# MIT 3.071
Amorphous Materials

3: Glass Forming Theories

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After-class reading list

- Fundamentals of Inorganic Glasses

  - Ch. 3 (except section 3.1.4)

- Introduction to Glass Science and Technology

  - Ch. 2

- 3.022 nucleation, precipitation growth and interface kinetics

- Topological constraint theory

  - M. Thorpe, "Continuous deformations in random networks"

  - J. Mauro, "Topological constraint theory of glass"

Glass formation from liquid
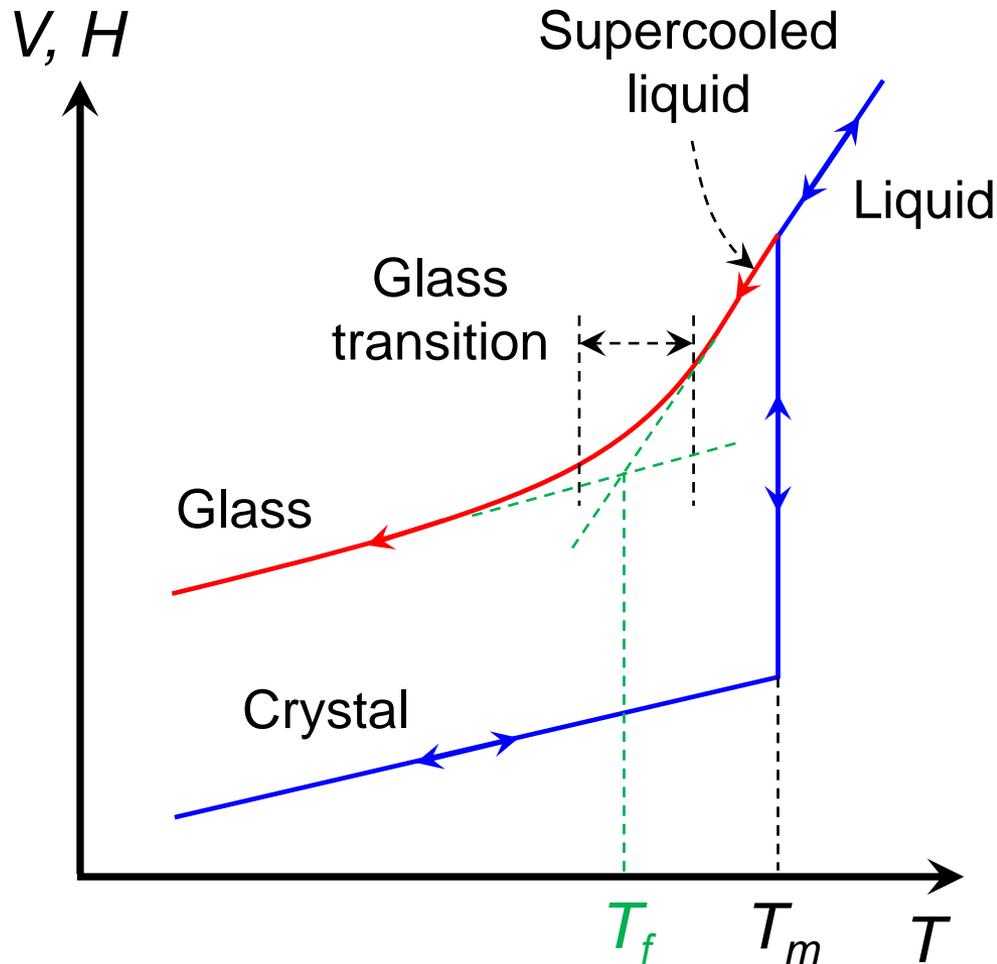
? Supercooling of liquid and suppression of crystallization

? Glass transition: from supercooled liquid to the glassy state

? Glass forming ability: the structural origin

Glass forming theories

- The kinetic theory

  - □ Nucleation and growth

  - □ *"All liquids can be vitrified provided that the rate of cooling is fast enough to avoid crystallization."*

- Laboratory glass transition

  - □ Potential energy landscape

- Structural theories

  - □ Zachariasen's rules

  - □ Topological constraint theory

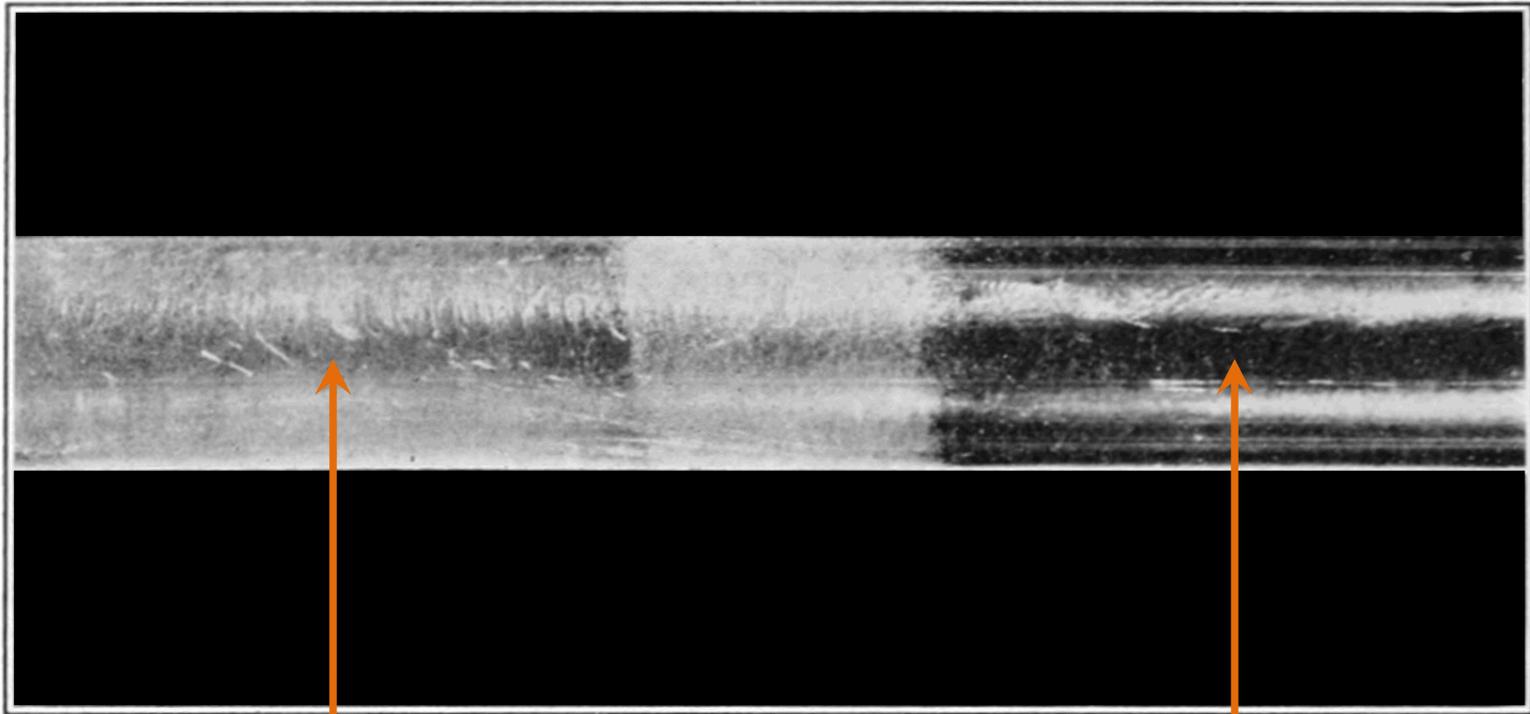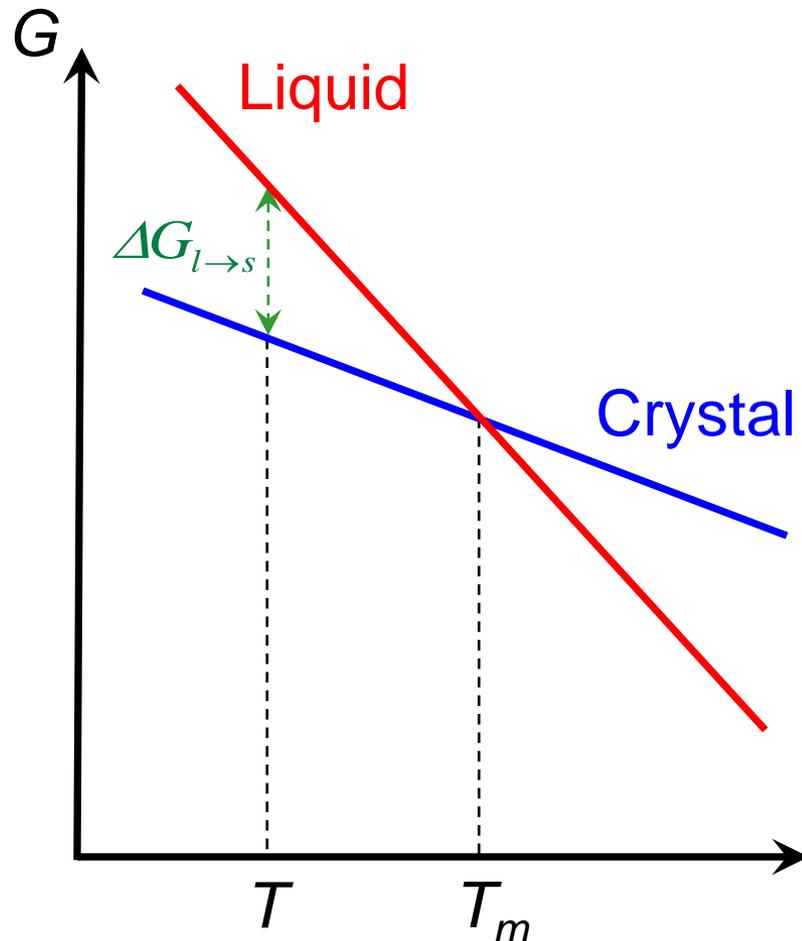# Crystallization is the opposite of glass formation

Image is in the public domain.

Crystallized

Amorphous

Suspended Changes in Nature, Popular Science 83 (1913).

Thermodynamics of nucleation

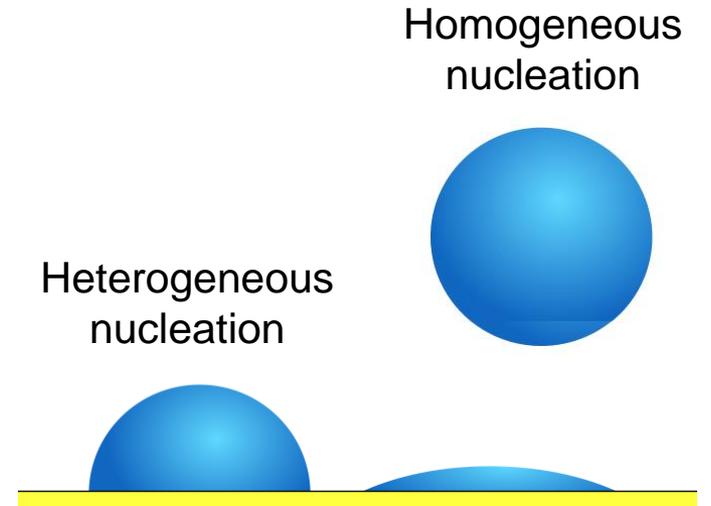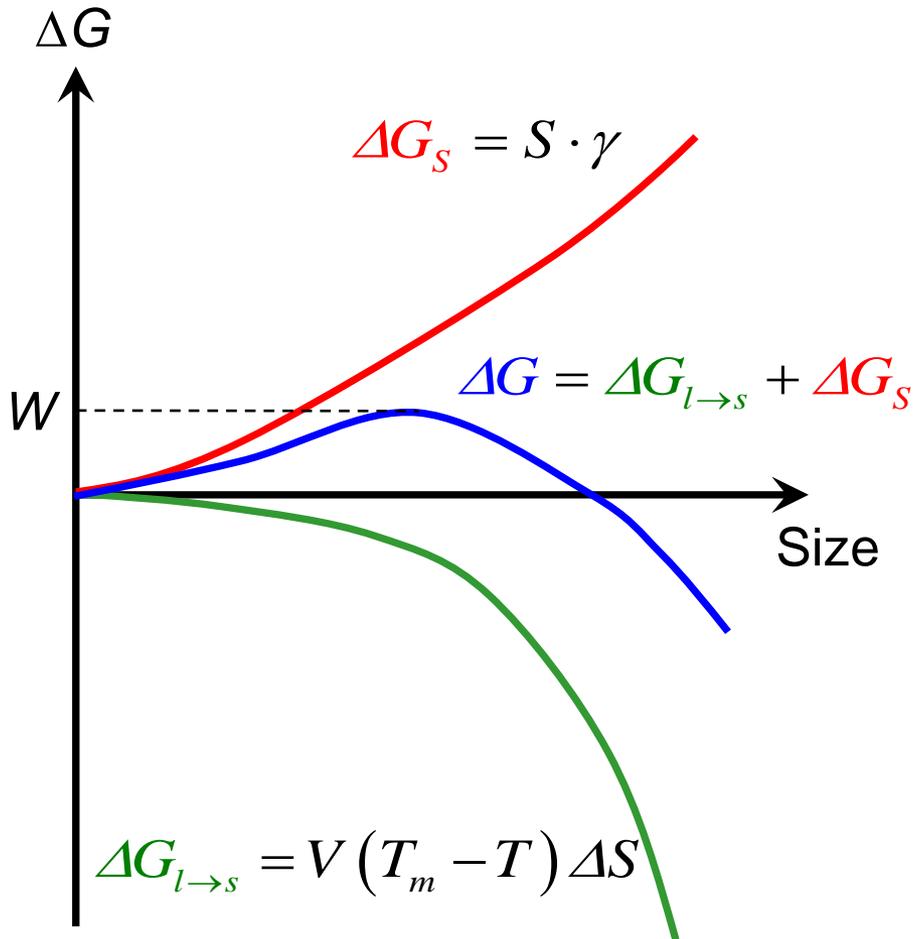$$G = H - TS \qquad \frac{\partial G}{\partial T} = -S$$

$$\because S_l > S_s$$

$$\therefore \left| \frac{\partial G_l}{\partial T} \right| > \left| \frac{\partial G_s}{\partial T} \right|$$

When $T < T_m$,

$$\Delta G_{l \to s} = G_s - G_l < 0$$

$$= V \cdot (T_m - T) \cdot \Delta S$$

Driving force for nucleation

Thermodynamics of nucleation

$$\Delta G_S = S \cdot \gamma$$
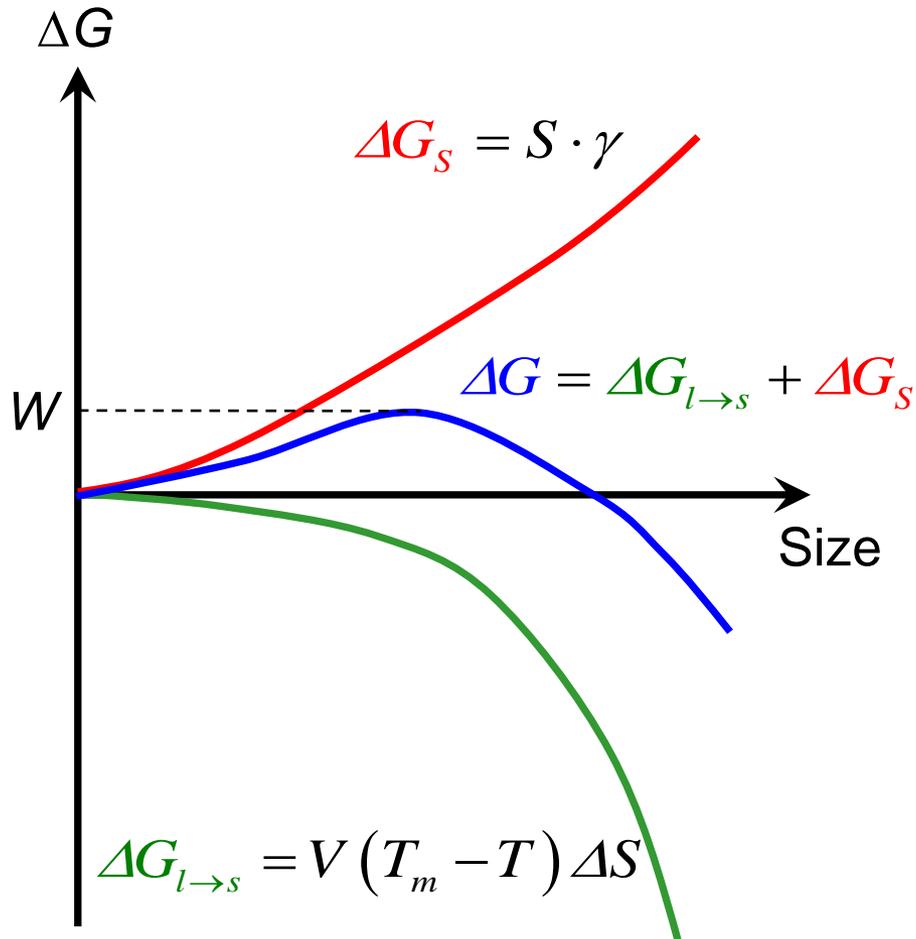
$$\Delta G = \Delta G_{l \to s} + \Delta G_S$$

W

Size

ΔG

$$\Delta G_{l \to s} = V \left(T_m - T \right) \Delta S$$

Homogeneous nucleation

Heterogeneous nucleation

Surface energy contribution

$$\Delta G_S = S \cdot \gamma$$

Energy barrier for nucleation

Kinetics of nucleation

$$\Delta G_S = S \cdot \gamma$$

$$\Delta G = \Delta G_{l \to s} + \Delta G_S$$

$$W$$

Size

$$\Delta G_{l \to s} = V(T_m - T)\Delta S$$

Nucleation rate:
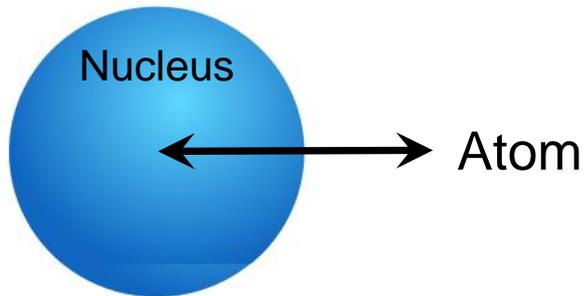
$$R_n \propto D \cdot \exp\left(-\frac{W}{k_B T}\right)$$

$$\because D = D \cdot \exp\left(-\frac{\Delta E_D}{k_B T}\right)$$

$$\therefore R_n = D \cdot \exp\left(-\frac{\Delta E_D + W}{k_B T}\right)$$

$$T \to T_m: W \to \infty, R_n \to 0$$

$$T \to 0: R_n \to 0$$

Kinetics of growth

Nucleus

⟷ Atom

Crystal Growth

Energy

liquid

Diffusional Energy Barrier (ΔE)

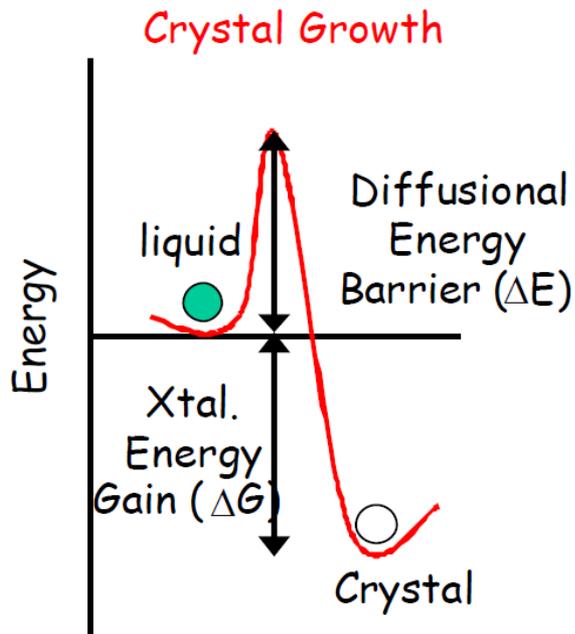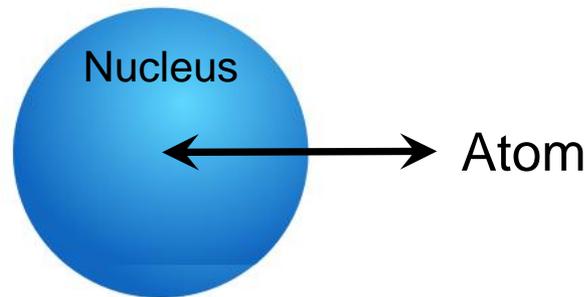Xtal. Energy Gain (ΔG)

Crystal

Flux into the nucleus:

$$F_{\leftarrow} \propto \nu \cdot \exp\left(-\frac{\varDelta E}{k_B T} \right)$$
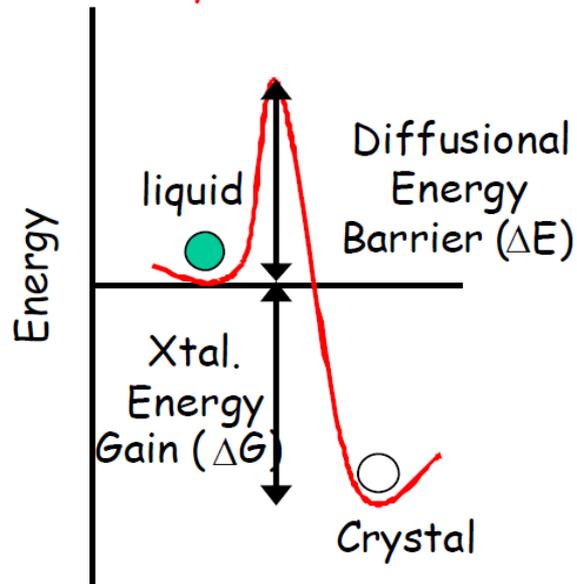
Flux out of the nucleus:

$$F_{\rightarrow} \propto \nu \cdot \exp\left(-\frac{\varDelta E + \varDelta G}{k_B T} \right)$$

Kinetics of growth

Nucleus

Atom

Crystal Growth

Energy

liquid

Diffusional Energy Barrier (ΔE)

Xtal. Energy Gain (ΔG)

Crystal

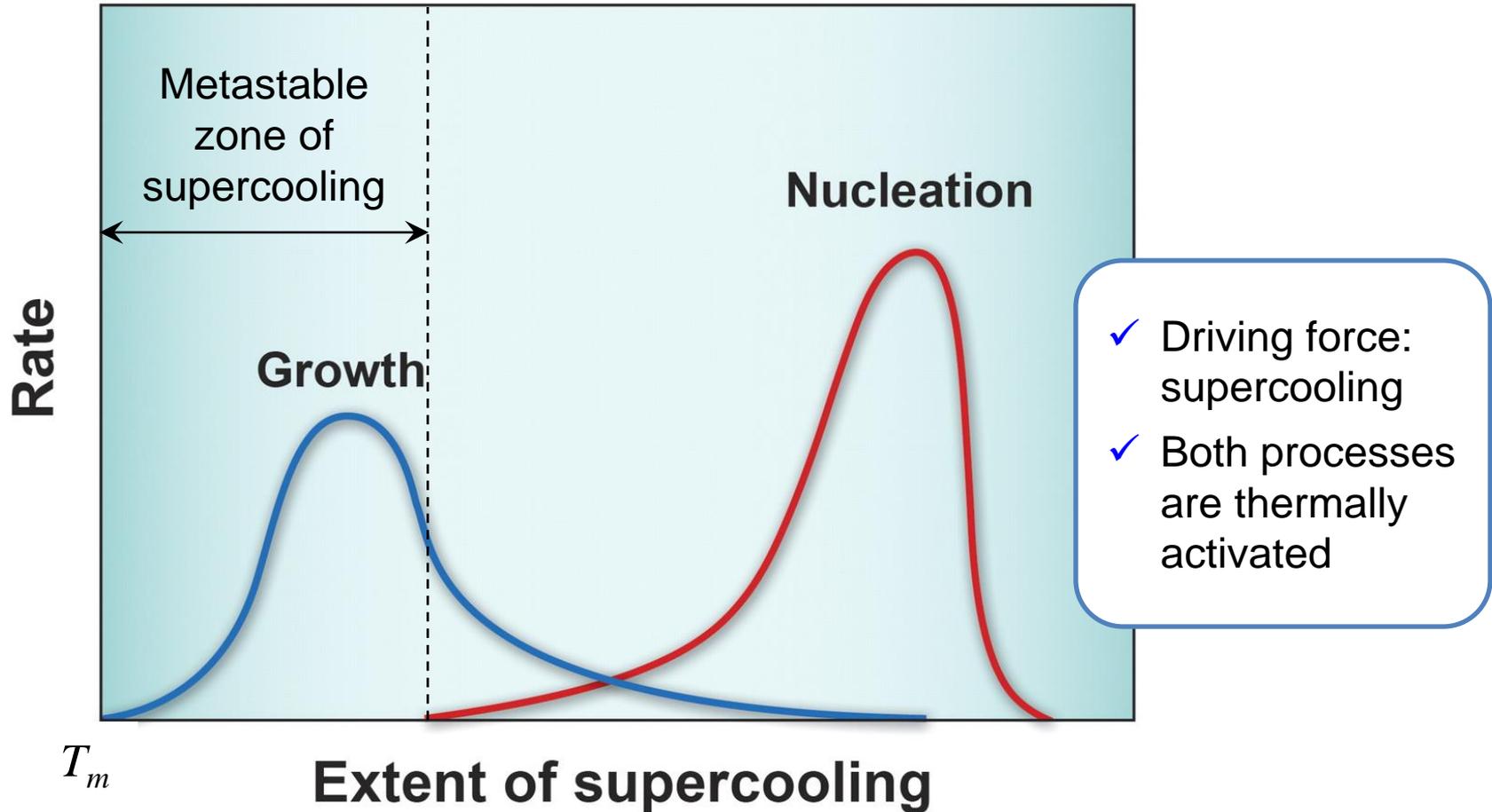Net diffusion flux:

$$R_g \propto F_{\leftarrow} - F_{\rightarrow}$$

$$= v \cdot \exp\left(-\frac{\Delta E}{k_B T}\right) \cdot \left[1 - \exp\left(-\frac{\Delta G}{k_B T}\right)\right]$$

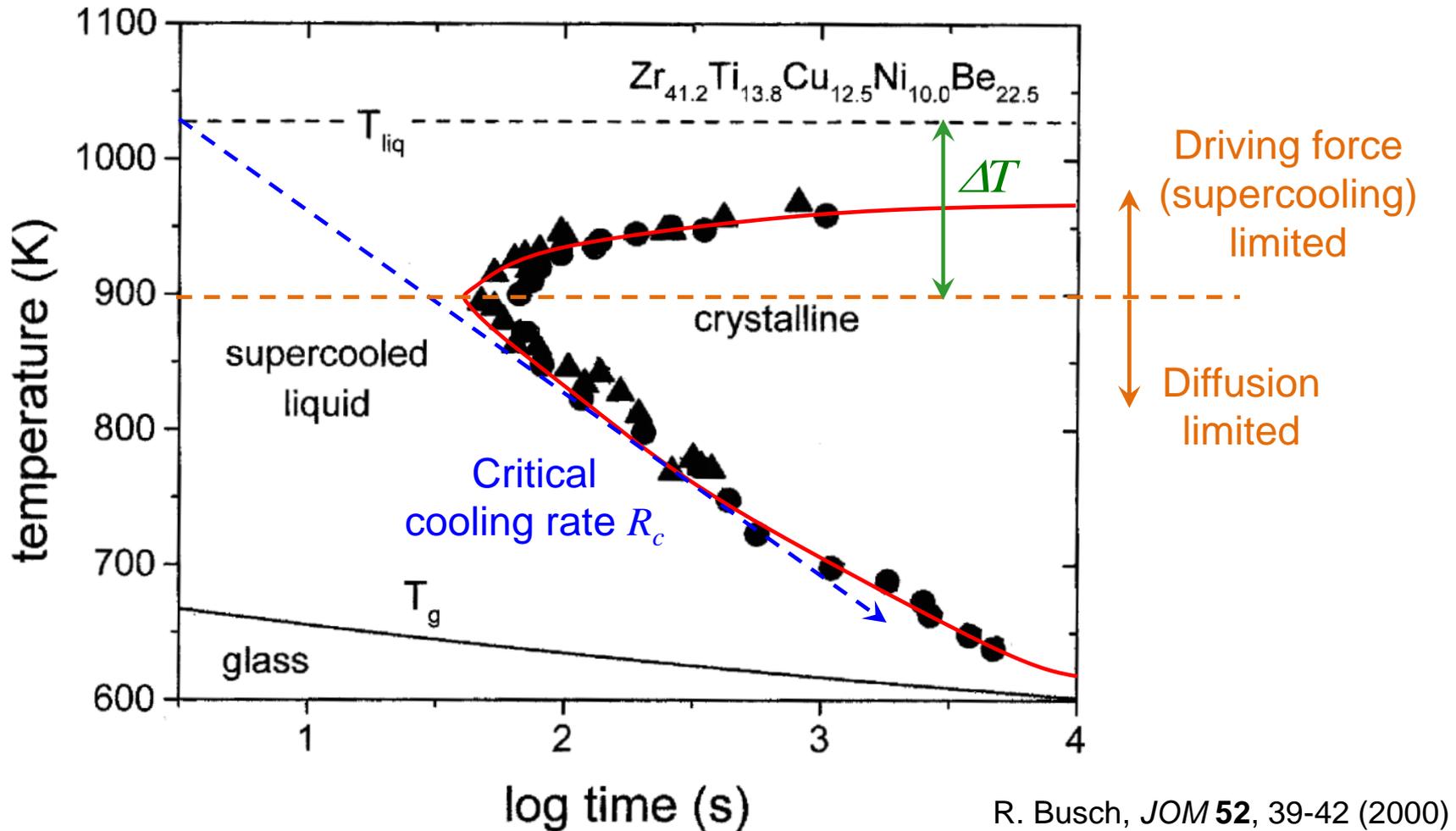$$\sim v \cdot \exp\left(-\frac{\Delta E}{k_B T}\right) \cdot \frac{\Delta G}{k_B T}$$

$$T \to T_m: \Delta G \to 0, R_g \to 0$$

$$T \to 0: R_n \to 0$$

Crystal nucleation and growth

Metastable zone of supercooling

Nucleation

Rate

Growth

T_m

Extent of supercooling

- ✓ Driving force: supercooling
- ✓ Both processes are thermally activated

Time-temperature-transformation diagram

R. Busch, *JOM* **52**, 39-42 (2000)

Critical cooling rate and glass formation

Material	Critical cooling rate (°C/s)
Silica	9×10^{-6}
GeO$_2$	3×10^{-3}
Na$_2$O·2SiO$_2$	6×10^{-3}
Salol	10
Water	10^7
Vitreloy-1	1
Typical metal	10^9
Silver	10^{10}

Technique	Typical cooling rate (°C/s)
Air quench	1-10
Liquid quench	10^3
Droplet spray	10^2-10^4
Melt spinning	10^5-10^8
Selective laser melting	10^6-10^8
Vapor deposition	Up to 10^{14}

Maximum glass sample thickness: $d_{\max} \sim \sqrt{\dfrac{\alpha \cdot \Delta T}{R_c}}$ $\quad \alpha$: thermal diffusivity
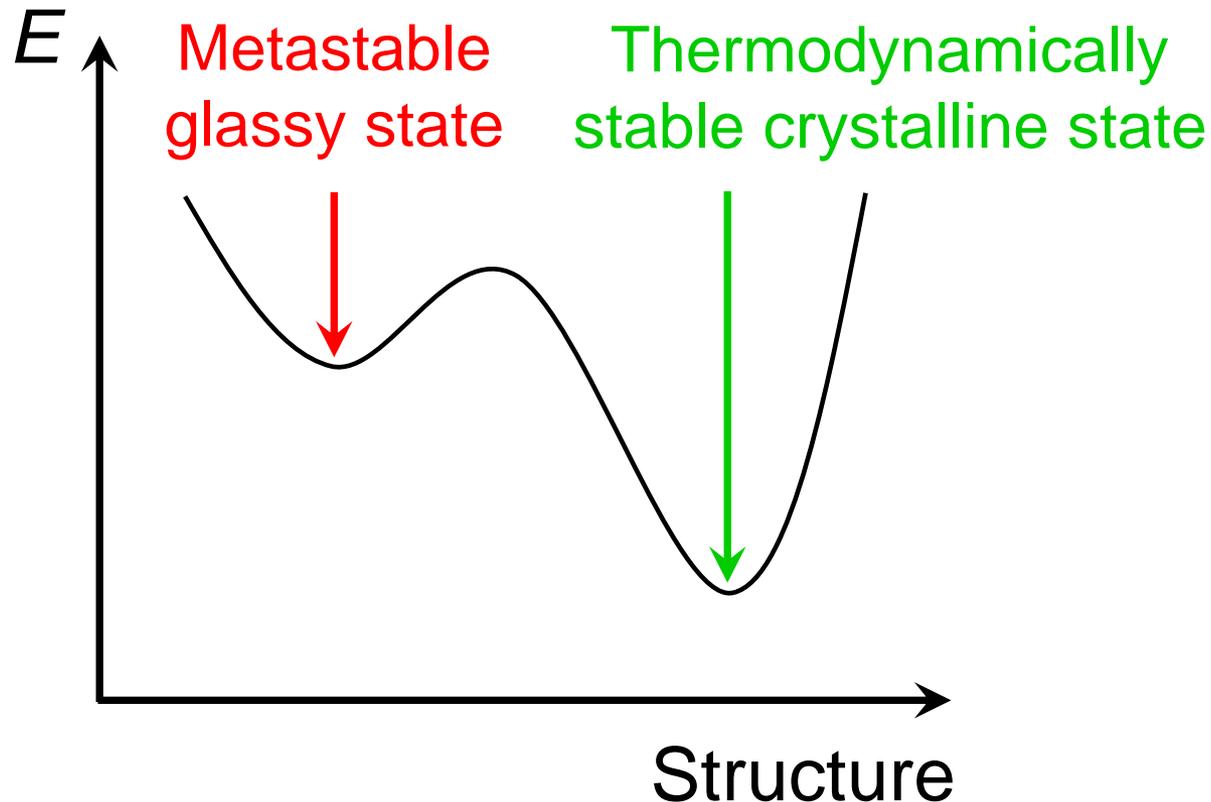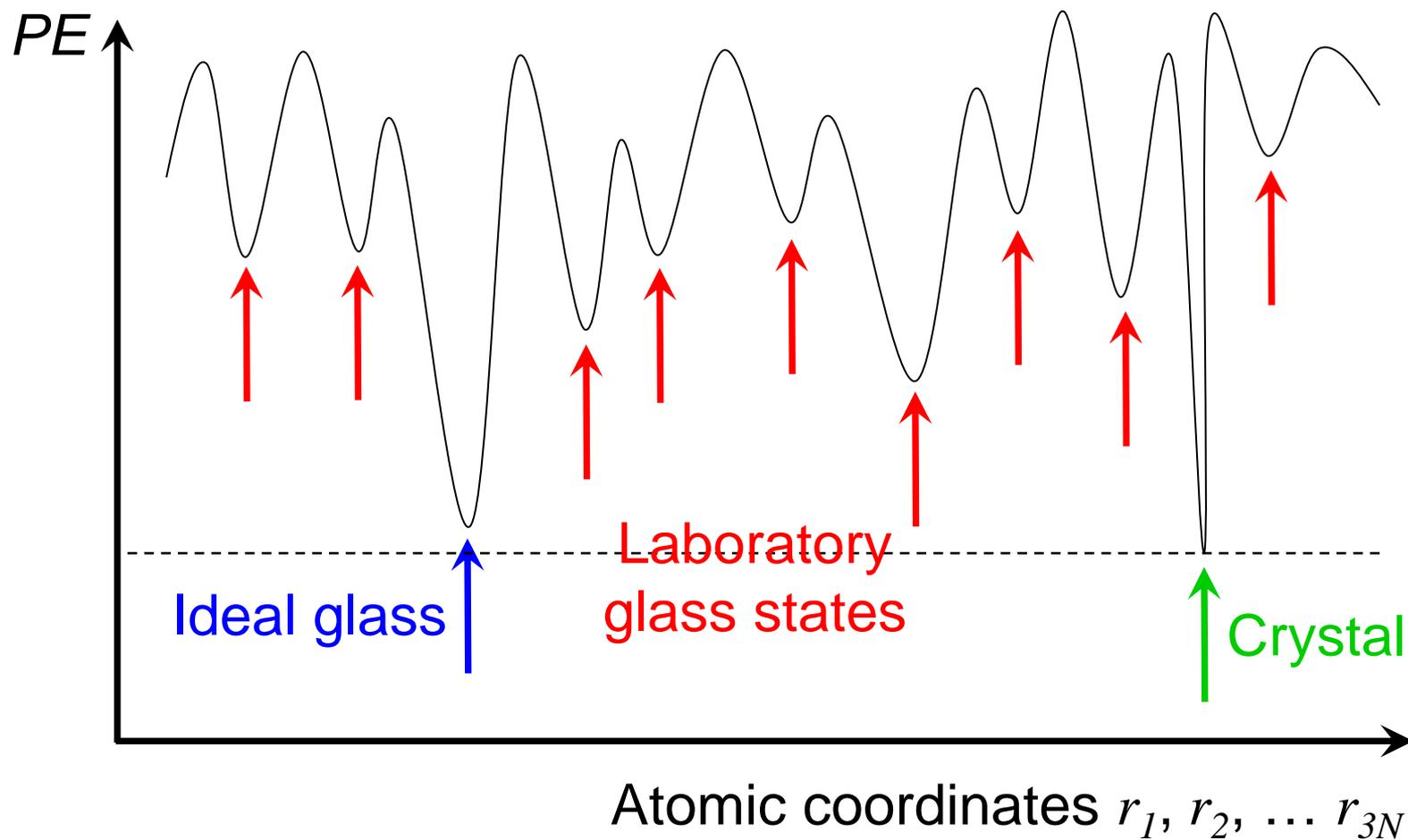
Glass formation from liquid
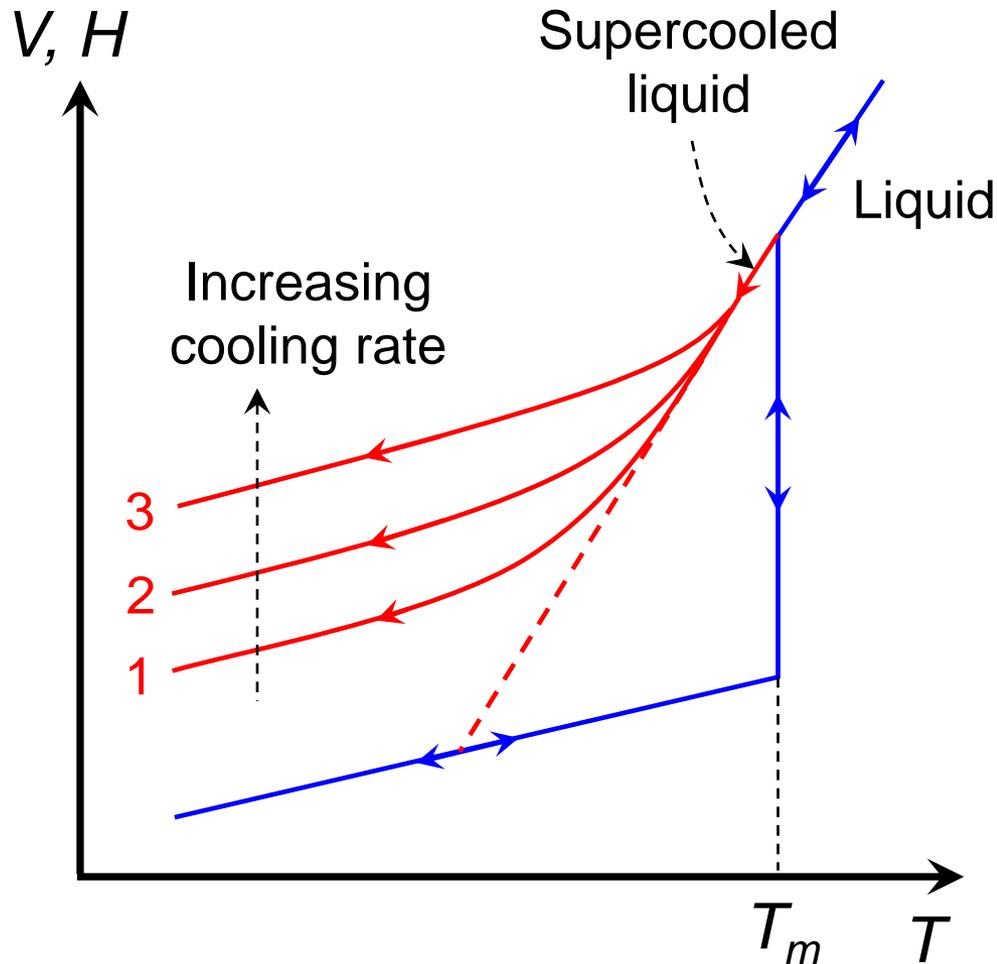
- ✓ Glasses obtained at different cooling rates have different structures
- ✓ With infinitely slow cooling, the ideal glass state is obtained

Potential energy landscape (PEL)

■ The metastable glassy state

E

Metastable
glassy state

Thermodynamically
stable crystalline state

Structure

Potential energy landscape (PEL)

Laboratory glass transition

- Liquid: ergodic

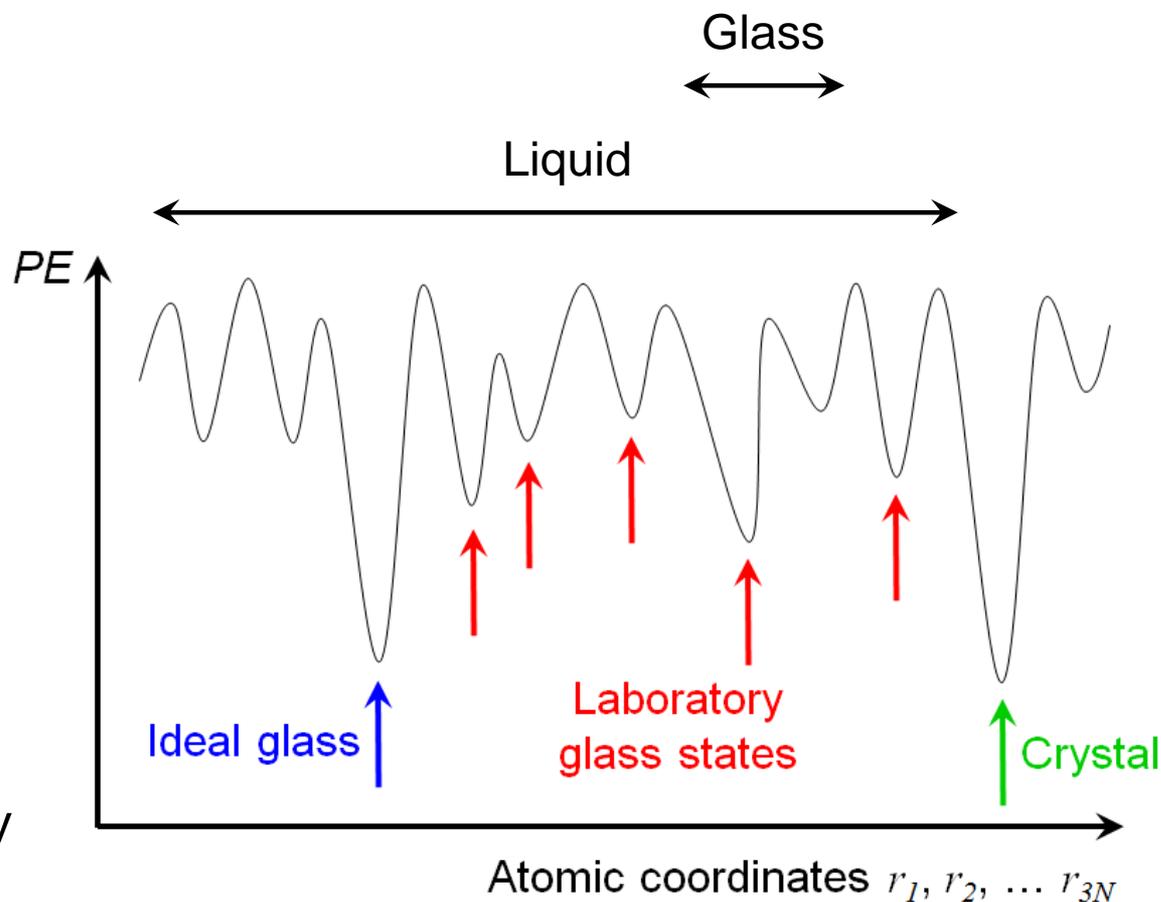- Glass: nonergodic, confined to a few local minima

$$t_{obs} < \tau$$

- Inter-valley transition time τ :

$$\tau = \frac{1}{\nu} \cdot \exp\left(-\frac{B}{k_B T} \right)$$

B : barrier height
ν : attempt frequency

Glass

Liquid

PE

Ideal glass   Laboratory glass states   Crystal

Atomic coordinates $r_1, r_2, \ldots r_{3N}$

✓ <u>Glass former:</u> high valence state, covalent bonding with O

✓ <u>Modifier:</u> low valence state, ionic bonding with O

Network modifiers   Glass formers   Intermediates

Zachariasen's rules

Rules for glass formation in an oxide A_mO_n

- An oxygen atom is linked to no more than two atoms of A
- The oxygen coordination around A is small, say 3 or 4
  - ☐ Open structures with covalent bonds
  - ☐ Small energy difference between glassy and crystalline states
- The cation polyhedra share corners, not edges, not faces
  - ☐ Maximize structure geometric flexibility
- At least three corners are shared
  - ☐ Formation of 3-D network structures

> ✓ Only applies to most (not all!) oxide glasses
> ✓ Highlights the importance of network topology

Classification of glass network topology

Floppy / flexible Underconstrained	Isostatic Critically constrained	Stressed rigid Overconstrained
• # (constraints) < # (DOF)	• # (constraints) = # (DOF)	• # (constraints) > # (DOF)
• Low barrier against crystallization	• Optimal for glass formation	• Crystalline clusters (nuclei) readily form and percolate

PE

PE

PE

$r_1, r_2, \ldots r_{3N}$

$r_1, r_2, \ldots r_{3N}$

$r_1, r_2, \ldots r_{3N}$
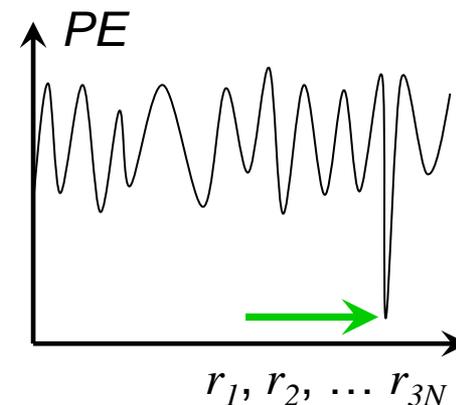
Number of constraints

Denote the atom coordination number as r

- Bond stretching constraint: $r/2$

- Bond bending constraint: $2r-3$ $(r \geq 2)$

  □ One bond angle is defined when $r = 2$

  □ Orientation of each additional bond is specified by two angles

- Total constraint number:

$$\sum_{r \geq 2} (2.5r - 3) = (2.5\langle r \rangle - 3) \cdot n_{r \geq 2}$$

- Mean coordination number:

$$\langle r \rangle = \frac{\sum_{r \geq 2} r}{n_{r \geq 2}}$$

Isostatic condition / rigidity percolation threshold

- **Total number of degrees of freedom:** $3n_{r\geq2}$

- **Isostatic condition:**

$$3n_{r\geq2} = \left(2.5\langle r \rangle - 3\right) \cdot n_{r\geq2} \;\Rightarrow\; \boxed{\langle r \rangle = 2.4}$$

- **Examples:**

  - Ge_xSe_{1-x} $\quad \langle r \rangle = x \cdot 4 + \left(1 - x\right) \cdot 2 = 2 + 2x$

  - As_xS_{1-x} $\qquad \langle r \rangle = x \cdot 3 + \left(1 - x\right) \cdot 2 = 2 + x$

  - Si_xO_{1-x} $\qquad \langle r \rangle = x \cdot 4 + \left(1 - x\right) \cdot 2 = 2 + 2x$

> Why oxides and chalcogenides make good glasses?

Temperature-dependent constraints

- The constraint number should be evaluated at the glass forming temperature (rather than room temperature)

- Silica glass Si_xO_{1-x}

  - Bond stretching

  $$\frac{r_{Si}}{2} \cdot n_{Si} + \frac{r_O}{2} \cdot n_O$$

  - O-Si-O bond angle

  $$\left(2r_{Si} - 3\right) \cdot n_{Si}$$

  - Isostatic condition

  $$x = 1/3 \quad SiO_2$$
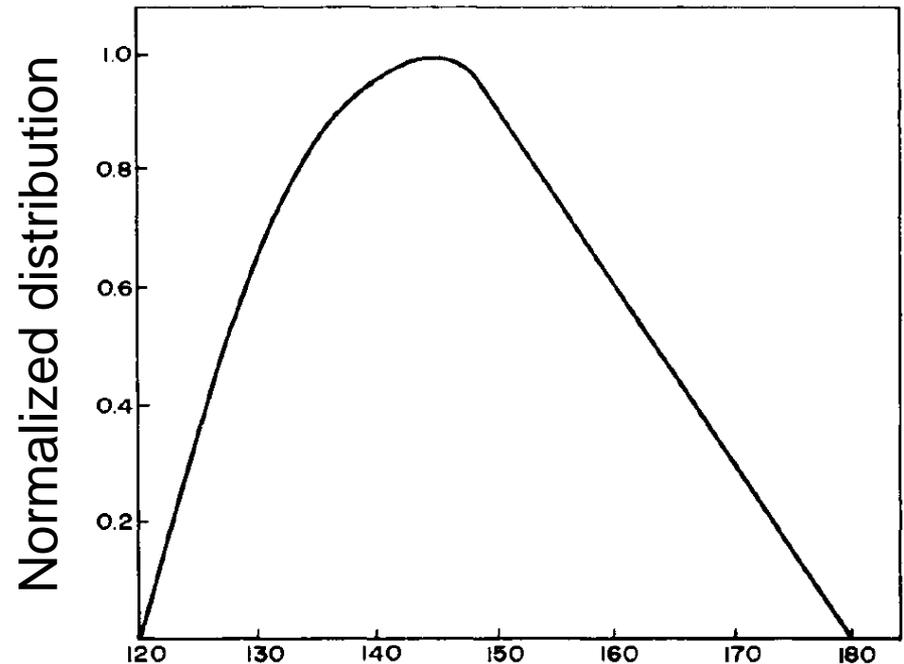
Si-O-Si bond angle in silica glass

Temperature-dependent constraints

■ Each type of constraint is associated with an onset temperature above which the constraint vanishes

Continuous form:

$$q_\alpha(T) = \left[1 - \exp\left(-\frac{\Delta F_\alpha^*}{kT}\right)\right]^{\nu t_{obs}}$$

$$\lim_{T\to 0} q_\alpha(T) = 1$$

"Rigid"

Conversion between discrete and continuous forms:

$$\Delta F_\alpha^* = -T_\alpha \ln\left(1 - 2^{-1/\nu t_{obs}}\right)$$

Discrete form:

$$q_\alpha(T) = \theta(T_\alpha - T)$$

"Floppy"

$$\lim_{T\to\infty} q_\alpha(T) = 0$$
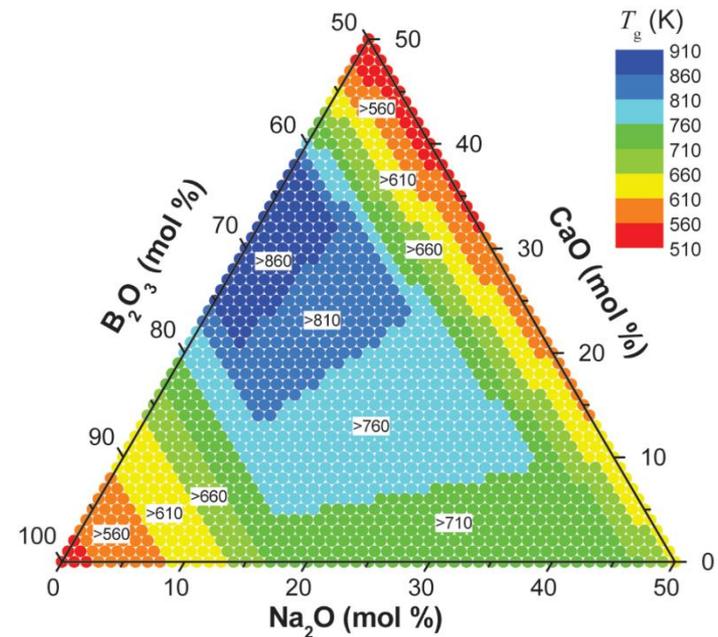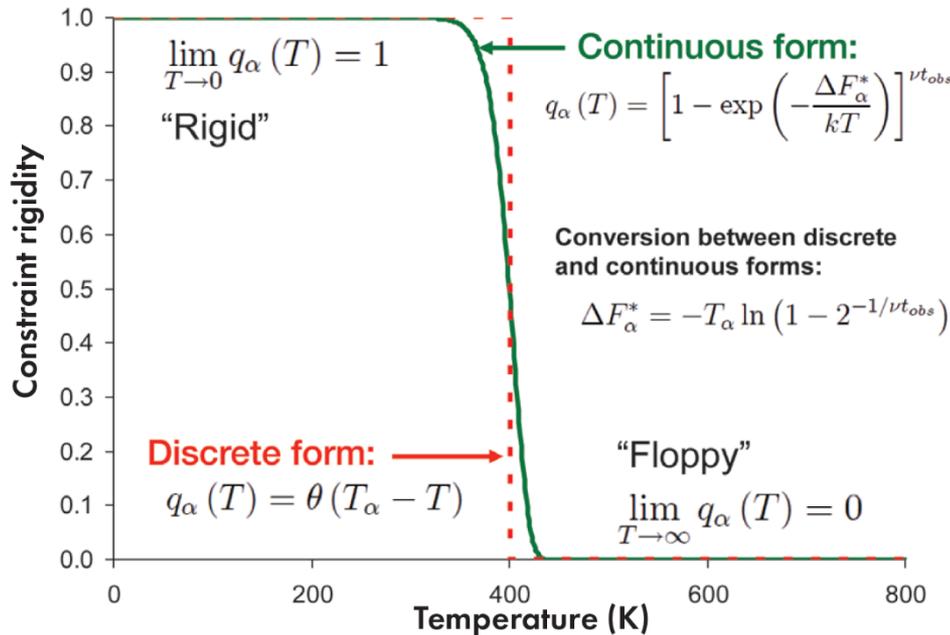
"Topological constraint theory of glass," *ACerS Bull.* **90**, 31-37 (2011).

Enumeration of constraint number

Bond stretching constraints (coordination number):

- 8-*N* rule: applies to most covalently bonded nonmetals (O, S, Se, P, B, As, Si, etc.)

- Exceptions: heavy elements (e.g. Te, Sb)

Bond bending constraints:

- Glasses with low forming temperature:

$$\#_{BB} = 2r - 3$$

- Atomic modeling or experimental characterization required to ascertain the number of active bond bending constraints

					2 **He** Helium 4.003
5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)

Property dependence on network rigidity

■ Many glass properties exhibit extrema or kinks at the rigidity percolation threshold $\langle r \rangle = 2.4$
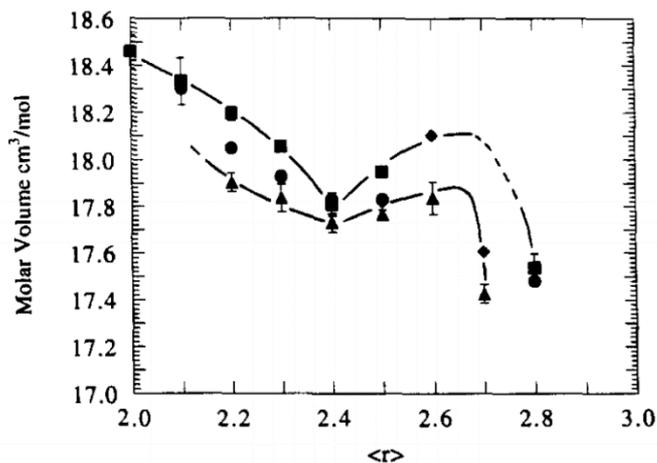

Fig. 6. Dependence of molar volume on $\langle r \rangle$ for binary Ge–Se and ternary Ge–Sb–Se systems. The molar volume at room temperature for the binary and ternary are represented by ■ and ▲, respectively. The molar volume values for the binary glasses given by Ota et al. [11] are represented by ● and those for the ternary glasses given by Savage et al. [23] are represented by ◆. The curves are drawn as a guide to the eye. The maximum measured error is 0.5%.
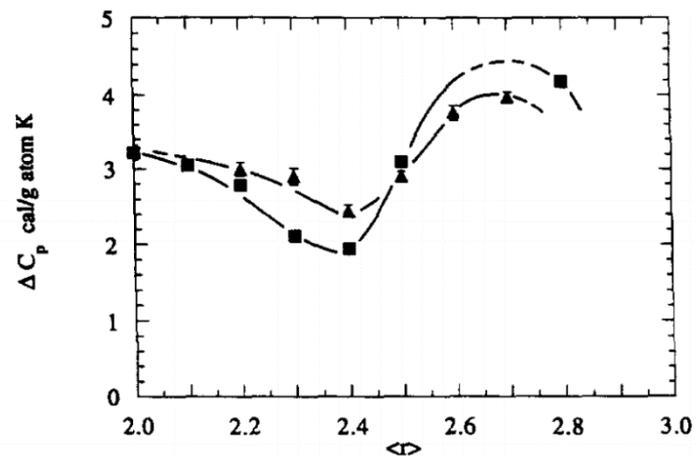
Fig. 10. ΔC_p versus $\langle r \rangle$ for binary Ge–Se and ternary Ge–Sb–Se systems. The ΔC_p values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 1.8%.

J. Non-Cryst. Sol. **185**, 289-296 (1995).

Measuring glass forming ability

- Figure of merit (FOM): $\Delta T = T_x - T_g$
- T_x : crystallization temperature
- T_g : glass transition temperature
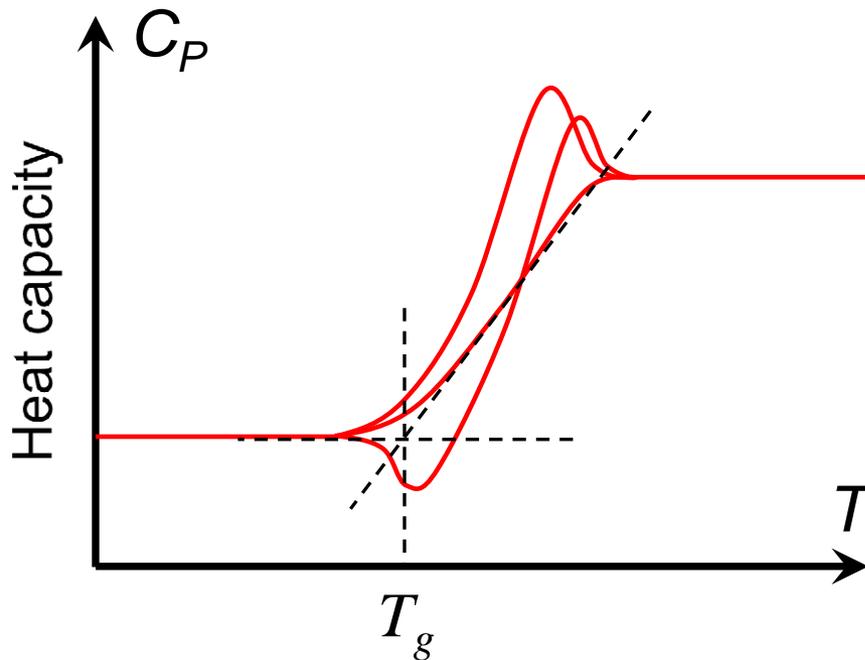
✓ T_g is dependent on measurement method and thermal history

✓ Alternative FOM:

$$\left(T_x - T_g \right) \big/ \left(T_m - T_x \right)$$

Hruby coefficient

Summary

- Kinetic theory of glass formation
  - ☐ Driving force and energy barrier for nucleation and growth
  - ☐ Temperature dependence of nucleation and growth rates
  - ☐ T-T-T diagram and critical cooling rate
- Laboratory glass transition
  - ☐ Potential energy landscape
  - ☐ Ergodicity breakdown: laboratory glass transition
  - ☐ Path dependence of glass structure
- Glass network topology theories
  - ☐ Zachariasen's rules
  - ☐ Topological constraint theory
- Parameters characterizing glass forming ability (GFA)

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