Breakdown of the Stokes-Einstein Relation in Supercooled Water

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Available at: https://works.bepress.com/fstarr/9/
Relation between the Widom line and the breakdown of the Stokes–Einstein relation in supercooled water

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Contributed by H. E. Stanley, March 24, 2007 (sent for review October 29, 2006)

Supercooled water exhibits a breakdown of the Stokes–Einstein relation between the diffusion constant D and the alpha relaxation time $\tau_\alpha$. For water simulated with two different potentials, TIPSP and ST2, we find that the temperature of the decoupling of diffusion and alpha relaxation correlates with the temperature of the maximum in specific heat that corresponds to crossing the Widom line $T_W(P)$. Specifically, we find that our results for $D\tau_\alpha/T$ collapse onto a single “master curve” if temperature is replaced by $T - T_W(P)$. We further find that the size of the mobile molecule clusters (dynamical heterogeneities) increases sharply near $T_W(P)$. Moreover, our calculations of mobile particle cluster size $n(t)^*$ for different pressures, where $t^*$ is the time for which the mobile particle cluster size largest, also collapse onto a single master curve if $T$ is replaced by $T - T_W(P)$. The crossover to a more locally structured low density liquid (LDL) as $T \rightarrow T_W(P)$ appears to be well correlated both with the breakdown of the Stokes–Einstein relation and with the growth of dynamic heterogeneities. Our results are consistent with the possibility that the breakdown of the SE relation in supercooled water at low pressures is associated with the hypothesized liquid–liquid phase transition.

(14, 15). One basic relation among dynamic properties is the Stokes–Einstein (SE) relation $D = \frac{k_B T}{6\pi \eta a}$, where $D$ is the diffusion constant, $T$ is the temperature, $k_B$ is the Boltzmann constant, $\eta$ is the viscosity, and $a$ is the effective hydrodynamic radius of a molecule. This expression provides a relation between mass and momentum transport of a spherical object in a viscous medium. The SE relation describes nearly all fluids at $T \geq (1.2–1.6) T_g$, where $T_g$ is the glass transition temperature. Because the hydrodynamic radius $a$ is roughly constant, $D\eta/T$ is approximately independent of $T$ (16–18). However, in most liquids, for $T \leq (1.2–1.6) T_g$, $D\eta/T$ is no longer a constant (19–28). For the case of water, the breakdown of the SE relation occurs at $\approx 1.8 T_g$ in the same temperature region in which many of the unusual thermodynamic features of water occur (5, 11, 14, 29).

Our aim is to evaluate to what degree the SE breakdown can be correlated with the presence of thermodynamic anomalies and the onset of spatially heterogeneous dynamics, and how these features relate to the location of the Widom line (22, 30–33). From prior studies of water, we can already form an expectation for the correlation between the SE breakdown and the Widom line by combining three elements: (i) the Widom line is approximately known from the extrapolated power-law divergence of $K_T$ (34); (ii) the locus of points $T_W(P)$ where $D$ extrapolates to zero is also known, and nearly coincides with $T_W(P)$ at low pressures (see Fig. 1 of ref. 12); (iii) the SE relation has been found to fail in liquids generally at the temperature $T_W(P)$ (35). Combining these three results, one might not be surprised if the breakdown of the SE relation should occur near the Widom line for $P < P_c$, and it should continue to follow $T_W(P)$ for $P > P_c$. We will see that our results are consistent with this expectation, but reveal some unexpected insights.

Our results are based on molecular dynamics (MD) simulations of $N = 512$ water-like molecules interacting via the TIPSP potential (36, 37), which exhibits a LL critical point at approximately $T_c \approx 217$ K and $P_c \approx 340$ MPa (37, 38). We carry out simulations in the isothermal isobaric ensemble for three different pressures $P = 0$, 100, and 200 MPa, and for temperatures $T$ ranging from 320 K down to $230$ K for $P = 0$ and 100 MPa, and down to 220 K for 200 MPa. We also analyze MD simulations of $N = 1,728$ water-like molecules interacting via the ST2 potential.


The authors declare no conflict of interest.

Abbreviations: LL, liquid-liquid; SE, Stokes–Einstein.
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(39, 40), which displays a LL critical point at \( T_C = 245 \) K and \( P = 180 \) MPa (41). The simulations for the ST2 model are performed at fixed volume and temperature (40).

**Results**

We explore the possible relation between the Widom line and the breakdown of the SE relation (Eq. 1). To locate the Widom line, we first analyze the isobaric heat capacity \( C_P \) for the TIP5P (Fig. 1a) and the ST2 (Fig. 1b) models.

We next calculate the diffusion constant via its asymptotic relation to the mean-squared displacement,

\[
D = \lim_{t \to \infty} \frac{\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{6t},
\]

where \( \mathbf{r}(t) \) is the position of oxygen \( j \) at time \( t \). It is difficult to accurately calculate the viscosity \( \eta \) in simulations, so we instead calculate the alpha relaxation time \( \tau_\alpha \) (which is expected to have nearly the same \( T \) dependence as \( \eta \) as the time at which the coherent intermediate scattering function

\[
F(q, t) = \frac{\langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle}{\langle \rho(\mathbf{q}, 0) \rho(-\mathbf{q}, 0) \rangle},
\]

decays by a factor of \( e \). Here \( \rho(\mathbf{q}, t) = \sum_j \exp(-i\mathbf{q}\cdot\mathbf{r}_j(t)) \) is the Fourier transform of the density at time \( t \), \( \mathbf{r}_j(t) \) is the position of oxygen \( j \) at time \( t \), \( \mathbf{q} \) is a wave vector and the brackets denote an average over all \( |\mathbf{q}| = q \) and many equilibrium starting configurations. We calculate \( F(q, t) \) at the value of \( q \) corresponding to the first maximum in the static structure factor \( F(q, 0) \). It is important that we use the coherent scattering function (as opposed to the incoherent, or self-scattering function), because we want to capture collective relaxation that contributes to \( \eta \). We expect that \( \tau_\alpha \) calculated this way would behave similar to \( \eta \) and hence the SE relation (Eq. 1) can be written as

\[
\frac{D\tau_\alpha}{T} \text{ = constant.}
\]

**Fig. 2.** \( \tau_\alpha \) and \( D \) as functions of \( T \) for \( P = 0 \), 100, and 200 MPa for the TIP5P model.

**Fig. 3.** Test for the TIP5P model of the key result of this paper: that the SE breakdown at low pressures is correlated with crossing the Widom line. (a) \( D\tau_\alpha/T \) as a function of \( T \) for \( P = 0 \) MPa, 100 MPa and 200 MPa for the TIP5P model. For all panels, \( D\tau_\alpha/T \) is scaled by its high \( T \) value to facilitate comparison of the different systems. (b) \( D\tau_\alpha/T \) as a function of \( T - T_W \) for TIP5P. The curves for different pressures overlap on the same master curve when \( T \) is replaced by \( T - T_W \).
We see that both $r_m$ and $D$ for the TIP5P (Fig. 2) display rapid changes at low $T$. Fig. 3a shows $D/r_m$ for different $T$ at $P = 0$ MPa (a) and different $P$ at $T = 230$ K (b). (c) $r(r^*)$ for $P = 0$, 100, and 200 MPa. (d) $r(r^*)$ as a function of $T - r_m(P)$ for three different $P$. All these plots are for the TIP5P model.

Fig. 4. Pressure and temperature dependence of clusters ("dynamic heterogeneities") that form at low temperatures and become more pronounced as the Widom line is approached. Mobile particle cluster size $r(r^*)_m$ for different $T$ at $P = 0$ MPa (a) and different $P$ at $T = 230$ K (b). (c) $r(r^*)_m$ for $P = 0$, 100, and 200 MPa. (d) $r(r^*)_m$ as a function of $T - r_m(P)$ for three different $P$. All these plots are for the TIP5P model.

Because we find a correlation between $T_w(P)$ and the breakdown of the SE relation, the hypothesized connection between the SE breakdown and the onset of dynamical heterogeneities (DH) suggests a connection between $T_w(P)$ and the onset of DH. To investigate the behavior of the dynamic heterogeneities, we study the clusters formed by the 7% most mobile molecules (43), defined as molecules with the largest displacements during a certain interval of time $t$. The clusters of the highly mobile molecules are defined as follows. If in a pair of mobile molecules determined in the interval $[t_0, t_0 + 1]$, two oxygens at time $t_0$ are separated by less than the distance corresponding to position of the first minimum in the pair correlation function (0.315 nm in TIP5P and 0.350 nm in ST2), this pair belongs to the same cluster.

The weight-averaged mean cluster size

$$
(r(t))^w = \frac{\langle r^2(t) \rangle}{\langle r(t) \rangle},
$$

measures the average cluster size to which a randomly chosen molecule belongs, where $r(t)$ is the number-averaged mean cluster size. We show $r(t)^w$ in Fig. 4 for TIP5P as a function of observation time interval $t$ for different $T$ at $P = 0$ MPa (Fig. 4a). The behavior at higher $P$ is qualitatively the same (Fig. 4b). At low $T$, $r(t)^w$ has a maximum at the time $r^*$ associated with the breaking of the cage formed by the neighboring molecules (see (44) and the references therein). Both the magnitude and the time scale $r^*$ of the peak grow as $T$ decreases. At high $T$, this peak merges and becomes indistinguishable from a second peak with fixed characteristic time $\tau = 0.5$ ps. By evaluating the vibrational density of states, we associate this feature with a low frequency vibrational motion of the system, probably the O–O–O bending mode (45).

To probe the temperature dependence of $r(t)^w$, we plot the peak value $r(r^*)_m$ in Fig. 4c as a function of $T$ for $P = 0$, 100, and 200 MPa for the TIP5P model. At high $T$, $r(r^*)_m$ is nearly constant, because at high $T$, clusters result simply from random motion of the molecules. Upon cooling near the Widom line, $r(r^*)_m$ increases sharply. When $r(r^*)_m$ is plotted as a function of $T - T_w(P)$ (see Fig. 4d), we find that (similar to the behavior of $D(r^*)$) the three curves for $P = 0$, 100, and 200 MPa overlap, and it is apparent that the pronounced increase in $r(r^*)_m$ occurs for $T \approx T_w(P)$.

Finally, we consider the correspondence between DH and static structural heterogeneity in the supercritical region; this region is characterized by large fluctuations spanning a wide range of structures, from HDL-like to LDL-like. To quantify these structural fluctuations, we calculate for the TIP5P model the temperature derivative of a local tetrahedral order parameter $Q$ (46). In Fig. 5, we show $|\langle Q \rangle_0 T|_l$ at different $T$ for $P = 0$, 100, and 200 MPa, and find maxima (10) at $T_w(P)$ (7, 47). The maxima in $|\langle Q \rangle_0 T|_l$ indicates that the change in local tetrahedrality is maximal at $T_w(P)$, which should occur when the structural fluctuations of LDL-like and HDL-like components is largest. We see that the growth of the dynamic heterogeneity coincides with the maximum in fluctuation of the local environment. Also, because $Q$ quantifies the orientational order, the fact...
that we find that \(\langle\partial Q/\partial T\rangle_P\) has a maximum at approximately the same temperature where \(C_P = T(\partial S/\partial T)_P\) has a maximum, supports the idea that water anomalies are closely related to the orientational order present in water.

To further test whether the breakdown of the SE relation in water is associated with the Widom line, we study another model of water, ST2, which displays a LL phase transition at low temperatures (6). Fig. 6a shows \(D_{\tau_w} / T\) as a function of \(T\) for the ST2 model. At high \(T\), \(D_{\tau_w} / T\) remains approximately constant. At low \(T\), \(D_{\tau_w} / T\) increases, indicating a breakdown of the SE relation (2), which, similar to the case for the TIP5P model, occurs near the Widom line \(T_w(P)\). For \(P < P_c\), we plot \(D_{\tau_w} / T\) against \(T - T_w(P)\) (Fig. 6b) and we again find, similar to the TIP5P model, all of the curves for different pressures overlap within the limits of accuracy, suggesting that \(D_{\tau_w} / T\) is a function only of \(T - T_w(P)\).

To alternatively quantify the temperature where the SE relation breaks down, we use the observation that by plotting parametrically \(\log D\) as a function of \(\log (\tau_w/T)\), one can identify the crossover temperature \(T_c(P)\) between the two regions by the intersection of the high \(T\) SE behavior and the low \(T\) “fractional SE behavior” \(D(\tau_w / T)^\alpha = \text{const}\) (19, 40). Fig. 7 shows the locus

**Fig. 5.** \(\langle\partial Q/\partial T\rangle_P\) as a function of \(T\) for \(P = 0, 100,\) and 200 MPa. We note that, although the temperature of the maximum decreases with increasing pressure, the value \(\langle\partial Q/\partial T\rangle_P\) at the maximum for \(P = 200\) MPa is lower than at lower pressures.

**Fig. 6.** Test for the ST2 model that the SE breakdown is correlated with crossing the Widom line at low pressures. (a) Analog of Fig. 3a for the ST2 model. The data for \(P > P_c\) are shown using thick dotted and dashed curves, whereas the data for \(P < P_c\) are shown in thin curves. For all panels, \(D_{\tau_w} / T\) is scaled by its high \(T\) value to facilitate comparison of the different systems. (b) Analog of Fig. 3b for the ST2 model including the experimental data of \(D_{\tau_w} / T\) (15, 48–50).

**Fig. 7.** Locus in \(P-T\) plane of \(C_{\text{max}}\) and crossover temperature \(T_c(P)\) for the ST2 model. Filled circle denotes the liquid–liquid critical point \((T_c, P_c)\) in the ST2 model (41). The behavior of \(T_c(P)\) changes dramatically below \(P_c\), suggesting a correlation between the Widom line and the breakdown of the SE relation for \(P < P_c\). \(T_c(P)\) for \(P > P_c\) is shown in dotted line.

**Fig. 8.** Dynamic heterogeneities in the ST2 model of water. (a) \(n(t)\) as a function of \(t\) at 5 K intervals for \(P = 0.63\) g/cm\(^3\) from 265 to 300 K. The bold line shows the \(T = 280\) K isotherm where the constant volume specific heat \(C_V\) has a maximum. (b) \(n(t^{*})\) as a function of \(T\) for \(P = 0.63\) g/cm\(^3\). We indicate the temperature at which \(C_V\) has a maximum by a vertical arrow. The maximum of \(C_V\) occurs in the same region where other response functions, such as \(C_h\), have maxima.
of $T_x$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in the P–T plane of the ST2 model. We confirm that the same collapse of $D/H$ in

Discussion and Summary

We have shown that the breakdown of the SE relation for $P < P_c$ can be correlated with the Widom line emanating from the LL critical point. In particular, rescaling $T$ by $T - T_w(P)$ yields data collapse of $Dw/T$ for different pressures. Rapid structural changes occur for $T$ near $T_w(P)$, where larger LDL “patches” emerge upon cooling (52–54). The size of the dynamic heterogeneities also increases sharply as the Widom line is crossed. The breakdown of the SE relation can be understood by the fact that diffusion at low $T$ is dominated by regions of fastest moving molecules (DH), whereas the relaxation of the system as a whole is dominated by the slowest moving molecules. Consistent with this, we find that the growth of mobile particle clusters occurs near the Widom line and also near the breakdown of the SE relation for $P < P_c$. Thus, the SE breakdown and sharp growth in dynamic heterogeneities in water are consistent with the LL critical point hypothesis (2–6). Our results are also consistent with recent experimental findings in confined water (8, 13, 14).

We thank C. A. Angell, S.-H. Chen, G. Frankenze, J. M. Hehlert Sengers, S. Han, L. Liu, M. G. Mazzia, F. Sciortino, M. Sperl, K. Stokely, B. Widom, L. Xu, Z. Yan, E. Zaccarelli, and especially S. Sastry for helpful discussions and the National Science Foundation Chemistry Program for support. We also thank the Boston University Computation Center, Yeshiva University, and ACEnet for allocation of computational time.