

Brownian Motion of Molecular Probes in Supercooled Liquids

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When a supercooled liquid approaches glass transition, viscous flow slows down greatly, but often the Brownian motion of a molecular probe in the host liquid does not slow down as much, causing the Stokes-Einstein relation to fail by orders of magnitude. Here we formulate a theory that relates the Brownian motion of the probe to two concurrent processes in the host liquid: viscous flow and molecular hopping. Molecular hopping prevails over viscous flow when the probe is small and the temperature is low. Our theory generalizes the Stokes-Einstein relation and fits the experimental data remarkably well.

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Einstein assumed that the Brownian motion of a probe in a host liquid is facilitated by viscous flow [1]. The host liquid consists of molecules of one species. The probe can be a colloidal particle, a molecule of another species, or a molecule of the same species as that of the host liquid. A decrease in the temperature slows down both the Brownian motion of the probe and the viscous flow of the host liquid. That is, as the temperature decreases, the diffusivity of the probe D_p decreases, and the viscosity of the host liquid η increases. The probe-liquid pair is said to obey the Stokes-Einstein relation if $D_p\eta/kT$ is independent of temperature, where kT is the temperature in units of energy. The Stokes-Einstein relation holds for many probe-liquid pairs over wide ranges of temperature [2,3].

The Stokes-Einstein relation, however, fails for some probes in some supercooled liquids, where a modest decrease in temperature slows down the viscous flow in a liquid greatly but does not slow down the Brownian motion of a probe as much. That is, the decrease in D_p does not cancel out the increase in η , causing $D_p\eta/kT$ to increase by orders of magnitude [4–11]. Figure 1 plots the experimental data of $D_p\eta/kT$ as functions of the temperature for seven probe-liquid pairs. The Stokes-Einstein relation approximately holds for the pairs 9,10-Bis(phenylethynyl)anthracene-Ortho-terphenyl (BPEA-OTP) and rubrene-OTP but fails for the other five pairs. The failure of the Stokes-Einstein relation has been studied as an important aspect of glass transition [12–14].

A plausible cause of this failure is as follows. Because of thermal agitation, molecules of the host liquid constantly bombard the probe. At a short time scale, the bombardments do not cancel out but give rise to a net force motivating the probe to drift. For the probe to drift, the surrounding molecules of the host liquid must move apart by changing neighbors. At high temperature when a substance is a liquid, molecules change neighbors through viscous flow, and the Stokes-Einstein relation holds. At low temperature when the

substance is a glass, molecules change neighbors by collective and localized molecular rearrangement, such as free volume activation and ring displacement [15]. The Stokes-Einstein relation does not apply. We call such collective and localized molecular rearrangement “molecular hopping.” As the substance cools from a liquid to a glass, molecular hopping gradually dominates over viscous flow. The flux of

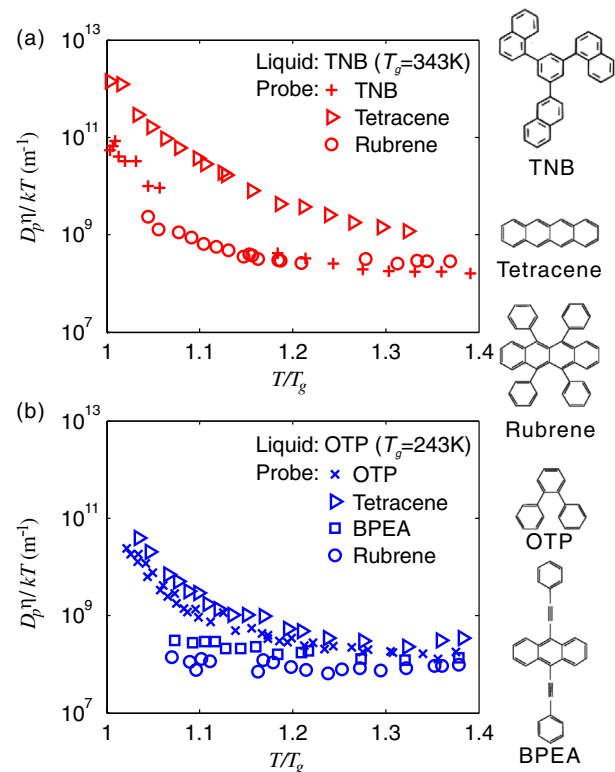


FIG. 1 (color online). Experimental data for molecular probes in supercooled liquids. (a) Data for several probes in 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene (TNB) [5]. (b) Data for several probes in Ortho-terphenyl (OTP) [8]. BPEA stands for 9,10-Bis(phenylethynyl)anthracene.

molecular hopping offers additional mobility to the probe and makes its Brownian motion faster than the prediction of the Stokes-Einstein relation. This picture is supported by molecular dynamic simulations which show that the self-diffusion flux of the host liquid splits into a fast group and a slow group [16–21], where it is further verified that the slow group of molecules satisfies the Stokes-Einstein relation [21] and, thus, corresponds to the self-diffusion by viscous flow.

Here we describe a theory that quantitatively relates the Brownian motion of a probe to the molecular hopping in a liquid. Although supercooled liquids are dynamically heterogeneous and show anomalous diffusion at a short time scale, transport becomes homogeneous and assumes Fickian behavior at a time scale longer than the time for structural relaxation [13,22,23]. Consequently, we model a supercooled liquid as a homogeneous and isotropic continuum and model molecular hopping as Fickian diffusion. We show that when molecular hopping is the prevailing mechanism of transport, the mobility of the probe is proportional to the hopping diffusivity of the host liquid and is inversely proportional to the volume of the probe. Furthermore, we hypothesize that in a supercooled liquid, the two processes—molecular hopping and viscous flow—facilitate the Brownian motion of the probe concurrently. Molecular hopping prevails over viscous flow when the probe is small and the temperature is low. Our theory generalizes the Stokes-Einstein relation with one additional term and fits the experimental data of the seven probe-liquid pairs to a single curve.

Einstein assumed that the probe drifts when molecules of the host liquid change neighbors by viscous flow [Fig. 2(a)]. We first recall the steps that lead to the Stokes-Einstein relation. Stokes [24] solved the boundary-value problem of a spherical particle radius a_p moving in a host liquid of viscosity η . His solution showed that the velocity V_p of the particle is linear in the force F acting on the

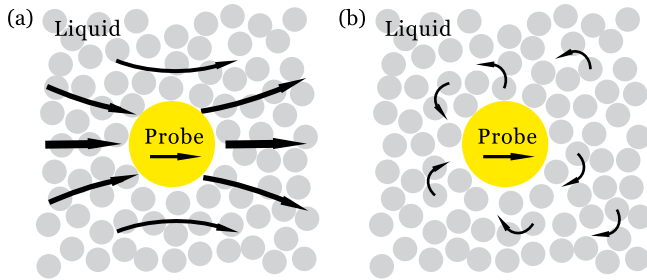


FIG. 2 (color online). Brownian motion of a probe facilitated by two mechanisms of molecular movements in the host liquid. (a) Molecules of the host liquid move by viscous flow. The probe drags the surrounding molecules of the liquid. (b) Molecules of the host liquid move by molecular hopping. The probe causes compression in the front and tension in the back, causing a hopping flux of molecules of the host liquid from front to the back of the probe.

particle, $V_p = M_p F$, with the mobility $M_p = 1/(6\pi a_p \eta)$. Einstein related the mobility and the diffusivity of the particle, $D_p = kTM_p$ [1]. The combination of the two results gives the Stokes-Einstein relation:

$$D_p = \frac{kT}{6\pi a_p \eta}. \quad (1)$$

In solving the boundary-value problem, Stokes assumed that the particle is a rigid sphere, the host liquid is a continuum, and the velocity of the host liquid at the liquid-particle interface is the same as that of the particle. These assumptions may not hold for probes of various shapes and sizes. In practice, one calculates a_p from Eq. (1) using the experimentally measured diffusivity of a probe and the viscosity of the host liquid. The result so obtained is called the Stokes radius of the probe. If the Stokes radius is independent of the temperature (namely, if $D_p \eta / kT$ is independent of the temperature), the probe-liquid pair is said to obey the Stokes-Einstein relation.

Here we assume that a probe can also drift when molecules of the host liquid change neighbors by hopping [Fig. 2(b)]. The molecules of the host liquid hop randomly due to thermal fluctuation, even in the absence of any probe. When a net force motivates the probe to drift forward, the liquid ahead of the probe is in compression, and the liquid behind the probe is in tension. This bias in stress drives molecules of the host liquid to hop from the front to the back of the probe more frequently than the other way around. As the molecules in the host liquid move to the back of the probe, the probe drifts forward.

We adapt Herring's [25] theory of self-diffusion in solids to model hopping in supercooled liquids. The theory adopts a Fickian-type model of diffusion, $\mathbf{J} = -(D_{\text{hop}}/\Omega kT)\nabla\mu$, where \mathbf{J} is the hopping flux of molecules of the host liquid, μ the chemical potential of molecules in the host liquid, D_{hop} the hopping diffusivity of the host liquid, and Ω the volume per molecule in the host liquid. Hopping keeps the density of the host liquid unchanged so that the flux is divergence-free, $\nabla \cdot \mathbf{J} = 0$. Consider a spherical probe radius b_p subject to force F drifting at velocity V_p . We require that the flux of molecules neither penetrate into the probe nor leave a gap on the boundary of the probe. Thus, on the boundary of the probe, the velocity of the probe sets up a flux of molecules of the host liquid in the radial direction, $J_r(b_p, \theta) = (V_p/\Omega) \cos \theta$, where θ is the angle of the radial direction measured from the direction of the velocity of the probe. The chemical potential exerts traction normal to the boundary, $\sigma_n = -\mu/\Omega$. This traction is compressive ahead of the probe and tensile behind the probe. Balancing the forces acting on the probe, we obtain that $F = -\int_0^\pi \sigma_n 2\pi b_p^2 \sin \theta \cos \theta d\theta$.

The above theory leads to a linear relation between the velocity of the probe and the force acting on the probe, $V_p = M_p F$, where M_p is the mobility of the probe due to the hopping of the molecules of the host liquid. The

hopping flux scales with the velocity of the probe, $J \sim V_p/\Omega$, the gradient of the chemical potential scales with the force acting on the probe, $\nabla\mu \sim \Omega F/b_p^3$, and the flux is proportional to the gradient of the chemical potential $J \sim (D_{\text{hop}}/\Omega kT)\nabla\mu$. These scaling relations link the mobility of the probe to the hopping diffusivity of the host liquid, $M_p \sim D_{\text{hop}}\Omega/kTb_p^3$. We determine the numerical coefficient in this relation by solving the boundary-value problem. Herring's theory shows that the chemical potential satisfies the Laplace equation, $\nabla^2\mu = 0$. Solving this partial differential equation in spherical coordinates, we obtain the distribution of the chemical potential, $\mu(r, \theta) = V_p kT b_p^3 \cos\theta / 2D_{\text{hop}} r^2$. We have set the chemical potential remotely from the probe to be zero. The chemical potential is positive ahead of the probe and negative behind the probe. This difference in chemical potential drives molecules of the host liquid to hop from the front to the back of the probe, facilitating the probe to drift forward. On the basis of this solution, we obtain the mobility of the probe due to the hopping of molecules in the host liquid, $M_p = 3D_{\text{hop}}\Omega/2\pi kTb_p^3$. Using the Einstein relation, $D_p = kTM_p$, we link the diffusivity of the probe to the hopping diffusivity of the host liquid:

$$D_p = \frac{3\Omega}{2\pi b_p^3} D_{\text{hop}}. \quad (2)$$

The diffusivity of the probe is linear in the hopping diffusivity of the host liquid and is inversely proportional to the volume of the probe. Our theory assumes that the probe is a rigid sphere, and the host liquid is a continuum. These assumptions may not hold in experiments. In the spirit of the Stokes-Einstein relation, we will calculate b_p from Eq. (2) using measured diffusivities and we will call the radius so obtained the Herring radius. If the Herring radius is independent of the temperature (namely, if D_p/D_{hop} is independent of the temperature), the probe-liquid pair is said to obey the Herring-Einstein relation.

As discussed earlier, in a supercooled liquid, viscous flow and molecular hopping are concurrent mechanisms of transport. We hypothesize that the diffusivity of the probe is the sum of the contributions from viscous flow (1) and molecular hopping (2):

$$D_p = \frac{kT}{6\pi a_p \eta} + \frac{3\Omega}{2\pi b_p^3} D_{\text{hop}}. \quad (3)$$

The viscosity η and the hopping diffusivity D_{hop} characterize molecular transport in the host liquid. Since viscous flow and molecular hopping are distinct processes, the Stokes radius a_p and the Herring radius b_p are distinct parameters. We say that a probe-liquid pair satisfies the hypothesis if Eq. (3) holds for temperature-independent values of a_p and b_p .

We determine the hopping diffusivities of the two host liquids TNB and OTP using the experimental data

of self-diffusion contained in Fig. 1. In the figure, the Stokes-Einstein relation is a horizontal line on which the experimental data at high temperature fall. For each host liquid, we use the data of self-diffusivity D_{self} at high temperature ($T/T_g > 1.37$ for TNB and $T/T_g > 1.36$ for OTP) in Fig. 1 to fit the Stokes radius a_{self} . That is, at high temperature we assume that the Stokes-Einstein relation is valid, $D_{\text{self}}\eta/kT = 1/6\pi a_{\text{self}}$, neglecting the effect of hopping. We obtain $a_{\text{self}} = 3.2 \text{ \AA}$ for TNB and $a_{\text{self}} = 3.4 \text{ \AA}$ for OTP. At low temperature, the self-diffusivities of the two host liquids violate the Stokes-Einstein relation by orders of magnitude. We assume that the difference between the experimentally determined $D_{\text{self}}\eta/kT$ from the prediction of the Stokes-Einstein relation is entirely due to hopping. Specializing Eq. (3) for self-diffusion, we write

$$D_{\text{self}} = \frac{kT}{6\pi a_{\text{self}}\eta} + D_{\text{hop}}. \quad (4)$$

In writing Eq. (4), we require that the Herring radius satisfies $2\pi b_{\text{self}}^3/3 = \Omega$. For the data of $D_{\text{self}}\eta/kT$ for the two host liquids TNB and OTP in Fig. 1, subtracting the contribution of the Stokes-Einstein relation, we obtain $D_{\text{hop}}\eta/kT$. In doing so, we cannot obtain any information on D_{hop} at the high-temperature ranges where the Stokes

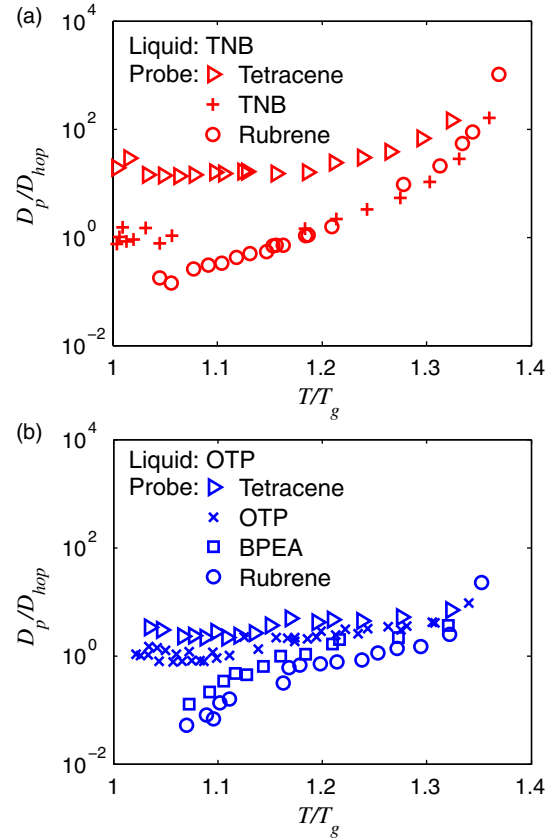


FIG. 3 (color online). Diffusivity of probes normalized by the hopping diffusivity in the host liquids. (a) Data for several probes in TNB. (b) Data for several probes in OTP.

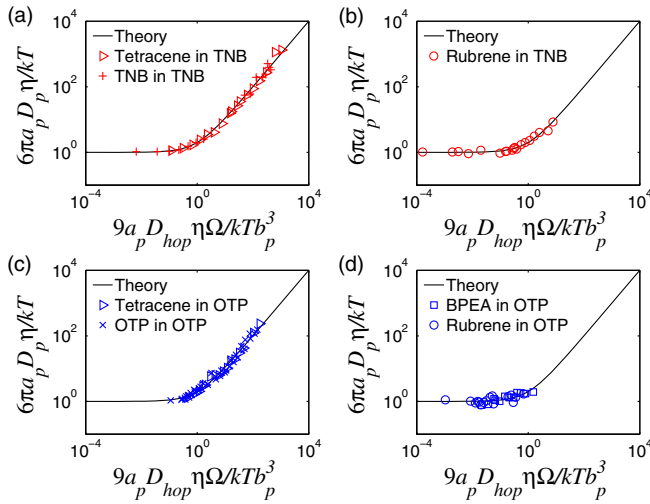


FIG. 4 (color online). The fitting of the experimental data for seven probe-liquid pairs to the theoretical prediction. (a) Small probes in TNB. (b) Large probes in TNB. (c) Small probes in OTP. (d) Large probes in OTP. In each plot, The horizontal line corresponds to the Brownian motion facilitated by viscous flow (i.e., the Stokes-Einstein relation). The linear relation corresponds to the Brownian motion facilitated by molecular hopping (i.e., the Herring-Einstein relation).

radii are calculated. Subsequent discussion and plots only use the data in the remaining ranges of temperature, which are more than 90% of the original ranges of temperature.

As noted before, some probe-liquid pairs (BPEA-OTP and rubrene-OTP) approximately obey the Stokes-Einstein relation but others do not (Fig. 1). In the latter cases, we find that the ratio D_p/D_{hop} approaches constant at low temperature (Fig. 3). For instance, for the probe tetracene in the liquid TNB, D_p/D_{hop} is constant at low temperature, when $T/T_g < 1.18$ (Fig. 3). That is, when a probe-liquid pair violates the Stokes-Einstein relation, the pair obeys the Herring-Einstein relation.

To ascertain our hypothesis that viscous flow and molecular hopping in a supercooled liquid facilitate Brownian motion concurrently, we compare Eq. (3) and the experimental data for the seven probe-liquid pairs (Fig. 4). The vertical axis is a dimensionless measure of the deviation from the Stokes-Einstein relation. The horizontal axis is a dimensionless measure of the relative magnitude of the two mechanisms of molecular transport—viscous flow and molecular hopping. For each probe-liquid pair, the

experimental data fit Eq. (3) remarkably well by temperature-independent a_p and b_p (Table I). The values a_p and b_p are on the order of the size of the molecules. Since the viscous flow and molecular hopping are independent processes, and the shape of each probe is very different from a sphere, a_p and b_p can be very different for the same probe-liquid pair. The transition from viscous flow to molecular hopping as a prevailing mechanism of transport is evident (Fig. 4). Viscous flow prevails when the temperature is high and the probes are large, as represented by the horizontal lines in Fig. 1. Molecular hopping prevails when the temperature is low and the probes are small, as represented by the horizontal lines in Fig. 3.

For each liquid, the two mechanisms of transport define a characteristic length, $\Lambda = \sqrt{\eta D_{\text{hop}} \Omega / kT}$ [26–28]. The characteristic length increases as the temperature drops (Fig. 5). The horizontal axis of Fig. 4 can be written as $9a_p \Lambda^2 / b_p^3$, which is a dimensionless measure of the size of a probe relative to the characteristic length Λ . When a probe is small compared to this characteristic length, the Brownian motion of the probe is mainly facilitated by molecular hopping in the host liquid. When a probe is large compared to this characteristic length, the Brownian motion of the probe is mainly facilitated by the viscous flow of the host liquid.

We have considered molecular probes undergoing Brownian motion in supercooled liquids facilitated by two concurrent mechanisms by which the molecules in the host liquid change neighbors. In principle, any probe undergoes Brownian motion in any host in which molecules change neighbors by any mechanism. For example, near the melting point of a crystal, diffusion of vacancies is a dominant mechanism of transport, but other concurrent mechanisms like power law creep exist [30]. We expect that a probe (e.g., a ceramic particle) undergoes Brownian motion in a crystal (e.g., a metal).

In summary, we have assumed that molecules of a supercooled liquid move by two concurrent processes: viscous flow and molecular hopping. We have developed a theory that allows both processes to facilitate the Brownian motion of a probe. Molecular hopping prevails over viscous flow when the probe is small and the temperature is low. Our approach quantitatively explains the experimental data and generalizes the Stokes-Einstein relation. The Brownian motion of a probe in a medium depends on the mechanisms of transport in the medium, the size of the probe, and

TABLE I. The Stokes radius and the Herring radius of various probes in different host liquids.

Liquid	Probe				
	Tetracene	OTP	TNB	BPEA	Rubrene
TNB	$a_p = 0.5 \text{ \AA}$	N/A	$a_{\text{self}} = 3.2 \text{ \AA}$	N/A	$a_p = 1.9 \text{ \AA}$
	$b_p = 2.7 \text{ \AA}$		$b_{\text{self}} = 6.8 \text{ \AA}$		$b_p = 12.4 \text{ \AA}$
OTP	$a_p = 3.2 \text{ \AA}$	$a_{\text{self}} = 3.4 \text{ \AA}$	N/A	$a_p = 3.3 \text{ \AA}$	$a_p = 6.4 \text{ \AA}$
	$b_p = 4.1 \text{ \AA}$	$b_{\text{self}} = 5.6 \text{ \AA}$		$b_p = 12.0 \text{ \AA}$	$b_p = 20.2 \text{ \AA}$

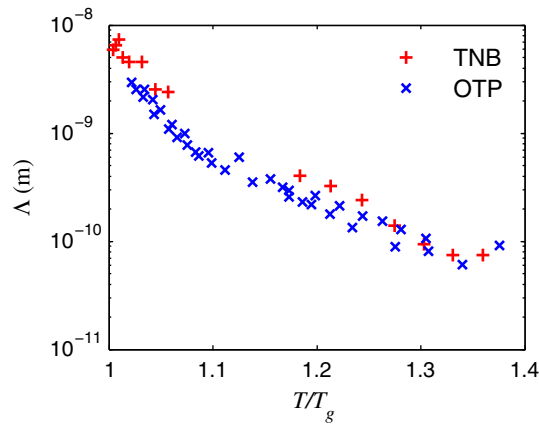


FIG. 5 (color online). The characteristic length $\Lambda = \sqrt{\eta D_{\text{hop}} \Omega / kT}$ plotted as a function of the temperature. The volume per molecule in the host liquid is $\Omega = 0.64 \text{ nm}^3$ for TNB and $\Omega = 0.37 \text{ nm}^3$ for OTP [29].

temperature. The Brownian motion of probes sheds light on mechanisms of molecular transport in complex matter.

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