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Stokes–Einstein–Debye relation in TIP5P water

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The Stokes–Einstein–Debye (SED) relation in TIP5P water is tested with the original formula and its variants within the temperature range 240–390 K. The results indicate that although the variants explicitly break down, the original SED relation is almost valid. Compared with the Stokes–Einstein relation, no explicit decoupling is observed in translational and rotational motion. Variation of the effective hydrodynamic radius is critical to testing the validity of the SED relation.

Keywords: Stokes–Einstein–Debye relation, TIP5P water, effective hydrodynamic radius, Stokes' formula

PACS: 61.20.Ja, 61.20.Gy

DOI: 10.1088/1674-1056/ad94e3 **CSTR:** 32038.14.CPB.ad94e3

1. Introduction

The Stokes–Einstein–Debye (SED) relation[1] relates the rotational diffusion constant D_r to the rotational frictional coefficient ς or the rotational relaxation time τ_r, and is expressed as $D_\mathrm{r} = k_\mathrm{B}T/\zeta$ or $D_\mathrm{r} = [n(n+1)\tau_{rn}]^{-1}$, where k_B is the Boltzmann constant, T is the temperature and τ_{rn} is the τ_r determined by the decay of the nth degree Legendre polynomial. ς is described by the Stokes formula $\zeta = 8\pi\eta a^3$ for a rigid sphere with a radius a moving in a fluid with viscosity η.

Variants are usually adopted to test the SED relation rather than the original formula. One gets the variant $D_\mathrm{r} \sim T/\eta$ if it is assumed that the effective hydrodynamic radius a is a constant and the Stokes formula $\zeta = 8\pi\eta a^3$ is also valid,[2,3] where the symbol $\sim$ means proportional to. Furthermore the variant $D_\mathrm{r} \sim T/\tau_\mathrm{t}$ is established with the approximated relation $\eta = G_\infty\tau_\mathrm{t}$,[4] where G_∞ is the instantaneous shear modulus presumed to be a constant and τ_t is the translational relaxation time. Moreover, if $D_\mathrm{r} = [n(n+1)\tau_{rn}]^{-1}$ is satisfied for any integer n, $n(n+1)\tau_{rn} = m(m+1)\tau_{rm}$ for different n, m is also a variant.[5] Combined with the Stokes–Einstein (SE) relation $D_\mathrm{t} = k_\mathrm{B}T/(6\pi\eta a)$ and using the assumption of constant a, one can get more variants, such as the independence of the ratios $D_\mathrm{t}\tau_{rn}$,[6] $D_\mathrm{t}/D_\mathrm{r}$[7] and $T\tau_{rn}/\eta$[8] with the temperature, where D_t is the translational diffusion constant.

Many studies have proposed that the SED relation is invalid in supercooled liquids using the variants. In particular its validity in supercooled water has attracted much attention. $D_\mathrm{r} \sim T/\eta$ is observed to break down in TIP4P/2005 under supercooling and the breakdown is much larger than the SE relation $D_\mathrm{t} \sim T/\eta$.[2] Without considering T, D_r is still proportional to η^{-1} down to the glass transition temperature T_g in ortho-terphenyl (OTP).[9] $D_\mathrm{t}\tau_{rn}$ with $n = 1$ or 2 is found to be temperature and density dependent in supercooled SCP/E, TIP5P and ST2 water.[6,10–13] The breakdown of $D_\mathrm{t}\tau_{r2}$ happens at $2T_\mathrm{g}$ in TIP5P and ST2, but not at the usually recognized $1.2T_\mathrm{g}$; this can be explained by a hierarchical two-state scenario.[14,15] The ratio $D_\mathrm{r}\tau_\mathrm{t}/T$ is almost a constant in supercooled SPC/E water[4] for $T > 280$ K but increases with cooling below 280 K. However, a controversial result is that only a fractional form $D_\mathrm{r} \sim (T/\tau_\mathrm{t})^{\xi}$ with $\xi = 0.75$ is shown for the whole temperature range. The ratio $D_\mathrm{t}/D_\mathrm{r}$ is found not to be a constant but decreases with decreasing temperature in SPC/E,[4] TIP4P/2005[2] and OTP.[7] $D_\mathrm{t}\tau_{rn}$ is observed to be size dependent[16] and the small probe increases by almost two orders of magnitude as T_g is approached. $T\tau_{r6}/\eta$ is almost established, but a fractional form $\tau_{r1} \sim (\eta/T)^{\xi}$ with $\xi = 0.8$ is shown in TIP4P/2005 water; however, Kawasaki and Kim proposed that the violation of SED in TIP4P/2005 water is spurious.[2] A deviation from $n(n+1)\tau_{rn} = m(m+1)\tau_{rm}$ is observed in both analytical models and experiments.[5,17–19] Both $D_\mathrm{r} \sim T/\tau_\mathrm{t}$ and $\tau_{r2}^{-1} \sim T/\tau_\mathrm{t}$ show a crossover with cooling in ST2 water;[20] $D_\mathrm{r} \sim T/\tau_\mathrm{t}$ is established at high temperatures and has a fractional form at low temperatures; $\tau_{r2}^{-1} \sim T/\tau_\mathrm{t}$ breaks downs over the whole temperature range with two fractional forms. There are several different explanations for the breakdown of the SED relation, such as a change in the mechanism due to transitional diffusion arising around $1.2T_\mathrm{g}$,[9,21,22] spatially heterogeneous dynamics[16,20] and a two-state transformation.[13]

Because the above results are mainly deduced from variants of the SED relation, some controversial results are observed with different variants and even the same variant with different data handling. Moreover, the assumption of constant a is ad hoc. Therefore, the validity of the SED relation is still elusive. It was found that considering how a varies under different conditions is critical for the validity of the SE relation

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for ions in ionic solutions.[23–27] Our previous results show that the Einstein relation is definitely established in TIP5P water and the Jagla model.[28] The SE relation should be valid under the assumption of the validity of the Stokes formula and then a should be varied with temperature. It is therefore necessary to explore the SED relation from the original formulae $D_{\mathrm{r}} = k_{\mathrm{B}}T/(8\pi\eta a^3)$ and $D_{\mathrm{r}} = [n(n+1)\tau_{rn}]^{-1}$ while also taking the variation of a into account. Because the validity of the SED relation in supercooled water has attracted much attention, in this work we test the validity of the SED in TIP5P water and also check the consistency between the original SED relation and its variants.

2. Simulation details and analysis methods

The configuration for the molecular dynamics (MD) simulation consists of 2048 TIP5P water molecules[29] with a constant density 0.976 g·cm^{-3}. All our MD simulations were performed with the GROMACS package.[30,31] Periodic boundary conditions were applied in all three directions of Cartesian space. The particle mesh Ewald algorithm[32] was employed to calculate the long-range electrostatic interactions with a cutoff of 1.2 nm in real space. The van der Waals interactions were calculated directly with a truncated spherical cutoff of 1.2 nm. The 25 temperatures simulated in this work are distributed within the range 240–390 K. The system temperature was kept constant by a Nosé–Hoover thermostat.[33,34]

To examine the SED relation, the rotational diffusion coefficient D_{r} is calculated via its asymptotic relation with rotational mean square displacement (RMSD)[2,4]

$$D_{\mathrm{r}} = \lim_{\Delta t\to\infty} \langle \varphi^2(\Delta t)\rangle/(4\Delta t), \tag{1}$$

where $\langle\varphi^2(\Delta t)\rangle$ is the RMSD and $\varphi_i(\Delta t)$ is the angular displacement. The rotational relaxation time τ_{rn} is calculated via the rotational correlation function[1,2]

$$C_n(t) = \sum_{i=1}^{N} \langle P_n[\boldsymbol{e}_i(t)\cdot\boldsymbol{e}_i(0)]\rangle/N, \tag{2}$$

where $P_n(x)$ is the nth-order Legendre polynomial, $e_i(t)$ is the unit vector of the dipole for the ith TIP5P molecule and τ_{rn} is determined by $C_n(\tau_{rn}) = e^{-1}$. The τ_{rn} values for $n = 1, 2, 3$ are determined. A time interval of 0.001 ps is adopted to calculate the RMSD and $C_n(t)$. Eight trajectories were simulated to calculate D_{r} and τ_{rn}. The related D_{r} and τ_{rn} for $n = 1, 2, 3$ are plotted in Figs. 1(a) and 1(b), respectively. The data show large fluctuations at low temperature, and the statistical error for D_{r} and τ_{rn} is about 10%. The heterogeneous rotational dynamics are characterized by the rotational non-Gaussian parameter[35] expressed as

$$\alpha_2(t) = 3\langle\varphi^4(t)\rangle/5\langle\varphi^2(t)\rangle^2 - 1. \tag{3}$$

The frictional coefficient α is taken directly from our previous work[28] and is determined by applying a constant external force F_{e} on the selected 128 molecules, with all other particles being regarded as the medium. In the linear response regime, the frictional force on an ion ($f_{\mathrm{r}} = \alpha v$) is equal to the applied force (F_{e}) after reaching the non-equilibrium steady state. The frictional coefficient $\alpha = C\eta v$ is determined by

$$\alpha = \frac{F_{\mathrm{e}}}{v}, \tag{4}$$

where v can be calculated by $v = \lim_{t\to\infty}\langle r(t)\rangle/t$.[36] The viscosity η, translational diffusion coefficient D_{t} and translation relaxation time τ_{t} (calculated with $k = 24.5$ nm^{-1} corresponding to the first maximum of the static structure factor) are also directly taken from our previous work.[28] The hydrodynamic radius is evaluated by $a \sim \alpha/\eta$.

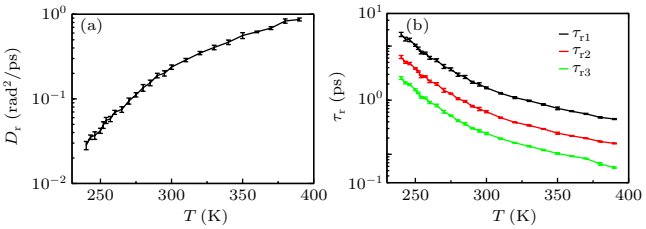


Fig. 1. The D_{r} and τ_{rn} for $n = 1, 2, 3$ as a function of T: (a) D_{r} versus T; (b) τ_{rn} versus T.

3. Results and discussion

Based on D_{r}, τ_{rn}, η, τ_{t} and α, we fit our simulation data with the two formulae $D_{\mathrm{r}} \sim (T/\eta)^{\xi_1}$ and $D_{\mathrm{r}} \sim (T/\tau_{\mathrm{t}})^{\xi_2}$ to test the two variants $D_{\mathrm{r}} \sim T/\eta$ and $D_{\mathrm{r}} \sim T/\tau_{\mathrm{t}}$, respectively. Moreover, the fitting of $D_{\mathrm{r}} \sim \tau_{rn}^{-\xi_3}$ is adopted to test the original SED relation $D_{\mathrm{r}} = [n(n+1)\tau_{rn}]^{-1}$. Based on the assumption of the validity of the Stokes formula $\alpha = 6\pi\eta a$, a is evaluated from $a \sim \alpha/\eta$. Due to η and α being large numbers and having large statistical errors at low temperatures, $D_{\mathrm{r}}\alpha^3 \sim (T\eta^2)^{\xi_4}$ is applied to test the original SED relation $D_{\mathrm{r}} = k_{\mathrm{B}}T/(8\pi\eta a^3)$. A variant or the original SED relation is valid if the corresponding exponent $\xi_i \approx 1.0$ ($i = 1, 2, 3$ or 4), and invalid otherwise. To facilitate the determination of the exponents, the related results are calculated and plotted in Fig. 2.

The $D_{\mathrm{r}} \sim (T/\eta)^{\xi_1}$ in Fig. 2(a) shows a crossover at a temperature around $T_x = 280$ K as temperature decreases. The variant $D_{\mathrm{r}} \sim T/\eta$ is almost established with an exponent $\xi_1 = 1.02$ for $T > T_x$ but explicitly breaks down when $T < T_x$ with an exponent $\xi_1 = 0.21$. $D_{\mathrm{r}} \sim (T/\tau_{\mathrm{t}})^{\xi_2}$ in Fig. 2(b) shows a similar crossover as $D_{\mathrm{r}} \sim (T/\eta)^{\xi_1}$ at the same T_x. However, the variant $D_{\mathrm{r}} \sim T/\tau_{\mathrm{t}}$ is invalid in the whole temperature range with $\xi_2 = 1.75$ for $T > T_x$ and $\xi_2 = 0.19$ for $T < T_x$. $D_{\mathrm{r}} \sim \tau_{rn}^{-1}$ for $n = 1, 2, 3$ is almost established, as shown in Fig. 2(c). The ξ_3 fitted in $D_{\mathrm{r}} \sim \tau_{rn}^{-\xi_3}$ for $n = 1, 2, 3$ are 0.95, 0.93, 0.93, respectively, and are close to the exact

result. $D_{\rm r}=k_{\rm B}T/(8\pi\eta a^3)$ is also almost valid for the fitted exponent $\xi_4=1.09$ shown in $D_{\rm r}\alpha^3\sim(T\eta^2)^{\xi_4}$.

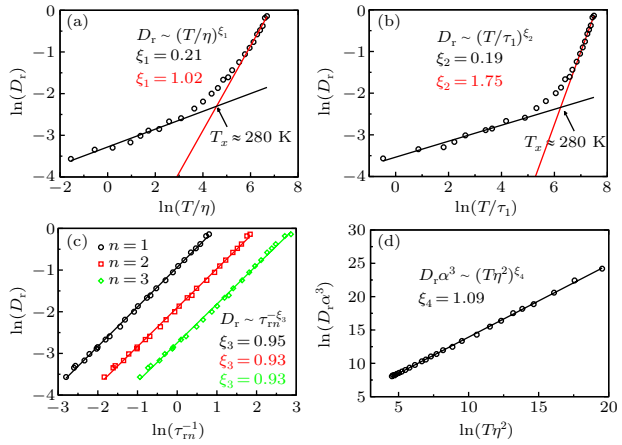


Fig. 2. Verification of the validity of the SED relations $D_{\rm r}\sim T/\eta$ (a), $D_{\rm r}\sim T/\tau_{\rm t}$ (b), $D_{\rm r}\sim\tau_{rn}^{-1}$ (c), $D_{\rm r}\sim T/\eta a^3$ (d). The calculated data are represented by symbols and the data are fitted by $D_{\rm r}\sim(T/\eta)^{\xi_1}$, $D_{\rm r}\sim(T/\tau_{\rm t})^{\xi_2}$, $D_{\rm r}\sim\tau_{rn}^{-\xi_3}$ and $D_{\rm r}\alpha^3\sim(T\eta^2)^{\xi_4}$ respectively. The fitted exponent ξ_i is written in the same color as the corresponding solid fitting line.

The results indicate that two variants, $D_{\rm r}\sim T/\eta$ and $D_{\rm r}\sim T/\tau_{\rm t}$, are both invalid in the temperature range 240–390 K. The crossover is similar to that observed for the variants of the SE relation but with different exponents,[28] and the validity of $D_{\rm r}\sim T/\eta$ above T_x is consistent with a being almost constant when $T>T_x$. The variant of the SED relation expressed as $D_{\rm t}\tau_{\rm r2}$ also breaks down at almost the same temperature in TIP5P and ST2 water.[13] A similar phenomenon is also found in TIP4P/2005 water,[2] i.e., $D_{\rm r}\sim T/\eta$ is valid when $T>250$ K. This is different from SPC/E water,[4] in which $D_{\rm r}\sim T/\tau_{\rm t}$ only shows a fractional form with an exponent $\xi_2=0.75$ within the 200–350 K range. Comparing the exponent in the variant of the SE relation $D_{\rm t}\sim T/\eta$,[28] one can get $D_{\rm t}/D_{\rm r}\sim(T/\eta)^{0.61}$ for $T<T_x$, and this will decrease with cooling similar to what is observed in SPC/E,[4] TIP4P/2005[2] and OTP.[7]

The $D_{\rm r}\sim\tau_{rn}^{-1}$ is similar to that observed by Cicerone and Ediger with four probes in OTP.[16] However, it is different from that observed in TIP4P/2005 water;[2] $D_{\rm r}\tau_{rn}$ for $n=1$, 2, 3, 6 can be increased by two orders from 300 K to 190 K. Comparing Figs. 2(a) and 2(d), the breakdown of $D_{\rm r}\sim T/\eta$ is restored to some extent by taking the variation of a into account, which implies that the variation of a is critical for the validity of the SED relation. The deviations of ξ_3 and ξ_4 from the exact result $\xi_i\approx 1.0$ are small, so we conclude that the original two SED relations $D_{\rm r}=[n(n+1)\tau_{rn}]^{-1}$ and $D_{\rm r}=k_{\rm B}T/(8\pi\eta a^3)$ are almost valid for TIP5P water within the range 240–390 K.

To further verify the validity of $D_{\rm r}\sim\tau_{rn}^{-1}$ and explore the origins for the small breakdown shown by ξ_3, the relation $\tau_{rn}=\gamma_n\tau_{\rm r1}$ for $n=2$, 3 is adopted and the non-Gaussian parameter $\alpha_2(t)$ is also calculated. If $D_{\rm r}\sim\tau_{rn}^{-1}$ is valid, $\gamma_n\simeq 2/[n(n+1)]$ and breaks down otherwise. Figure 3(a) shows $\gamma_2=0.372$ and $\gamma_3=0.152$, which are close to the exact results $\gamma_2=1/3$ and $\gamma_3=1/6$. The results also imply that $D_{\rm r}\sim\tau_{rn}^{-1}$ is established, which is consistent with the result shown in Fig. 2(c).

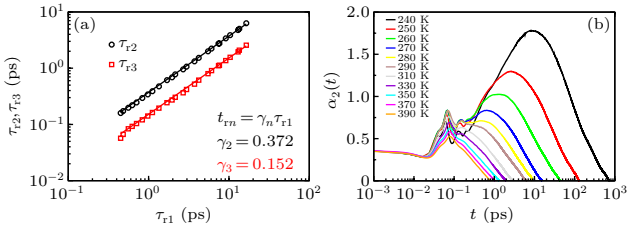


Fig. 3. Verification of the validity of the SED relation by $\tau_{rn}=\gamma_n\tau_{\rm r1}$ (a) and the non-Gaussian parameter $\alpha_2(t)$ (b).

If the angular displacement $\varphi_i(\Delta t)$ follows a Gaussian distribution, $D_{\rm r}\sim\tau_{\rm r1}^{-1}$ is an exact result because $\langle P_1(\cos\varphi)\rangle=\exp\left(-\langle\varphi^2\rangle/2\right)$. However, the rotational dynamics are also observed to deviate from Gaussian and show a heterogeneous dynamics like the translational dynamics.[19,35,37,38] The non-Gaussian parameter $\alpha_2(t)$, plotted in Fig. 3(b), is similar to that observed in SPC/E water[35] and TIP4P/2005.[3] The value of $\alpha_2(t)$ deviates from zero and the deviation increases with decreasing temperature. However, the deviations are small and the maximum is less than 2.0 even at 240 K. This is consistent with the small breakdown in $D_{\rm r}\sim\tau_{\rm r1}^{-1}$.

The $D_{\rm r}\sim\tau_{rn}^{-1}$ for different n is valid if the molecular rotation follows a free angular diffusion equation. Because of the deviations from Gaussian, the net torque applied on a molecule may deviate from zero at an instant. The net torque will prevent the molecule from rotating freely and lead to a deviation from the exact result $D_{\rm r}\sim\tau_{rn}^{-1}$. Because of the small deviations from Gaussian, the breakdown of $D_{\rm r}\sim\tau_{rn}^{-1}$ is small. The same mechanism may also lead to the small breakdown in $D_{\rm r}\alpha^3\sim T\eta^2$, because $D_{\rm r}=k_{\rm B}T/(8\pi\eta a^3)$ is also established without net torque. Moreover, the small breakdown in $D_{\rm r}=k_{\rm B}T/(8\pi\eta a^3)$ may result from the assumption of the validity of the Stokes formula $\zeta=8\pi\eta a^3$. The water molecule is considered to be effectively a sphere in $\zeta=8\pi\eta a^3$; however, it is a planar molecule. To what extent it can be considered a sphere needs further study.

Many studies have proposed that translational and rotational motion decouple in supercooled liquids, and different decoupling temperatures have been proposed, such as $1.2T_{\rm g}$,[14] $1.5T_{\rm g}$[4] and $2.0T_{\rm g}$.[13] However, this proposition is usually based on the variants of the SE and SED relations. Decoupling is also tested in this work, and the related SE relation $D_{\rm t}\sim T/\alpha$, SED relation $D_{\rm r}\sim\tau_{\rm r1}^{-1}$ and $D_{\rm r}\alpha^3\sim T\eta^2$ are plotted in Fig. 4(a). Shi and co-workers tested the decoupling with $D_{\rm t}\tau_{\rm r2}\sim a^2$.[13,15] The same testing method is also adopted in this work using $D_{\rm t}\sim\tau_{\rm r2}^{-1}$ if a is considered to be a constant and $D_{\rm t}\eta^2\sim\alpha^2\tau_{\rm r2}^{-1}$ otherwise. The related data are plotted in Fig. 4(b). All data are rescaled with the data at 390 K.

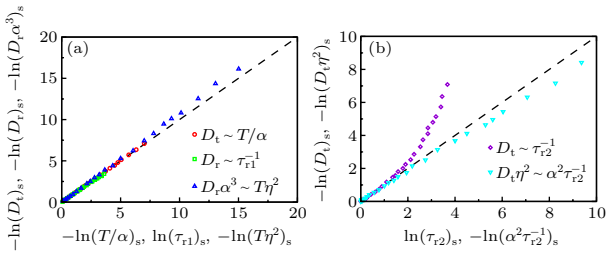


Fig. 4. Verification of the decoupling of translational and rotational motion: (a) $D_t \sim T/\alpha$ versus $D_r \sim \tau_{r1}^{-1}, D_r\alpha^3 \sim T\eta^2$; (b) $D_t \sim \tau_{r2}^{-1}$, $D_t\eta^2 \sim \alpha^2\tau_{r2}^{-1}$. The dotted line is the reference line $y = x$.

As our previous work indicates that the SE relation is definitely valid if we assume that the Stokes formula $\alpha = 6\pi\eta a$ is valid,[28] the same data are plotted by red circles, as shown in Fig. 4(a); these fall well on the reference line $y = x$. The green squares for $D_r \sim \tau_{r1}^{-1}$ almost fall on the reference line and only a small deviation is observed by comparison with $D_t \sim T/\alpha$. No explicit decoupling is observed by comparing $D_r \sim \tau_{r1}^{-1}$ and $D_t \sim T/\alpha$. The data for $D_r\alpha^3 \sim T\eta^2$ are also almost on the reference line at high temperature ($T \geq 260$ K) and show deviations at a lower temperature. The deviation from the exact line is about 6.7% at $T = 240$ K. $D_t \sim \tau_{r2}^{-1}$ in Fig. 4(b) shows that decoupling happens around 280 K. This is similar to the observations in TIP5P and ST2 water,[13,15] but different from TIP4P/2005 water, where decoupling occurs at 250 K.[2] However, the decoupling is almost restored by considering that the variation of a and $D_t\eta^2 \sim \alpha^2\tau_{r2}^{-1}$ only shows explicit deviations from the reference line for $T \leq 260$ K. The deviation is about 10% at $T = 240$ K. A possible reason for the deviation is the strong correlation at low temperatures; molecules cannot rotate freely[7] and it may not be appropriate to consider the molecules to be effectively spherical. The deviations for $D_r\alpha^3 \sim T\eta^2$ and $D_t\eta^2 \sim \alpha^2\tau_{r2}^{-1}$ at low temperature are still within statistical error; the data error is about 10% at $T = 240$ K, as shown in Fig. 1. Moreover, the deviations are much smaller in this work compared with previous studies.[2,4,7,15] So we conclude there is no explicit decoupling in translational and rotational motion and the variation of a should be considered to test the SED relation.

4. Conclusion

We have performed atomistic MD simulations to explore the validity of the SED relation in supercooled water with the TIP5P model in the temperature range 240–390 K. Our results confirm that the original SED relation is almost valid in supercooled TIP5P water, even though its two variants, $D_r \sim T/\tau_t$ and $D_r \sim T/\eta$, definitely break down (and in their fractional forms). The variant $D_r \sim T/\eta$ gives rational results only when a can be considered as a constant above 280 K but explicitly breaks down below 280 K. $D_r \sim T/\tau_t$ is invalid in the whole temperature range; two fractional forms are observed with a crossover at 280 K. $D_r \sim \tau_{rn}^{-1}$ shows a smaller deviation from the exact result which can be explained by the dynamic heterogeneity observed in the non-Gaussian parameter. After taking the variation of a into account, the rationality of $D_r \sim T/\eta$ is restored, and $D_r \sim T/(\eta a^3)$ is almost established. By comparing $D_t \sim T/\alpha$, $D_r \sim \tau_{r1}^{-1}$ and $D_r \sim T/(\eta a^3)$, no explicit decoupling of the translational and rotational motion is observed. $D_t \sim \tau_{r2}^{-1}$ show evident decoupling below 280 K but is almost restored by taking the variation of a into account. Overall, the two variants $D_r \sim T/\eta$ and $D_r \sim T/\tau_t$ are usually not good substitutes for the original SED relation, and they should be critically and quantitatively evaluated when being used to inspect the validity of the SED relation. Besides supercooled TIP5P water, the inconsistency between the original SED relation and its variants may appear in other supercooled liquids. The effective hydrodynamic radius a is an important parameter for the validity of the SED relation and its variation with conditions should be seriously evaluated when testing the SED relation.

Acknowledgments

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References

[1] Debye P 1929 *Polar Molecules* (New York: The Chemical Catalog Company))
[2] Kawasaki T and Kim K 2019 *Scientific Reports* **9** 8118
[3] Kawasaki T and Kim K 2019 *Journal of Statistical Mechanics: Theory and Experiment* **2019** 084004
[4] Mazza M G, Giovambattista N, Stanley H E and Starr F W 2007 *Phys. Rev. E* **76** 031203
[5] Kivelson D and Kivelson S A 1989 *J. Chem. Phys.* **90** 4464
[6] Netz P A, Buldyrev S V, Barbosa M C and Stanley H E 2006 *Phys. Rev. E* **73** 061504
[7] Lombardo T G, Debenedetti P G and Stillinger F H 2006 *J. Chem. Phys.* 125
[8] Dehaoui A, Issenmann B and Caupin F 2015 *Proc. Natl. Acad. Sci. USA* **112** 12020
[9] Fujara F, Geil B, Sillescu H and Fleischer G 1992 *Zeitschrift für Physik B Condensed Matter* **88** 195
[10] Stanley H E, Barbosa M C, Mossa S, Netz P A, Sciortino F, Starr F W and Yamada M 2002 *Physica A* **315** 281
[11] Netz P A, Starr F W, Barbosa M C and Stanley H E 2002 *Physica A* **314** 470
[12] Netz P A, Starr F, Barbosa M C and Stanley H E 2002 *J. Mol. Liq.* **101** 159
[13] Shi R, Russo J and Tanaka H 2018 *Proc. Natl. Acad. Sci. USA* **115** 9444
[14] Debenedetti P G 2003 *J. Phys.: Condens. Matter* **15** R1669
[15] Shi R, Russo J and Tanaka H 2018 *J. Chem. Phys.* **149** 224502
[16] Cicerone M T and Ediger M D 1996 *J. Chem. Phys.* **104** 7210
[17] Kivelson D and Miles D 1988 *J. Chem. Phys.* **88** 1925
[18] Diezemann G, Sillescu H, Hinze G and Böhmer R 1998 *Phys. Rev. E* **57** 4398
[19] De Michele C and Leporini D 2001 *Phys. Rev. E* **63** 036702
[20] Becker S R, Poole P H and Starr F W 2006 *Phys. Rev. Lett.* **97** 055901
[21] Rössler E 1990 *Phys. Rev. Lett.* **65** 1595
[22] Thirumalai D and Mountain R D 1993 *Phys. Rev. E* **47** 479

[23] Lee S H and Rasaiah J C 1994 *J. Chem. Phys.* **101** 6964
[24] Lee S H and Rasaiah J C 1996 *The Journal of Physical Chemistry* **100** 1420
[25] Ren G, Chen L and Wang Y 2018 *Phys. Chem. Chem. Phys.* **20** 21313
[26] Hubbard J and Onsager L 1977 *J. Chem. Phys.* **67** 4850
[27] Varela L M, García M and Mosquera V C 2003 *Phys. Rep.* **382** 1
[28] Ren G and Wang Y 2021 *Phys. Chem. Chem. Phys.* **23** 24541
[29] Mahoney M W and Jorgensen W L 2000 *J. Chem. Phys.* **112** 8910
[30] Berendsen H J C, van der Spoel D and van Drunen R 1995 *Comput. Phys. Commun.* **91** 43
[31] Van Der Spoel D, Lindahl E, Hess B, Groenhof G, Mark A E and Berendsen H J 2005 *J. Comput. Chem.* **26** 1701
[32] Essmann U, Perera L, Berkowitz M L, Darden T, Lee H and Pedersen L G 1995 *J. Chem. Phys.* **103** 8577
[33] Nosé S 1984 *J. Chem. Phys.* **81** 511
[34] Hoover W G 1985 *Phys. Rev. A* **31** 1695
[35] Mazza M G, Giovambattista N, Starr F W and Stanley H E 2006 *Phys. Rev. Lett.* **96** 057803
[36] Shi R and Wang Y 2013 *J. Phys. Chem. B* **117** 5102
[37] Kämerer S, Kob W and Schilling R 1997 *Phys. Rev. E* **56** 5450
[38] Mishra C K and Ganapathy R 2015 *Phys. Rev. Lett.* **114** 198302