Translational diffusion (and crystal growth rates) in supercooled liquids and glasses: Influence of spatially heterogeneous dynamics

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NOTE: recent preprints can be downloaded at:
www.chem.wisc.edu/~ediger
Outline

- Self-diffusion in liquids far above Tg
- Self-diffusion in liquids just above Tg
- Crystal growth rates just above Tg
- Translational motion in extremely stable glasses
Self-diffusion far above $T_g$

Sillescu and coworkers pioneered the study of diffusion in supercooled liquids. At 1.2 $T_g$, diffusion is already slightly “enhanced” compared to SE.

Stokes Einstein equation

$$D = \frac{kT}{6\pi \eta r_H}$$

(Chang and Sillescu, JPCB, 1997)
Outline

• Self-diffusion in liquids far above Tg
• **Self-diffusion in liquids just above Tg** (TNB revisited, OTP, PS, Si in SiO$_2$)
• Crystal growth rates just above Tg
• Translational motion in extremely stable glasses
Physical vapor deposition allows the preparation of isotopically patterned samples.
SIMS measurements of isotopic concentration profiles

\[ \text{SIMS} \]

\[ \text{O}_2^+ \]

H\(^+\) and D\(^+\) counted by mass spectrometer

From SIMSworkshop.org

SIMS measurements performed by Tom Mates at the Materials Department, University of California - Santa Barbara
Sample preparation and measurement

Each deposition yields ~ 10 samples with identical concentration profiles
Self-diffusion of TNB near $T_g$

SIMS data with annealing at 353 K ($T_g + 6$ K); red lines showing Fickian diffusion with $D = 8 \times 10^{-16} \text{ cm}^2/\text{s}$; Swallen et al. (nearly submitted)
TNB self-diffusion is significantly enhanced near $T_g$

High temperature D value from NMR measurement by Chang and Sillescu (1997); Viscosity data from Plazek and Magill (1966)
Cross-over to non-Fickian diffusion at high q

Neutron reflectivity (NR) from Swallen et al. (2006)

\[ \xi = 1.4 \text{ nm}; \]
\[ \text{rms jump} = 3.4 \text{ nm} \]

Robust upper bound for \( \xi \)

First expts near \( T_g \)

\[ D(q) = \frac{1}{q^2 \tau(q)} \]

Neutron reflectivity (NR) from Swallen et al. (2006)
Cross-over to non-Fickian diffusion is consistent with simulation and theory

- Schweizer and Saltzman (2004) - Entropic barrier hopping theory
- Seen in simulations --->
- Cross-over length in TNB at Tg is 14 times larger than length indicated by high temperature experiments (Wuttke PRE 1996, glycerol at 1.6 Tg)
- Cross-over consistent with spatially heterogeneous dynamics => crossover length tied to SE enhancement => should increase with lower T

Berthier, PRE (2004)

Self-diffusion in o-terphenyl (OTP) near Tg

Isothermal desorption data for OTP

Desorbed at $T_g + 9$ K

Fickian model

Film ~ 400 nm
o-Terphenyl self-diffusion coefficients: large enhancement at Tg
Comparison of enhanced translation in TNB and OTP

Here comparison is made to rotational correlation times from NMR
Self-diffusion of polystyrene 20-mers: Minimal Stokes-Einstein enhancement

![Graph showing self-diffusion data and fit parameters.](image-url)

- \( \log (D / \text{cm}^2\text{s}^{-1}) = A + \log \left( \frac{T}{\eta} \right) \)
- \( T_g \)
- \( D(\text{FReS}) \)
- \( D(\text{NMR}) \)
- \( \frac{T}{\eta} \)
- \( B - \log a_T \) (G-mode)

Si diffusion in $\text{SiO}_2$ (data compiled by Nascimento and Zanotto): Minimal Stokes-Einstein enhancement

**Si diffusion and viscosity have the same T dependence down to $T_g$**
Enhanced diffusion at Tg vs. fragility (experiments = points)

- Polymers don’t show SE enhancement - too large to utilize spatially heterogeneous dynamics for fast transport
- Trend of RFOT prediction seems correct

**Figure 4.** Fragility of the supercooled liquids ans thier important effect on the observed Stokes—Einstein Relation deviation. For fragile liquids such as o-terphenyl, such deviation is as large as 3 orders of magnitude, whereas in strong liquids like SiO₂, it should be only minor. The plot is for self-diffusion at glass transition temperature Tg.

Temperature-dependent distribution of relaxation times???

- Early explanations of enhanced diffusion assumed strong T dependence for width of relaxation time distribution: e.g., $D$ and $\eta$ (or $\tau_c$) sample different moments of the distribution.
- RFOT-based calculation also has T dependent distribution width.
- For TNB and OTP, DR experiments indicate $KWW \beta$ is independent of T near $T_g$; for OTP, some other experiments reach a different conclusion.
Is enhanced diffusion associated with spatially heterogenous dynamics?

- Hard sphere simulations show growing enhancement without growing width and show strong connection between SHD and enhanced translation (Kumar, et al. JCP 2006). Hard sphere theory shows first two features (Saltzman and Schweizer, PRE 2006).
- Facilitated dynamics view argues that no correlation between distribution width and growing enhancement is necessary.
- ON THE OTHER HAND, simulations of ST2 water lead Becker et al. (PRL 2007) to conclude that dynamic heterogeneity does not “cause” SE breakdown.

Thought experiment: Predict the SE enhancement at Tg for DHIQ\((m=158)\) and glycerol\((m=51)\)? What approach would you use? Is fragility really the key variable?
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Crystal growth rates at low temperatures are controlled by structural relaxation of the liquid.

We can extract the kinetic growth rate $u_{\text{kin}}$ from experimental measurements of the growth rate $u$ by removing the contribution of the thermodynamic driving force.
The crystal growth rate is another measure of mobility in a spatially heterogeneous supercooled liquid.

For TNB, kinetic part of crystal growth rate has an even weaker T dependence than self-diffusion.
We can test relation between crystal growth rate and $\eta$ (but not D) for a large number of organic systems.

Crystal growth rates always have a weaker temperature dependence than $\eta$

IMC polymorph data => $u_{kin}$ is really a measure of liquid mobility

Data from Scherer/Uhlmann, Magill/Plazek, Yu, and Wu/Yu; Comparison made by Ediger et al., JCP 2008
We can also test the relation between crystal growth rate and $\eta$ (but not $D$) for a large number of inorganic systems.

Crystal growth rates often have a weaker temperature dependence than $\eta$.

Data from laboratories of Wagstaff, Weinberg, Zanotto, Uhlmann, Bergeron, and Gutzow. Comparison made by Ediger et al., JCP 2008.
Connection between crystal growth rate and $\eta$ depends systematically upon fragility.

Our interpretation - Note similarity to behavior predicted for diffusion.

most homogeneous

most heterogeneous
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Vapor-deposition of TNB can create high density glasses - likely the most stable glasses ever prepared in a laboratory.

Bulk molar volume data from Plazek and Magill, JCP 1966.
Substrate temperature and deposition rate control the stability of vapor-deposited glasses

- $T_{\text{substrate}} < 0.7 \ T_g$ Unstable glass  
  (literature view prior to 2007)
- $T_{\text{substrate}} \approx 0.98 \ T_g$ Ordinary glass  
  (used up to this point in this talk)
- $T_{\text{substrate}} \approx 0.85 \ T_g$ Highly stable glass  
  (“superaged” glass results from equilibration in a liquid-like layer at the surface of the glass during deposition)

(Swallen et al., Science, 2007; Kearns et al., JPC B, 2008)
Translational motion in stable TNB glasses during annealing above $T_g$: a growth front converts stable glass to liquid.

Swallen et al. (nearly submitted)
Sample preparation and measurement

Vapor deposition produces ordinary glass.

Annealing produces stable glass.

SIMS measurement at Tg.
Another view of liquid growth front moving into stable glass upon annealing near $T_{\text{g}}$

$T_{\text{anneal}} = 345$ K
Growth front moves into stable glass from free surface with a constant velocity.

\[ T_{\text{anneal}} = 345 \text{ K} \]
Why a growth front?

• Packing in stable glass is so dense and so low in energy that very few molecules can escape stable glass cage even above $T_g$
• A “defect” is required; surface and interfaces act as defects
• Unprecedented
• Incompatible with standard models of glass to liquid transformation, e.g., TNM; these are *homogeneous* descriptions of glass $\rightarrow$ liquid transformation
• Useful for understanding supercooled liquids?
Supercooled liquids vs. Annealed stable glasses

- Spontaneous
- Many simultaneous transformations
- Hard to isolate a single “event” or rate

- Controlled
- One transformation
- Expt focused on one event

(Thanks to Peter Harrowell for this idea!)
NOTE: Our 2003 publication of TNB self-diffusion coefficients is incorrect because stable glasses were unknowingly prepared and the growth front mechanism was not recognized (low spatial resolution).

Old data; NOT diffusion
\[ T_{\text{substrate}} \sim 0.85 \, T_g \]

New and correct data:
\[ T_{\text{substrate}} \sim T_g \]

Swallen et al. (nearly submitted)
Summary of diffusion in liquids and glasses

- High T liquids do not feel energy landscape => SE works
- As T is lowered to Tg, liquids exhibit spatially heterogeneous dynamics => SE breakdown and crossover to non-Fickian diffusion at increasingly larger length scales
- Crystal growth rates suggest a systematic relation between spatially heterogeneous dynamics and fragility
- Extremely stable glasses, when annealed above Tg, exhibit a heterogeneous transformation into a liquid; engineered version of spatially heterogeneous dynamics in supercooled liquid