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# Supercooled liquids analogous fractional Stokes–Einstein relation in NaCl solution above room temperature*

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The Stokes–Einstein relation $D \sim T/\eta$ and its two variants $D \sim \tau^{-1}$ and $D \sim T/\tau$ follow a fractional form in supercooled liquids, where $D$ is the diffusion constant, $T$ the temperature, $\eta$ the shear viscosity, and $\tau$ the structural relaxation time. The fractional Stokes–Einstein relation is proposed to result from the dynamic heterogeneity of supercooled liquids. In this work, by performing molecular dynamics simulations, we show that the analogous fractional form also exists in sodium chloride (NaCl) solutions above room temperature. $D \sim \tau^{-1}$ takes a fractional form within 300–800 K; a crossover is observed in both $D \sim T/\tau$ and $D \sim T/\eta$. Both $D \sim T/\tau$ and $D \sim T/\eta$ are valid below the crossover temperature $T_x$, but take a fractional form for $T > T_x$. Our results indicate that the fractional Stokes–Einstein relation not only exists in supercooled liquids but also exists in NaCl solutions at high enough temperatures far away from the glass transition point. We propose that $D \sim T/\eta$ and its two variants should be critically evaluated to test the validity of the Stokes–Einstein relation.

**Keywords:** sodium chloride solutions, supercooled liquids, molecular dynamics, Stokes–Einstein relation

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## 1. Introduction

The dynamic properties of liquids dramatically change as temperature decreases into the supercooled region. For example, the shear viscosity will sharply increase with supercooling, but the diffusion constant will dramatically decrease. However, the rate of the increase in the shear viscosity can be much larger than that of the decrease in the diffusion constant.[1] The Stokes–Einstein relation is observed to be invalid in supercooled liquids[2–7] and the ratio $D\eta/T$ is almost a constant for temperature $T > (1.2\text{–}1.6)T_g$, but no longer a constant when $T < (1.2\text{–}1.6)T_g$, where $D$ is the diffusion constant, $\eta$ is the shear viscosity, and $T_g$ is the glass transition temperature.[8]

The shear viscosity is difficult to be accurately determined via simulation especially at low temperatures. Because of similar changes between structural relaxation and shear viscosity when temperature changes,[5,8–10] the structural relaxation time is usually adopted as a substitute to evaluate the shear viscosity. It is proposed that the breakdown of the Stokes–Einstein relation in supercooled liquids is due to the fact that the dynamic heterogeneity causes decoupling of the diffusion and relaxation.[6,9] Two functional forms, $\eta \sim T\tau$ and $\eta \sim \tau$, are usually adopted to evaluate $\eta$, and the corresponding variants of the Stokes–Einstein relations are $D \sim \tau^{-1}$ [9,10] and $D \sim T/\tau$,[5,8] respectively. The former is based on the exponential relaxation of the self-intermediate scattering function $F_s(k,t) \sim e^{-t/\tau}$ in simple liquids, which can be described by $F_s(k,t) = \exp\left(-k^2Dt\right)$ if the displacements of particles follow Gaussian distribution.[6] So $D$ is coupled with $\tau$ like $D \sim \tau^{-1}$. The same variant is also proposed by Debye[11] as well as in the mode coupling theory when temperature is close to the glass transition point.[6] The latter variant is based on the Maxwell relation $\eta = G_\infty\tau$, where $G_\infty$ is the instantaneous shear modulus.[8] The structural relaxation $\tau$ will greatly change with a little decrease in temperature in the deep supercooling region. Thereafter, $D \sim \tau^{-1}$ and $D \sim T/\tau$ will give almost the same results. The hydrodynamic radius is considered to be a constant in $D \sim T/\eta$, $D \sim \tau^{-1}$, and $D \sim T/\tau$. However, it is not likely to be a constant in any case. For example, the hydrodynamic radius of ions in ionic solutions is mainly determined by the ion atmosphere.[12] Moreover, the diffusion and relaxation show different rate of changes under supercooled states, and are likely to show different changes at high temperatures. An interesting question is raised: the fractional Stokes–Einstein relation exists in supercooled liquids near the glass transition point, does it also exist at high temperature far away from the glass transition point?

The main idea of the fractional forms is the decoupling of the diffusion and relaxation, namely, the rate of the decrease in diffusion is different from that of the increase in shear viscosity under supercooling. Debye and Hückel proposed[13] that the ion is not free in ionic solutions, but is surrounded by the solvation shell consisting of counterions and solvent molecules. The solvation shell is coupled with the center ion.

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It is completely or partially moving with the center ion and plays a significant role in the dynamics of the ion. The center ion will be decoupled from the solvation shell under extreme conditions, like in a strong electric field or at high temperature. A classic example is the Wien effect:[14] the strong electrolyte solution deviates from Ohm's law under strong electric fields. The electric field accelerates the ion to decouple from its surrounding shells and leads to the nonlinear increase of conductivity.[15] Because of the importance of the solvation shell in the dynamics of the ion, we propose that a similar fractional Stokes–Einstein relation may also exist in ionic solution at high temperatures. In light of the advantages of directly following each particle individually,[16–19] in this work, we have performed molecular dynamics (MD) simulations with aqueous sodium chloride (NaCl) solutions above room temperature to examine whether the fractional Stokes–Einstein relation also exists in aqueous NaCl solutions far away from the glass transition temperature. Moreover, the rationality of the three forms of the Stokes–Einstein relation is also discussed.

## 2. Simulation details

All our MD simulations were performed with the GROMACS package.[20,21] The CHARMM force field[22] for NaCl and the TIP3P[23] water were adopted to model aqueous sodium chloride solutions. The same model has been adopted to study the cluster formation and nucleation in aqueous NaCl solutions.[24–26] The ions and atoms were modeled as charged Lennard–Jones particles. The interactions between atoms and/or ions are described as

$$u(r_i, r_j) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}}, \qquad (1)$$

where $r_i$ is the $i$th atom (ion) position, $\sigma$ and $\varepsilon$ are the Lennard–Jones distance and energy constant, respectively, and $q_i$ is the partial charge of the $i$th atom (ion). The force field data are listed in Table 1. The periodic boundary conditions were applied to all three dimensions and the particle mesh Ewald algorithm[27] was employed to calculate the long-range electrostatic interactions with a cutoff of 1.2 nm in the real space. The van der Waals interactions were calculated directly with the same cutoff of 1.2 nm.

The simulated system contains 200 ion pairs and 3000 water molecules with a constant density $\rho = 1.136$ g/cm$^3$. Twenty six temperatures uniformly distributed within 300–800 K were adopted to investigate the diffusion, relaxation, and Stokes–Einstein relation in aqueous NaCl solution. To avoid possible disturbance of the thermostat, at each temperature, the system was firstly equilibrated in the $NVT$ ensemble for 10 ns with Nosé-Hoover thermostat,[28,29] followed by another 10 ns $NVE$ MD simulation for sample data. All chosen temperatures are above room temperature, which is high enough and far away from the glass transition point for NaCl solution. The time step for all MD simulations was 1 fs and the configurations were sampled every 10 steps for data analysis.

**Table 1.** CHARMM force field parameters for $Na^+$ and $Cl^-$ and TIP3P water model parameters.

| Atom/ion | $\sigma$/nm | $\varepsilon$/kJ·mol$^{-1}$ | Charge/e |
|---|---|---|---|
| $Na^+$ | 0.243 | 0.196 | +1 |
| $Cl^-$ | 0.405 | 0.628 | −1 |
| O | 0.315 | 0.636 | −0.834 |
| H | – | – | 0.417 |

## 3. Results

To examine whether the fractional Stokes–Einstein relation exists in aqueous NaCl solution above room temperature, we firstly consider the solvation structures and dynamics at different temperatures, and then calculate the diffusion constants and structural relaxation time to evaluate the two variants of the Stokes–Einstein relation. Next, the shear viscosity is determined to evaluate the Stokes–Einstein relation $D \sim T/\eta$, and the rationality of the variants of the Stokes–Einstein relation is discussed.

### 3.1. Solvation shell structures and dynamics

Ions exist as solvated ions in aqueous ionic solution. We adopted the radial distribution function (RDF) to characterize the solvation shells.[30] RDF is defined as $g(r) = \langle\delta(r - r_1)\rangle$, where $r_1$ is the position of center ion. The calculated RDFs for the $Na^+$–$Cl^-$ shell, $Na^+$–$H_2O$ shell, and $Cl^-$–$H_2O$ shell at temperatures $T = 300$, 400, 500, 600, 700, and 800 K are plotted in Fig. 1. Figure 1(a) shows that the main peak of the $Na^+$-$Cl^-$ shell increases slightly with increasing temperature, but the second peak decreases a little. The main peak corresponds to the ion atmosphere. The results suggest that $Na^+$ and $Cl^-$ are more strongly spatially correlated in the ion atmosphere, which results from the decrement of dielectric constant as temperature increases.[31] Both the main peak and the second peak of the $Na^+$–$H_2O$ shell and $Cl^-$–$H_2O$ shell decrease with increasing temperature, as shown in Figs. 1(b) and 1(c). Ions and water molecules get more weakly spatial-correlated at a higher temperature. The hydration structures are more likely to be disrupted by the thermal random movement with increasing temperature.

To further characterize the coupling of the center-ion and solvation shell, we calculate the residence correlation function of the ion with its solvation shells. The residence correlation function is defined as $C(t) = \langle p(0)\, p(t)\rangle$,[30,32] where $p(t)$ is 1 if a given ion is still in the solvation shell at time $t$ and otherwise zero. The solvation shell is mainly described by the first solvation shell. Its position corresponds to the first minimum of RDF, the first minimum is 0.36 nm for $Na^+$-$Cl^-$ shell, 0.32 nm for $Na^+$-$H_2O$ shell and 0.44 nm for $Cl^-$-$H_2O$ shell.

The $C(t)$ usually follows a exponential relaxation and the lifetime $\tau_s$ of solvation shell is defined as $\tau_s = \int_0^\infty C(t)\mathrm{d}t$.

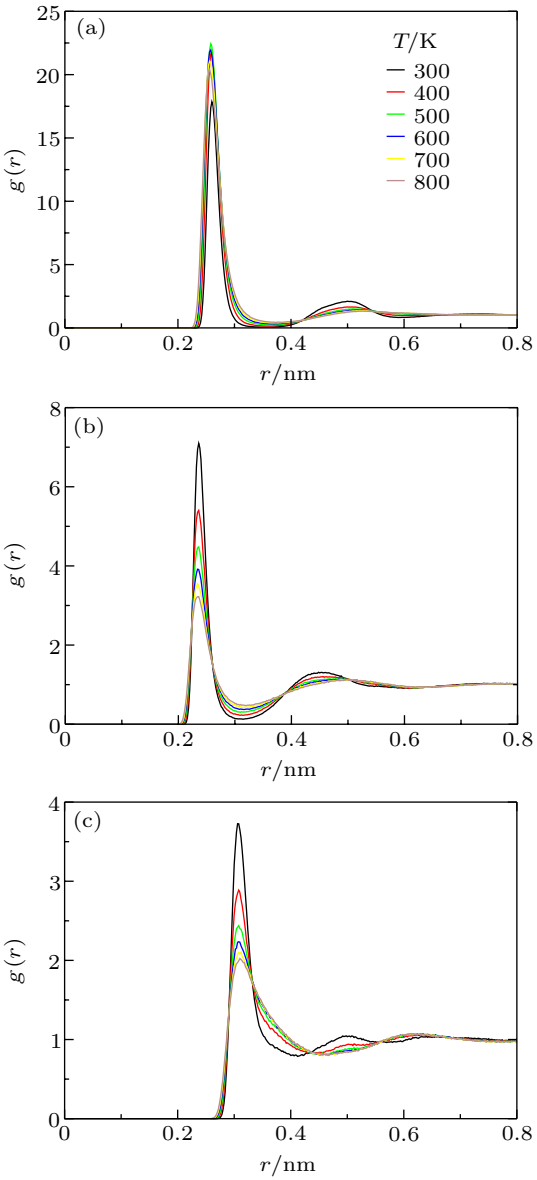



**Fig. 1.** Radial distribution functions (RDFs) of solvation shells: (a) $Na^+$–$Cl^-$ shell, (b) $Na^+$–$H_2O$ shell, (c) $Cl^-$–$H_2O$ shell.

The lifetimes $\tau_s$ for each shell are plotted in Fig. 2. It is shown that $\tau_s$ for each solvation shell are all decreased with increasing temperature. Ions get less temporally correlated with their surrounding shells with increasing temperature. The results also suggest that solvation is more likely to be destroyed at a higher temperature. Ions can more easily get rid of the constraint of solvation shells. The changes in solvation structure and dynamic may lead different rate in increases of the diffusion and the decreases of the relaxation with increasing temperature, and further lead the analogous fractional Stokes–Einstein relation as observed in supercooled liquids. In the following, we will calculate the diffusion constant and structural relaxation time as well as discuss the variants of the Stokes–Einstein relation.

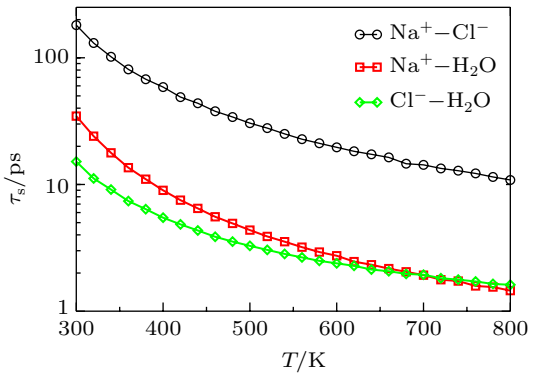



**Fig. 2.** Life time $\tau_s$ for $Na^+$–$Cl^-$ shell, $Na^+$–$H_2O$ shell, and $Cl^-$–$H_2O$ shell.

### 3.2. Diffusion and structural relaxation

To evaluate the variants of the Stokes–Einstein relation $D \sim \tau^{-1}$ and $D \sim T/\tau$, the diffusion constant of ions is calculated via the mean square displacement as

$$D = \lim_{t\to\infty} \frac{\left\langle \sum_i^N |\boldsymbol{r}_i(t) - \boldsymbol{r}_i(0)|^2 \right\rangle}{6Nt}, \tag{2}$$

where $N$ is the number of ions, $\boldsymbol{r}_i(t)$ is the position of the $i$th ion at time $t$, $\langle\rangle$ denotes the ensemble average. The mean square displacements (MSDs) of $Na^+$ and $Cl^-$ at $T = 300$, 400, 500, 600, 700 and 800 K are plotted in Fig. 3. The MSD can be separated into three parts for both $Na^+$ and $Cl^-$ at each temperature. The ballistic regime, MSD $\sim t^2$, the diffusive regime, MSD $\sim t$, the intermediate corresponds to the cage regime. Although the time ranges of each regime are different at different temperatures, the ballistic regime and cage regime are much smaller than the diffusive regime at each temperature. The time ranges of ballistic regime for both $Na^+$ and $Cl^-$ are smaller than 0.1 ps, the cage regime is within 0.1–1 ps, and the diffusive regime is locate at the time regime $t > 1$ ps. The diffusion constant is determined by linearly fitting with the data in the diffusive regime. The structural relaxation of ions is described by the self-intermediate scattering function $F_s(k,t)$, which is defined as

$$F_s(k,t) = \frac{1}{N}\sum_j^N \left\langle \exp\left\{ \mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}_j(0) - \boldsymbol{r}_j(t)] \right\} \right\rangle, \tag{3}$$

where $\boldsymbol{k}$ is a wavevector and usually chosen as the first maximum of the structure factor, in this work, $k = 22.0$ nm$^{-1}$ for $Na^+$ and 18.5 nm$^{-1}$ for $Cl^-$. $F_s(k,t)$ usually follows an exponential relation $F_s(k,t) \sim \mathrm{e}^{-t/\tau}$ in simple liquids, and the structural relaxation time $\tau$ is implicitly determined by $F_s(k,\tau) = \mathrm{e}^{-1}$ with the chosen $k$.

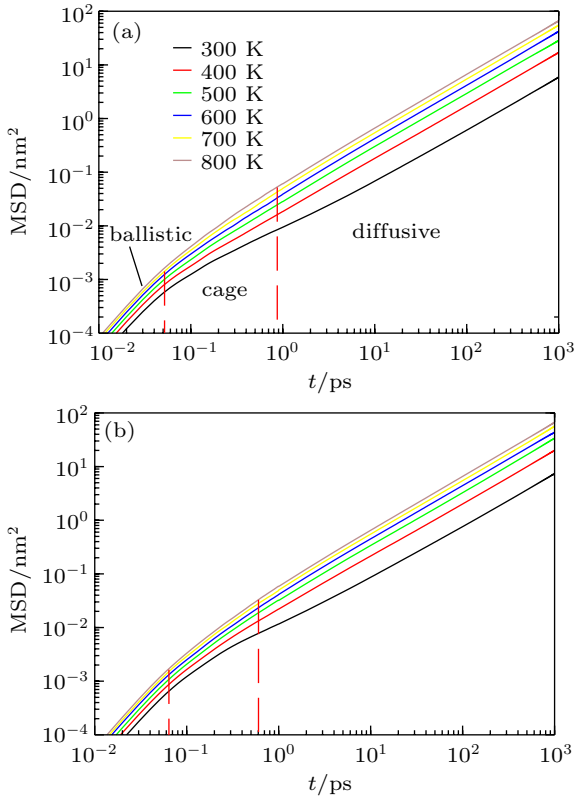



**Fig. 3.** The mean square displacement of the ion as a function of time $t$: (a) $Na^+$, (b) $Cl^-$. The two red dotted lines separate the MSD to three parts: ballistic, cage and diffusive.

The diffusion constants and structural relaxation times for $Na^+$ and $Cl^-$ at different temperatures within 300–800 K are plotted in Fig. 4(a) and 4(b), respectively. It is shown that the diffusion constants for both $Na^+$ and $Cl^-$ are increasing with temperature, whereas the diffusion constant of $Na^+$ increases faster than $Cl^-$. Due to the solvation differences as shown in Fig. 1 and Fig. 2,[33] $Cl^-$ exhibits a faster diffusion than $Na^+$ at $T = 300$ K, but the differences of diffusion between $Na^+$ and $Cl^-$ decrease with increasing temperature, which are almost the same at $T = 660$ K, $Na^+$ even exhibits a faster diffusion than $Cl^-$ above $T = 660$ K. Figure 4(b) shows the structural relaxation time $\tau$ is decreasing with increasing temperature. $\tau$ first get a large decrease at lower temperatures, but the the rate of the decreases becomes smaller at higher temperatures.

Comparing the diffusion constant with relaxation time, it is shown that an ion with a faster relaxation has a larger diffusion constant. However, the increases of the diffusion constant for both $Na^+$ and $Cl^-$ are more than the decreases of the relaxation time within 300–800 K. The increase of diffusion constant is about eight times the temperature increases from 300 K to 800 K, but the relaxation time only decreases around six times. It is different from what is observed in supercooled liquids, that the relaxation time increases faster than the diffusion decreases when cooling.[8,9,34] The increase of the temperature will lead to the increase of the diffusion and the decrease of the relaxation. Moreover, it also leads the whole or partially decoupling of the center ion with the solvation shells, and leads to fewer water molecules and counterions moving with the center ion. The effect will also intensify the diffusion of ion. So the different changes of the diffusion and relaxation with increasing temperature are due to the disruption of the solvation shells.

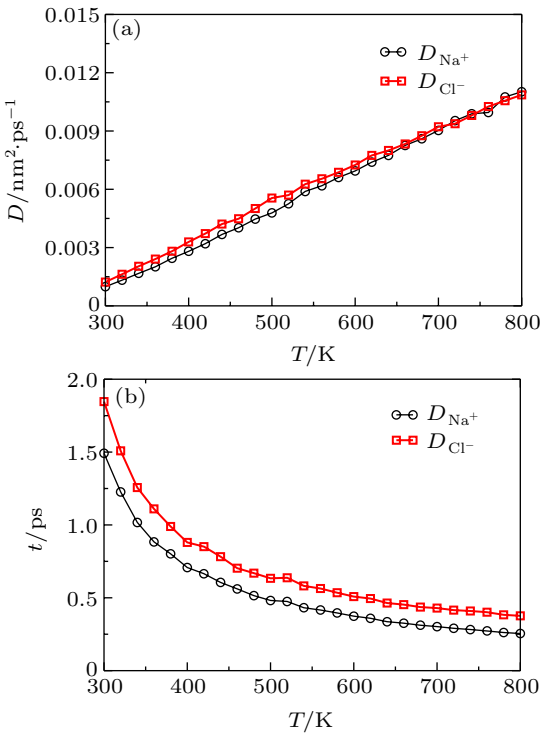



**Fig. 4.** (a) The diffusion constants $D$ of $Na^+$ and $Cl^-$ versus temperature $T$, (b) The structural relaxation time $\tau$ of $Na^+$ and $Cl^-$ as a function of temperature within 300–800 K.

### 3.3. Variants of the Stokes–Einstein relation

To examine the existence of the fractional Stokes–Einstein relation in NaCl solution above room temperature, the two variants $D \sim \tau^{-1}$ and $D \sim T/\tau$ were evaluated by $D \sim \tau^{\xi}$ and $D \sim (\tau/T)^{\xi}$, respectively. The variants are valid if $\xi = -1$ and otherwise the variant of Stokes–Einstein relation follows a fractional form. The logarithms of $\tau$ and $D$ for $Na^+$ and $Cl^-$ are plotted in Fig. 5. The fitted $\xi$ are not equal to $-1$ for both $Na^+$ and $Cl^-$ for all temperatures: $\xi = -1.34$ for $Na^+$ and $-1.38$ for $Cl^-$. The results suggest that the variant $D \sim \tau^{-1}$ is invalid and has taken a fractional form. As shown in Fig. 4, the diffusion constant increases faster than the decreases of the relaxation time in aqueous NaCl solution within 300–800 K, and then $\xi < -1$. It is different from what is observed in supercooled liquids at low temperatures, the rate of increases of the relaxation is greater than the decreases of the diffusion in supercooled liquids when cooling,[8,9,34] and the exponent $\xi$ is greater than $-1$ in supercooled liquids.

The logarithms of $\tau/T$ and $D$ are plotted in Fig. 6 to test the variant of the Stokes–Einstein relation described by $D \sim T/\tau$. $D \sim T/\tau$ gets a crossover at temperature $T_x$ for $Na^+$

and $Cl^-$. The data for $T < T_x$ are well fitted with $\xi \approx -1$ for both $Na^+$ and $Cl^-$, but $\xi > -1$ when $T > T_x$, where $\xi = -0.66$ for $Na^+$ and $-0.67$ for $Cl^-$. The results show the diffusion and relaxation also decouple for $T > T_x$, and a fractional $D \sim T/\tau$ is also observed. The crossover temperatures are a little different for $Na^+$ and $Cl^-$, $T_x = 500$ K for $Na^+$ and 480 K for $Cl^-$. The differences may be caused by the solvation differences between $Na^+$ and $Cl^-$ as shown in Fig. 1 and Fig. 2. The solvation for $Na^+$ is stronger than $Cl^-$.

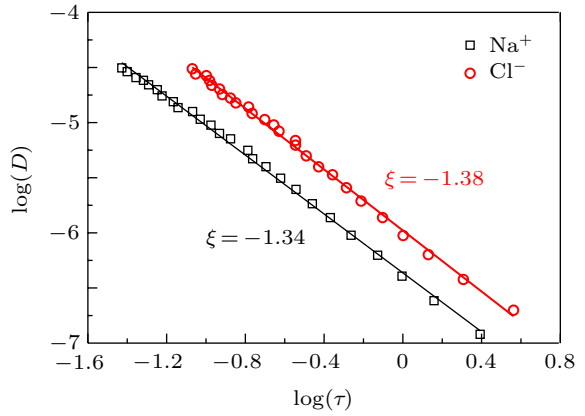



**Fig. 5.** Testing the variant of Stokes–Einstein relation described by $D \sim \tau^{-1}$ for $Na^+$ and $Cl^-$. The symbols are the simulated data and the solid lines are fitted by $D \sim \tau^{\xi}$. The colored exponent $\xi$ is corresponding to the same colored solid line.

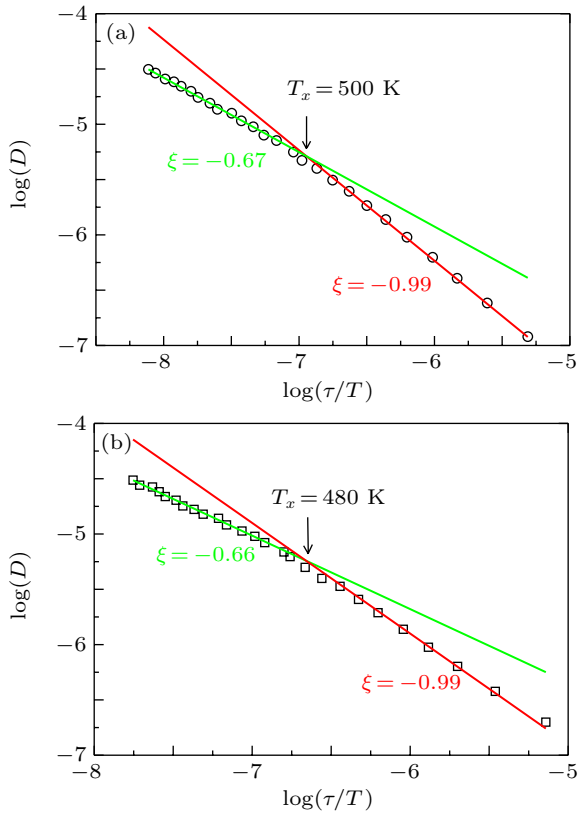



**Fig. 6.** Testing the variant of the Stokes–Einstein relation described by $D \sim T/\tau$: (a) $Na^+$ and (b) $Cl^-$. The symbols are the simulated data and the solid lines are fitted by $D \sim (\tau/T)^{\xi}$. The temperature $T_x$ labels the crossover temperature.

### 3.4. The Stokes–Einstein relation

The variants of the Stokes–Einstein relation described by $D \sim \tau^{-1}$ and $D \sim T/\tau$ are taken a fractional form, but is the Stokes–Einstein relation $D \sim T/\eta$ really in a fractional form in aqueous NaCl solution above room temperature. The shear viscosity is evaluate by $\eta \sim T\tau$, $\eta \sim \tau$ in $D \sim \tau^{-1}$ and $D \sim T/\tau$, respectively. To examine the Stokes–Einstein relation described by $D \sim T/\eta$, we need to calculate the shear viscosity. Because of its reliability and fast convergence, the method proposed by Hess is adopted in this work.[35] An external force $a_x$ is applied in the $X$ direction. The Navier–Stokes equation for liquids with $a_x$ is

$$\rho \frac{\partial_x u_x(z)}{\partial t} = \rho a_x(z) + \eta \frac{\partial^2 u_x(z)}{\partial z^2}, \tag{4}$$

where $a_x(z) = A\cos(kz)$, $u_x(z)$ is the velocity in $X$ direction and a function of $z$ only, $\rho$ is the density of fluid, $A$ is the maximum of $a_x$, $k = 2\pi/l$, $l$ is the simulation box size. The generated velocity is

$$u_x(z) = V\left(1 - e^{-t/\tau}\right)\cos(kz), \tag{5}$$

where the prefactor $V = A\rho/\eta k^2$ can be determined from $u_x(z)$ after the system reaches a non-equilibrium steady state. The shear viscosity can be determined by

$$\eta = \frac{A\rho}{Vk^2}. \tag{6}$$

The force $a_x$ should be chosen carefully[35] to avoid being too large or too small. The system moves too far away from the equilibrium if $a_x$ is too large, in contrast, it is difficult to determine the shear viscosity for large fluctuation. To get the correct shear viscosity, we tested different $A$ to determine the linear dependence regime between $V$ and $A$ at $T = 300$, 400, 500 and 800 K. Figure 7(a) shows that $V$ is proportional to $A$ when $A$ is within 0.002–0.05 nm/ps$^2$. To get good statistics, we chose five $A = 0.01$, 0.02, 0.03, 0.04 and 0.05 nm/ps$^2$ to determine the shear viscosity. The calculated shear viscosity is plotted in Fig. 7(b). The shear viscosity is decreasing with increasing temperature, which initially gets a fast decrease but the rate of the decrease gets smaller with increasing temperature. The rate of the decrease for $T > 500$ K is much smaller than that for $T < 500$ K.

To test the Stokes–Einstein relation described by $D \sim T/\eta$, the logarithms of $\eta/T$ and $D$ are plotted in Fig. 8. Similar to $D \sim T/\tau$, $D \sim T/\eta$ is also taken a crossover at $T_x \approx$ 500 K for both $Na^+$ and $Cl^-$, $\xi \approx$ -1 for both $Na^+$ and $Cl^-$ for $T < T_x$, but $\xi < -1$ for $T > T_x$, $\xi = -1.41$ for $Na^+$ and $-1.22$ for $Cl^-$. It is shown that $D \sim T/\eta$ is valid for both $Na^+$ and $Cl^-$ for $T < T_x$, but breaks down when $T > T_x$. The results are analogous with those observed in supercooled liquids while cooling, however, $D \sim T/\eta$ is invalid below a crossover temperature in supercooled liquids[8] and an invalidity is observed above a crossover temperature in our case.

To test the validity of the two variants of the Stokes–Einstein relation, by comparing the results given by $D \sim \tau^{-1}$ with $D \sim T/\eta$, it is shown that they give different $\xi$s especially for temperature $T < T_x$, $\xi$s are close to each other when $T > T_x$, but a difference around 0.1 still exists. Although both $D \sim \tau^{-1}$ and $D \sim T/\eta$ show the breakdown of the Stokes–Einstein relation, yet the different $\xi$s confirm that $D \sim \tau^{-1}$ is not a good variant of $D \sim T/\eta$. The functional form $\eta \sim T\tau$ used to evaluate shear viscosity in $D \sim \tau^{-1}$ is invalid. Then comparing the results given by $D \sim T/\tau$ with $D \sim T/\eta$, both formulas show a crossover as temperature increases, and the crossover temperature are almost the same for $D \sim T/\tau$ and $D \sim T/\eta$, $\xi \approx -1$ for $T < T_x$ in both $D \sim T/\tau$ and $D \sim T/\eta$. So $D \sim T/\tau$ is a good variant of $D \sim T/\eta$ for $T < T_x$. While temperature $T > T_x$, $\xi > -1$ for both $Na^+$ and $Cl^-$ in $D \sim T/\tau$, but $\xi < -1$ in $D \sim T/\eta$, so $D \sim T/\tau$ is not a good variant of $D \sim T/\eta$ for $T > T_x$.

To evaluate $\eta \sim \tau$ in $D \sim T/\tau$, we scaled the relaxation time and shear viscosity with the data at $T = 300$ K and plotted all data in Fig. 9. The scaled relaxation time and viscosity are almost coincident for temperature $T < 400$ K, but they start to deviate from each other above $T = 400$ K and the deviations increase with increasing temperature especially when $T > 500$ K. The decreases of viscosity are very small for $T > 500$ K while the relaxation continuously decreases with increasing temperature as shown in Figs. 4 and 7. Comparing

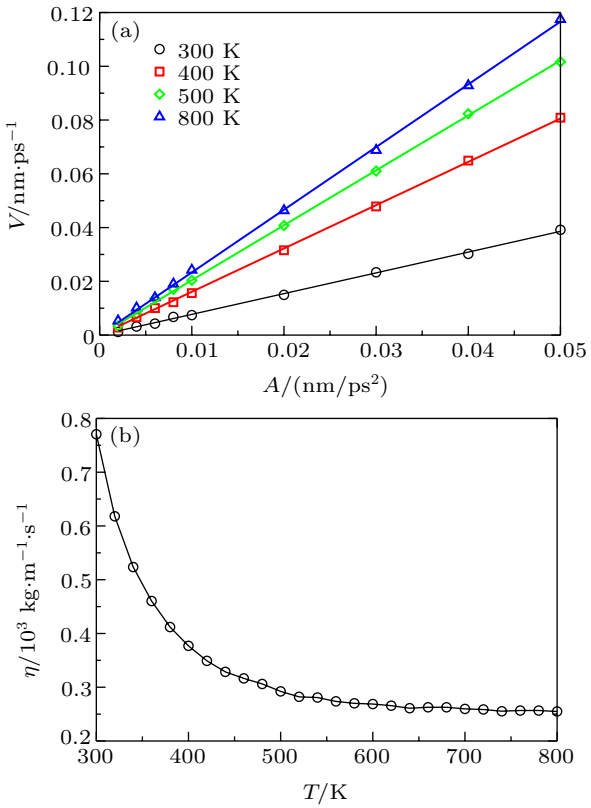



**Fig. 7.** (a) The prefactor $V$ as a function of the maximum of force $A$ while $A$ is within 0.002–0.05 nm/ps$^2$ at temperatures $T = 300$, 400, 500 and 800 K. The symbols are simulation data and the solid lines are fitted by $V \sim A$. (b) The shear viscosity $\eta$ versus temperature $T$.

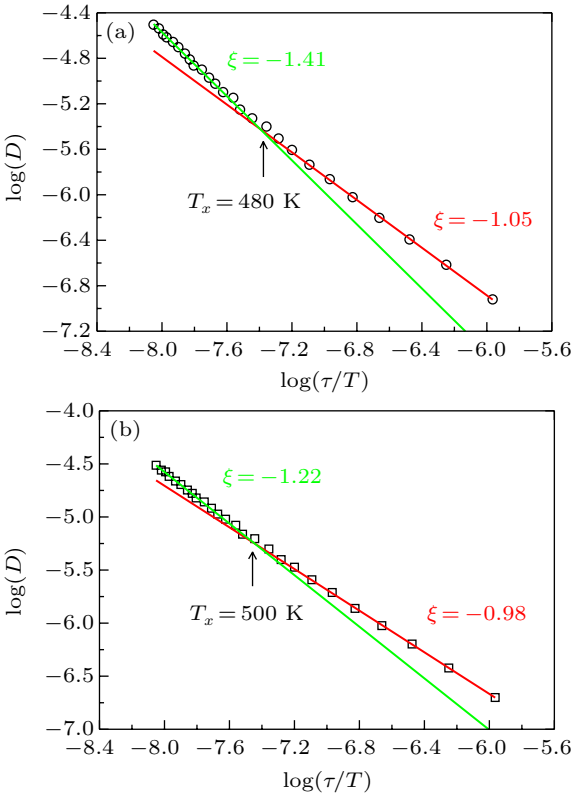



**Fig. 8.** Testing the Stokes–Einstein relation described by $D \sim T/\eta$ for $Na^+$ and $Cl^-$: (a) $Na^+$ and (b) $Cl^-$. The symbols are the simulated data and the solid lines are fitted by $D \sim (\eta/T)^{\xi}$. The temperature $T_x$ labels the crossover temperature.

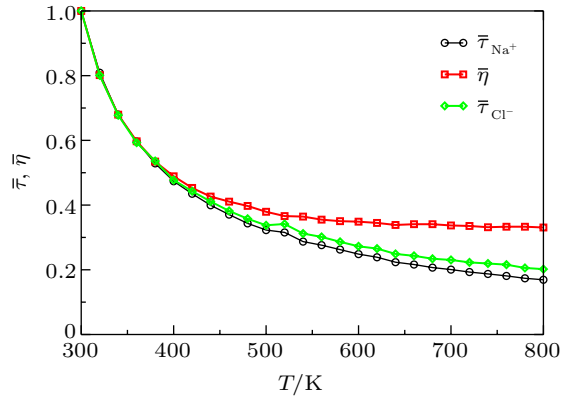



**Fig. 9.** The scaled relaxation time $\overline{\tau}$ and scaled shear viscosity $\overline{\eta}$ with the data at $T = 300$ K versus temperature $T$.

with the crossover shown in $D \sim T/\tau$ and $D \sim T/\eta$ at $T_x \approx 500$ K for $Na^+$ and $Cl^-$, we propose the breakdown of the Stokes–Einstein described by $D \sim T/\eta$ occurred at the temperature for the decoupling of the shear viscosity and relaxation.

Overall, the fractional Stokes–Einstein relation explicitly exists in NaCl solution far away from the glass transition temperature. $D \sim \tau^{-1}$ and $D \sim T/\tau$ give different $\xi$ s compared with $D \sim T/\eta$ within 300–800 K. Although some coincidence is observed between $D \sim T/\tau$ and $D \sim T/\eta$ within 300–500 K, both variants are not good variants of the Stokes–Einstein relation described by $D \sim T/\eta$. The results are sim-

ilar to those observed by Shi *et al.*[1] So one should critically evaluate the rationality of the two variants, $D \sim \tau^{-1}$ and $D \sim T/\tau$, while using them to test the Stokes–Einstein relation.

## 4. Discussion

The results indicate that the two variants of the Stokes–Einstein relation $D \sim T/\tau$ and $D \sim \tau^{-1}$ are invalid above room temperature and follow a fractional form. It is proposed that the invalidity is due to the dynamic heterogeneity.[6,36,37] However, $D \sim T/\tau$ and $D \sim \tau^{-1}$ give contradictory results, especially for $T < T_x$. It has been observed that the dynamic heterogeneity is decreased with increasing temperature.[38] But $D \sim T/\tau$ is breakdown at a higher temperature. So it is not likely that the breakdown of $D \sim T/\tau$ and $D \sim \tau^{-1}$ results from the dynamic heterogeneity as proposed in supercooled liquids. As shown in Fig. 4, the diffusion constant and relaxation time show different increase and decrease with increasing temperature, we propose the breakdown of $D \sim T/\tau$ and $D \sim \tau^{-1}$ results from the disruption of the solvation shells.

$D \sim \tau^{-1}$ is an approximate relation resulting from $F_s(k,t) = \exp\left(-k^2 Dt\right)$. However, $F_s(k,t) = \exp\left(-k^2 Dt\right)$ is only valid while the displacements of particle rigorously follow Gaussian distribution. It is only established in simple liquids under hydrodynamic limit. $F_s(k,t)$ is generally relaxed with a long time tail even in diluted hard sphere liquid for the molecular chaos.[39] $D \sim T/\tau$ is based on the approximation relation $\eta = G_\infty \tau$. The Maxwell relation $\eta = G_\infty \tau$ is only valid when the bulk modulus gets a fast relaxation, whereas the relation is not strictly established generally. Besides, the hydrodynamic radius is considered to be a constant in $D \sim T/\tau$, $D \sim \tau^{-1}$ and $D \sim T/\eta$. Actually, the molecule is solvated in liquid and is not free while moving. So the fractional form of Stokes–Einstein relation $D \sim T/\eta$ may be a result of not considering the changes of the hydrodynamic radius.

## 5. Conclusion

In this work, we performed atomistic molecular dynamics simulations to examine the diffusion, structural relaxation and the variants of the Stokes–Einstein relation in aqueous ionic solutions above room temperature far away from the glass transition temperature. We simulated 26 temperatures uniformly distributed within 300–800 K to monitor the fractional Stokes–Einstein relation. The results indicate $D \sim \tau^{-1}$ is invalid for both $Na^+$ and $Cl^-$ above room temperature, and follows a fractional form within 300–800 K. $D \sim T/\tau$ takes a crossover for both $Na^+$ and $Cl^-$ at $T_x \approx 500$ K. It is valid for both $Na^+$ and $Cl^-$ with an exponent $\xi \approx$ -1 for $T < T_x$, but breaks down with $\xi > -1$ for $T > T_x$. Combining the results given by $D \sim \tau^{-1}$ and $D \sim T/\tau$, indicates that the fractional variants of the Stokes–Einstein relation also exist in aqueous NaCl solutions above room temperature far away from the glass transition temperature, which is analogous with what is observed in supercooled liquid at a much lower temperature near the glass transition temperature. Moreover, the fractional forms are observed in the heating process. The center ion will be partially or whole decoupled with the solvation shells. We proposed the fractional Stokes–Einstein relation is due to the decoupling of the center-ion and its surrounding solvation shells.

Comparing the results given by $D \sim \tau^{-1}$ and $D \sim T/\tau$ with $D \sim T/\eta$, $D \sim \tau^{-1}$ is not a good variant of $D \sim T/\eta$ for both $Na^+$ and $Cl^-$ within 300–800 K, $D \sim T/\tau$ is a good variant of $D \sim T/\eta$ only for $T < T_x$ but is not a good variant above $T_x$. The shear viscosity decreases slower than the relaxation when $T > T_x$, they decouple at $T \approx 400$ K and the deviations increases as temperature increases especially for $T > T_x$. We propose the breakdown of $D \sim T/\tau$ and $D \sim T/\eta$ occurs at the temperature of the decoupling between the shear viscosity and structural relaxation. In conclusion, the fractional Stokes–Einstein relation not only exists in supercooled liquids at low temperatures near the glass transition point, but also exists in aqueous NaCl solution at high temperatures far away from the glass transition temperature. One should critically evaluate the two variants of the Stokes–Einstein relation, $D \sim T/\tau$ and $D \sim T/\eta$, while using to test the validity of Stokes–Einstein relation.

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## References

[1] Shi Z, Debenedetti P G and Stillinger F H 2013 *J. Chem. Phys.* **138** 12A526
[2] Swallen S F, Bonvallet P A, McMahon R J and Ediger M D 2003 *Phys. Rev. Lett.* **90** 015901
[3] Mapes M K, Swallen S F and Ediger M D 2006 *J. Phys. Chem. B* **110** 507
[4] 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
[5] Xu L, Mallamace F, Yan Z, Starr F W, Buldyrev S V and Eugene Stanley H 2009 *Nat. Phys.* **5** 565
[6] Binder K, Kob W, *Glassy materials and disordered solids: An introduction to their statistical mechanics* World Scientific: 2011
[7] Habasaki J, Leon C and Ngai K 2017 *Top. Appl. Phys.* **132**
[8] Kumar P, Buldyrev S V, Becker S R, Poole P H, Starr F W and Stanley H E 2007 *Proc. Natl. Acad. Sci.* **104** 9575
[9] Jeong D, Choi M Y, Kim H J and Jung Y 2010 *Phys. Chem. Chem. Phys.* **12** 2001
[10] Ikeda A and Miyazaki K 2011 *Phys. Rev. Lett.* **106** 015701
[11] Grant E H 1957 *J. Chem. Phys.* **26** 1575
[12] Varela L M, García M and Mosquera V c 2003 *Phys. Rep.* **382** 1
[13] Varela L M, Garcia M and Mosquera V 2003 *Phys. Rep.* **382** 1-111
[14] Onsager L and Kim S K 1957 *J. Phys. Chem.* **61** 198
[15] Onsager L and Kim S K 1957 *J. Phys. Chem.* **61** 198

[16] Vázquez-Raygoza A, Cano-González L, Velázquez-Martínez I, Trejo-Soto P, Castillo R, Hernández-Campos A, Hernández-Luis F, Oria-Hernández J, Castillo-Villanueva A, Avitia-Domínguez C, Sierra-Campos E, Valdez-Solana M and Téllez-Valencia A 2017 *Molecules* **22** 2055
[17] Balatti G, Ambroggio E, Fidelio G, Martini M and Pickholz M 2017 *Molecules* **22** 1775
[18] Ishak S, Aris S, Halim K, Ali M, Leow T, Kamarudin N, Masomian M and Rahman R 2017 *Molecules* **22** 1574
[19] Shu C, Xiao K, Cao C, Ding D and Sun X 2017 *Molecules* **22** 1342
[20] Berendsen H J C, van der Spoel D and van Drunen R 1995 *Comput. Phys. Commun.* **91** 43
[21] Van Der Spoel D, Lindahl E, Hess B, Groenhof G, Mark A E and Berendsen H J 2005 *J. Comput. Chem.* **26** 1701
[22] Brooks B R, Bruccoleri R E, Olafson B D, Swaminathan S and Karplus M 1983 *J. Comput. Chem.* **4** 187
[23] Jorgensen W L, Chandrasekhar J, Madura J D, Impey R W and Klein M L 1983 *J. Chem. Phys.* **79** 926
[24] Hassan S A 2008 *J. Phys. Chem. B* **112** 10573
[25] Hassan S A 2008 *Phys. Rev. E* **77** 031501
[26] Hassan S A 2011 *J. Chem. Phys.* **134** 114508
[27] Essmann U, Perera L, Berkowitz M L, Darden T, Lee H and Pedersen L G 1995 *J. Chem. Phys.* **103** 8577
[28] Nosé S 1984 *J. Chem. Phys.* **81** 511
[29] Hoover W G 1985 *Phys. Rev. A* **31** 1695
[30] Lee S H and Rasaiah J C 1994 *J. Chem. Phys.* **101** 6964
[31] Anderson J, Ullo J J and Yip S 1987 *J. Chem. Phys.* **87** 1726
[32] Bloomfield V, Dalton W and Van Holde K 1967 *Biopolymers* **5** 135
[33] Koneshan S, Rasaiah J C, Lynden-Bell R and Lee S 1998 *J. Phys. Chem. B* **102** 4193
[34] Becker S R, Poole P H and Starr F W 2006 *Phys. Rev. Lett.* **97** 055901
[35] Hess B 2002 *J. Chem. Phys.* **116** 209
[36] Berthier L 2011 *Physics* **4** 42
[37] Giovambattista N, Mazza M G, Buldyrev S V, Starr F W and Stanley H E 2004 *J. Phys. Chem. B* **108** 6655
[38] Kob W, Donati C, Plimpton S J, Poole P H and Glotzer S C 1997 *Phys. Rev. Lett.* **79** 2827
[39] Alder B J and Wainwright T E 1967 *Phys. Rev. Lett.* **18** 988