19/07/2017 M. EDIGER — EXPERIMENTAL PERSPECTIVE ON SUPERCOOLED LIQUIDS AND GLASSES (MOLECULAR AND ATOMIC SYSTEMS).

introductory words.

Glasses as materials – polymer glasses / composites, optical fiber (scattering section very small due to homogeinity making possible to transmit over 100s kilometers without amplification), OLEDs –

Dramatic slowdown with temperatures between 10 and 19 orders of magnitude – 10^9–10^{19} and over.

Different types of interactions: Van der Waals, dipole-dipole, hydrogen bonding, metallic bonding.

↳ Crystallization? Problem for metallic glass

VTF $\log \tau/\tau_0 = A + \frac{B}{T - T_0}$ → Super Arrhenius behavior.

Little experiment in office: tube of metallic system — $T_m \sim 30K$, 10^{21} molecules, $\tau_\alpha \sim$ instantaneous, 20 years $\sim 10^{9} s$ → if critical nucleus ~ 100 molecules

$\left(\frac{10^{21}}{10^2}\right)\left(\frac{10^9}{10^{-9}}\right) \sim 10^{37}$ chances to nucleate

(possible # nucleus × time to wait × # of attempts)

still a liquid, super stable!

fragile / strong: fragile = with respect to perturbation caused by temperature

def: kinetic fragility $m = \left.\frac{d \log \tau}{d(T_g/T)}\right|_{T_g}$

SiO_2 $m \simeq 16$ → strong limit

highest value ~ 180 – → fragile limit.

"single time scale": Dielectric relaxation – collective measurement of dipole reorientation

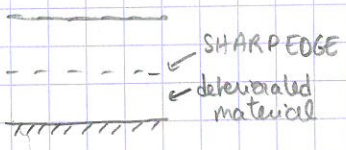
- Correlation function $CF(t) \sim \langle \left(\sum \vec{\mu}_i(t)\right) \cdot \left(\sum \vec{\mu}_i(0)\right) \rangle$ starting times

  NMR $CF(t) \sim \langle P_2 \vec{y}(t) \vec{y}(0) \rangle$ starting times, molecules.

4 liquids – Dielectric relaxation / Heat capacity spectroscopy → input: power (ω), measure: T(ω) → Eastwood et al J Phys Chem B 2008

* IMPORTANT EXCEPTION: translational diffusion coefficient → does not depend as much on temperature –

↓ method of measurement:

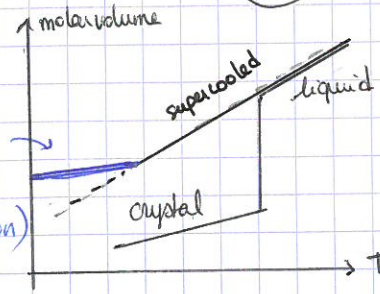


probe after heating and cooling how much the interface blurs ⇔ how much diffusion took place in the sample –

$$\frac{(D\tau_\alpha)_{H_2O,T}}{(D\tau_\alpha)_{EOT}} = 100 = \frac{(D\tau_c)_{air}}{(D\tau_c)_{EOT}}$$

molecular reorientation time

thermodynamics –



glasses, gets stuck in conf with too much volume (depends on the preparation)

Convention for T_g: → cool at 10 K/min → τ_α = 100s at equilibrium.

(LC)

… supercooled liquid (SCL) → liquid crystal → Class of LC

Kauzmann entropy crisis:

the excess entropy is $S_{ex} = S_{SCL} - S_{CR}$

What we want is the configurational entropy, that can be estimated as: $S_c \approx S_{SCL} - S_{Gaus}$.

some words about structure:

→ changes in $S(Q)$ with respect to T are small.

↪ connection between structure and dynamics.

connections between dynamics and thermodynamics ?