

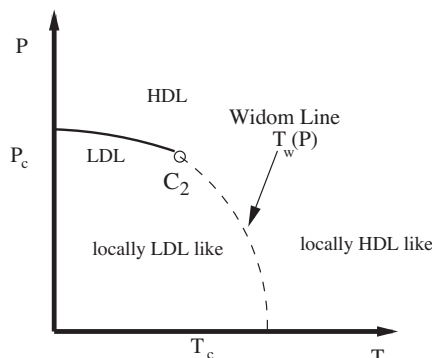
# Breakdown of the Stokes–Einstein relation in supercooled water

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Almost everyone would agree that water is probably the most important liquid for life, but few fully appreciate that water is also the most puzzling among the liquids. Water is anomalous in many ways compared with simple liquids. One of the most well known anomalies is the decrease of density of water upon cooling below 4°C. Other anomalies of water include the increase of specific heat and compressibility upon cooling.

Apart from the thermodynamic anomalies, the dynamics of water also displays surprising properties, such as the increase of diffusivity and decrease of viscosity upon compression (1) and a breakdown of the Stokes–Einstein (SE) relation (2) in supercooled water. The SE relation is a hydrodynamic equation relating the diffusivity,  $D$ , the temperature,  $T$ , and relaxation time,  $\tau$  (assuming that  $\tau$  is proportional to the viscosity). Specifically, it states that  $D$  is proportional to  $T$  and inversely proportional to the relaxation time  $\tau$ . Hence, the product  $D\tau/T$  should be temperature independent. This important hydrodynamic relation is obeyed by many liquids (3, 4) at relatively high temperatures, but it usually fails to describe the dynamics in supercooled states. Breakdown of the SE relation has also been seen in simple liquids near the glass transition (3–6). It was hypothesized that the presence of large dynamic heterogeneities might cause the breakdown of SE relation (7, 8). Dynamic heterogeneities in liquids are the consequence of highly mobile molecules forming a cluster and moving cooperatively. The size of these spatially heterogeneous dynamical regions increases as the temperature is decreased. Dynamic heterogeneities facilitate diffusion (and local structural relaxation) but do not facilitate the relaxation of the entire system. Hence, the large size of these dynamic heterogeneities should “decouple” diffusion and relaxation so  $D\tau/T$  is no longer a constant. The presence of dynamic heterogeneities in supercooled liquids has been verified by both experiments (6, 9) and computer simulations (10). In molecular liquids as well as in colloidal suspensions, the glass transition is followed by a sharp growth in dynamic heterogeneities (6, 9). Hence, it is common to assume that SE breakdown is related to glass transition

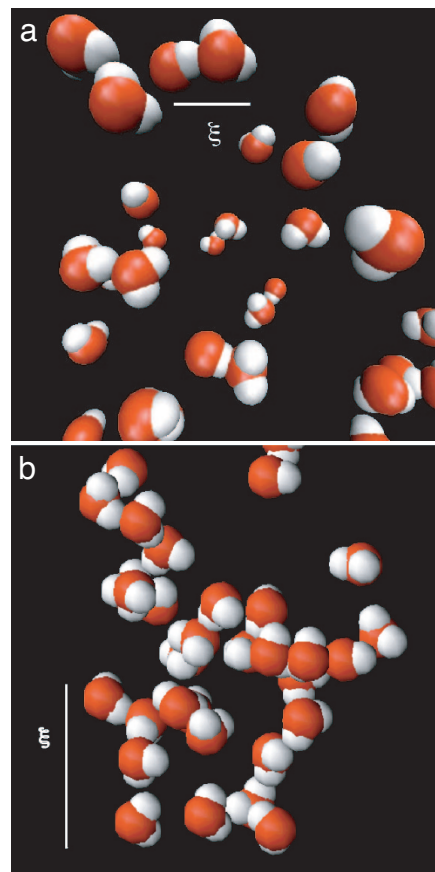


**Fig. 1.** Low-temperature liquid–liquid critical point  $C_2$  of water and corresponding Widom line. The coexistence line between LDL and HDL is represented by a solid curve, whereas the Widom line  $T_w(P)$  emanating from the liquid–liquid critical point is represented by a dashed curve. Widom line separates the water with HDL-like feature at high temperature from the LDL-like feature at low temperatures.

because the sizes of dynamic heterogeneities grows sharply near the glass transition (3, 4, 8, 11, 12).

In this issue of PNAS, the work by Chen *et al.* (13) on water confined in nanopores sheds light on the long standing issue of decoupling of diffusion and structural relaxation in supercooled water. They measure the diffusivity  $D$  by NMR experiments and the relaxation time  $\tau$  by neutron scattering experiments for temperatures down to  $-83^\circ\text{C}$  or 190 K. Confinement prevents the freezing of water below the bulk homogeneous nucleation temperature of  $-38^\circ\text{C}$ . Chen *et al.* find that the product  $D\tau/T$  is a constant at higher temperatures but increases sharply at low temperatures, signaling the breakdown of the SE relation. They further find that the breakdown of the SE relation occurs well above water’s glass transition temperature (13). Hence, their experiments call out for a scenario different from that believed for simple colloidal suspensions and liquids. A possible clue for this new scenario arises from the fact that Chen *et al.* discover that the SE relation breaks down at the same temperature where the behavior of the dynamics of water changes from non-Arrhenius at high temperatures to Arrhenius at low temperatures, which is estimated to be  $\approx 136$  K (14).

One possible interpretation of the breakdown of SE relation in super-



**Fig. 2.** Effect on the size of dynamic heterogeneities on crossing the Widom line  $T_w(P)$ . Clusters of 7% most mobile molecules showing the dynamic heterogeneities for  $T > T_w(P)$  (a) and for  $T < T_w(P)$  (b). The characteristic size of the dynamic heterogeneities  $\xi$  increases sharply upon crossing  $T_w(P)$  from high temperature side to low temperature side because of the emergence of a locally LDL-like structure.

cooled water consistent with experimental results (15) is the presence of a hypothesized liquid–liquid critical point (16, 17) in the deep supercooled region of water. The liquid–liquid critical point gives rise to a Widom line  $T_w(P)$  (see Fig. 1), the locus of the correlation length maxima, which emanates from the liquid–liquid critical point and extends into the one-phase region

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(18–20). When water is cooled along a constant pressure path below the critical point, it changes from a predominance of a “local high-density liquid (HDL) structure” to a predominance of a “local low-density liquid (LDL) structure” upon crossing the Widom line. Two consequences of this interpretation are as follows.

- The dynamics in the HDL-like region above  $T_W(P)$  is expected to be non-Arrhenius, whereas the dynamics in LDL-like region is expected to be Arrhenius. These expectations are borne out by the experiments (14, 20, 21).
- In the HDL-like region diffusion is a cooperative phenomenon but with

small length and time scales of dynamic heterogeneities, so we expect the SE relation to hold, whereas in the LDL-like region, emergence of a large, more ordered local structure below  $T_W(P)$  causes a growth of dynamic heterogeneities. Hence, in the LDL-like region, diffusion would be more cooperative compared with the HDL-like region. Indeed, we find that the size of the dynamic heterogeneities has a sharp increase at  $T_W(P)$ . Fig. 2 shows the formation of clusters by most mobile molecules of water in computer simulations above (Fig. 2a) and below (Fig. 2b)  $T_W(P)$ . The size  $\xi$  of these dynamic heterogeneities in-

creases as the temperature is lowered and has a sharp increase at the Widom line temperature  $T_W(P)$ , and thus a breakdown of the SE relation.

In summary, the discovery of Chen *et al.* (13) that the breakdown of the SE relation in supercooled water does not occur near the glass transition temperature raises the question of what causes the SE breakdown in supercooled water. It is possible that the cause is crossing the Widom line, which arises from the liquid–liquid critical point.

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