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Gilles Tarjus Daniel Kivelson

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# Breakdown of the Stokes–Einstein relation in supercooled liquids

Gilles Tarjus

Laboratoire de Physique Theorique des Liquides, Universite Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05, France

Daniel Kivelson

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

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The Stokes–Einstein and Stokes–Einstein–Debye relations hold well in nonsupercooled liquids; however, sizeable deviations from the former appear in supercooled liquids, leading to a “decoupling” of translational diffusion from viscosity and reorientational relaxation. We attribute this breakdown and this “decoupling” to the existence of structured domains in the supercooled liquid. © 1995 American Institute of Physics.

For nearly a century, a pillar of insight into the molecular dynamics of liquids has been the brilliantly inspired Stokes–Einstein (SE) relation,<sup>1</sup>

$$D\eta/k_B T = \frac{1}{3} \pi d, \quad (1)$$

where  $D$  is the translational diffusion constant,  $k_B$  the Boltzmann constant,  $T$  the temperature,  $\eta$  the coefficient of shear viscosity, and  $d$  a  $T$ -independent length closely associated with the diameter of a molecule. For the reorientational diffusion correlation time  $\tau_l$ , which describes relaxation of spherical harmonics of order  $l$ , there is a closely related relation, often called the Stokes–Einstein–Debye (SED) relation,<sup>2</sup> which is subject to similar conditions:

$$\tau_l k_B T / \eta = 6v/l(l+1), \quad (2)$$

where  $v$  is closely related to the molecular volume. In the Brownian (large) particle limit, the connection between both  $d$  and  $v$  and the size, shape, and boundary conditions of the diffusing particle can be specified.<sup>3–10</sup> Equations (1) and (2) can be combined:

$$D\tau_l = 2v/\pi dl(l+1). \quad (3)$$

The feature of most interest here is the fact that the right sides of all three equations are independent of  $T$ .

The success of these relationships is astonishing once one recognizes that for them to hold rigorously they should be applied, not to molecules, but to “Brownian” particles that are large compared to solvent molecules. Indeed, difficulties with these expressions, particularly with Eqs. (2) and (3), have been identified in cases where the diffusing particle is not appreciably larger than the solvent molecules.<sup>8,10</sup> However, on the whole, these relations have been very successfully applied, particularly if  $d$  and  $v$  are taken as slightly adjustable molecular parameters. Of course, slight  $T$  dependences of the right sides of Eqs. (1)–(3) are easily rationalized.<sup>11</sup> Recently, however, evidence has mounted of sizeable and systematic deviations from the Stokes–Einstein relation, Eq. (1), as well as from Eq. (3) in supercooled liquids.<sup>12–14</sup> It is these deviations, specifically associated with the properties of supercooled liquids, that are denoted “breakdown of the Stokes–Einstein relation,” or “decoupling” from  $\eta$ , or else “decoupling” between translational

and rotational diffusion; it is this phenomenon that we study here and for which we offer a different explanation than previously suggested.<sup>12,13,15</sup>

The most striking feature of supercooled liquids is that somewhat below the melting point ( $T_m$ ), the viscosity ( $\eta$ ), and the structural relaxation time ( $\tau_\alpha$ ) increase dramatically with slight decreases in  $T$ .<sup>16</sup> In many treatments, this is attributed to the formation of some species of correlated regions or domains.<sup>17–28</sup> (A bibliography and excellent brief history of domain-models applied to supercooled liquids is given in Ref. 28.) Thus, above some temperature  $T^*$ , which should be close to  $T_m$ , the liquid is “ordinary” and does not form domains, but below this  $T^*$  such domains dominate many of the relaxation processes. If a domain volume is given by  $L^3$ , the distribution of domain sizes can be characterized by a normalized function  $\rho(L)$  such that  $\rho(L)L^2 dL$  represents the probability of finding a molecule in a domain of size between  $L$  and  $L+dL$ . If the domain structures relax independently, and if the structural relaxation time of a domain of size  $L$  is described by

$$\tau_L = \tau_\infty \exp[E(L)/k_B T], \quad (4)$$

where  $\tau_\infty$  is a molecular, temperature-independent (or at most weakly temperature-dependent) relaxation time, and  $E(L)$  is a size-dependent activation free energy which goes to zero when  $L$  goes to zero, then the structural (or  $\alpha$ -) relaxation time for the liquid sample is given by

$$\tau_\alpha = \tau_\infty \int_0^\infty dL L^2 \rho(L) \exp[E(L)/k_B T]. \quad (5)$$

For  $T > T^*$ , there are no domains, so  $\rho(L) = \delta(L^3)/3$  and  $\tau_\alpha = \tau_0$ , where  $\tau_0 = \tau_\infty \exp[E(0)/k_B T]$  is associated with the relaxation time of molecules not in domains.

We postulate that reorientational relaxation of solvent molecules, or of probe molecules that are no larger than the most probable domain size, occurs independently in the various domains and that it is controlled by domain restructuring, so that  $\tau$  is proportional to  $\tau_\alpha$ . The viscosity is proportional to the stress-relaxation time which is also expected to be proportional to domain restructuring, i.e., to  $\tau_\alpha$ . It then follows that the (SED) relation, Eq. (2), holds at  $T$ 's both above and below  $T^*$ . Of course, if the molecular  $\tau_\infty$ 's are somehow different for the different processes, then break-

down of the SED relation can occur even at temperatures above  $T^*$ , but such effects do not constitute a breakdown associated specifically with the fact that the liquid is supercooled.<sup>11</sup> Note, as indicated in Eq. (2), that at  $T$ 's above  $T^*$ , i.e., not in the supercooled liquid, the  $\tau_l$  is proportional to  $\eta/T$ , not simply to  $\eta$ ; we interpret this as indicating that the *molecular*  $\tau_\infty$  for rotations is proportional to  $T^{-1}$  times that for stress relaxation.

Translational diffusion is different than reorientational relaxation because it may involve the motion of molecules over many domains. Actually, when measured by recording the relaxation of concentration fluctuations in a forced Rayleigh scattering experiment,<sup>13</sup> translational diffusion occurs over the scattering wavelength  $q^{-1}$  which is very large compared to the mean domain size  $L_D$ ; therefore, on the experimental time scale, a given molecule diffuses through a great number of different domains. Just like rotational diffusion, translational diffusion across a *given* domain of size  $L$  is controlled by the domain restructuring, so that the diffusion coefficient within the domain,  $D(L)$ , is proportional to  $T/\eta(L)$ , where  $\eta(L) \propto \exp[E(L)/k_B T]$  is the local domain viscosity. However, contrary to rotational diffusion (which is completed within a single domain), translational diffusion involves passage through different domains, which leads to different averaging over the distribution  $\rho(L)$ . The simplest model which encompasses the physics described earlier is a random walk in a random environment formed by the independently relaxing domains. The diffusion coefficient,  $D(\mathbf{r})$ , varies in space in such a way that it stays constant within a domain,  $D(\mathbf{r})=D(L)$  if  $\mathbf{r}$  belongs to a domain of size  $L$ , and changes abruptly at the boundary between two domains. It has been shown<sup>29</sup> that such a process converges asymptotically to regular Brownian motion with a diffusion constant given by

$$D = \langle D(\mathbf{r}) \rangle - \frac{1}{6} \int_0^\infty dt \langle \nabla D(\mathbf{r}) \cdot \nabla D(\mathbf{r}(t)) \rangle, \quad (6)$$

where the average  $\langle \rangle$  is taken for an isotropic, translationally invariant, ergodic, bounded distribution. [The process is that of a random walk in a random environment; ergodic means that the whole space of environments is fully sampled, and bounded means that  $D(r) < \infty$  and that the effect of the regions of  $D(\mathbf{r})=0$  be of measure zero.] Although in one-dimension the second term in Eq. (6) can never be neglected, and, in fact, the expression leads to  $D = \langle D(\mathbf{r})^{-1} \rangle^{-1}$ , in three dimensions, where the correlation between the position of the random walker at sequential times decays rapidly, the second term may be negligible. In the model described here, where  $D(\mathbf{r})$  changes only at domain boundaries, one expects the effect of gradients to be minimal so that Eq. (6) becomes

$$\begin{aligned} D \approx \langle D(\mathbf{r}) \rangle &= \int_0^\infty dL L^2 \rho(L) D(L) \\ &= D_0 \int_0^\infty dL L^2 \rho(L) \exp[-E(L)/k_B T], \quad (7) \end{aligned}$$

where  $D_0$  is a molecular diffusion constant. Note that the averaging over domains for translational diffusion is quite different than that for rotational diffusion and stress relax-

ation; thus the simple existence of domains of various size leads to a breakdown of the SE relation, Eqs. (1) and (3), at  $T$ 's below  $T^*$ , i.e., for supercooled liquids. Such a breakdown has been observed, and can amount to a change of 2 orders of magnitude of the right side of Eq. (3).<sup>12–14</sup> As already explained, at  $T > T^*$  there are no domains, and so the SE relation should hold.

The results discussed earlier require only that the relaxation properties of supercooled liquids at  $T$ 's below  $T^*$  be a consequence of the existence of structured, polydisperse domains, and that the restructuring activation energy of a domain be a function of its size  $L$ . The restructuring could involve the breakup of the domain or, quite possibly,<sup>2,4</sup> merely the relaxation of a local domain order parameter. To obtain quantitative results with Eqs. (5) and (7), we need a theory that yields an expression for  $\rho(L)$  and for  $E(L)$ .

Previous explanations for the SE breakdown also introduced domains, but domains with very special properties designed specifically to describe this phenomenon. In one model, the domains are fluidlike channels through which a particle can readily diffuse translationally without rotating appreciably.<sup>13</sup> In another model,<sup>15</sup> rotations take place instantaneously within large, but sparse, fluidized domains, so that while rotational relaxation frequencies are determined by the domain appearance rate, translational diffusion depends also upon the domain lifetimes because diffusion, although rapid within these domains, is interrupted by solidification of the domain before completion of transversal.

A recently introduced theory<sup>24,25</sup> envisages the liquid at  $T < T^*$  as composed of self-forming frustration-limited domains which relax through the creation and movement of walls. In this theory the activation energy  $E(L)$  is proportional to  $\sigma L^2$ , and both the surface tension  $\sigma$  and the square  $L_D^2$  of the most probable domain size are proportional to  $|T^* - T|^{4/3}$ ; with decreasing  $T$  the distribution of domain sizes  $\rho(L)$  becomes more peaked around  $L_D$ . This model, in contrast to the others mentioned earlier, was not developed specifically to rationalize the SE breakdown;<sup>24–26</sup> together with Eqs. (5) and (7), it leads to a decrease of the translational diffusion constant  $D$  with decreasing temperature that is *slower than predicted by the SE relation*, as is indeed observed experimentally.<sup>12,13</sup>

The material above completes the discussion of the Stokes–Einstein breakdown in supercooled liquids, the central topic of this article. However, we would also like to add a few words about the applicability of the model of structured domains to some closely related phenomena.

Although it seems reasonable to assume that the structural relaxation function for a single domain of size  $L$  should be exponential, if there is a distribution of domain sizes, the observed structural relaxation function in supercooled liquids would be nonexponential, perhaps stretched exponential. If, as postulated, rotational relaxation is tightly coupled to structural relaxation it, too, would be nonexponential; this nonexponential behavior is indeed found and it increases as  $T$  decreases.<sup>28,30</sup> We believe this trend with  $T$  occurs because as  $T$  decreases and domain sizes grow, the spread in domain sizes decreases more slowly than does the spread in activation energies.<sup>24,25</sup> However, studies of the rotational relax-

ation of probe molecules in supercooled liquids indicate that the nonexponentiality decreases with increasing probe size, a result to be expected as the size of the probe molecule approaches and exceeds the most probable size of the structured domains in the supercooled liquid.<sup>28</sup> On the basis of their studies, Cicerone *et al.*<sup>28</sup> argue that domains in supercooled orthoterphenyl, if they exist, must be less than 2.5 nm; we point out that estimates of cluster size according to the model of frustration-limited domains are indeed small,<sup>24,25</sup> only small clusters being needed to induce a gigantic increase in relaxation time.

In contrast to the nonexponentiality observed in rotational relaxation, the relaxation of concentration fluctuations measured by forced Rayleigh scattering is exponential.<sup>13</sup> This is to be expected because, as already mentioned, it involves translational diffusion over the scattering wavelength,  $q^{-1}$ , which is large compared to the mean domain size  $L_D$ . As a consequence, during the process a given diffusing particle resides in all different domains, and it depends upon an averaged or “motionally narrowed” relaxation function. This should lead to exponential,  $\exp(-q^2Dt)$ , rather than stretched exponential decay. This conclusion is also supported by considering the random-walk model with position-dependent diffusion coefficient since it predicts asymptotic convergence to regular Brownian motion.

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