MIT 3.071
Amorphous Materials

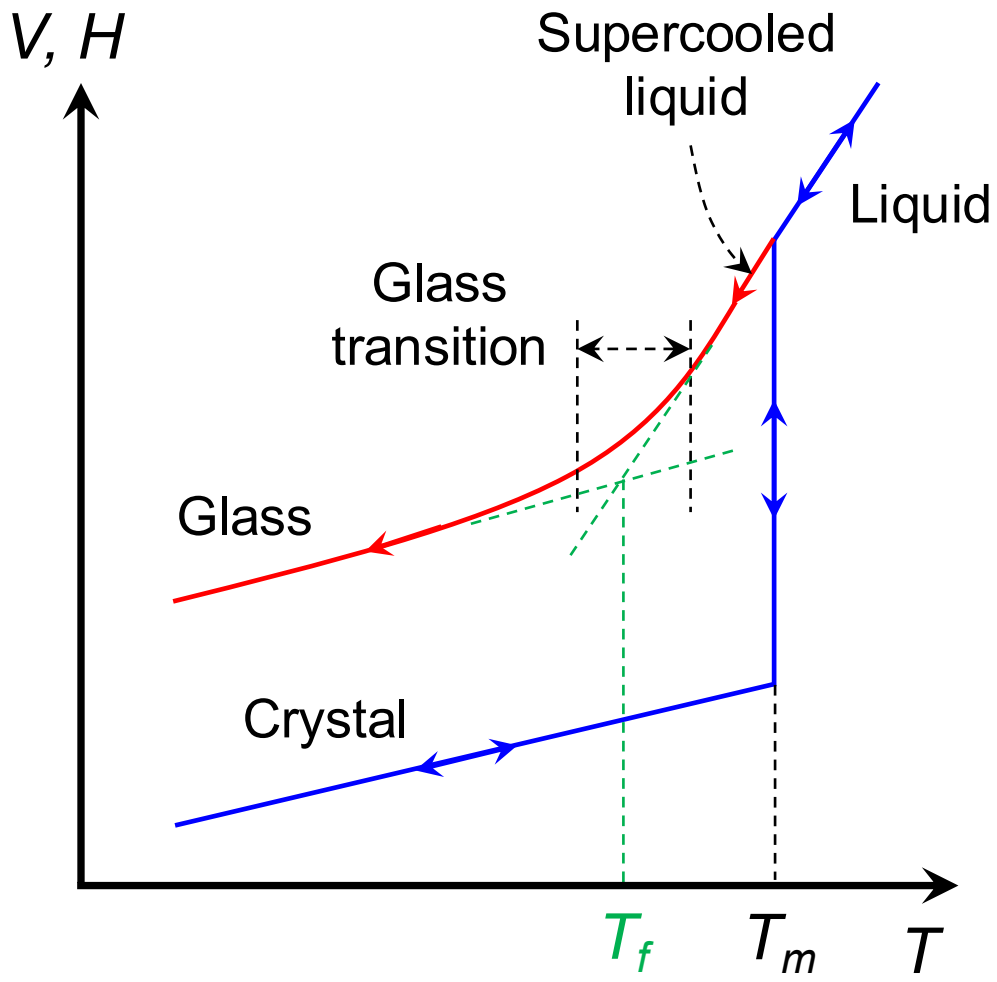
3: Glass Forming Theories

Juejun (JJ) Hu

After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 3 (except Section 3.1.4 in the 1994 version)
- 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

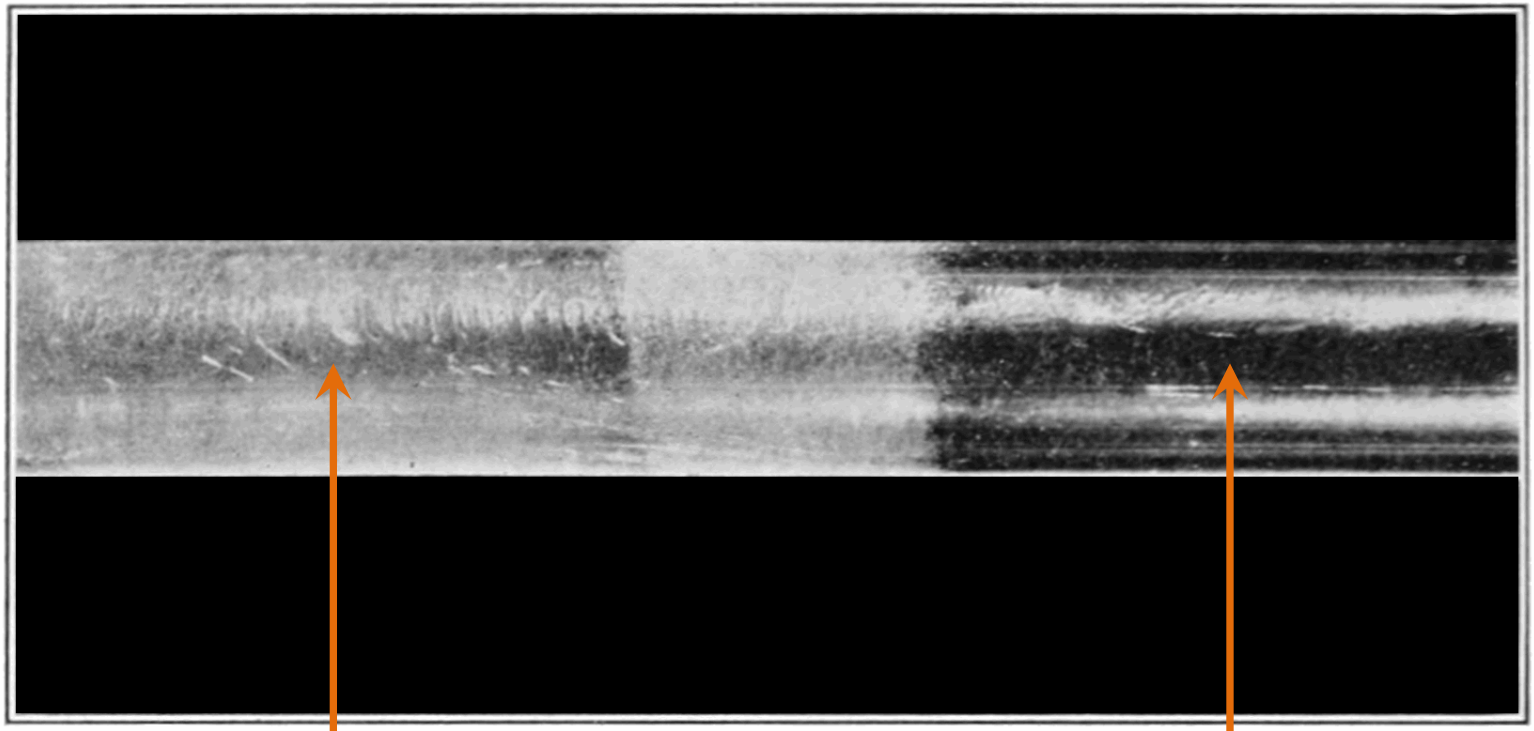


- ? Supercooling of liquid and suppression of crystallization
- ? Glass transition: from supercooled liquid to the glassy state
- ? Glass forming ability: the structural origin

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



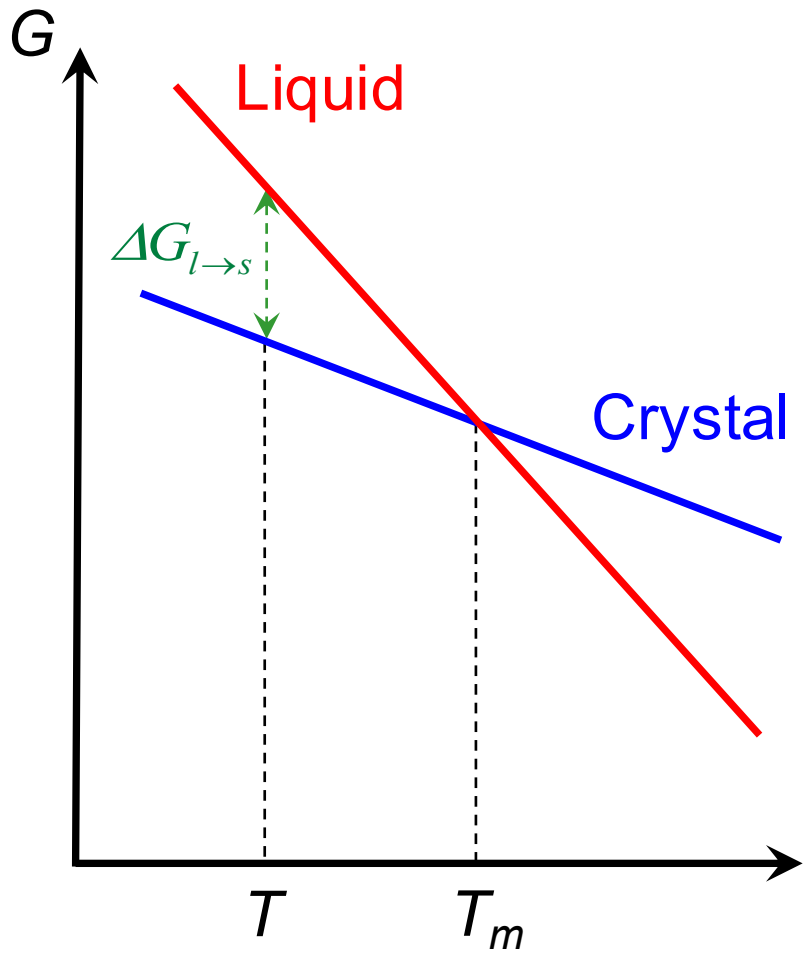
Source: public domain

Crystallized

Amorphous

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

Thermodynamics of nucleation



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

$$\text{Q } S_l > S_s$$

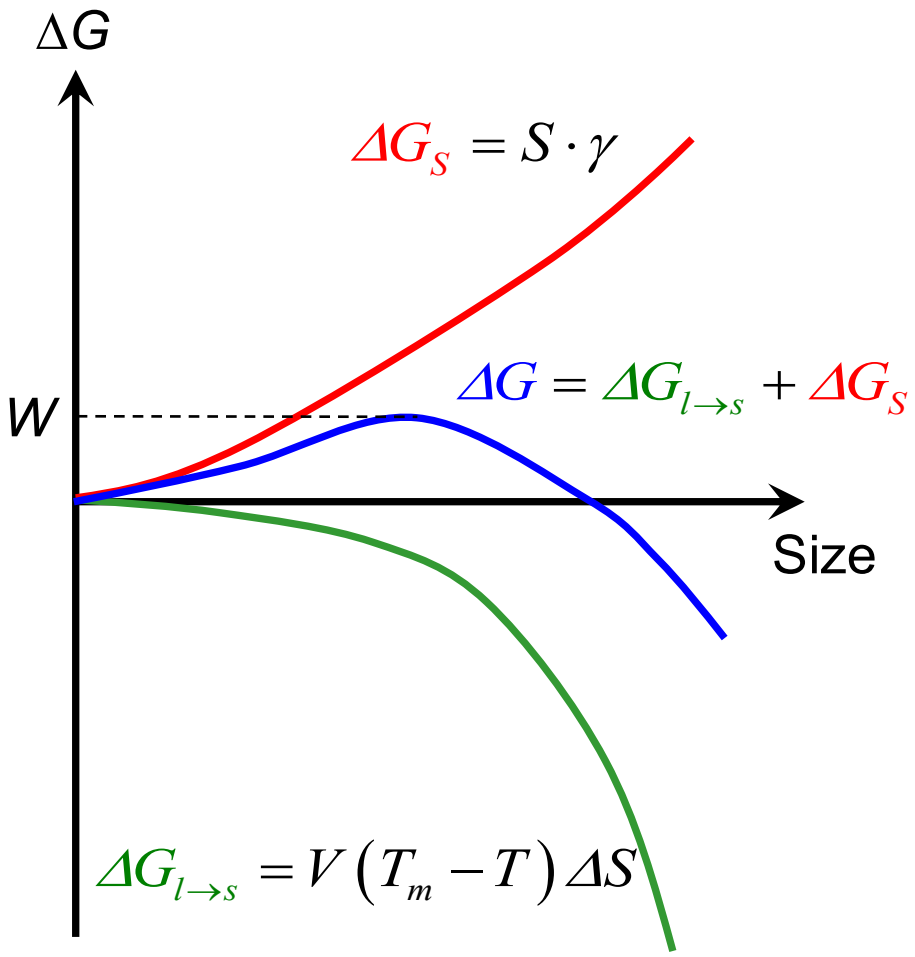
$$\therefore \left|\frac{\partial G_l}{\partial T}\right| > \left|\frac{\partial G_s}{\partial T}\right|$$

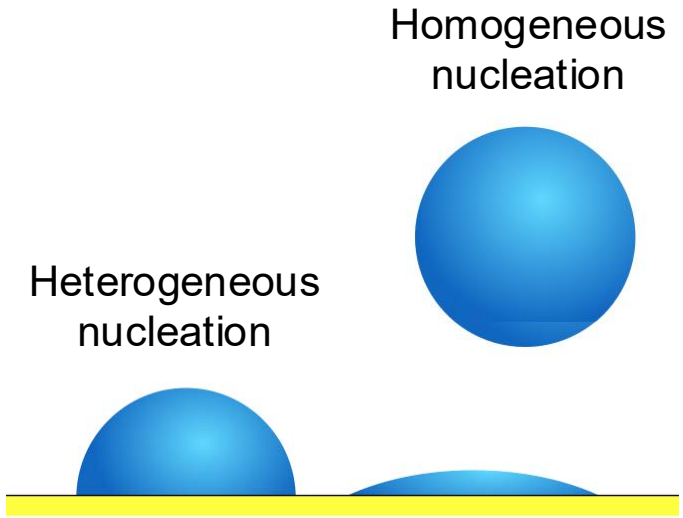
When $T < T_m$,

$$\Delta G_{l\to s} = G_s - G_l < 0$$
$$= V \cdot (T_m - T) \cdot \Delta S$$

Driving force for nucleation

Thermodynamics of nucleation



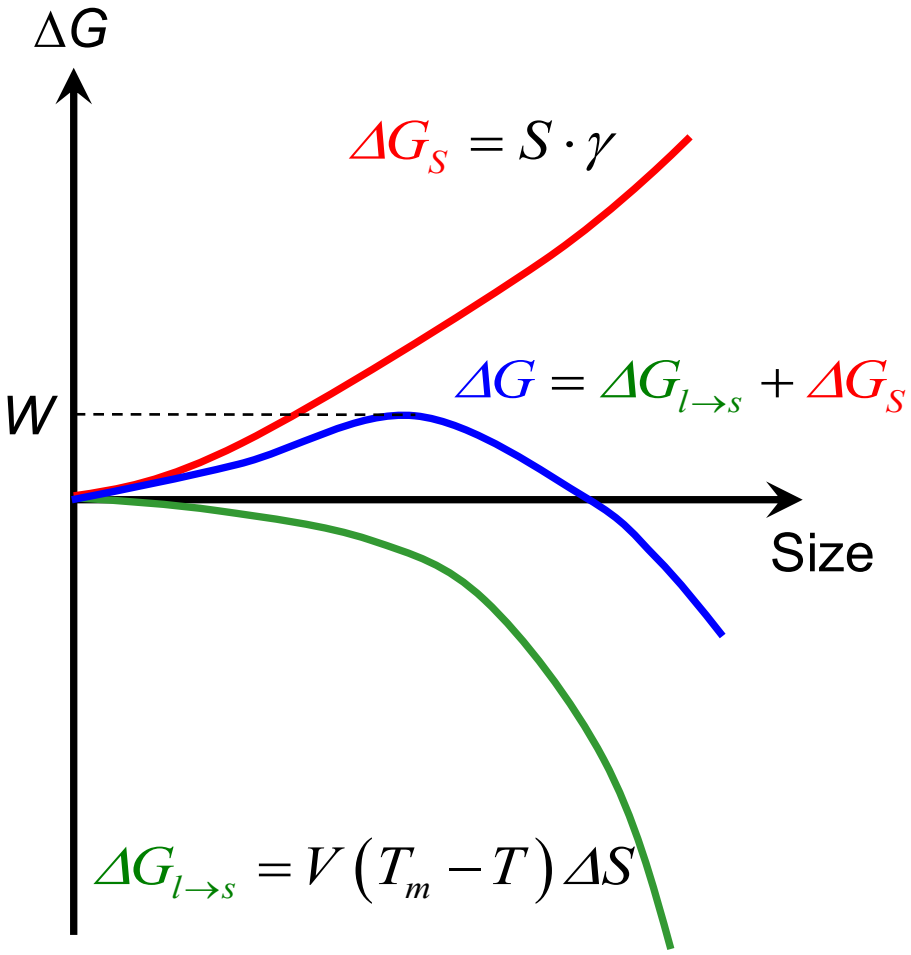


Surface energy contribution

$\Delta G_S = S \cdot \gamma$

Energy barrier for nucleation

Kinetics of nucleation



Nucleation rate:

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

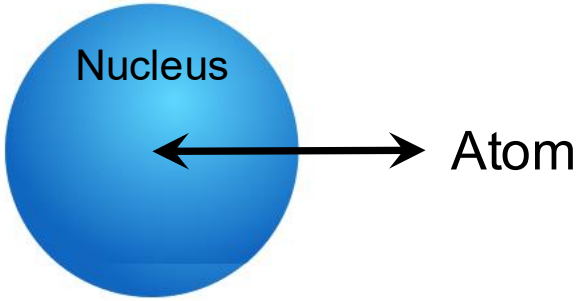
$$\text{Q } D = D_0 \cdot \exp\left(-\frac{\Delta E_D}{k_B T}\right)$$

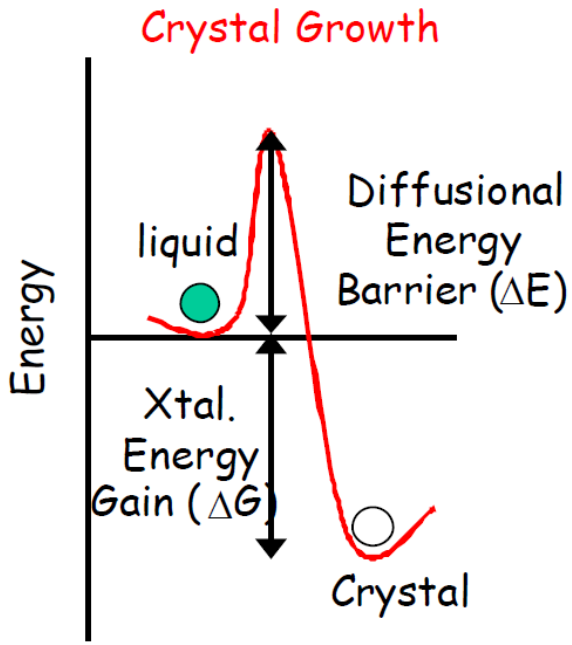
$$\therefore R_n = D_0 \cdot \exp\left(-\frac{\Delta E_D + W}{k_B T}\right)$$

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

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

Kinetics of growth





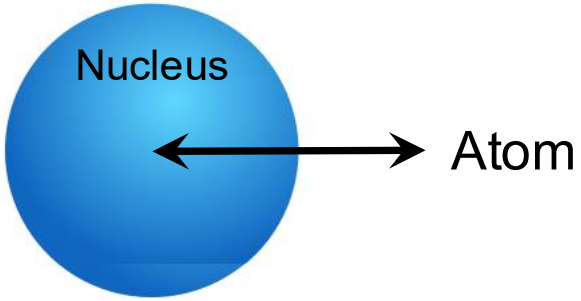
Flux into the nucleus:

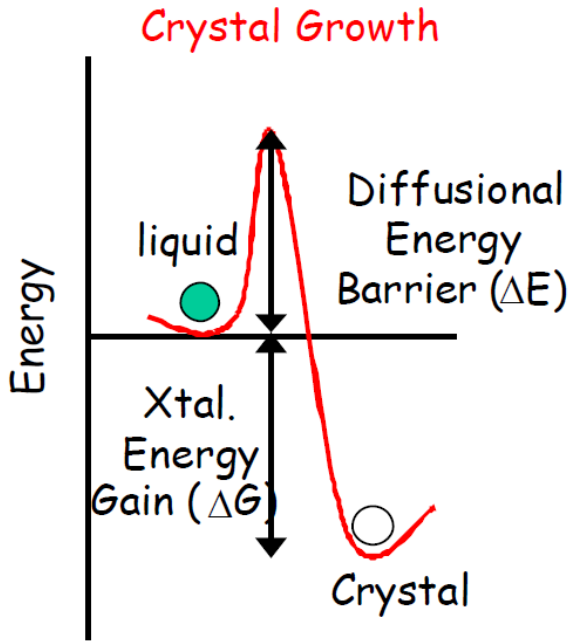
$$F_{\leftarrow} \propto \nu \cdot \exp\left(-\frac{\Delta E}{k_B T}\right)$$

Flux out of the nucleus:

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

Kinetics of growth





Net diffusion flux:

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

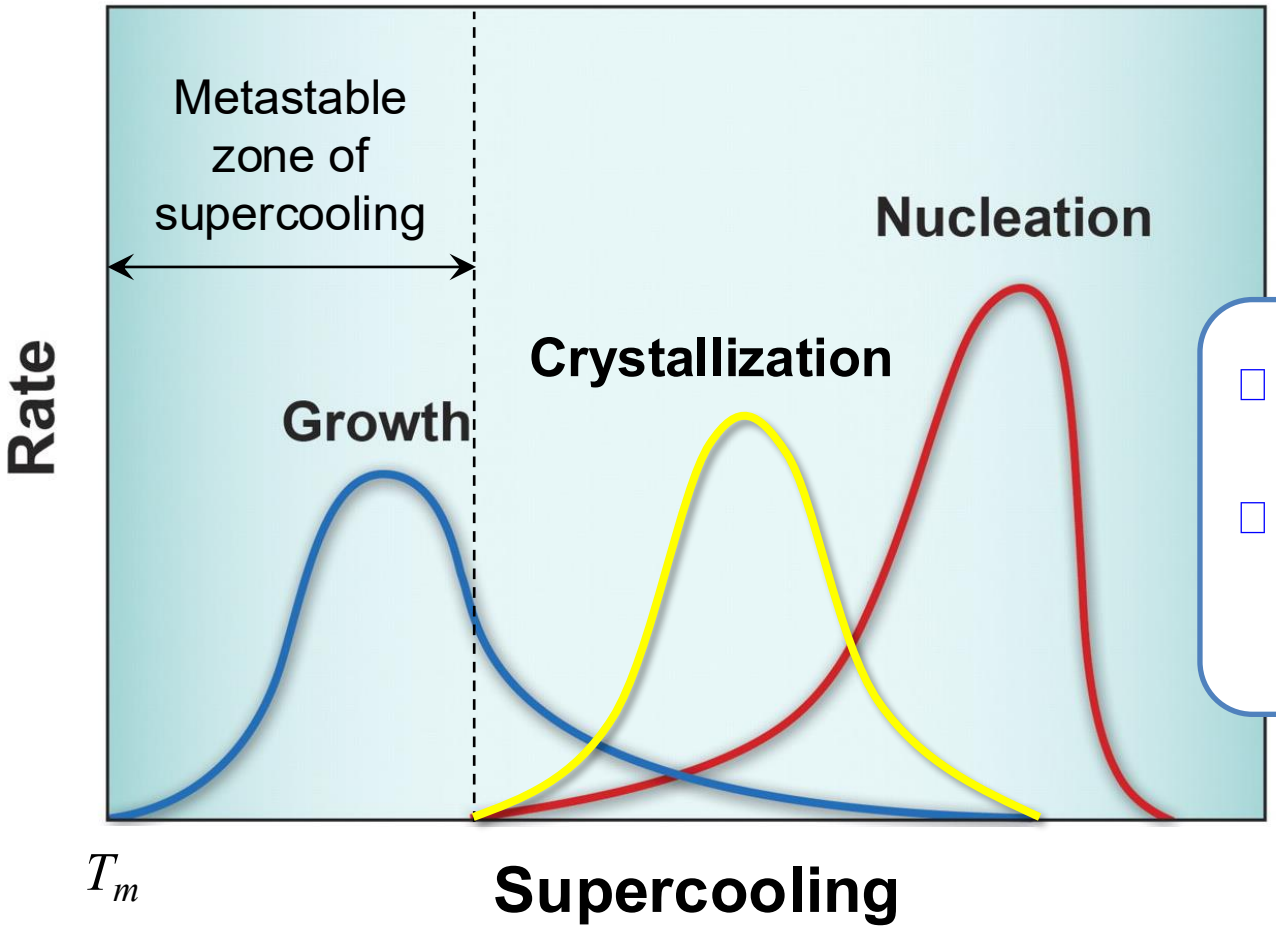
$$= \nu \cdot \exp\left(-\frac{\Delta E}{k_B T}\right) \cdot \left[1 - \exp\left(-\frac{\Delta G}{k_B T}\right)\right]$$

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

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

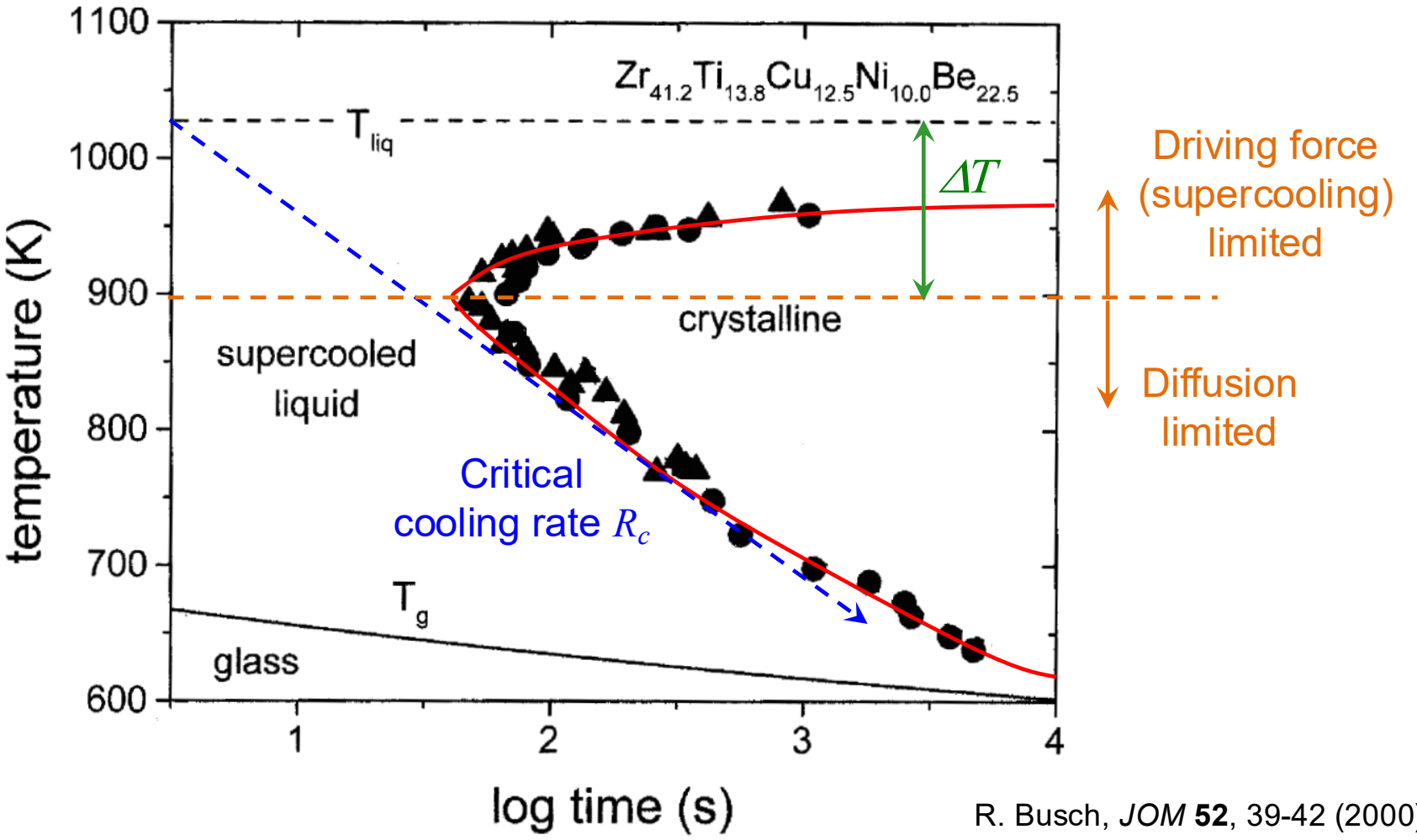
$$T \to 0 : R_n \to 0$$

Crystal nucleation and growth



- Driving force: supercooling
- Both processes are thermally activated

Time-temperature-transformation diagram



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

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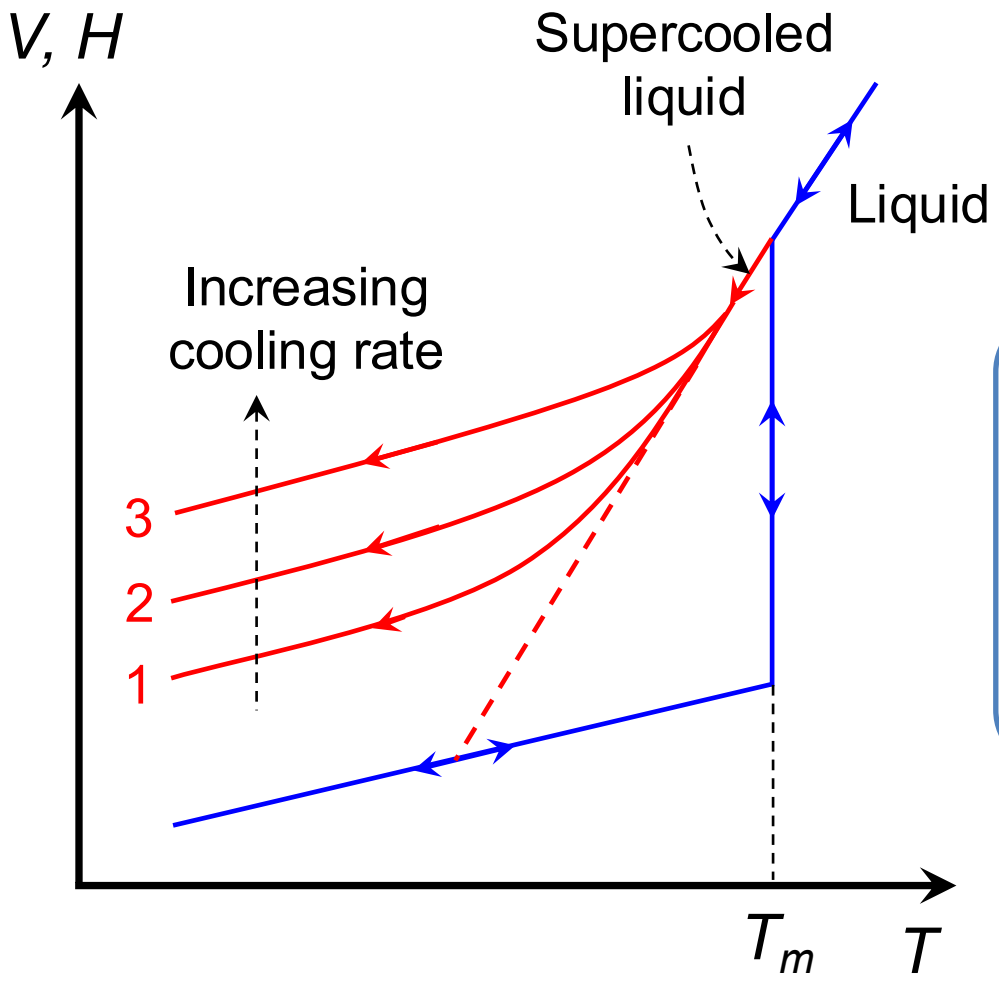
Critical cooling rate and glass formation

Material	Critical cooling rate (°C/s)
Silica	9×10^{-6}
GeO_2	3×10^{-3}
$Na_2O \cdot 2SiO_2$	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: $d_{\max} \sim \sqrt{\frac{\alpha \cdot \Delta T}{R_c}}$ α : thermal diffusivity

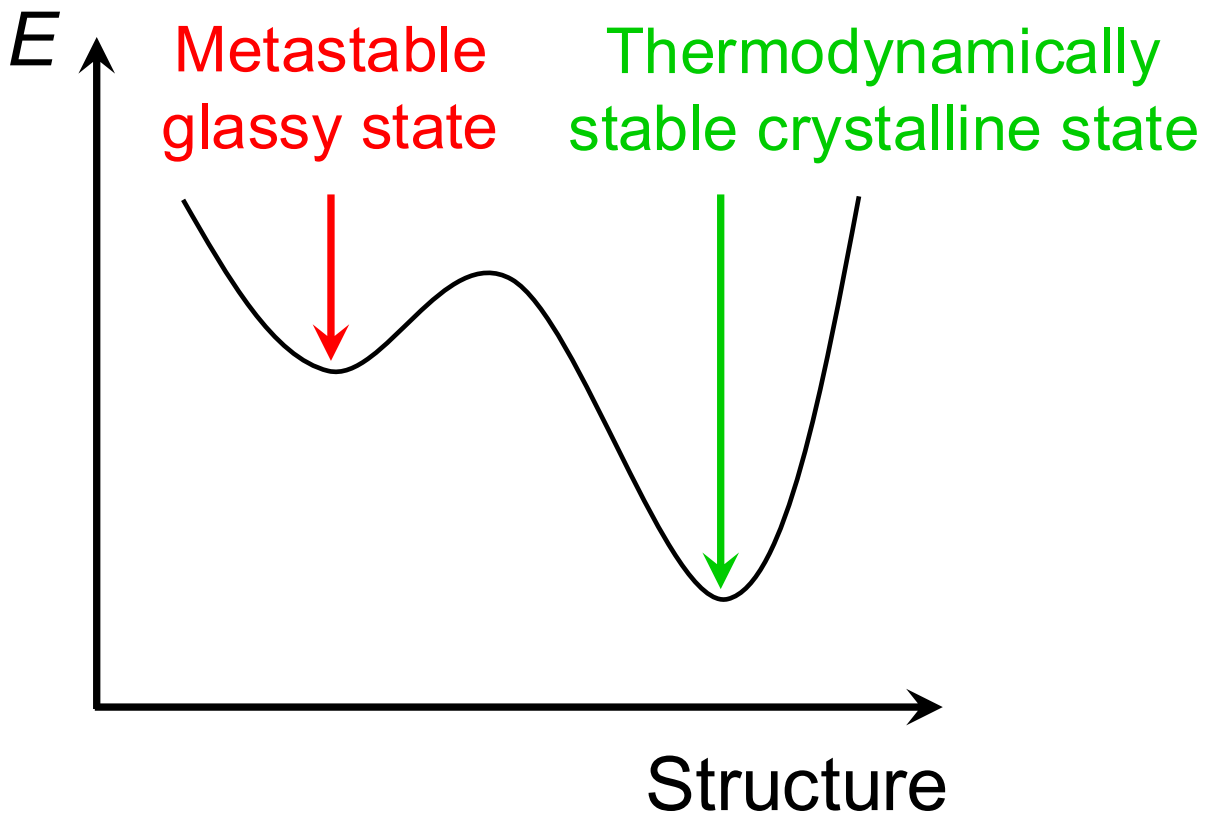
Glass formation from liquid



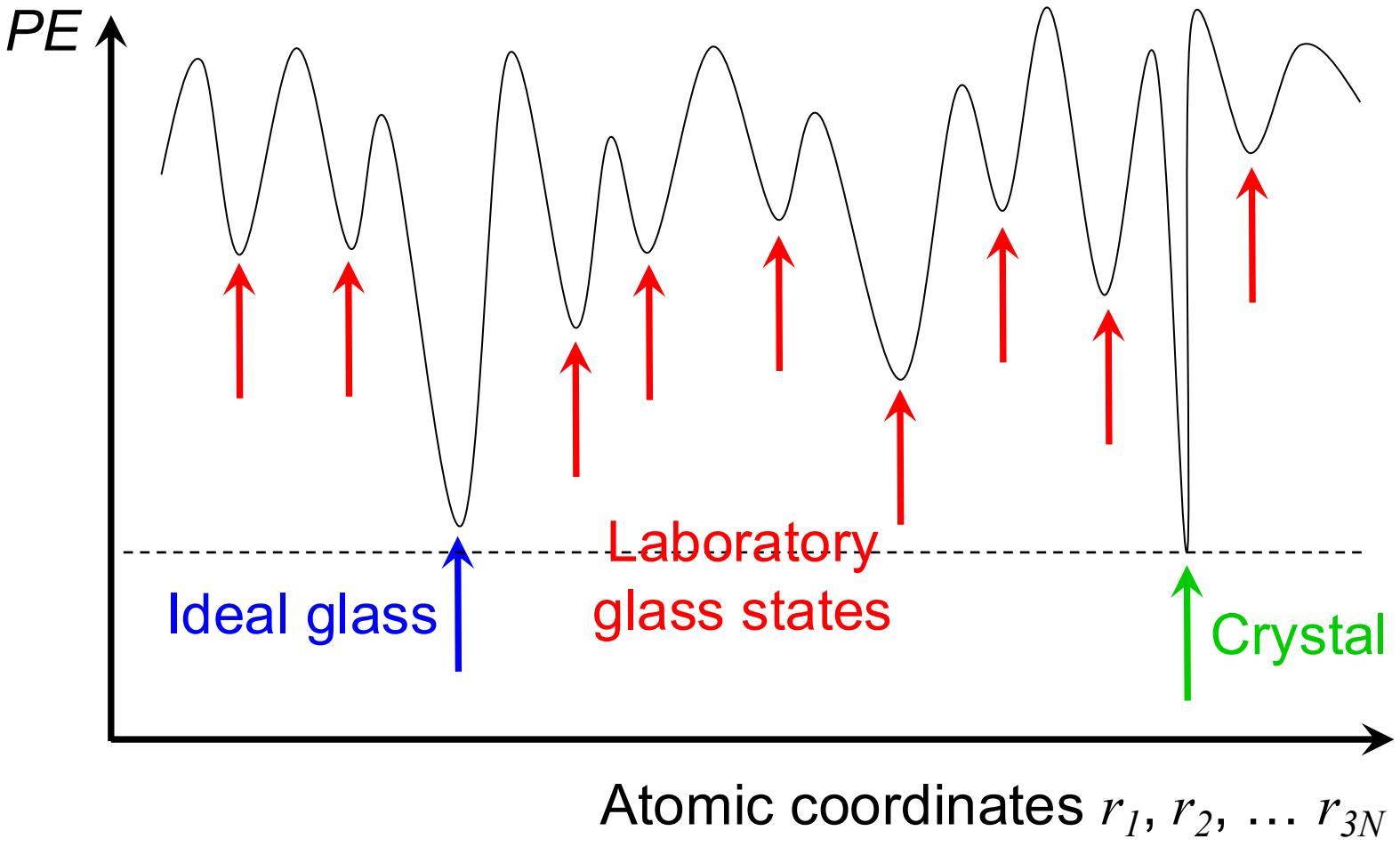
- Glasses obtained at different cooling rates have different structures
- With infinitely slow cooling, the ideal glass state is obtained

Potential energy landscape (PEL)

- The metastable glassy state



Potential energy landscape (PEL)



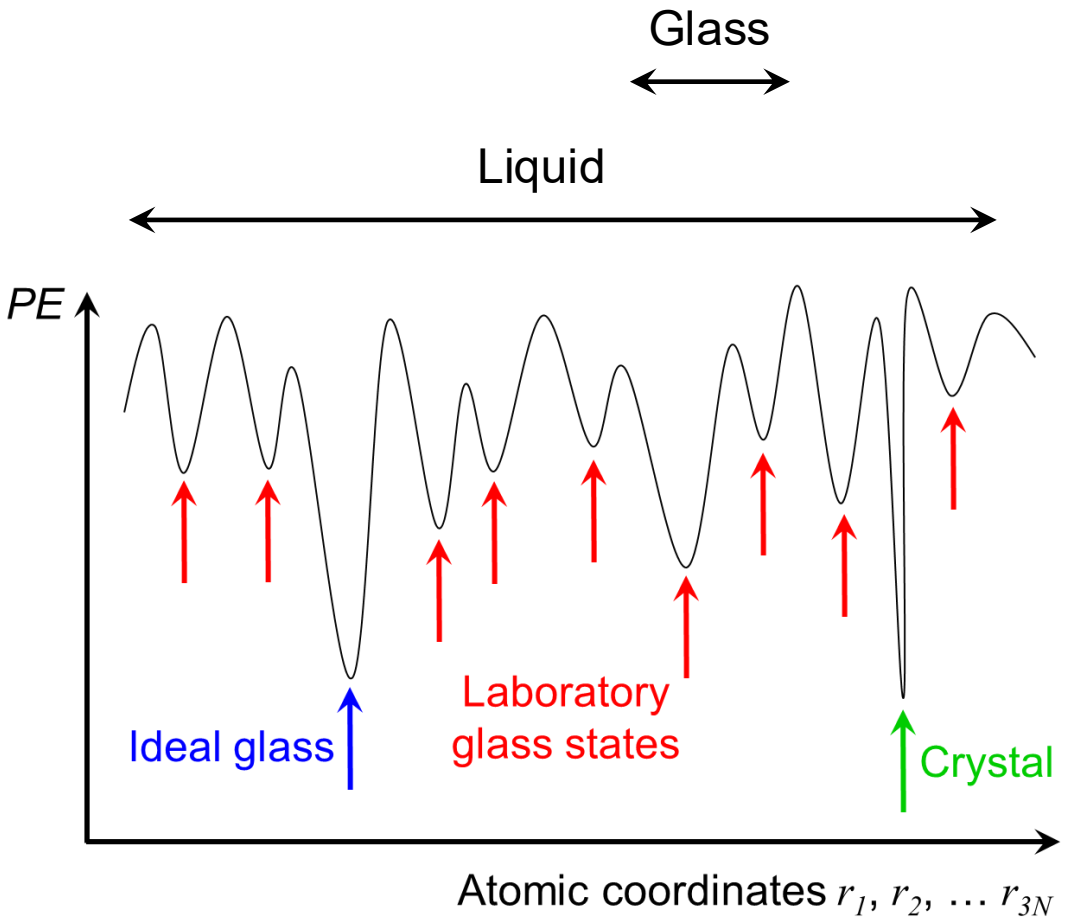
Laboratory glass transition

- 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 former: high valence state, covalent bonding with O
- Modifier: low valence state, ionic bonding with O

1 H Hydrogen 1.00794																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012182											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
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050											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
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	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
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	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
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	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)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

Network modifiers Glass formers Intermediates

Zachariasen's rules

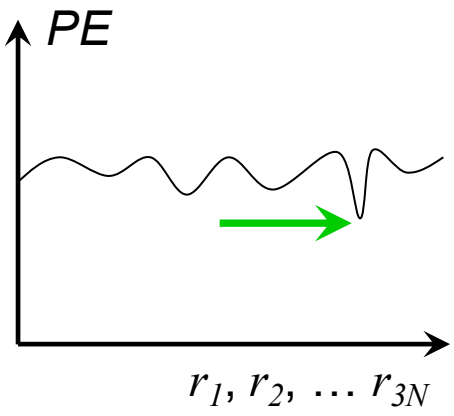
Rules for glass formation in an oxide A_mO_n

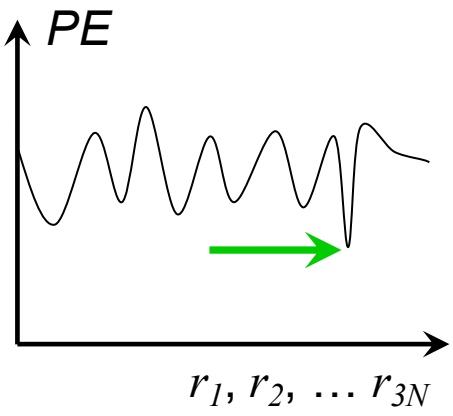
- An oxygen atom is linked to no more than two atoms of A
- The oxygen coordination around A is small, say 3 or 4
  - Open structures with covalent bonds
  - Small energy difference between glassy and crystalline states
- The cation polyhedra share corners, not edges, not faces
  - Maximize structure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

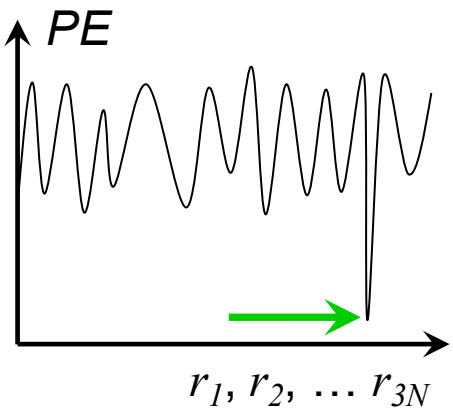
- Only applies to most (not all!) oxide glasses
- Highlights the importance of network topology

Classification of glass network topology

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







Number of constraints

Denote the atom coordination number as r

- Bond stretching constraint: $r/2$
- Bond bending constraint: $2r-3 \quad (r \geq 2)$
  - One bond angle is defined when r = 2
  - Orientation of each additional bond is specified by two angles
- Total constraint number:

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

- 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: $3n_{r\geq 2}$
- Isostatic condition:

$$3n_{r\geq 2} = \left(2.5\langle r\rangle - 3\right)\cdot n_{r\geq 2} \Rightarrow \boxed{\langle r\rangle = 2.4}$$

Phillips' "magic" coordination number

- Examples:
  - Ge_xSe_{1-x} $\langle r\rangle = x\cdot 4 + (1-x)\cdot 2 = 2 + 2x$
  - As_xS_{1-x} $\langle r\rangle = x\cdot 3 + (1-x)\cdot 2 = 2 + x$
  - Si_xO_{1-x} $\langle r\rangle = x\cdot 4 + (1-x)\cdot 2 = 2 + 2x$

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

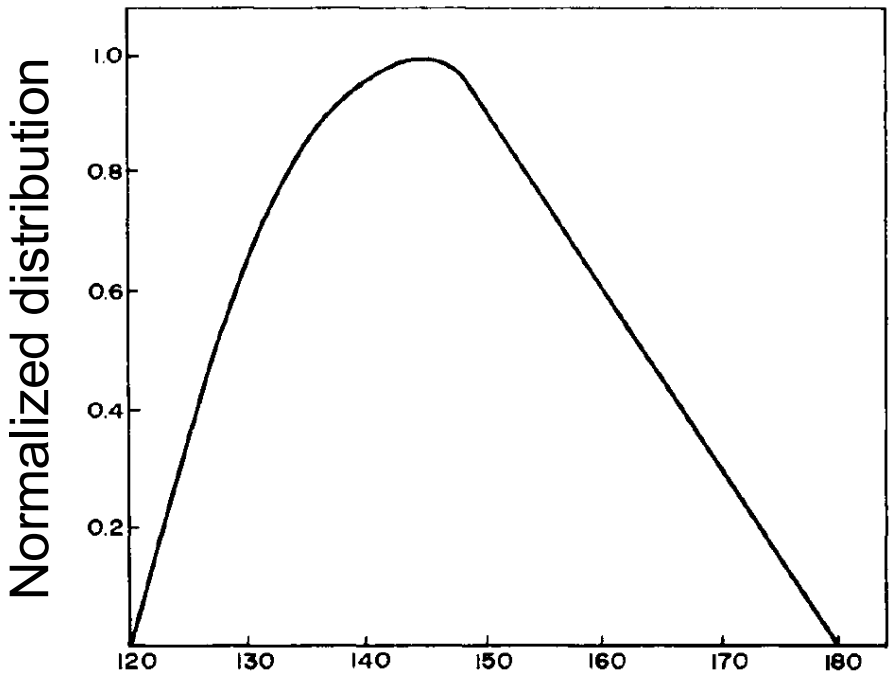
$$\frac{r_{Si}}{2}\cdot n_{Si}+\frac{r_O}{2}\cdot n_O$$

  - O-Si-O bond angle

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

  - Isostatic condition

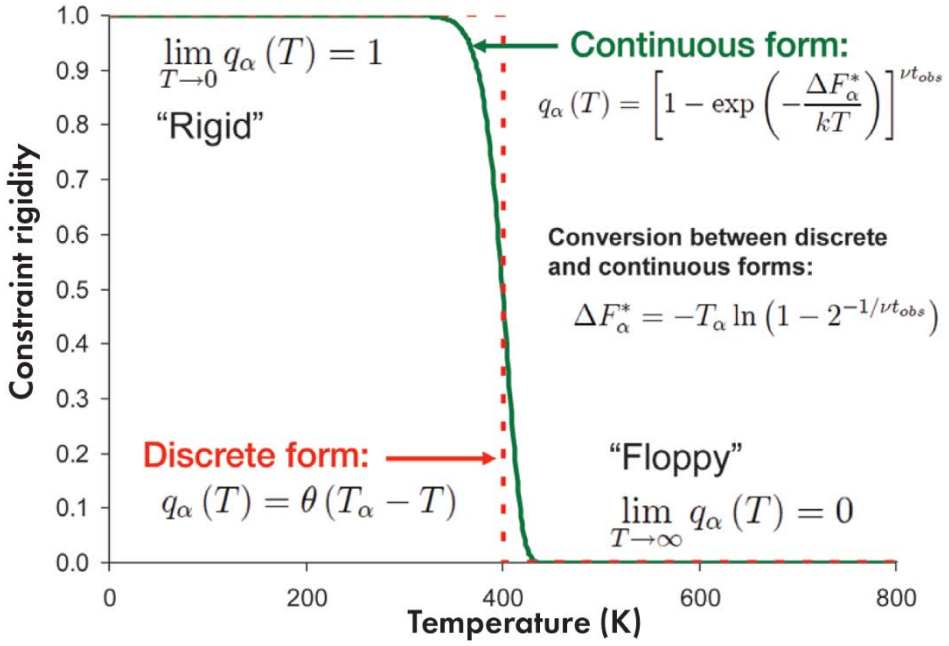
$$x=1/3 \quad SiO_2$$

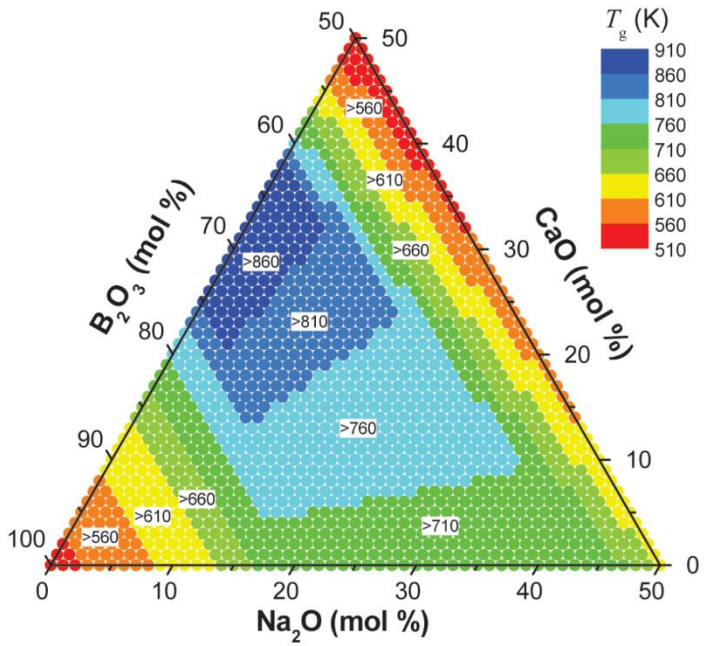


Si-O-Si bond angle in silica glass

Temperature-dependent constraints

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





"Topological constraint theory of glass," *ACerS Bull.* **90**, 31-37 (2011)

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Enumeration of constraint number

Bond stretching constraints (coordination number):

- 8-*N* rule: applies to most covalently bonded nonmetals (O, S, Se, P, As, Si, etc.)
- Exceptions: heavy elements (e.g. Te, Sb), boron anomaly

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 $\langle r \rangle = 2.4$

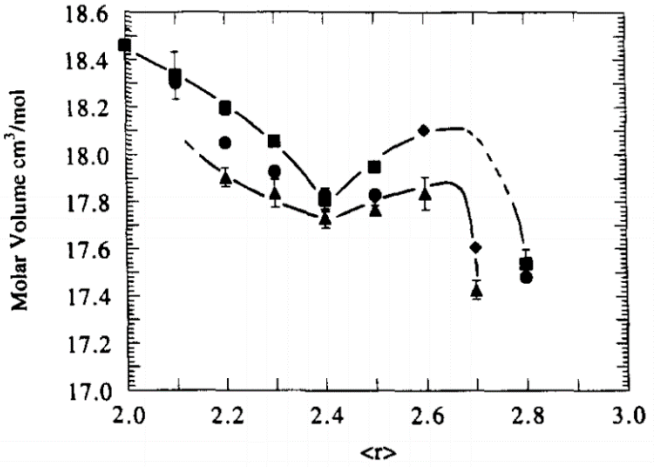


Fig. 6. Dependence of molar volume on $\langle r \rangle$ for binary Ge–Se and ternary Ge–Sb–Se systems. The molar volume at room temperature for the binary and ternary are represented by ■ and ▲, respectively. The molar volume values for the binary glasses given by Ota et al. [11] are represented by ● 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%.

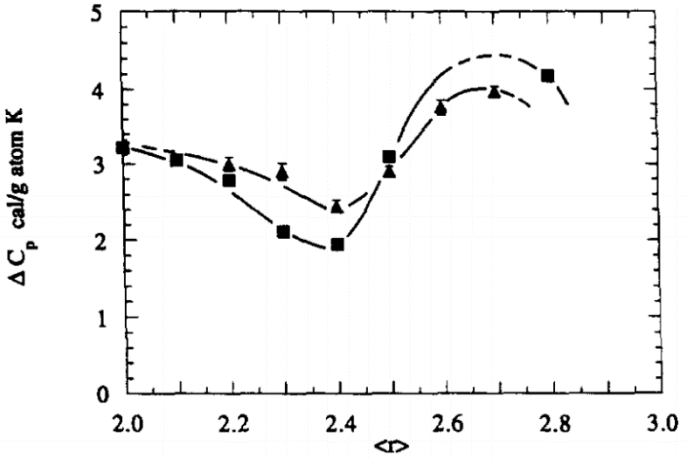


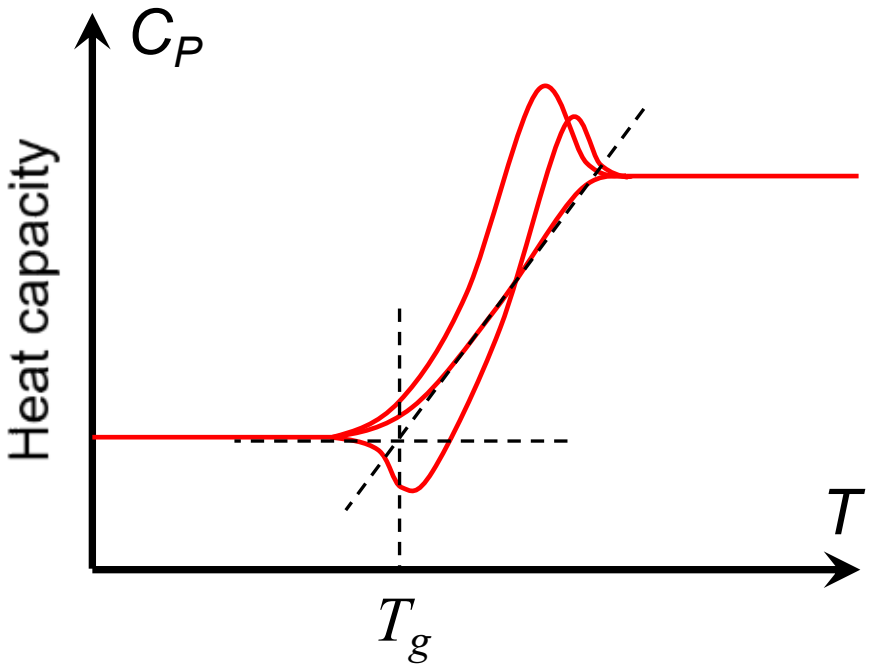
Fig. 10. ΔC_p versus $\langle r \rangle$ for binary Ge–Se and ternary Ge–Sb–Se systems. The ΔC_p values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 1.8%.

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

Udayan Senapati, Arun K. Varshneya, "Configurational arrangements in chalcogenide glasses: A new perspective on Phillips' constraint theory," Journal of Non-Crystalline Solids, Volume 185, Issue 3, 1995, Pages 289-296, https://www.sciencedirect.com. Used with permission.

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:

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

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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