

Rigidity Onset in Liquids

Are glasses like crystals - only disordered?
Once we change symmetry, is solid the same?

or

Are glasses like liquids - only slower?
Is there liquid-to-glass transition or is it just fuzzy?

or

Are glasses *essentially* different?

Crystal is essence of order
What is essence of disorder?
Why ask that?

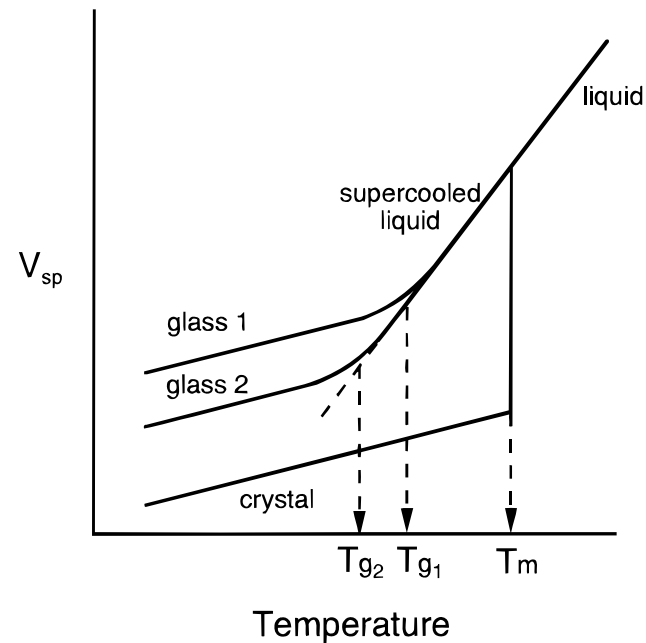
Crystallization: 1st-order nucleation transition

Cannot perturb a crystal (add defects) to get a glass

Need opposite limit: complete disorder

What (non-equilibrium) process → complete disorder?

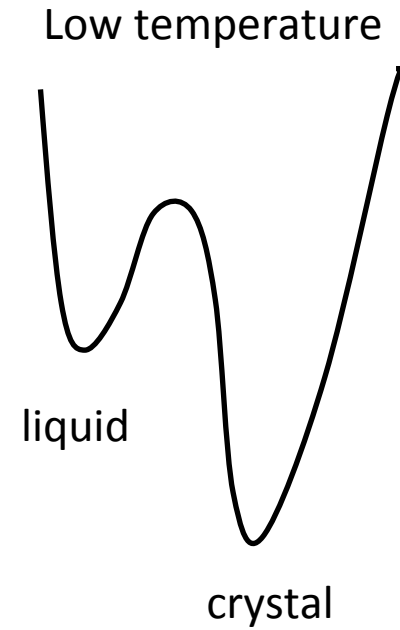
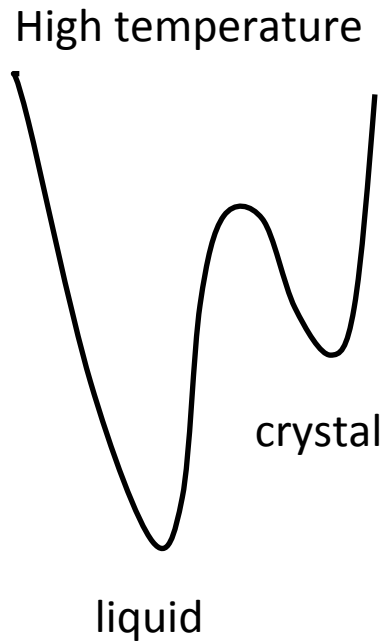
Supercooling a liquid into a glass



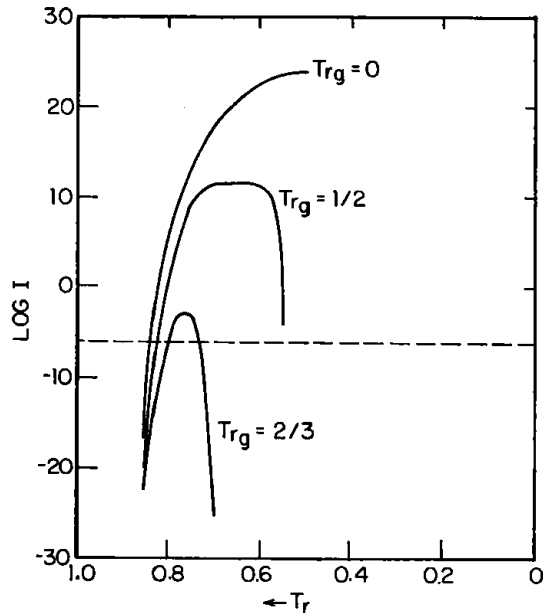
Schematic representation of specific volume vs. temperature for a liquid. Properties of glass depend upon cooling rate; glass 2 was cooled slower than glass 1. Glass transition temperature T_g can be defined by extrapolating V_{sp} in glass back to supercooled liquid line.

T_g depends upon cooling rate. Typical experimental rates $\sim 0.1-100$ K/min.

Slower liquid is cooled the more likely it will nucleate into crystal
but longer it has to relax to liquid ground state



Nucleation rates



$$I = \frac{k_n}{\eta} \exp [-b\alpha^3\beta/T_r(\Delta T_r)^2] \quad (6)$$

where k_n is a constant specified by the model, b is a constant determined by the nucleus shape, α and β are dimensionless parameters defined as:

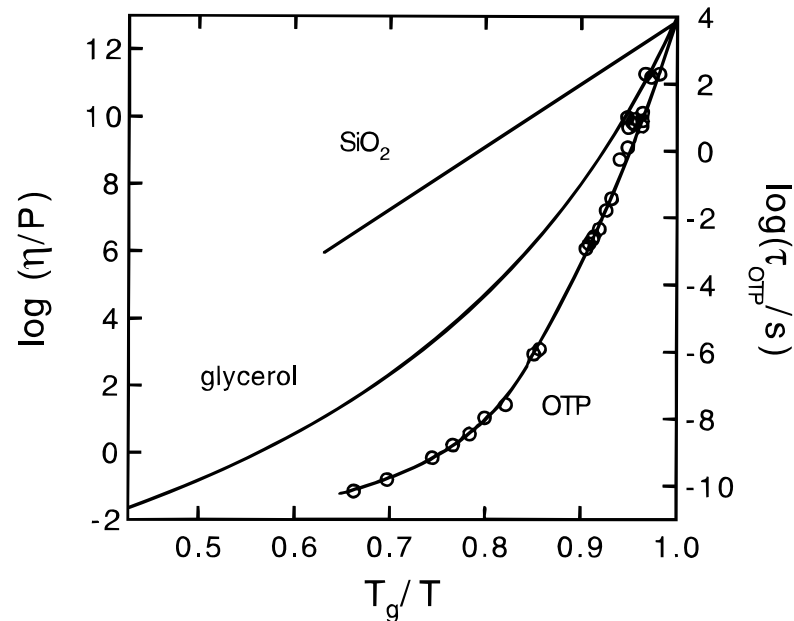
$$\alpha = \frac{(N\bar{V}^2)^{1/3}\sigma}{\Delta H_m} \quad (6a)$$

$$\beta = \frac{\Delta H_m}{RT_m} = \frac{\Delta S_m}{R} \quad (6b)$$

$$T_r = \frac{T}{T_m}, \quad \Delta T_r = \frac{T_m - T}{T_m}$$

Variation of logarithm of frequency (in $\text{cm}^{-3} \text{s}^{-1}$) of homogeneous nucleation of crystals in liquids with reduced temperature calculated from eqn. (6). $\alpha\beta^{1/3}$ was set equal to 1/2 and viscosity was calculated from the Fulcher equation with indicated assignments of T_{rg} in Fulcher equation.

Viscosity and relaxation times in supercooled liquids



Viscosity vs. reduced inverse temperature for 3 liquids: SiO_2 , glycerol, and *o*-terphenyl. Reorientation times are shown for *o*-terphenyl only. A nearly Arrhenius temperature dependence for relaxation times and the viscosity is characteristic of *strong* liquids, while *fragile* liquids show quite non-Arrhenius behavior.

Experimental definition of T_g . $\eta = 10^{13}$ poise (solid on scale of hours)
 $\tau \propto \eta/G$ so τ diverges as well

Nearly all materials can form a glass:
covalent, ionic, metallic, van der Waals, hydrogen bonding

Insulators: SiO_2 , S,

Molecular liquids: Glycerol, Salol

Polymers:

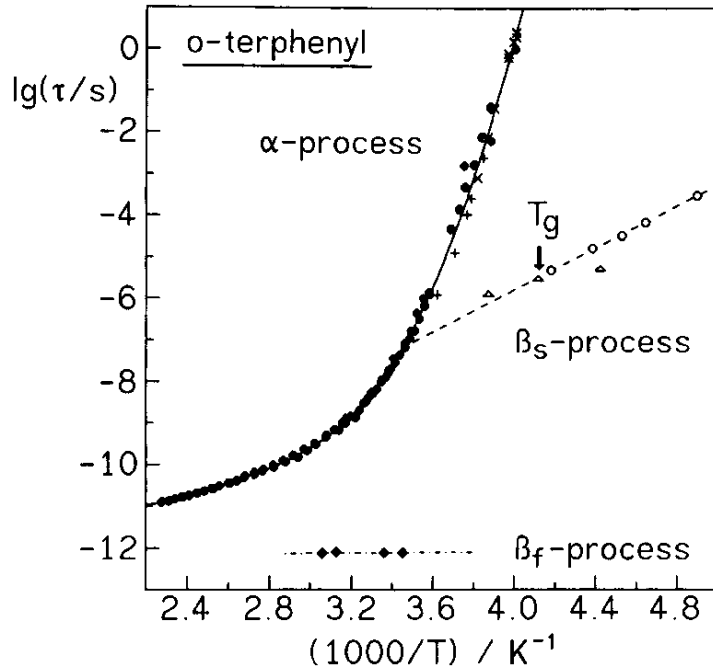
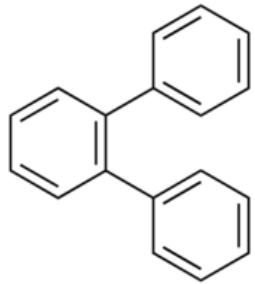
Semiconductors: Si, Ge, As_2Se_3 ,

Metals: $\text{Pd}_{0.8}\text{Si}_{0.2}$, Ni_4P ,

Need to cool fast enough to avoid nucleation

(Not liquid He or water)

Different relaxation times in glasses and supercooled liquids



Super- Arrhenius relaxation:
No unique expression.

Vogel - Tammann - Fulcher fit:
$$\tau = \tau_0 \exp\left(\frac{B}{T - T_\infty}\right)$$

Power law:

$$\tau = \tau_0 [(T - T_0)/T_0]^\alpha$$

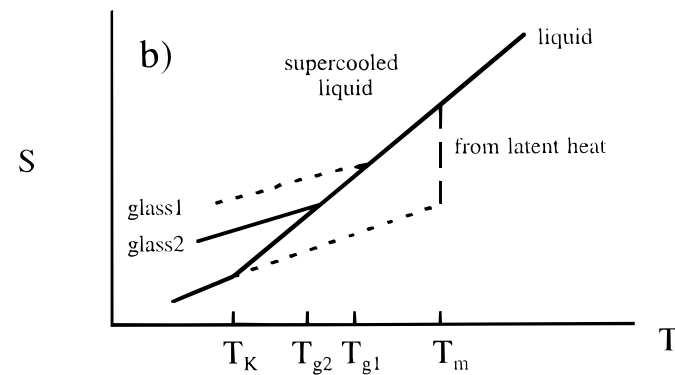
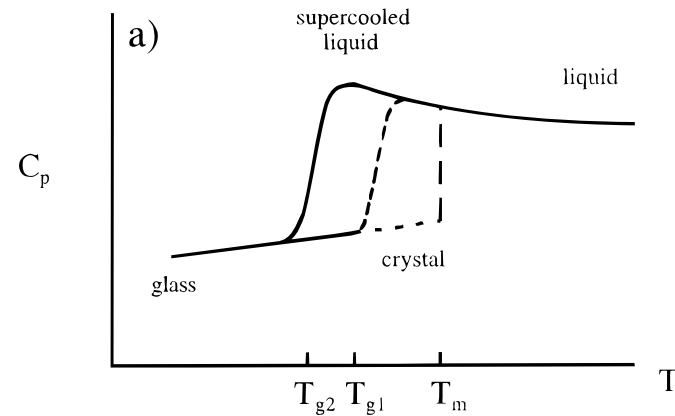
Various relaxation times measured for *o*-terphenyl.

α -relaxation: (dielectric relaxation, dynamic Kerr effect, light scattering, NMR).

β_s -relaxation (dielectric relaxation, time-resolved optical spectroscopy).

β_f -relaxation: (neutron scattering).

Kauzmann entropy catastrophe

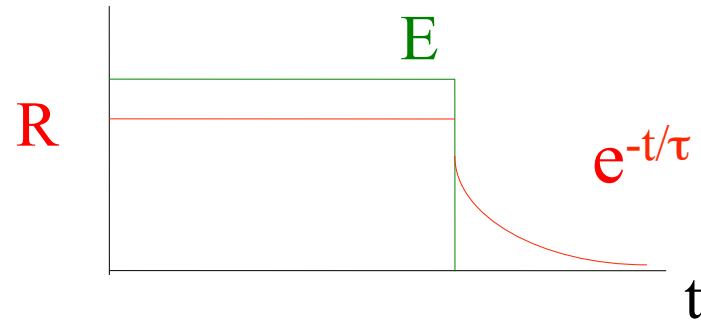


$$s(T_2) - s(T_1) = \int_{T_1}^{T_2} \frac{c_p(T)}{T} dT$$

Schematic diagram of temperature dependence of (a) specific heat, c_p , and (b) specific entropy, s , of crystal, liquid, supercooled liquid, and glass.

Glasses 1 and 2 are obtained at different cooling rates and have different apparent glass transition temperatures. Glass 1, shown by dashed curve, has faster cooling rate than that used for glass 2, solid curve.

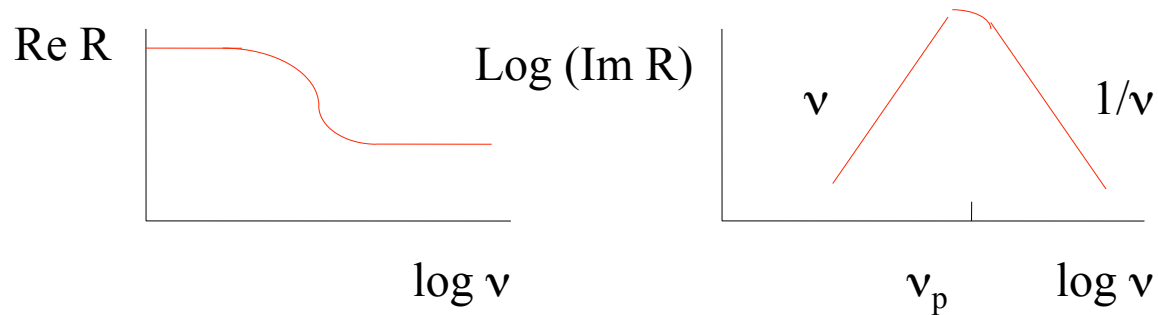
Single relaxation time: Debye model



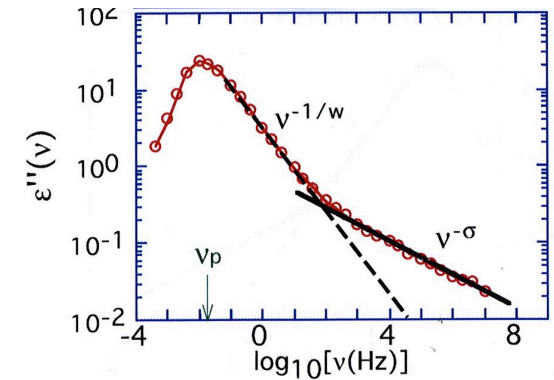
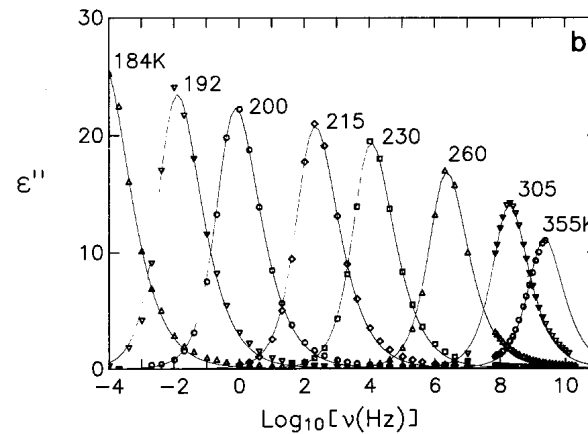
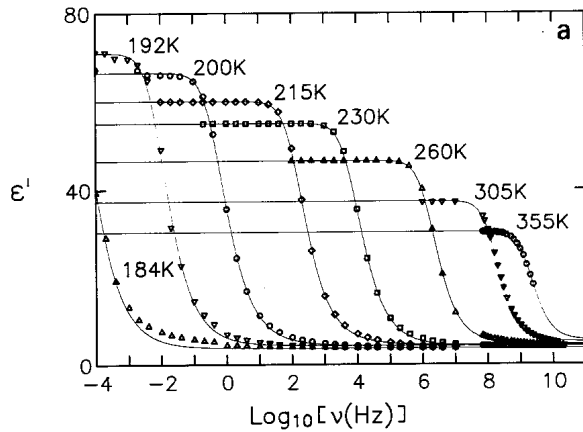
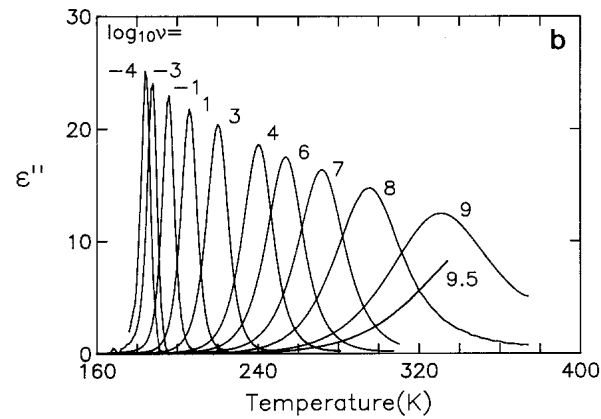
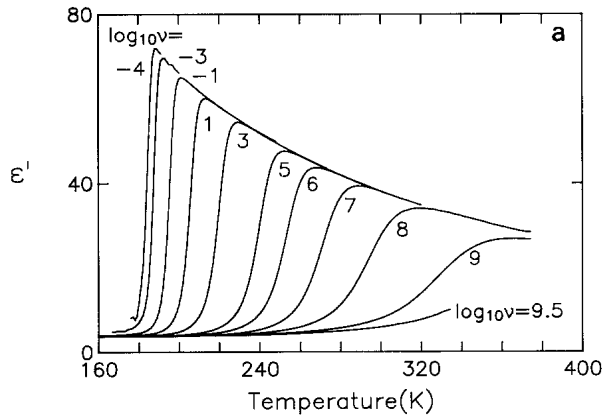
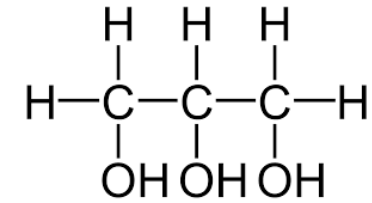
$$R(\omega) = R_{\infty} + [R_0 - R_{\infty}] / [1 - i \omega \tau]$$

Peak in imaginary (out-of-phase) part is at $\omega_p = 2\pi\nu_p = 1/\tau$
and has width

$$W_D = 1.14 \text{ decades}$$



Dielectric susceptibility of glycerol



Real and imaginary parts of the dielectric susceptibility of glycerol vs. temperature at labeled frequencies and vs. frequency at labeled temperatures.

Relaxation forms

$$\phi(t) = \phi_0 \exp -[t/\tau]^\beta$$

$$0 < \beta < 1$$

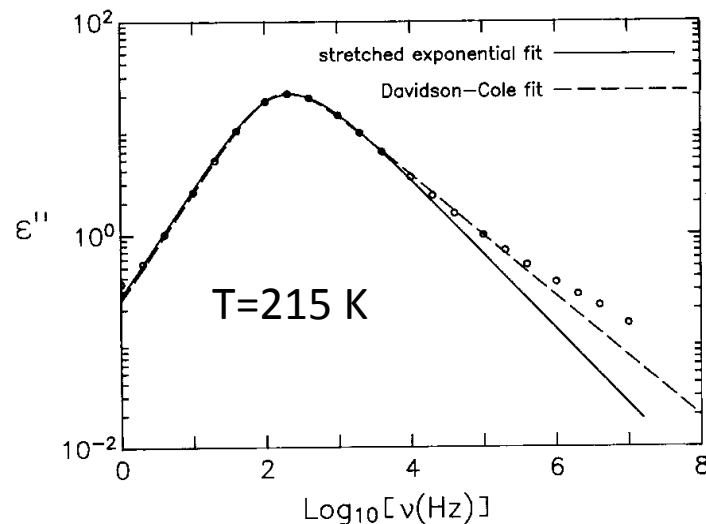
$$\phi(\omega) = \text{FT}\{-d/dt\} \phi_0 \exp [t/\tau]^\beta$$

Stretched exponential

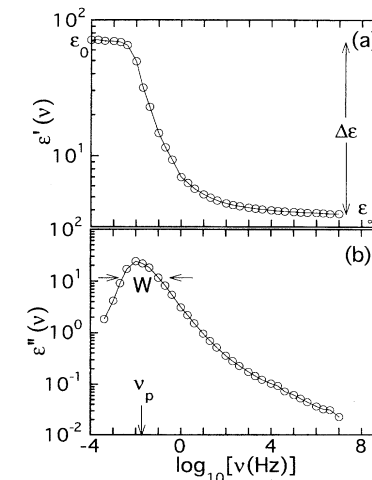
$$\varepsilon(\nu) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)[1/(1 + i2\pi\nu\tau)^\alpha]$$

$$0 < \alpha < 1$$

Cole-Davidson

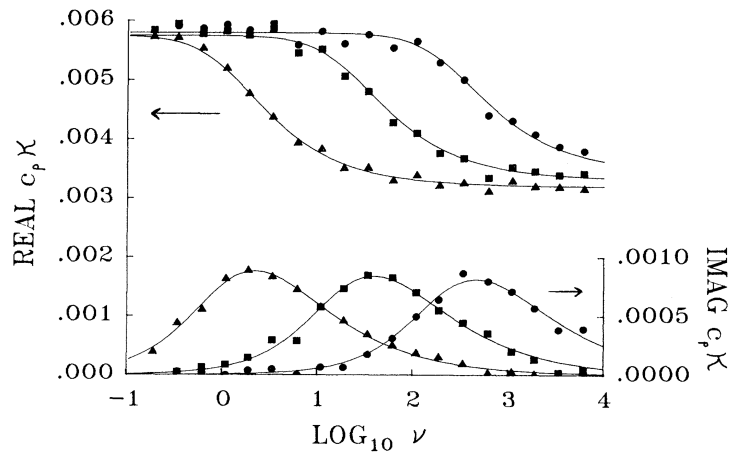


Glycerol at T = 215 K

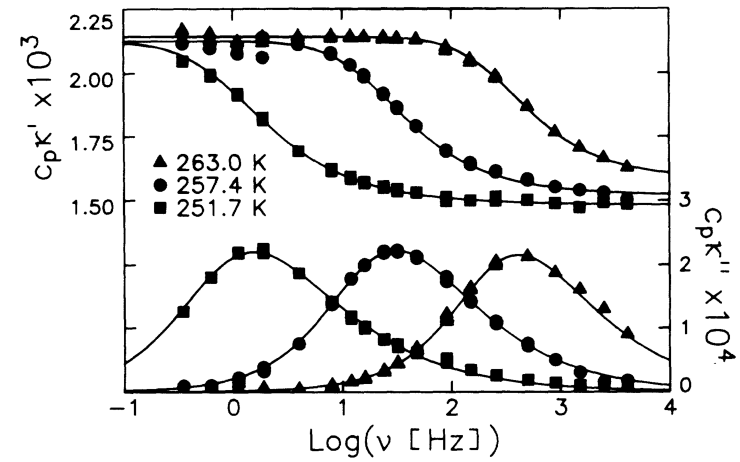


Glycerol at T = 192 K

Specific heat spectroscopy

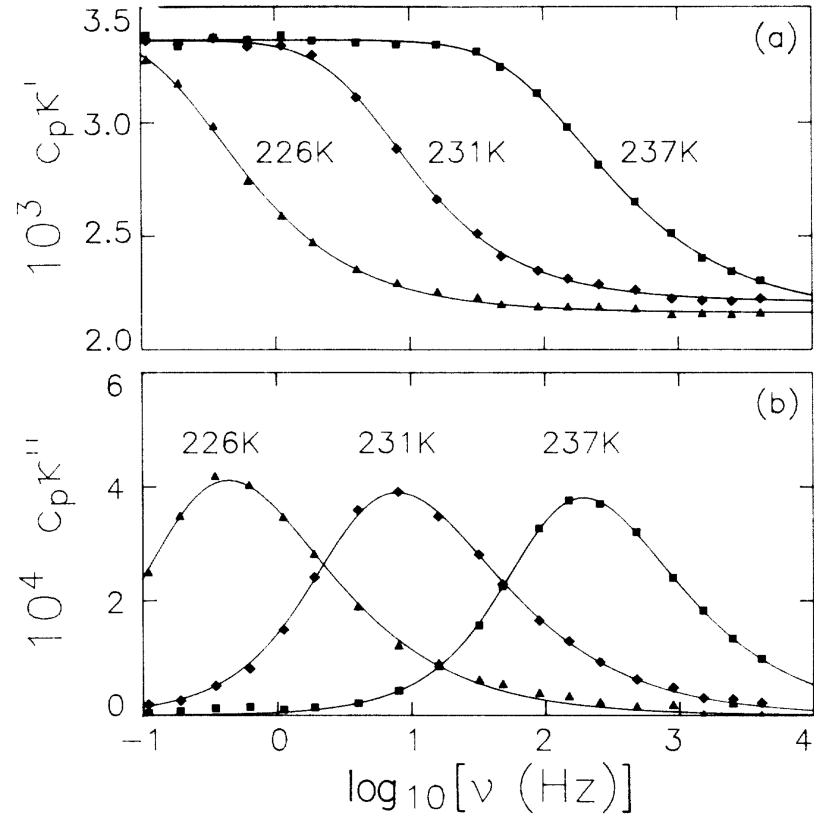
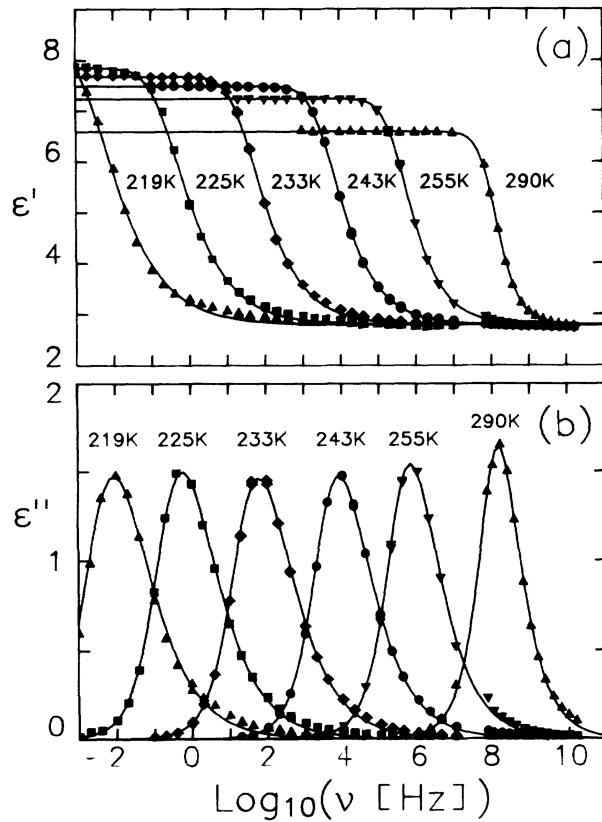


Glycerol



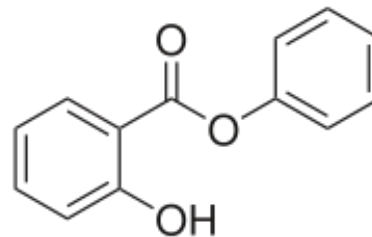
O-terphenyl mixtures

Dielectric and specific heat of salol

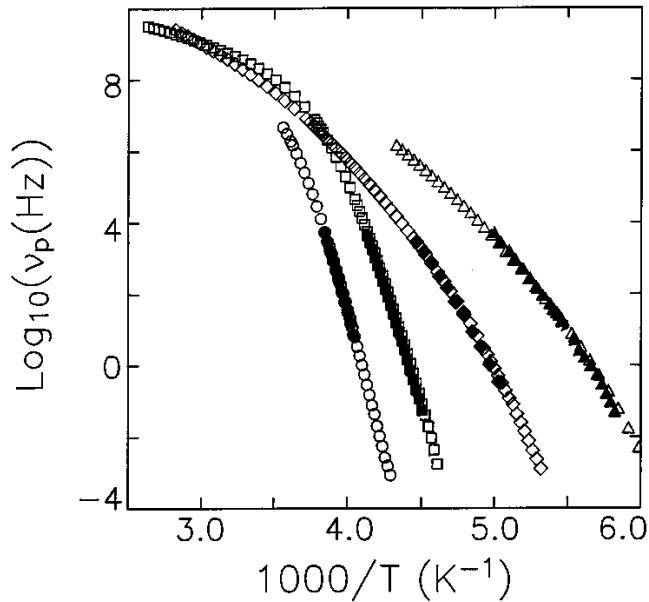


Real and imaginary parts of the dielectric susceptibility of salol vs. frequency at labeled temperatures.

Specific heat of salol

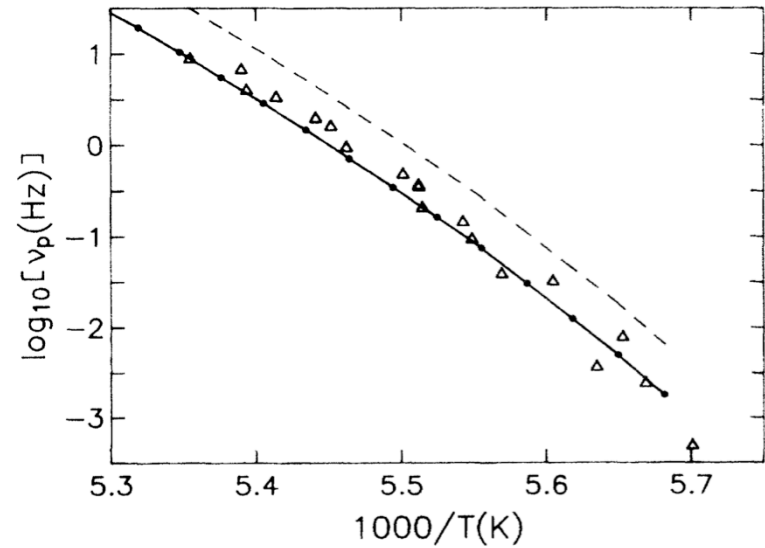


Peak frequency vs. $1/T$ (specific heat, dielectric, shear modulus)



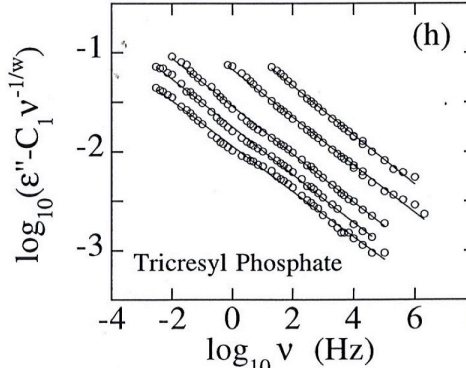
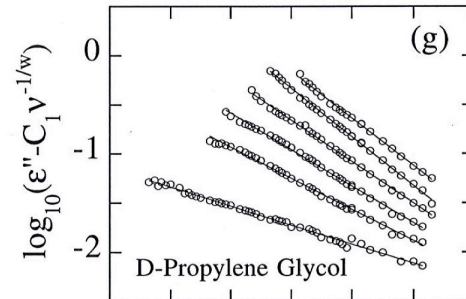
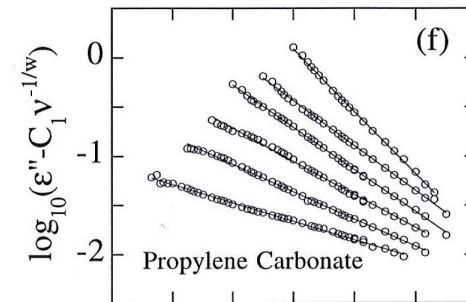
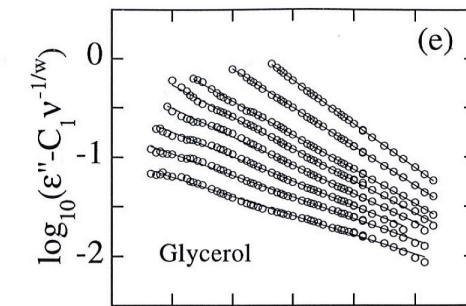
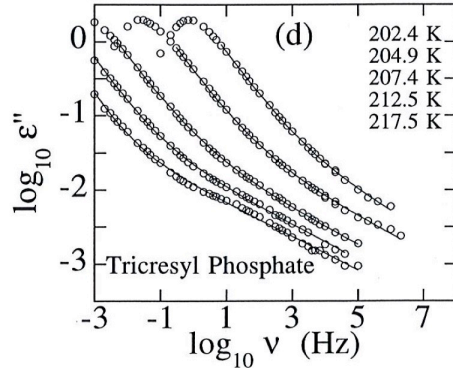
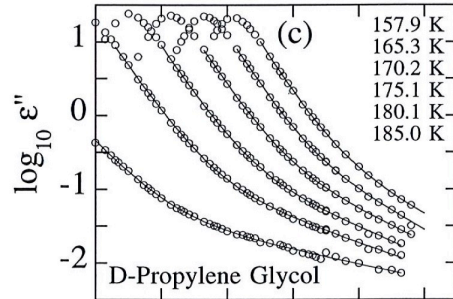
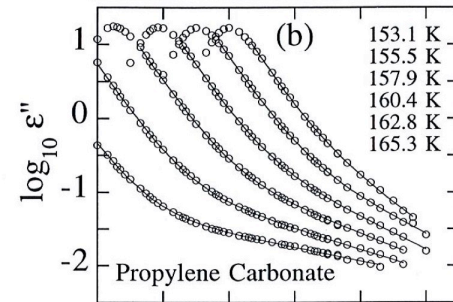
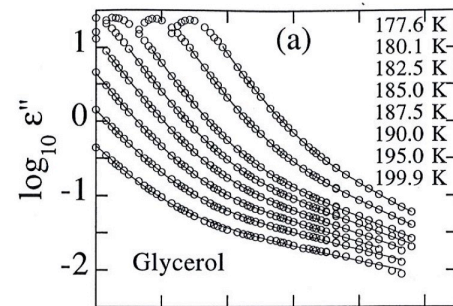
Log of peak frequency ν_p vs. $1/T$ for 4 samples: glycerol (\diamond), propylene glycol (Δ), salol (\square), and *o*-terphenyl mixed with 33% *o*-phenylphenol (O).

Open symbols for dielectric relaxation, and solid symbols for specific heat spectroscopy.



Temperature dependence of peak frequency of DBP from shear modulus (Δ) compared with dielectric spectroscopy (connected solid dots). Dashed line is electric modulus: $M(\nu) = 1/\epsilon(\nu)$

High-frequency tail: power law extending ~ 13 decades above peak



Susceptibility of Glasses

Dielectric susceptibility of liquids has 3 distinct frequency regimes.

