$ is a good variant of the Stokes–Einstein relation for TIP5P water within 400 K–510 K, but $D \sim \tau^{-1}$ is not for all temperatures within 400 K–800 K. The displacement of water molecule deviates from a Gaussian distribution as demonstrated by the non-Gaussian parameter; although the deviation is much smaller than that in supercooled water, yet it leads to the breakdown of $D \sim \tau^{-1}$. The $D \sim T/\eta$ and $D \sim T/\tau$ are broken down into a fractional form at high temperature with smaller deviations from the Gaussian distribution; but both are valid with a larger dynamic heterogeneity below T_x. It is different from the observed breakdown in supercooled water at low temperatures. As the water is at high temperature and in an equilibrium state, we should expect the validity of the Stokes–Einstein relation. The thermal ran-

dom movement is likely to disrupt the hydration shell of water and the local tetrahedral structure while heating; moreover, the system may enter into the super critical region while heating, which lead to different increases of diffusion and decreases of relaxation as well as the two Arrhenius laws displayed in diffusion and relaxation. Moreover, the hydration effect decreases and less water molecules are correlated with the center water molecule with temperature increasing; the population of HDA increases with temperature increasing but increases more slowly as the temperature further increases. The effective hydrodynamic radius is not a constant for all temperatures but decreases with temperature increasing for $T > 660$ K. We propose that the fractional forms of $D \sim \tau^{-1}$ and $D \sim T/\tau$ are due to the disruption of the hydration shells and local tetrahedral structure as well as the increase of shear viscosity; the breakdown of $D \sim T/\eta$ may be due to the system entering into a critical region when heating; the effective hydrodynamic radius should be critically evaluated while testing the Stokes–Einstein relation when the conditions experience a large change.

Acknowledgment

The author Gan Ren thanks Yanting Wang (Institute of Theoretical Physics, Chinese Academy of Sciences) for his suggestions.

References

[1] Gallo P, Amann-Winkel K, Angell C A, Anisimov M A, Caupin F, Chakravarty C, Lascaris E, Loerting T, Panagiotopoulos A Z, Russo J, Sellberg J A, Stanley H E, Tanaka H, Vega C, Xu L and Pettersson L G M 2016 *Chem. Rev.* **116** 7463

[2] Xu L, Mallamace F, Yan Z, Starr F W, Buldyrev S V and Eugene Stanley H 2009 *Nat. Phys.* **5** 565

[3] Kumar P, Buldyrev S V, Becker S R, Poole P H, Starr F W and Stanley H E 2007 *Proc. Natl. Acad. Sci. USA* **104** 9575

[4] Chen S H, Mallamace F, Mou C Y, Broccio M, Corsaro C, Faraone A and Liu L 2006 *Proc. Natl. Acad. Sci. USA* **103** 12974

[5] Shi Z, Debenedetti P G and Stillinger F H 2013 *J. Chem. Phys.* **138** 12A526

[6] Hubbard J and Onsager L 1977 *J. Chem. Phys.* **67** 4850

[7] Kumar D H, Patel H E, Kumar V R R, Sundararajan T, Pradeep T and Das S K 2004 *Phys. Rev. Lett.* **93** 144301

[8] Schultz S G and Solomon A K 1961 *The Journal of General Physiology* **44** 1189

[9] Noda A, Hayamizu K and Watanabe M 2001 *J. Phys. Chem. B* **105** 4603

[10] Mallamace F, Broccio M, Corsaro C, Faraone A, Wanderlingh U, Liu L, Mou C Y and Chen S H 2006 *J. Chem. Phys.* **124** 161102

[11] Mapes M K, Swallen S F and Ediger M D 2006 *J. Phys. Chem. B* **110** 507

[12] Swallen S F, Bonvallet P A, McMahon R J and Ediger M D 2003 *Phys. Rev. Lett.* **90** 015901

[13] Binder K and Kob W 2011 *Glassy materials and disordered solids: An introduction to their statistical mechanics* (Scientific: World Scientific)

[14] Habasaki J, Leon C and Ngai K 2017 *Top Appl. Phys.* 132

[15] Mazza M G, Giovambattista N, Stanley H E and Starr F W 2007 *Phys. Rev. E* **76** 031203

[16] Jeong D, Choi M Y, Kim H J and Jung Y 2010 *Phys. Chem. Chem. Phys.* **12** 2001

[17] Ikeda A and Miyazaki K 2011 *Phys. Rev. Lett.* **106** 015701

[18] Becker S R, Poole P H and Starr F W 2006 *Phys. Rev. Lett.* **97** 055901

[19] Giovambattista N, Mazza M G, Buldyrev S V, Starr F W and Stanley H E 2004 *J. Phys. Chem. B* **108** 6655

[20] de J. Guevara-Rodríguez F and Medina-Noyola M 2003 *Phys. Rev. E* **68** 011405

[21] Ramírez-González P E, López-Flores L, Acuña-Campa H and Medina-Noyola M 2011 *Phys. Rev. Lett.* **107** 155701

[22] Ramírez-González P E and Medina-Noyola M 2009 *J. Phys.: Condens. Matter* **21** 075101

[23] Mahoney M W and Jorgensen W L 2000 *J. Chem. Phys.* **112** 8910

[24] Berendsen H J C, van der Spoel D and van Drunen R 1995 *Comput. Phys. Commun.* **91** 43

[25] Van Der Spoel D, Lindahl E, Hess B, Groenhof G, Mark A E and Berendsen H J 2005 *J. Comput. Chem.* **26** 1701

[26] Essmann U, Perera L, Berkowitz M L, Darden T, Lee H and Pedersen L G 1995 *J. Chem. Phys.* **103** 8577

[27] Nosé S 1984 *J. Chem. Phys.* **81** 511

[28] Hoover W G 1985 *Phys. Rev. A* **31** 1695

[29] Hess B 2002 *J. Chem. Phys.* **116** 209

[30] Weingärtner H and Franck E U 2005 *Angew. Chem. Int. Ed.* **44** 2672

[31] Yamada M, Mossa S, Stanley H E and Sciortino F 2002 *Phys. Rev. Lett.* **88** 195701

[32] Kob W, Donati C, Plimpton S J, Poole P H and Glotzer S C 1997 *Phys. Rev. Lett.* **79** 2827

[33] Varela L M, García M and Mosquera V C 2003 *Phys. Rep.* **382** 1

[34] Koneshan S, Rasaiah J C, Lynden-Bell R and Lee S 1998 *J. Phys. Chem. B* **102** 4193