Web Course
Physical Properties of Glass

Glass Transformation-Range Behavior

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Materials Science & Engineering

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Glass Transformation-1

Glass Transformation-Range Behavior

- Structural relaxation and the glass transition

- Rheology and configurational entropy

- Thermal history effects on glass properties

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Supplementary References on Glass transformation-range behavior
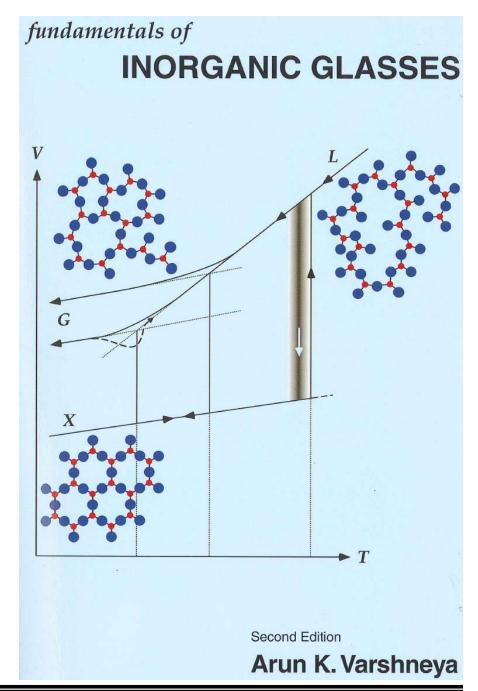
- Chapter 13 in 'the good book'*
- Structure, Dynamics and Properties of Silicate Melts, *Reviews in Mineralogy*, Vol. 32 (1995), ed. JF Stebbins, PF McMillan and DB Dingwell (Mineralogical Society of America)
  - CT Moynihan, Chap. 1, Structural relaxation and the glass transition
    - CT Moynihan et al, "Dependence of the Fictive Temperature of Glass on Cooling Rate," *J. Amer. Ceram. Soc.* **59** 12 (1976)
  - DB Dingwell, Chap. 2, Relaxation in silicate melts
  - P Richet and Y. Bottinga, Chap. 3, Rheology and configurational entropy of silicate melts
- GW Scherer, Glass formation and Relaxation, Chap. 3 in Materials Science and Technology, Vol. 9, ed. J. Zarzycki, VCH, 1991.

*AK Varshneya, Fundamentals of Inorganic Glasses, 2nd Ed (2006)

Why should we care?

- Glass properties depend on thermal history

- The nature of the glass transition is 'the deepest and most interesting unsolved problem in solid state theory'
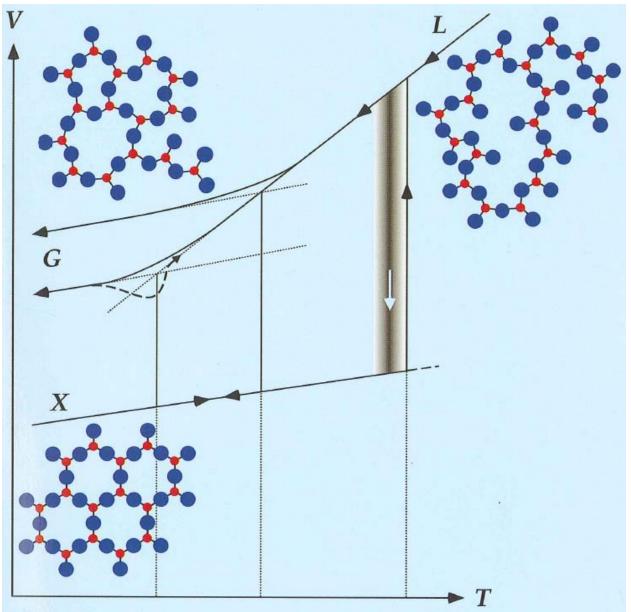-Philip W. Anderson, 1995

fundamentals of
INORGANIC GLASSES

Second Edition
Arun K. Varshneya

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Class Exercise- Consider the question 'What is the glass transition?'

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Structural relaxation and the glass transition

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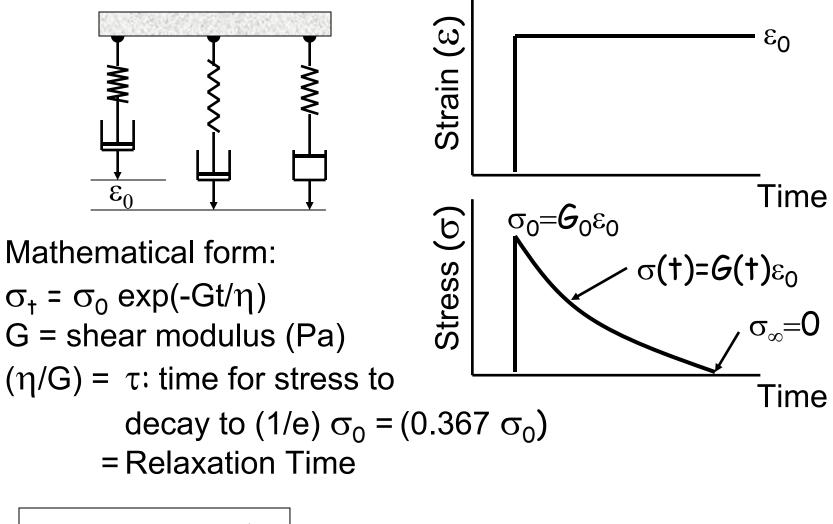
Glass transition:

- Changes in the structure of a super-cooled liquid 'fall out of equilibrium' as the liquid is cooled
- Relaxation time is long compared with the observational time
- Properties (including T_g) depend on thermal history; viz., quench rate through the glass transition region

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Structural relaxation

- Average structure specifies thermo-dynamic state of the liquid (T,P,V specified)
  - At equilibrium, average structure is time-independent
- Relaxation involves breaking/remaking network bonds
  - Dynamic equilibrium
  - Viscous characteristics of super-cooled liquid
  - Contribute to ΔH, ΔS, ΔV of the liquid as f(T,P)
- Structural relaxation rate decreases with decreasing temperature

Stress Relaxation- Maxwell Model

Mathematical form:

$\sigma_t = \sigma_0 \exp(-Gt/\eta)$

G = shear modulus (Pa)

$(\eta/G) = \tau$: time for stress to

     decay to $(1/e)\,\sigma_0 = (0.367\,\sigma_0)$

    = Relaxation Time

$$\boxed{\sigma_t = \sigma_0 \exp(-t/\tau)} \longleftarrow \text{Exponential relaxation curve}$$

Strain (ε)

ε_0

Time

Stress (σ)

$\sigma_0 = G_0 \varepsilon_0$

$\sigma(t) = G(t)\varepsilon_0$

$\sigma_\infty = 0$

Time

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Voigt-Kelvin Element-
Anelastic behavior

(a)

$2G\,\epsilon_{12}$ $2\eta\,\dot{\epsilon}_{12}$

S_{12}

(b)

$\dfrac{S_{12}}{2G}$

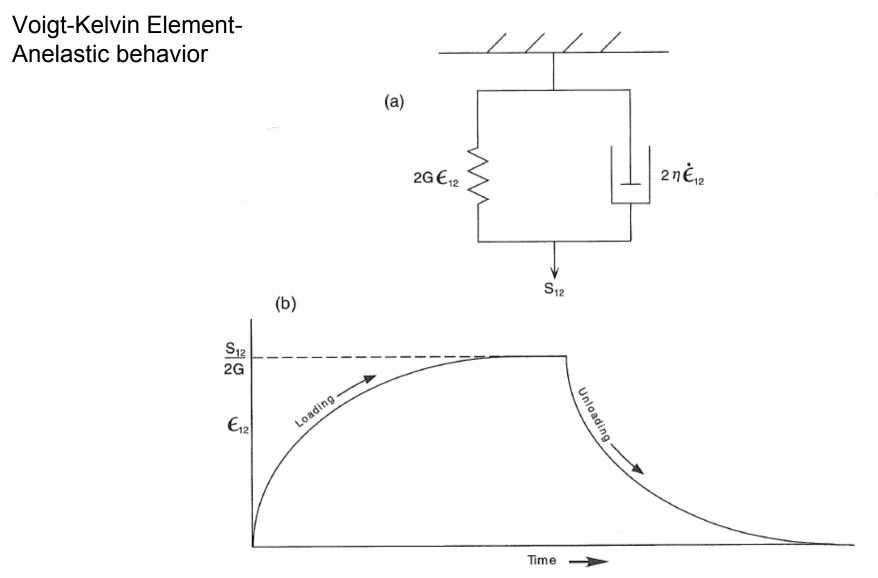ϵ_{12}

Loading

Unloading

Time

Figure 13-7. Voigt–Kelvin element. (a) Its composition. (b) Response after the application of a constant stress.

Burger element-permanent deformation

Note: viscoelastic substances may be modeled by a distribution of mechanical elements representing a distribution of structural features
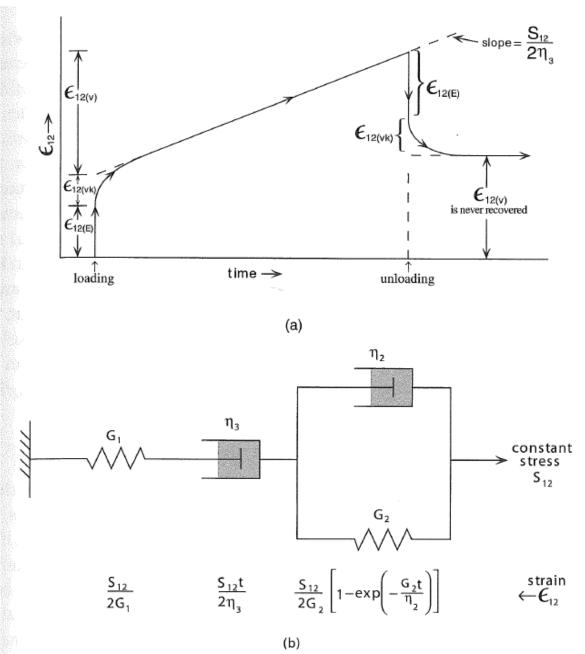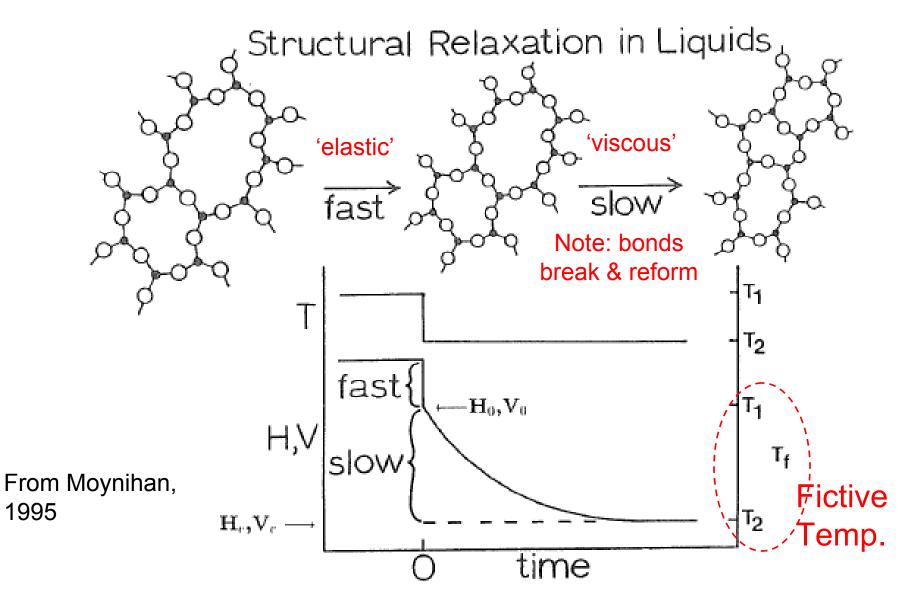

(a)

(b)

Figure 13-8. Delayed elasticity. (a) Variation of strain with time after loading and unloading. (b) Burger element.
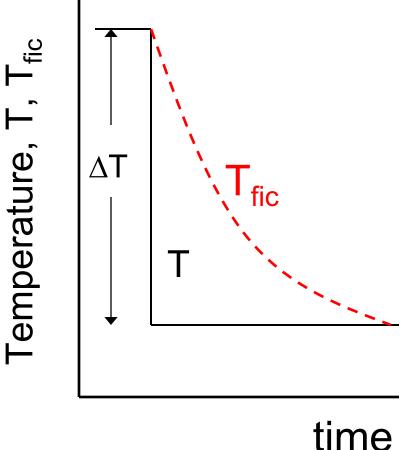
Consider isothermal relaxation after ΔT

Structural Relaxation in Liquids

'elastic' $\xrightarrow{\text{fast}}$ 'viscous' $\xrightarrow{\text{slow}}$

Note: bonds break & reform

From Moynihan, 1995

Fictive Temp.

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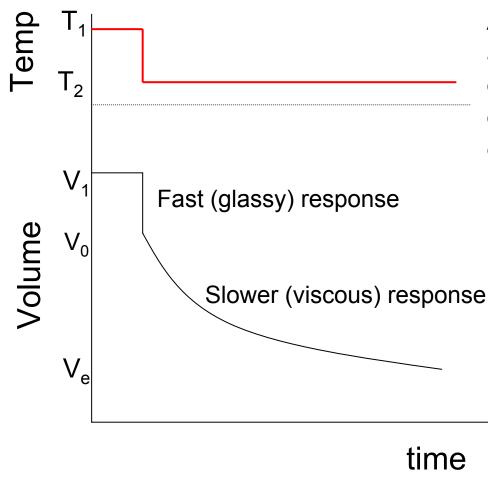Web-based Course
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Fictive Temperature

- Introduced by Tool, NBS (1946)

- Describes the contribution of structural relaxation to a property, expressed in units of temperature

- In equilibrium: $T_{fic}=T$ and $dT_{fic}/dT=1$

- For glass with 'frozen structure': $T_{fic}=$const. and $dT_{fic}/dT=0$

- *Not a fundamental property*, but a conceptual view

Fictive: feigned, sham (from fiction)

Relaxation Time

Assumption 1: the rate of structural relaxation is described by a characteristic relaxation time, τ

Assumption 2: rate at which volume approaches equilibrium defined by first order rate constant (k=1/t) and depends on deviation of volume from the new equilibrium value (at T_2):

$$\frac{d(V - V_e)}{dt} = k(V - V_e)$$

$$\Phi(t) = \frac{V - V_e}{V_0 - V_e} \equiv \frac{T_{fic} - T_2}{T_1 - T_2}$$

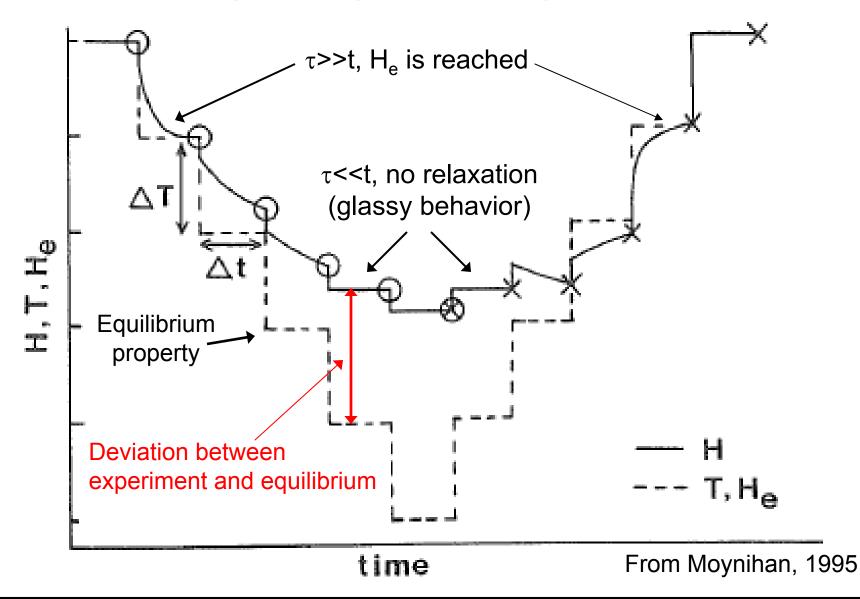$$\Phi(t) = \exp(-kT) = \exp\left(\frac{-t}{\tau}\right)$$

$\Phi(t)$ is a relaxation function
$\Phi(t) = 1$ at t=0, $\Phi(t) = 0$ at t=∞

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Assumption 3: for small departures from equilibrium and small ΔT, the temperature dependence of τ is described by the Arrhenius relationship:

$$\tau = \tau_0 \exp\left(\Delta H^*/RT\right)$$

where ΔH^* is the activation enthalpy

$\Delta H^* > 0$, so as T decreases, τ increases and the *rate* of structural relaxation decreases

Relaxation during heating and cooling

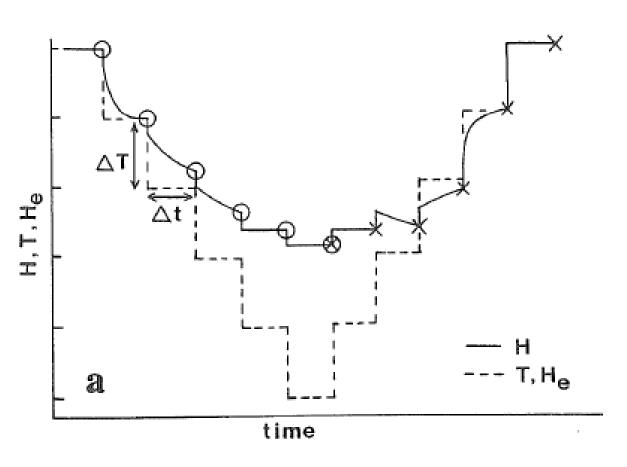τ>>t, H$_e$ is reached

τ<<t, no relaxation
(glassy behavior)

ΔT

Δt

H,T,H$_e$

Equilibrium
property

Deviation between
experiment and equilibrium

—— H

---- T,H$_e$

time

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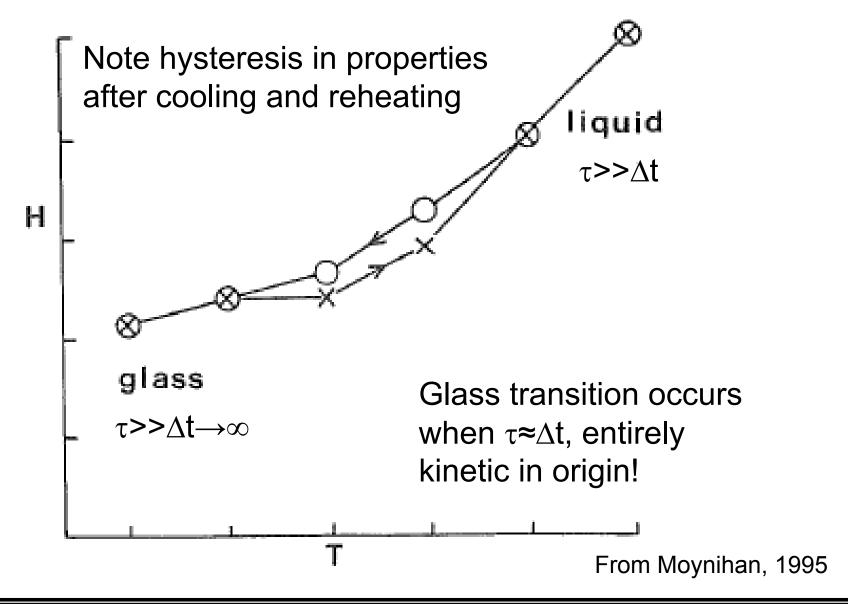Some observations:

On cooling, $H > H_e$ after Δt
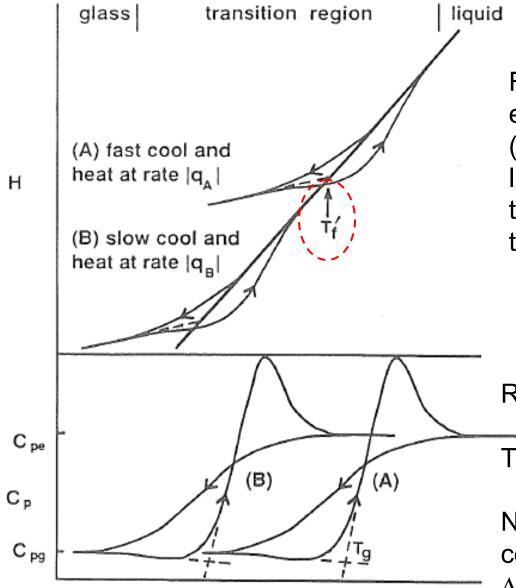On heating, $H < H_e$ after Δt

Note on heating: H initially *decreases* when approaching H_e, then *increases* at greater temperatures

cooling/heating rates are defined by $q = dT/dt$;
series of 'isothermal' holds for $\Delta t = \Delta T/q$

Information about relaxation time can be obtained by measuring property changes at different 'q'....

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Note hysteresis in properties after cooling and reheating

liquid

$\tau >> \Delta t$

H

glass

$\tau >> \Delta t \rightarrow \infty$

Glass transition occurs when $\tau \approx \Delta t$, entirely kinetic in origin!

T

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glass | transition region | liquid

(A) fast cool and heat at rate $|q_A|$

(B) slow cool and heat at rate $|q_B|$

T_f'

H

C_{pe}

C_p

C_{pg}

(B)   (A)
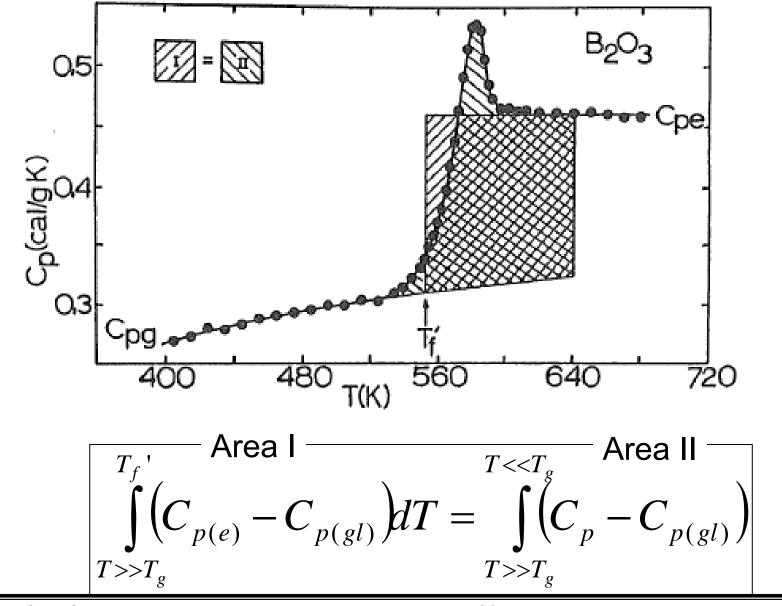
T_g

From Moynihan, 1995   Temperature

Fast cooling rate: 'fall out of equilibrium' at greater temperature (shorter relaxation time), greater limiting fictive temperature (T_f')- the intersection of the H-values for the glass and liquid

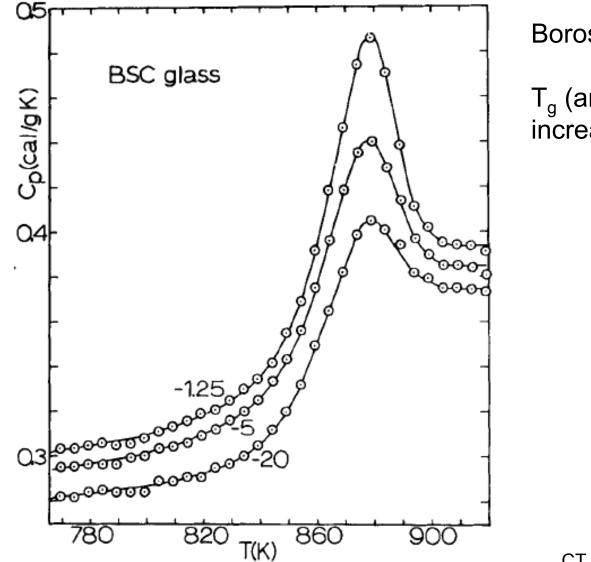Recall Heat Capacity C_p=dH/dT

T_g is 'observed' when t≈Δt=ΔT/q

Note: sigmoidal shape of $C_p(T)$ is a consequence of the hysteresis in the ΔH/ΔT due to the relaxation kinetics

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Measuring the 'limiting fictive temperature'- one measure of T_g

$$\underbrace{\int_{T\gg T_g}^{T_f{}'}\left(C_{p(e)} - C_{p(gl)}\right)dT}_{\text{Area I}} = \underbrace{\int_{T\gg T_g}^{T\ll T_g}\left(C_p - C_{p(gl)}\right)}_{\text{Area II}}$$

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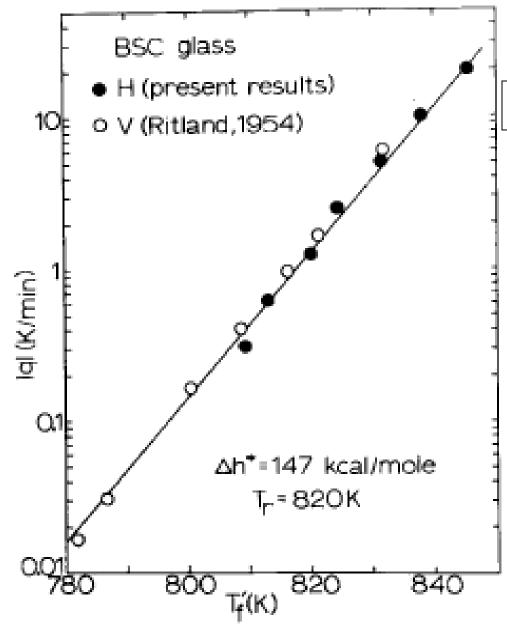# The glass transition temperature depends on the thermal history

Borosilicate crown glass

T_g (and T_{fic}) increases with increasing quench rates (q_c)

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BSC glass
● H (present results)
○ V (Ritland, 1954)

$\Delta h^* = 147$ kcal/mole
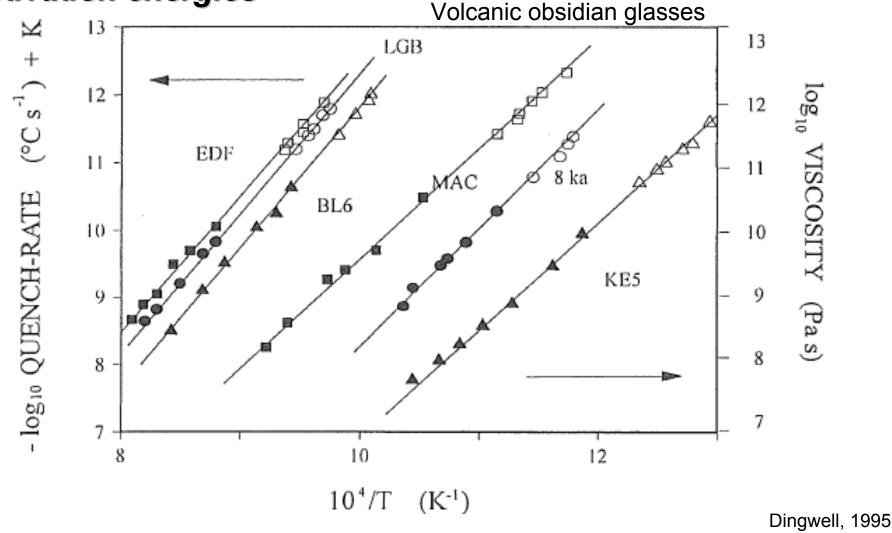$T_r = 820K$

$$d(\ln q_c)/d(1/T_f') = -\Delta H^*/R$$

Note: Over small temperature intervals, centered on T_r, the activation energies for enthalpy relaxation are equivalent to those from shear-viscosity measurements (solid line) and from volume relaxation measurements (Ritland)

CT Moynihan, et al., JACerS, 59 12 (1976)

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Shear viscosity relaxation (closed symbols) and enthalpy relaxation (open symbols) processes have the same activation energies

Volcanic obsidian glasses

Dingwell, 1995

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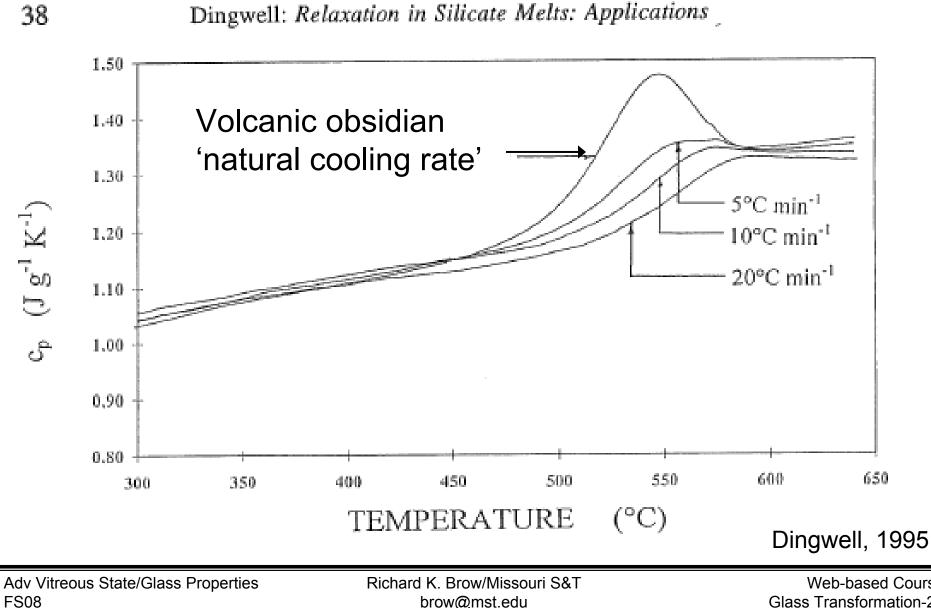Web-based Course
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Table 1. Glass transition temperatures Tg measured by DSC at 10 K/min heating rate, logarithms of mean equilibrium enthalpy structural relaxation times $< \tau >$ and shear viscosities η at Tg, and activation enthalpies ΔH^* and ΔH_η^* for structural relaxation and viscous flow in the glass transition region.

Glass	Tg(K)	$\log < \tau >$(s)	$\log\eta$(Pa·s)	ΔH^* (kJ/mol)	ΔH_η^* (kJ/mol)
As$_2$Se$_3$	454	2.4	10.8	342	322
B$_2$O$_3$	557	2.6	11.4	385	385
ZBLA	587	2.8	11.6	1400	1140
lead silicate (NBS 711)	714	2.6	11.9	374	411
0.25Na$_2$O-0.75SiO$_2$	748	2.7	11.6	410	435
GeO$_2$	810	—	11.5	—	303
alkali lime silicate (NBS 710)	832	2.6	11.8	612	612
alkali borosilicate (BSC)	836	—	12.1	615	615
diopside (CaMgSi$_2$O$_6$)	973	—	12.7	—	965
anorthite (CaAl$_2$Si$_2$O$_8$)	1109	—	12.6	—	1084

Enthalpy Relaxation
vs.
Viscous Flow

From Moynihan, 1995

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Table 1. Glass transition temperatures Tg measured by DSC at 10 K/min heating rate, logarithms of mean equilibrium enthalpy structural relaxation times $< \tau >$ and shear viscosities η at Tg, and activation enthalpies ΔH^* and ΔH_η^* for structural relaxation and viscous flow in the glass transition region.

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Enthalpy Relaxation
vs.
Viscous Flow

From Moynihan, 1995

Example: Geospeedometry

38 Dingwell: *Relaxation in Silicate Melts: Applications*

Volcanic obsidian 'natural cooling rate'

5°C min⁻¹
10°C min⁻¹
20°C min⁻¹

c_p (J g⁻¹ K⁻¹)

TEMPERATURE (°C)

Dingwell, 1995

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Example: Geospeedometry

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Kinetics of structural relaxation

- Qualitative 'first order' kinetic model

$$\Phi(t) = \exp\left(\frac{-t}{\tau}\right)$$

$$\tau = \tau_0 \exp\left(\Delta H * / RT\right)$$

- Quantitative model must account for
  - **Non-linear character** of the relaxation function
  - **Non-exponential character** of the relaxation function

Non-linear isothermal relaxation

Figure 8. Isothermal relaxation at 530°C of the density of a soda lime silicate glass following an upward step change in temperature from 500°C (upper curve) and a downward step in temperature from 565°C (lower curve). Solid lines are calculated from Equations (8), (14) and (15) using the parameters $\tau_0 = 3.9 \times 10^{-37}$ s, $\Delta H^* = 607$ kJ/mol, x = 0.45 and $\beta = 0.62$.

Note that the relaxation time depends on the instantaneous structure (fictive temp)

$$\tau = \tau_0 \exp\left[\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f} \right]$$

Tool-Narayanaswamy (TN) Equation
x is the nonlinear parameter (0≤x≤1)

From Moynihan, 1995

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Relaxation is non-exponential

Plot with x-axis "Normalized time" (0 to 1.2) and y-axis "Normalized property" (0 to 1.2).

Legend:
- beta=1.0
- beta=0.8
- beta=0.6
- beta=0.4

$$\Phi(t) = \exp\left(\frac{-t}{\tau}\right)^{\beta}$$

Stretched exponential function (KWW)- β is the non-exponentiality parameter ($0 \leq \beta \leq 1$)

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Distribution of relaxation times

$$\exp\left[-\left(\frac{t}{\tau_p}\right)^{\beta}\right] \approx \sum_{k=1}^{N} w_k \exp\left(-\frac{t}{\tau_k}\right)$$

Broader distributions are associated with smaller values of β

Figure 3-18. Distribution of relaxation times obtained when the KWW function is represented by sum of exponential terms, as in Eq. (3-44); $\beta = 1$ corresponds to a single relaxation time. As β decreases the distribution broadens, but always remains skewed to short times.

Scherer, 1991

Is there a physical source for non-exponentiality?

Consider a distribution of relaxation times (τ_i) incorporated into the relaxation function with a weighting coefficient (g_i, where $\Sigma g_i = 1$), and each relaxation time described by the T-N form:

$$\Phi(t) = \sum_i g_i \exp\left[-\int_0^t dt'/\tau_i\right]$$

$$\tau_i = \tau_0 \exp\left[\frac{x\Delta H*}{RT} + \frac{(1-x)\Delta H*}{RT_f}\right]$$
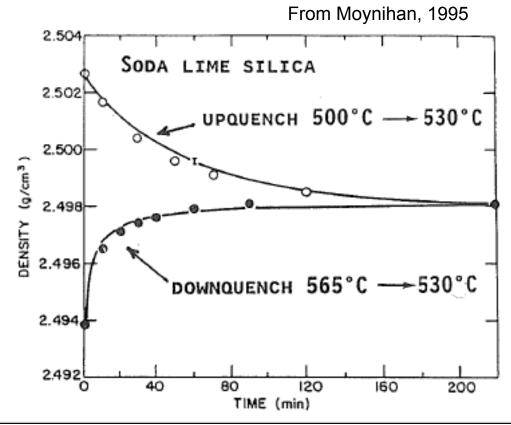
Microscopic interpretation:
- Relaxation involves coupled responses of a series of processes with different 'reaction rates'- bond 1 breaks, then bond 2…..
- Different regions within liquid relax at different rates because of structural differences (differences in configurational entropy from μ-region to μ-region)

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Structural relaxation models

- Four adjustable parameters: τ_0, ΔH^*, x, β

From Moynihan, 1995

$$\Phi(t) = \frac{P(t) - P_e}{P_0 - P_e} \equiv \frac{T_{fic}(t) - T_2}{T_1 - T_2}$$

Figure 8. Isothermal relaxation at 530°C of the density of a soda lime silicate glass following an upward step change in temperature from 500°C (upper curve) and a downward step in temperature from 565°C (lower curve). Solid lines are calculated from Equations (8), (14) and (15) using the parameters $\tau_0 = 3.9 \times 10^{-37}$ s, $\Delta H^* = 607$ kJ/mol, $x = 0.45$ and $\beta = 0.62$.

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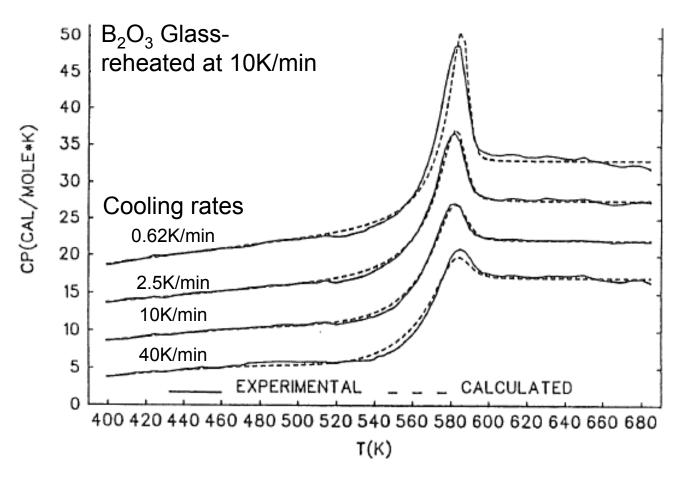brow@mst.edu

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Figure 9. Heat capacities of B_2O_3 glass measured during heating at 10 K/min after cooling through the transition region at rates of 0.62, 2.5, 10 and 40 K/min (top curve to bottom curve). Heat capacity scale is correct for top curve; other curves have been displaced downward for clarity. Solid lines are experimental data. Dashed lines are calculated from Equations (8), (16), (17) and (18) using the parameters $\tau_0 = 1.3 \times 10^{-33}$ s, $\Delta H^* = 377$ kJ/mol, x = 0.39 and $\beta = 0.62$.

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Structural Relaxation Summary

- The glass transition is a kinetic phenomena
  - Thermal history dependence
- Thermal history effects on glass properties described using the 'fictive temperature' concept.
  - T_{fic} represents the contribution of structural relaxation to the property of interest, expressed in temperature units
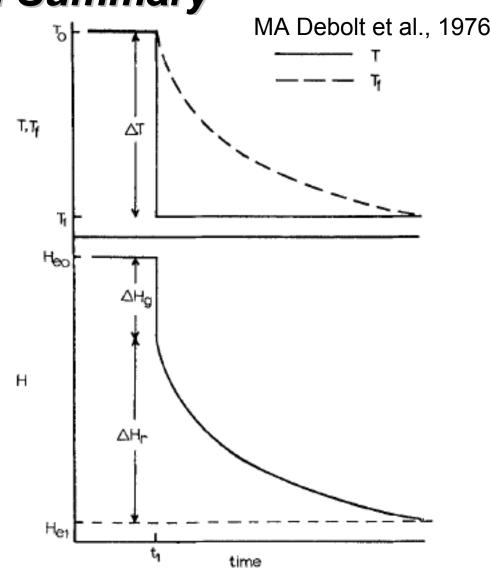
MA Debolt et al., 1976

Fig. 1.   Schematic of isothermal evolution of enthalpy and fictive temperature following a single temperature jump.

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Structural Relaxation Summary

The relaxation function $\Phi(t)$

1. Is **non-linear**

- Up-quench $\neq$ down-quench relaxation rates
- $\Phi(t)$ depends on instantaneous structure (T_{fic})
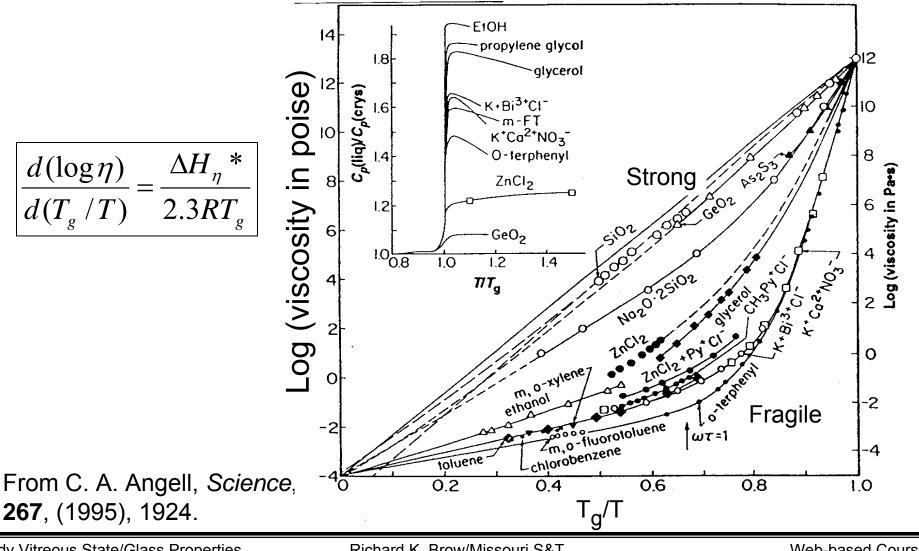- Tool-Narayanaswamy 'non-linearity' parameter 'x'

$$\tau = \tau_0 \exp\left[\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f}\right]$$

2. Is **non-exponential**

- 'Stretched exponential' function (KWW)- β

$$\Phi(t) = \exp\left(\frac{-t}{\tau}\right)^{\beta}$$

- Modeled by a distribution of relaxation times
- Is their a 'microscopic' explanation?

How is enthalpy relaxation connected to viscosity?

$$\frac{d(\log \eta)}{d(T_g / T)} = \frac{\Delta H_\eta {}^*}{2.3 R T_g}$$

From C. A. Angell, *Science*, **267**, (1995), 1924.

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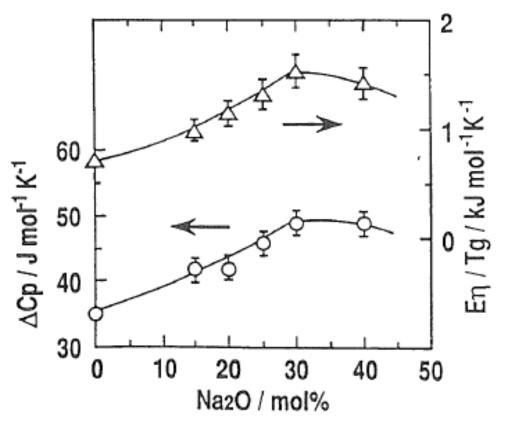# *How is enthalpy relaxation connected to viscosity?*

xNa$_2$O (1-x)B$_2$O$_3$ glasses

Fragile melt behavior (greater E$_\eta$/T$_g$) correlated with larger ΔC$_p$ at T$_g$…

$$\frac{d(\log \eta)}{d(T_g / T)} = \frac{E_\eta}{2.3RT_g}$$

Related to greater structural changes as glass is heated through transition range?

Figure 12. Composition dependences of ΔC_P and H$_\eta$*/Tg (= E$_\eta$/Tg) at Tg for $x\cdot$Na$_2$O-(100-x)$\cdot$B$_2$O$_3$ melts (Lee et al., 1995).

Moynihan, 1995

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Relaxation time at $T_g \approx$ 400-600 sec

Angell defines T_g at 10^{12} Pa·

Enthalpy Relaxation and Viscous Flow have similar activation energies- similar 'structural' mechanisms?

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$0.25Na_2O-0.75SiO_2$	748	2.7	11.6	410	435
GeO_2	810	—	11.5	—	303
alkali lime silicate (NBS 710)	832	2.6	11.8	612	612
alkali borosilicate (BSC)	8:		12.1	615	615
diopside ($CaMgSi_2O_6$)	973	—	12.7	—	965
anorthite ($CaAl_2Si_2O_8$)	1109	—	12.6	—	1084

From Moynihan, 1995

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Glass Transition Theories

- Free Volume-Viscosity
- Adam-Gibbs Cooperative Relaxations
  - Configurational Entropy

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Free Volume Theory

- Turnbull, Cohen, J Chem Phys 52 3038 (1970); Cohen, Grest Phys Rev B, 20 1077 (1979)

- Consider 'ideal' close-packed structure representing a thermodynamic minimum volume, V_0

- Flow occurs by movement of molecules into voids or holes larger than a critical size, V_h

  - Thermal/density fluctuations open up voids

  - Increase temperature, increase specific volume (V) of melt

  - Free volume (V_f) within a structure becomes available to accommodate viscous flow

$$\eta = \eta_0 \exp\left[\frac{V_0}{V_f(T,P,...)}\right]$$

hole

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Free volume depends melt properties

$$V_f(T,P) = V_0 \left[\int\limits_{T_0,P_0}^{T,P_0} \Delta\alpha_P dT - \int\limits_{T_0,P_0}^{T_0,P} K_T dP \right]$$

α_P=isobaric expansion coefficient
K_T=isothermal compressibility
For constant pressure,

$$\frac{V_f}{V_0} \approx \int\limits_{T_0}^{T} \left(\alpha_{liq} - \alpha_{glass} \right) dT \approx \left(\alpha_{liq} - \alpha_{glass} \right)\left(T - T_0 \right)$$

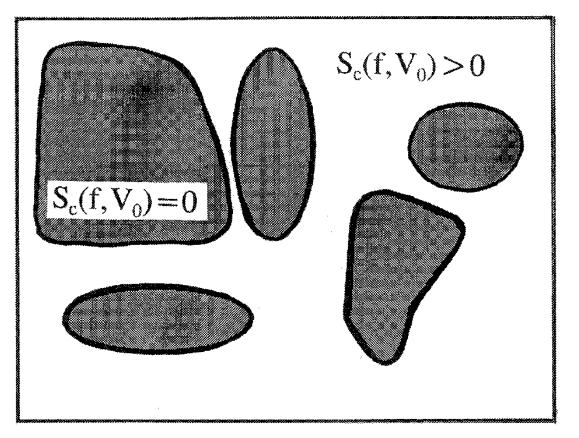Substitute into the Arrhenian η equation to get the VFT eq.:

$$\boxed{\log\eta = A + \frac{B}{T - T_0}}$$

"T_0" represents the temperature at which free volume disappears

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Configurational Entropy Model

- G. Adam, JH Gibbs, J. Chem. Phys., 43 139 (1965); GW Scherer, J. Am Ceram Soc, 67 504 (1984)

- Fluidity of a system depends on the rate of disappearance of the configurational entropy

- A system at the ideal glass transition temperature (T_2) has no more configurational entropy to lose
  – System is 'frozen' into 'ground state' of amorphous packing

- Adam-Gibbs model assumes that a liquid consists of a number of regions that can cooperatively rearrange
  – Each region consists of 'Z' molecules that can rearrange independently in response to an enthalpy fluctuation

- As a liquid is supercooled, configurational entropy of the system is reduced and the size of the cooperatively rearranging subsystems grows larger
  – Increased coupling between neighboring molecules with decreasing temp.

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Visualizing configurational entropy…

$$S_c(f, V_0) > 0$$

$$S_c(f, V_0) = 0$$

Lattice model version: glass regions imbedded in sea of liquid-glass transition occurs (on cooling) when the percolation limit for imbedded regions is reached

EA DiMarzio, J. Res. Natl. Inst. Stand. Technol. **102**, 135 (1997)

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Adam-Gibbs (cont.)

- Probability for a single cooperative transition:

$$p(T) = A \exp\left(-\frac{z\delta\mu}{k_B T} \right)$$

where A is a frequency factor and $\delta\mu$ is the energy barrier (per molecule) to rearrangement. The average transition probability depends on the lower limit to the sizes of the cooperative regions (z^*):

$$\langle p(T) \rangle = \sum_{z=z^*}^{\infty} A \exp\left(-\frac{z\delta\mu}{k_B T} \right) \approx \langle A \rangle \exp\left(-\frac{z^*\delta\mu}{k_B T} \right)$$

Entropy of the entire system (S_c) depends on the number (n) of rearranging units of size z and the entropy contribution of each unit: $S_c = n s_c$. For one mole of molecules, there are $n = N_A/z$ independent regions, so $z^* = s_c^* N_A / S_c$ and $s_c^* \approx k_B \ln 2$ is the configurational entropy of a minimally sized region.

$$\langle p(T) \rangle = \langle A \rangle \exp\left(-\frac{s_c^* N_A \delta\mu}{k_B T S_c} \right) = \langle A \rangle \exp\left(-\frac{C}{T S_c} \right)$$

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Adam-Gibbs (cont.)

Since fluidity ($1/\eta$) is proportional to the transition probability, then

$$\eta = \eta_0 \exp\left(\frac{C}{TS_c}\right)$$

Note that $\eta \to \infty$ as S_c decreases ($\Delta s \to 0$); viz., fewer configurations are accessible, more molecules must cooperate to permit flow. At some temp (T_K), $Z \to \infty$ and flow no longer occurs.

$$S_c \approx \int_{T_K}^{T} \frac{\Delta C_p}{T}, \quad \Delta C_p = \frac{D}{T}$$

Angell: Fragile liquids have small values for 'D', strong liquids have large values.

$$S_c \approx D\left(\frac{1}{T_K} - \frac{1}{T}\right)$$

$$\boxed{\eta \approx \eta_0 \exp\left(\frac{B}{T - T_K}\right)}$$ VFT-form

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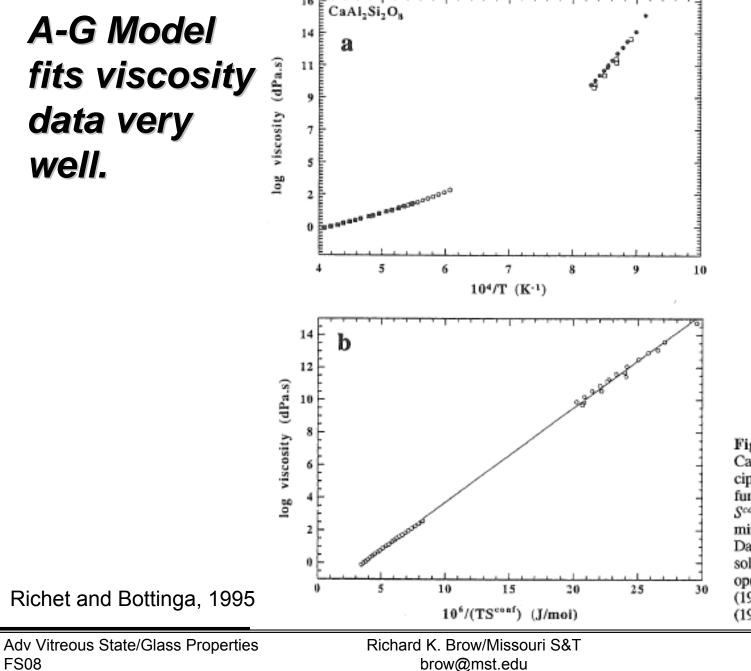
A-G Model fits viscosity data very well.

Figure 7. Viscosity of liquid $CaAl_2Si_2O_8$ as a function of reciprocal temperature (a) and as a function of $1/TS^{conf}$ (b), where S^{conf} is the calorimetrically determined configurational entropy. Data from Urbain et al. (1982; solid squares), Scarfe et al. (1983; open circles), Hummel and Arndt (1985; open squares) and Sipp (1993; solid circles).

Richet and Bottinga, 1995

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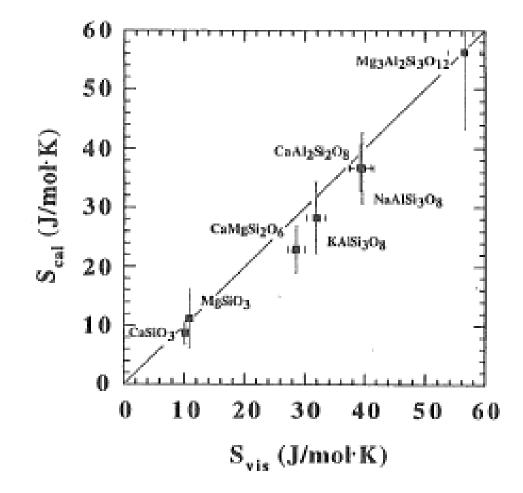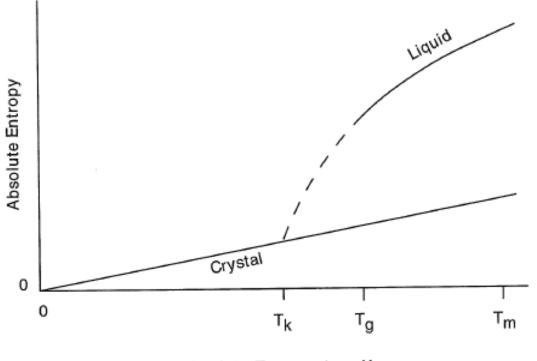
A-G Model fits viscosity data very well.

Figure 8. Comparison between configurational entropies at the glass transition determined from either calorimetric or viscosity measurements.

Richet and Bottinga, 1995
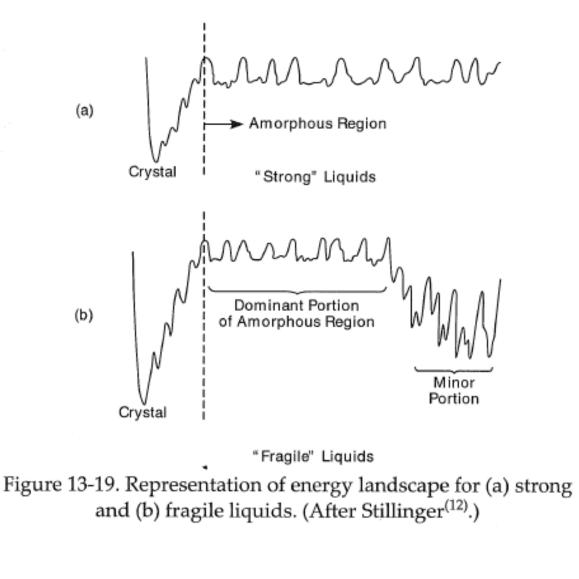
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Kauzmann Temperature (T_K)

Figure 13-16. Absolute entropy of liquid and crystal with temperature. Note discontinuity of slope at T_K (Kauzmann temperature).

Does the extension of the supercooled liquid entropy below T_g by slower cooling lead to the condition where this entropy is equal to that of the crystal?

•Kinetic barrier to a thermodynamic catastrophe
•*"Frozen in transition" without any specific thermodynamic order**
•T_K provides a thermodynamic basis for the VFT relationship

*Varshneya (p.328)

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Figure 13-19. Representation of energy landscape for (a) strong and (b) fragile liquids. (After Stillinger[12].)

Potential energy landscapes represent configuration distributions in a system

From Adam-Gibbs, each transition probability depends on $\delta\mu$, the energy barrier (per molecule) to rearrangement

$$p(T) = A\exp\left(-\frac{z\delta\mu}{k_B T}\right)$$

Fragile liquids are characterized by many different configurations that are accessible at greater temps: greater S_c, lower η.

Strong liquids have few local minima- single barrier, Arrhenius dependence?

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Summary- Glass Transition

- Upon cooling a liquid through the supercooled region, viscosity rapidly rises
  - Glass transition range: 10^8-10^{15} Pa-s
  - Glass transition temperature sometimes defined at 10^{12} Pa-s
- Rapid rise in viscosity implies a rapid reduction in free volume and a loss of configurational entropy
- Fictive temperature
  - Divergence of the temperature dependent properties of a supercooled liquid and glass; e.g., V-T curve
  - structure of a glass corresponding to the structure of the liquid at T_{fic}
- A change in temperature in the transition range produces a nonlinear approach to equilibrium for glass properties, like viscosity
  - Properties depend on changing experimental temperature and changing fictive temperature
  - Fictive temperature history determines the physical properties of a glass

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