Spatially heterogeneous dynamics in supercooled organic liquids

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Image from Weeks and Weitz, Science (2000)
Outline

• Molecular reorientation and the $\alpha$ relaxation process
• Translational diffusion
• Spatially heterogeneous dynamics
• Solid state NMR experiments
• Computer simulations
The $\alpha$ relaxation process controls many aspects of dynamics in supercooled liquids and glasses

- $\alpha$ or structural relaxation process: dielectric relaxation, dynamic Kerr effect, light scattering, NMR, probe rotation
- Conventional view: $\alpha$ relaxation controls diffusion, rate of crystal growth, and ability to equilibrate a glass

Molecular reorientation closely tracks $\eta/T$

Debye-Stokes-Einstein:

$$\tau = \frac{\eta V}{kT}$$

Cicerone et al. JCP (1995)
High fragility glassformers show a non-Arrhenius temperature dependence as $T_g$ is approached from above.

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Self-diffusion in liquids far above $T_g$

- $<r^2> = 6Dt$
- $D$ for water at 298 K
- First four decades of slowing diffusion tracks viscosity quite well (SE)
- SE derived for large spheres in a continuum

\[ D = \frac{kT}{6\pi \eta r_H} \]

Figure 1. Self-diffusion coefficients $D$ in glass forming liquids: salol (●), glycerol (□), PDE (○), CDE (△). The full lines were obtained from the Stokes–Einstein relation, eq 8, using the hydrodynamic radii, $R_{\text{trans}} = R_H$, from Table 1, and the shear viscosities, $\eta$, from the literature quoted in section III.

(Chang and Sillescu, JPCB, 1997)
Sillescu and coworkers pioneered the study of diffusion in supercooled liquids. At 1.2 $T_g$, diffusion appears to be slightly “enhanced” compared to SE.

Stokes Einstein equation

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

(Chang and Sillescu, JPCB, 1997)
Self-diffusion near $T_g$ (trisnaphthylbenzene or TNB)

SIMS data with annealing at 353 K ($T_g + 6$ K); red lines showing Fickian diffusion with $D = 8 \times 10^{-16}$ cm$^2$/s; Swallen et al., JPCB (2009)

From SIMSworkshop.org
TNB self-diffusion is significantly enhanced near $T_g$ relative to viscosity (SE equation)

Self-diffusion in o-terphenyl (OTP) near $T_g$

Isothermal desorption data for OTP

Desorbed at $T_g + 9$ K
Fickian model
Film $\sim 400$ nm
OTP self-diffusion coefficients: large enhancement at $T_g$ relative to viscosity

Mapes et al., JPCB 2006.
100 microsecond simulations of OTP

- Eastwood et al., J. Phys. Chem B 2013, 117, 12898
- Fully atomistic classical MD
- Diffusion is enhanced relative to rotational motion, in good agreement with experiments
Indomethacin (IMC) self-diffusion is significantly enhanced near $T_g$ (SIMS)

Note: $\tau_\alpha$ and viscosity have same $T$ dependence
Swallen et al, Soft Matter 2011
The crystal growth rate is more closely connected with diffusion than with viscosity or structural relaxation (more to come…)

Diffusion: Swallen et al., Soft Matter 2011
Crystal growth rates: Wu and Yu, JPCB 2006
TNB, OTP, IMC show similar enhancement of D near $T_g$ relative to $\tau_\alpha$ (or viscosity)

Swallen et al, Soft Matter 2011
Self-diffusion of polystyrene 20-mers: Minimal enhancement of $D$

Figure 8  Urakawa et al. Macromolecules (2004)
Check of Fickian diffusion for PS 20-mers

Figure 6  Urakawa et al.
Si diffusion in SiO$_2$ (data compiled by Nascimento and Zanotto): Minimal Stokes-Einstein enhancement

Si diffusion and viscosity have the same $T$ dependence down to $T_g$. 
Summary this far

• Structural relaxation, molecular reorientation and viscosity have very nearly the same T dependence

• For IMC, TNB, and OTP – T dependence of D is weaker

• For Si in SiO$_2$ and PS 20-mer, D has same T dependence as all the others

• Why?
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Non-exponential correlation functions

Non-exponential correlation and relaxation functions

- Most prominent in fragile glassformers
- Often fit to KWW form: $\exp[-(t/\tau)^\beta]$
- Often $\beta = 0.5$ near $T_g$
- Two possible interpretations
- $\beta$ places upper bound on the width of the local relaxation time distribution

Richert (1994)
Solid-state NMR allows selection and study of slow subensembles

- o-terphenyl (OTP) at $T_g + 11$ K
- Slow ensemble = slowest 29%
- Slow ensemble decays considerably slower and more exponentially
- Results => $\beta_{\text{intr}} \sim 1$, i.e., distribution of relaxation times is really the spatial distribution of relaxation times
- Heterogenous interpretation is correct

Size of regions with distinct dynamics can be measured by spin diffusion

- 4D3CP NMR expt developed by Tracht et al (PRL 1998)
- 3.7 nm at $T_g + 10$ K in PVAc
- $\xi_{\text{het}}$ may be the same thing as $\xi_{\text{coop}}$
Simulations illustrate spatially heterogeneous dynamics at moderately high temperatures

- 17,500 identical spheres, near $T_c$, Dzugutov potential
- Most mobile 6% of particles are highlighted
- Similar color means a connected group

Colloidal particles show spatially heterogeneous dynamics

Weeks, Weitz …
Science (2000)

Confocal microscopy, 1.2 µm spheres, fastest spheres are colored.
Probe diffusion is enhanced relative to reorientation at lower temperature

- big Stokes-Einstein violation
- rotation and translation have different T dependences
- explained by spatially heterogeneous dynamics?

Cicerone and Ediger (1996)
Why does SE breakdown as $T_g$ is approached in single component supercooled liquids (for low molecular weight, fragile glassformers)?

- A better question: Why does molecular rotation and translation apparently decouple with decreasing $T$? (comparison of two single particle correlation times).
- Homogeneous answer: Molecules translate further and further without rotating.
- Heterogeneous answer: For any individual molecule, rotation and translation is tight coupled (seen in simulations). Then, apparently decoupling must result from the diversity of local relaxation rates => heterogeneous dynamics. Translation should becomes non-Fickian on short length scales near $T_g$. 
Cross-over to non-Fickian diffusion at high $q$

$\xi = 1.4$ nm; rms jump $= 3.4$ nm

Robust upper bound for $\xi$

First expts near $T_g$

Enhanced translational diffusion is associated with spatially heterogeneous dynamics

- Hard sphere simulations show strong connection between SHD and enhanced translation (Kumar, et al. JCP 2006).
- Molecular simulations show an increasing correlation between fast rotators and fast translators as the temperature is lowered towards $T_g \Rightarrow$ enhanced translation only appears when averaging over entire ensemble (Lombardo/Debenedetti JCP 2006, Chong/Kob, PRL 2006)
- Decoupling results from an increasing length scale associated with heterogeneous dynamics. See simulations by Chong and Kob, PRL 2009.
Hard sphere simulations show Stokes-Einstein breakdown

Dumbbell simulations by Chong/Kob (PRL 2009)

Left: Correlation between local rotation rate and local translation rate increases with decreasing T.
Right: Decoupling between average D and tau results from correlated motion with an increasing length scale.
Summary

• High T liquids do not feel energy landscape => all relaxation processes have the same T dependence and SE works
• As T is lowered to $T_g$, fragile liquids exhibit spatially heterogeneous dynamics => SE breakdown
• Dynamics can vary spatially by 1-4 decades near $T_g$
• Tracer and self diffusion can be enhanced relative to reorientation or viscosity by 1-4 decades
• Regions of slow dynamics extend 1-3 nm; polymers too large to show enhanced diffusion
• How important is heterogeneous dynamics for strong glassformers?? (recall D for Si in SiO$_2$)