

Chapter 10

Shear Viscosity and Diffusion in Supercooled Liquids

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Under normal liquid conditions (at equilibrium or when moderately supercooled), molecular rotational and translational diffusion adhere closely to the simple Stokes-Einstein-Debye hydrodynamic model. Deeply supercooled “fragile” liquids present a striking exception, with translational diffusion alone occurring up to $10^2 - 10^3$ times “too fast”. This anomaly rests upon the statistics of fluctuating local viscosity in the fragile glass-forming medium. The simplest version of this picture identifies large fluidized domains that spontaneously appear and disappear in a dynamically inert matrix. Plausible and self-consistent values characterizing these fluctuations are cited for orthoterphenyl (OTP) at its glass transition.

Liquids that supercool easily and form glasses have presented many conceptual puzzles, whose resolution has led to deeper understanding of these substances at the molecular level. This paper focusses on one of those puzzles that mainly concerns the so-called “fragile” glass formers, identified by the markedly non-Arrhenius temperature dependences of their shear viscosity $\eta(T)$ and various mean relaxation times $\tau(T)$ (1, 2). Specifically, the need to reconcile separate measurements of translational and of rotational diffusion rates in fragile liquids just above their glass transition temperature T_g leads inevitably to a molecular picture of the medium that is strongly inhomogeneous in both space and time.

Translational and rotational diffusion constants, D_{trans} and D_{rot} , measure rates of increase with time of the mean-square positional and angular displacements for tagged molecules:

$$\begin{aligned}\langle(\delta\mathbf{r})^2\rangle &\cong 6D_{\text{trans}}\delta t, \\ \langle(\delta\theta)^2\rangle &\cong 4D_{\text{rot}}\delta t.\end{aligned}\quad (1)$$

It has been traditional to assess measured values of these diffusion constants by means of the elementary Stokes-Einstein-Debye (SED) hydrodynamic model of a Brownian sphere with radius R embedded in a homogeneous, incompressible, viscous medium (3)–(6). Assuming that “sticking” boundary conditions apply in this model, one has

$$\begin{aligned}D_{\text{trans}} &= k_B T / 6\pi\eta(T)R, \\ D_{\text{rot}} &= k_B T / 8\pi\eta(T)R^3,\end{aligned}\quad (2)$$

where k_B is Boltzmann's constant. These expressions apply both to the case of a pure liquid (where the "sphere" represents the same chemical species as that composing the surrounding viscous medium), as well as to the cases of selected "probe" molecules of various sizes dissolved in the viscous liquid of interest.

The SED expressions 2 enjoy surprising success at representing measured diffusion rates for a wide variety of substances in their equilibrium liquid ranges, and under modest amounts of supercooling. The temperature variations of D_{trans} and D_{rot} track that of $T/\eta(T)$, and the implied hydrodynamic radii R from equation 2 have reasonable values for the molecules examined. Furthermore, the SED model retains its validity under elevated pressure conditions (7).

Recent experiments on deeply supercooled fragile liquids have revealed strong violations of the simple SED model that produces equation 2 (8)–(11). The second of equation 2 continues to describe rotational diffusion down to T_g (at which point η may be approximately 15 orders of magnitude larger than its melting temperature value); however measured translational diffusion rates below about $1.2T_g$ display positive deviations from the first of SED expressions 2 that can grow to an enhancement factor of 10^2 or more (8)–(11).

Even though the selective breakdown of the SED description at first sight seems paradoxical, the large magnitude of the phenomenon at T_g suggests that an explanation need only be straightforward, not subtle. Indeed, such an explanation is available (12, 13). The following Section II lays the groundwork for resolving the puzzle by presenting some general remarks about the "rugged potential energy landscape" that describes intermolecular interactions in fragile liquids. This leads naturally into Section III, a mesoscopic description of the fragile glass-forming medium in terms of a fluctuating local viscosity field. Section IV then shows how certain combinations of length and time scale parameters characterizing this field create a selective bottlenecking scenario that decouples the rotational and translation diffusion processes, just as experiment demands. Section V concludes the presentation with a discussion of several issues, including stretched-exponential (KWW) relaxation, and connections between the SED model violations and the Adam-Gibbs theory of relaxation processes in glass formers (14).

I Potential Energy Landscape

Molecular interactions in a glass-forming substance, and consequently its thermal and dynamical behaviors, are determined by a potential energy function $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N)$. Here the \mathbf{r}_i represent coordinates of the individual molecules, N in number, and generally will include internal degrees of freedom (orientation, conformation) as well as center position. The total number of variables for a macroscopic material sample may be some multiple of Avogadro's number, and the geometry of the Φ hypersurface in this huge multidimensional configuration space is incredibly complicated. Yet some simple features of the " Φ -scape" and their implications for the SED puzzle can be extracted from basic measurements.

Orthoterphenyl (OTP) has become one of the most widely studied fragile glass formers. Plazek, Bero, and Chay (15) have tabulated its shear viscosity $\eta(T)$ over a wide temperature range, from well above its melting point ($T_m = 329\text{K}$) to the vicinity of its

glass transition ($T_g \cong 240\text{K}$). One can represent this data in the following manner:

$$\eta(T) = \eta_0 \exp[F^*(T)/k_B T] \quad (3)$$

where η_0 is temperature independent, and F^* is an activation free energy for viscous flow. Formal activation energy E^* and activation entropy S^* then follow:

$$\begin{aligned} E^*(T) &= \partial[F^*(T)/T]/\partial(1/T), \\ S^*(T) &= -\partial F^*(T)/\partial T. \end{aligned} \quad (4)$$

One finds that E^* is approximately 4.3 kcal/mole in the hot OTP liquid regime ($T \cong 500\text{K}$), but increases dramatically to approximately 86 kcal/mole at T_g . Over the same range S^*/k_B increases by about 140. Similar results would be found for other fragile liquids.

The large increases in E^* and S^* as T declines stem from the strongly non-Arrhenius character of $\eta(T)$ for OTP, and indicate a change in kinetic mechanism for molecular rearrangements. In view of the fact that the heat of fusion of OTP is 4.103 kcal/mole (1δ), the above numbers suggest that while molecular motions in high-temperature shear flow can be resolved into shifts of single molecules or small groups of molecules, the corresponding motions near T_g entail concerted rearrangements of much larger groups.

Figure 1 translates this notion into a schematic view of the multidimensional Φ -scape. The topography shown in 1(a) represents a portion of the multidimensional configuration space inhabited by the system at high temperature; the texture is uniformly rough with modest barriers separating neighboring minima. By contrast, 1(b) illustrates a nonuniform topography that applies to the region inhabited at low temperature; modest barriers still exist between neighboring minima, but over a larger distance scale a substantial degree of "cratering" appears. The low-temperature preference is to reside near the low-potential-energy crater bottoms, but in order for the system to relax structurally to even lower energy, it is necessary to exit the initial crater and search for an even deeper one. The activation energy E^* in this low-temperature scenario involves the net rise required to move between craters, substantially larger than the mean barrier height separating neighboring single minima. The low-temperature activation entropy measures the extent of configuration space explored between successively inhabited craters, evidently quite large in magnitude.

II Local Mobility Variations

The structural relaxation process indicated in Figure 1(b) for cold fragile liquids requires unbundling a large local region in the medium, and repacking the loosened molecules in an alternative pattern to yield an equally low or lower potential energy. The kinetic sequence that accomplishes this process temporarily transforms an initially nearly rigid region into a more mobile, or fluid, state and then back to a rigid condition. In a macroscopic system, many locales of varying size and lifetime can simultaneously experience this scenario. Consequently one could describe the state of the glass-forming material in conventional 3-space by means of a position and time dependent mobility field. An equivalent description for the present analysis utilizes a space and time dependent local viscosity $\eta_{\text{loc}}(\mathbf{r}, t)$. Autocorrelation functions of this scalar field identify characteristic mean lengths and lifetimes for the spontaneous structural fluctuations.

Full characterization of the statistical properties of the fluctuating field η_{loc} is unnecessary for present purposes. Instead, it suffices just to distinguish regions of high and of low molecular mobility, and to assign mean values of η_{loc} to these regions:

$$\begin{aligned}\eta_{\text{loc}}(\mathbf{r}, t) &\cong \eta_0 \quad (\text{high mobility region}), \\ &\cong \eta_\infty \quad (\text{low mobility region}).\end{aligned}\quad (5)$$

A similar binary view of the local kinetics, stated in terms of translational diffusion rates and their fluctuations, appears in a Zwanzig study (17). If the cutoff criterion between "high mobility" and "low mobility" is biased in favor of the latter, regions of the former type will be rare and disconnected, as schematically illustrated in Figure 2.

III Selective Bottlenecking

We are now in a position to explain the gross violation of the SED expression for D_{trans} , while that for D_{rot} remains approximately valid, in the case of fragile liquids near T_g . As mentioned earlier, only a simple picture should be required to rationalize this strong qualitative effect, and so we use the simplifying assumption that η_∞ is substantially infinite compared to η_0 , and to the macroscopic measurable viscosity η for the material. Therefore we need only to be concerned with four parameters that represent mean-value properties of the individual fluidized domains that spontaneously appear and disappear in the glass-forming medium. These are (a) the domain internal viscosity η_0 , (b) domain mean volume v_0 , (c) domain appearance rate per unit volume of the medium r_0 , and (d) the mean domain lifetime t_0 . One must keep in mind that these parameters are all temperature dependent, presumably increasing toward well-defined limits as T declines to T_g .

The macroscopic rate of shear relaxation in a viscoelastic medium is determined by the Maxwell relaxation time (18)

$$\tau_s = \eta(T)/G_\infty, \quad (6)$$

where G_∞ is the (essentially) temperature-independent high-frequency shear modulus. Imagine that near T_g the system were in a uniform state of shear stress. The dominating inert and rigid matrix is incapable of relaxing that stress. However, a fluctuation that suddenly converts a portion of that inert matrix into a fluidized domain permits its unbundled molecules to rearrange within its volume $\cong v_0$ so as to relieve the imposed stress there. Other locales must await the stochastic appearance of their own fluidizing fluctuations to experience similar stress reduction. Consequently, appearance rate r_0 and volume v_0 control overall stress relaxation. This is equivalent to recognizing that the Maxwell time $\tau_s(T)$, and hence $\eta(T)$ itself, will be proportional to the combination

$$\tau_s(T), \eta(T) \propto (r_0 v_0)^{-1}, \quad (7)$$

and so the temperature dependence of this combination becomes that of τ_s and η . As T_g is approached from above, τ_s increases to the maximum time normally available for experiments, approximately $10^3 - 10^4$ s.

With the four nominally independent parameters combined in different ways, several characteristic times can be identified. In fact it is a separation of these time scales that

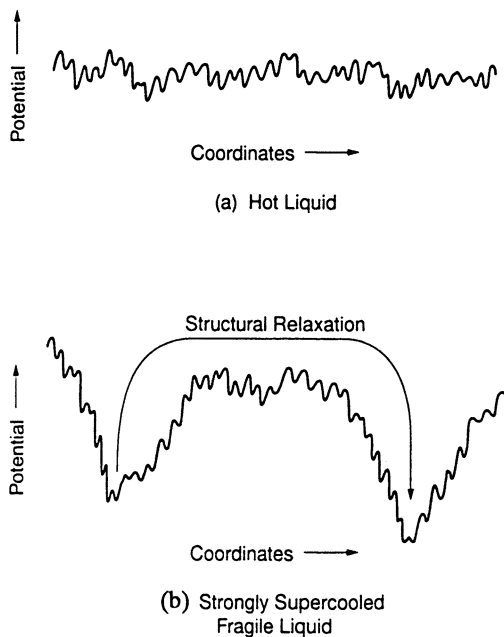


Figure 1. Schematic views of the rugged potential energy landscape for a fragile glass-forming liquid. Part (a) represents the uniformly rough topography in the region of the coordinate space occupied by the system when it is a hot liquid above its thermodynamic melting point. Part (b) indicates the deeply cratered topography in the region visited by the strongly supercooled fragile liquid.

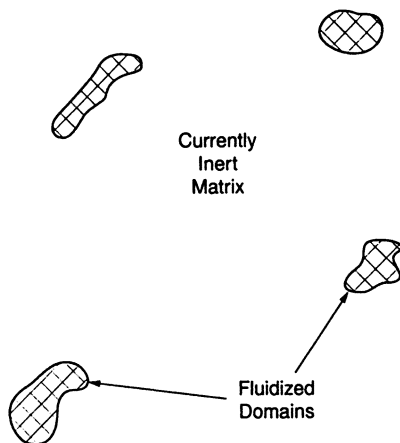


Figure 2. Binary classification of an amorphous glass-forming medium into high-mobility fluidized domains, and a relatively inert, low-mobility matrix. The criterion for distinction between the two has been selected so that the former are rare and disconnected.

provides a mechanism for violating the SED results 2. Specifically, consider the case where t_0 substantially exceeds the rotational relaxation time within a fluidized domain, while the mean domain volume v_0 is sufficiently large so that intradomain translational diffusion can span only a small fraction of the domain diameter in t_0 . Assuming that the SED expressions 2 with η_0 hold within fluidized domains, these statements convert into the following strong inequalities (12):

$$\frac{4\pi\eta_0 R^3}{k_B T} \ll t_0 \ll \frac{\pi\eta_0 v_0^{2/3} R}{k_B T}. \quad (8)$$

The physical significance of this time-scale ordering is that once a domain appears its interior molecules rotationally relax during an early small portion of its lifetime, so that the dominant remainder of t_0 has no further effect, and thus is "dead time." By contrast, the entire t_0 contributes to overall translational diffusion.

The picture just advocated requires both rotational and translational Brownian motion to rely on spontaneous appearance and later disappearance of fluidized domains, but this stochastic process exerts quite distinct bottlenecking influences on the two. When translated into expressions for the respective diffusion constants, this picture of selective bottlenecking leads to the following (12):

$$\begin{aligned} D_{\text{rot}}(T) &\cong r_0 v_0 / 2, \\ D_{\text{trans}}(T) &\cong k_B T r_0 v_0 t_0 / 6\pi\eta_0 R. \end{aligned} \quad (9)$$

The earlier equation 7 implies that D_{rot} should have the same temperature dependence (non-Arrhenius) as η^{-1} , in agreement with the second of equation 2. However, D_{trans} exhibits the additional factor t_0/η_0 , which provides the mean to enhance D_{trans} by the required two or more orders of magnitude near T_g .

Insufficient experimental data is currently available for any fragile substance to assign η_0 , v_0 , r_0 , and t_0 at all relevant temperatures. However it is possible to find reasonable estimates that are consistent with experimental measurements and with the time-scale separation 8. Table I, taken from reference (13), displays such a set of estimates for OTP at its T_g ; this set produce an enhancement factor of 10^2 for translational diffusion compared to the SED value, and exhibits the time-scale separation demanded by equation 8.

IV Discussion

Legitimate concerns might well be raised about the use of four mean value parameters (η_0 , v_0 , r_0 , t_0) to describe fluctuating, distributed, attributes of fluidized regions. For example, the right members of equation 7 and of the first of equation 9 respectively contain the combinations $(r_0 v_0)^{-1}$ and $r_0 v_0$. If r_0 and v_0 were fluctuating variables, then generally the average $\langle (r_0 v_0)^{-1} \rangle$ would differ from $\langle r_0 v_0 \rangle^{-1}$. However in the present context we expect anticorrelated fluctuations, with small domains spontaneously appearing more frequently than larger ones. Mathematically it is easy to demonstrate that if two random variables fluctuate with perfect anticorrelation such that their product is a constant, then indeed

$$\langle (xy)^{-1} \rangle \equiv \langle xy \rangle^{-1}. \quad (10)$$

Table I: Fluidized domain parameters and related quantities for OTP at T_g ^{a, b}

η_0 (P)	6.10×10^6
v_0 (\AA^3)	1.70×10^5
r_0 ($\text{cm}^{-3}\text{s}^{-1}$)	2.11×10^{15}
t_0 (s)	0.426
n_0 ^c	500
ϕ_0 ^d	1.53×10^{-4}
R (\AA)	3.5
$4\pi\eta_0 R^3/k_B T_g$ (s)	9.92×10^{-2}
$\pi\eta_0 v_0^{2/3} R/k_B T_g$ (s)	6.21

^a Values taken from ref. 13.

^b $T_g = 240\text{K}$, $\eta(T_g) = 4 \times 10^{12}\text{P}$.

^c n_0 = mean number of molecules in v_0 .

^d ϕ_0 = volume fraction of fluidized domains.

While it is too much to expect fluidized domain characteristics to follow this behavior precisely, it may be appropriate to suggest that rough conformity obtains, sufficient to justify the simple level of description utilized here.

Deeply supercooled glass-forming liquids seem universally to exhibit stretched-exponential relaxation functions (2, 19):

$$\phi(t) \cong \exp\{-[t/\tau(T)]^\beta\}, \quad 0 < \beta < 1. \quad (11)$$

Strong experimental evidence now exists not only that glassy media are dynamically heterogeneous, but that such heterogeneity underlies stretched exponential relaxation (20)–(22). The fluctuating field $\eta(\mathbf{r}, t)$ is the means for describing this situation in the present context, and its inverse controls the local (in space and time) rate of decay of structure. Consequently, near the glass transition we must have the mathematical connection:

$$\left\langle \exp \left\{ K \int_0^t [\eta(\mathbf{r}, t')]^{-1} dt' \right\} \right\rangle = \exp\{-[t/\tau(T)]^\beta\}, \quad (12)$$

where K is a positive constant dependent on the property whose relaxation is examined, and where $\langle \dots \rangle$ indicates a spatial average over all \mathbf{r} in the system volume. Experimental determinations of β and τ thus provide partial information about $\eta(\mathbf{r}, t)$.

Translational diffusion rates for probe molecules of various sizes have been studied experimentally as a means to determine the average size of dynamical heterogeneities — fluidized domains in the present analysis (11, 23). Certainly a spherical probe whose volume far exceeds v_0 would be expected to conform to the SED norm, though probes utilized so far are likely not in this size range. Although this large-probe strategy has merit, considerable caution needs to be exercised in its interpretation. Uncertainties exist about how foreign probes in a glass-forming medium might locally perturb the dynamics, and the larger the probe the larger such a perturbation would tend to be. Nevertheless, the resulting estimates of the mean linear dimension of inhomogeneities is in

the range of several nanometers for OTP at T_g (20), which is in rough agreement with Table I.

The Adam-Gibbs theory of cooperative relaxation in glass-forming liquids has maintained prominence in the field over the more than thirty years since its inception (14). That approach connects the temperature-dependent mean relaxation time to calorimetric entropy, using the concept of “cooperatively rearranging regions.” It is tempting, though probably not correct, to identify these Adam-Gibbs regions with the fluidized domains of the present paper. By themselves, the four parameters used here to characterize the fluidized domains do not suffice to determine configurational entropy, so at least one further postulate would be required to connect to the Adam-Gibbs viewpoint. One class of theoretical models suggests in fact that the Adam-Gibbs theory cannot be generally valid (24); whether it properly describes a restricted class of theoretical models and real substances remains an open issue.

For additional perspectives on the phenomena discussed in this paper, the reader may wish to consult the presentations (25) and (26).

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