Crystal Growth in Glass Forming Liquids

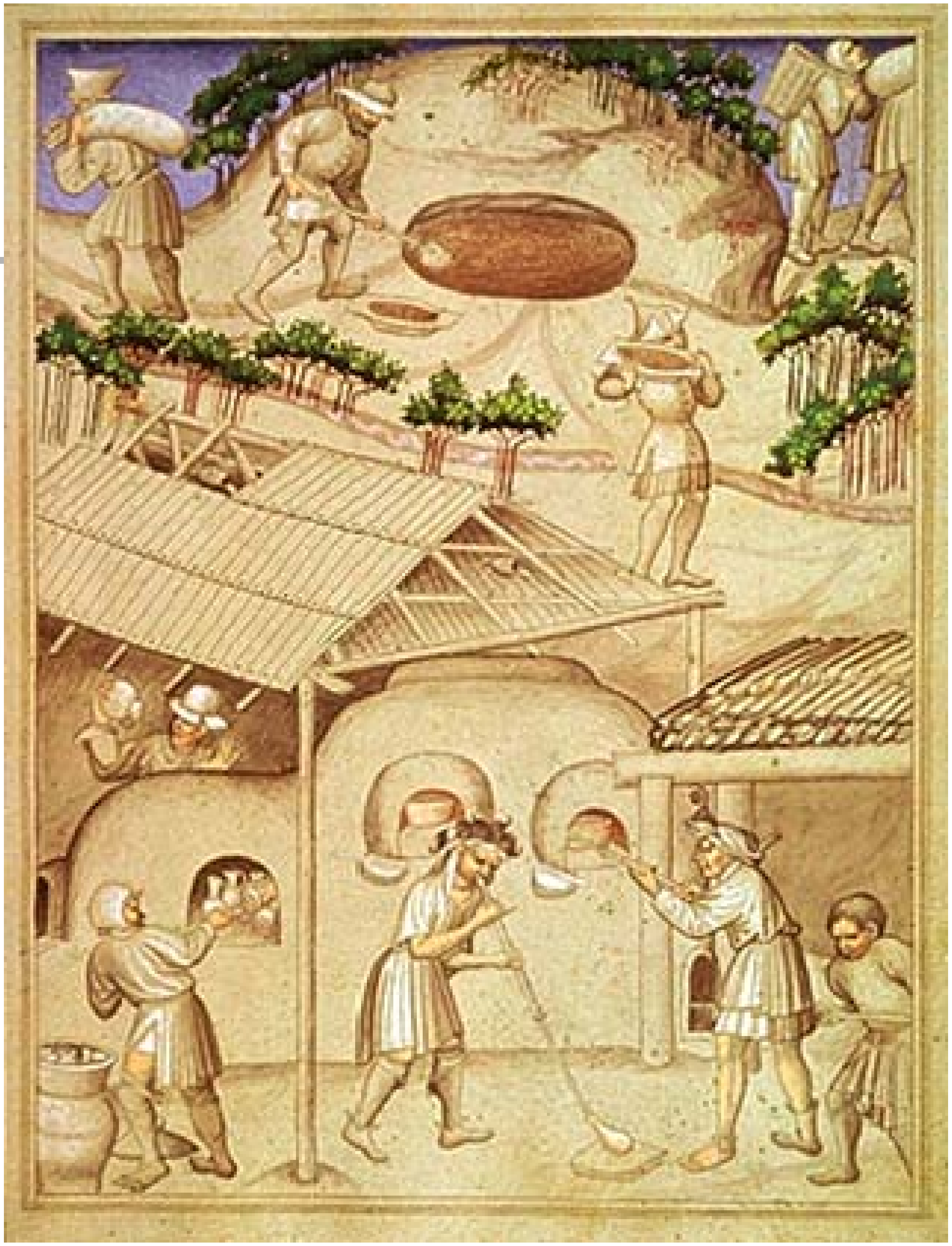
Marcio Luis Ferreira Nascimento
Edgar Dutra Zanotto

Federal University of São Carlos, Brazil
Vitreous Materials Laboratory
www.lamav.ufscar.br

Presented at the IMI-NFG US-Japan Winter School , Jan 14, 2008 and Reproduced by the International Materials Institute for Glass for use by the glass research community; Available at: www.lehigh.edu/imi

Outline

- Introduction
- Growth models?
- Normal Growth
- Screw Dislocation Growth
- Surface Nucleation Growth
- Some Examples
- Experimental Results
- Acknowledgments
- Bibliography



Introduction

Crystal growth rates depend basically on three factors:

i) **The undercooling, which is a measure of the driving force for crystal growth;**

ii) **The site factor, which is the fraction of sites on the crystal/ glass interface that can incorporate molecules;**

iii) **The effective diffusivity in the crystal/liquid interface, which is a measure of the resistance to molecular motion and rearrangement.**

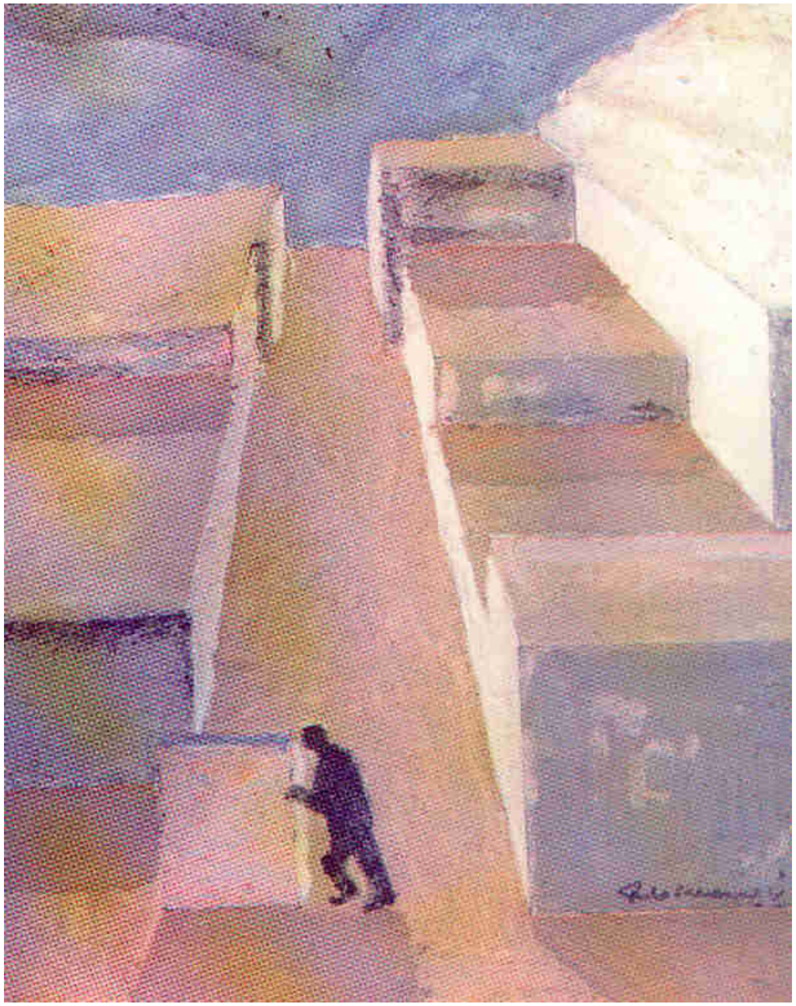
Relevance

Crystallization kinetics allows or not the existence of vitreous state

The development of glass-ceramics depend on the controlled crystallization of certain glasses

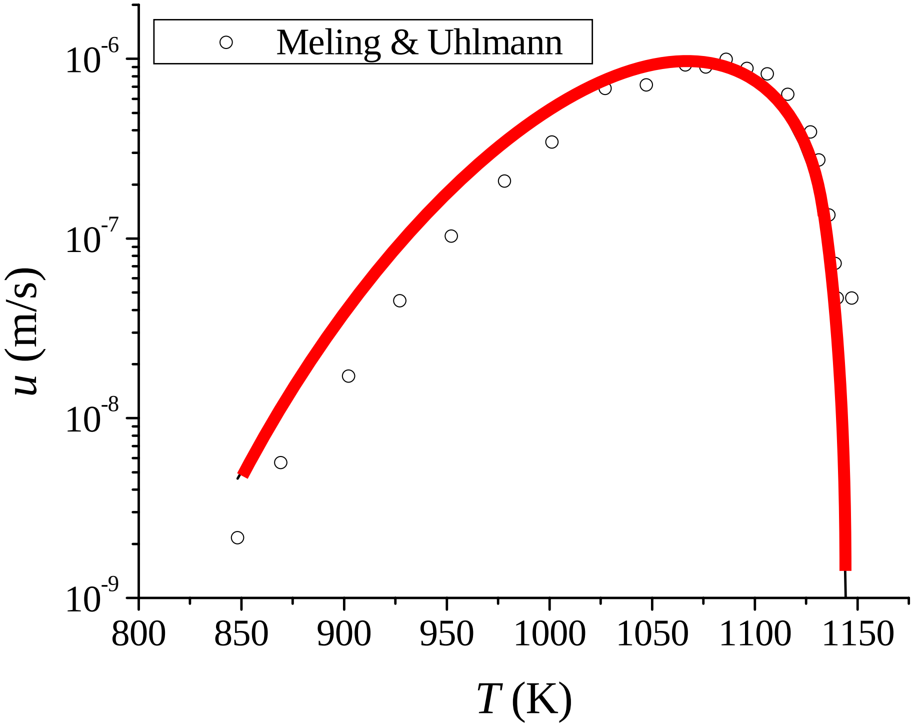
THEORY

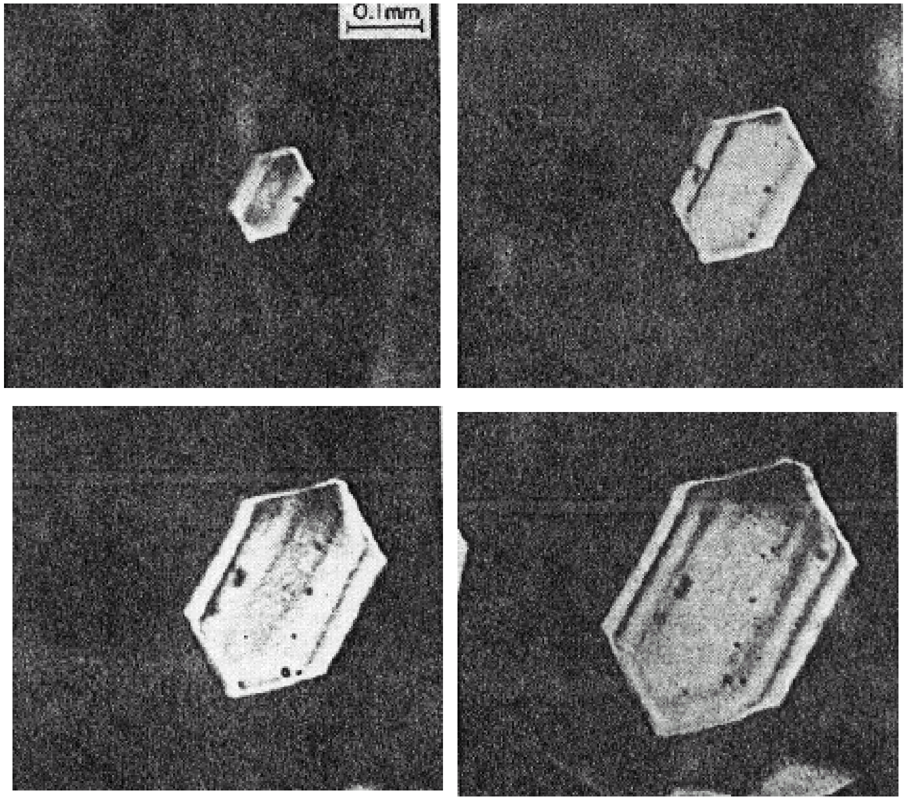
How Crystals Grow?



Painting by Paolo Massacci

Example of Crystal Growth



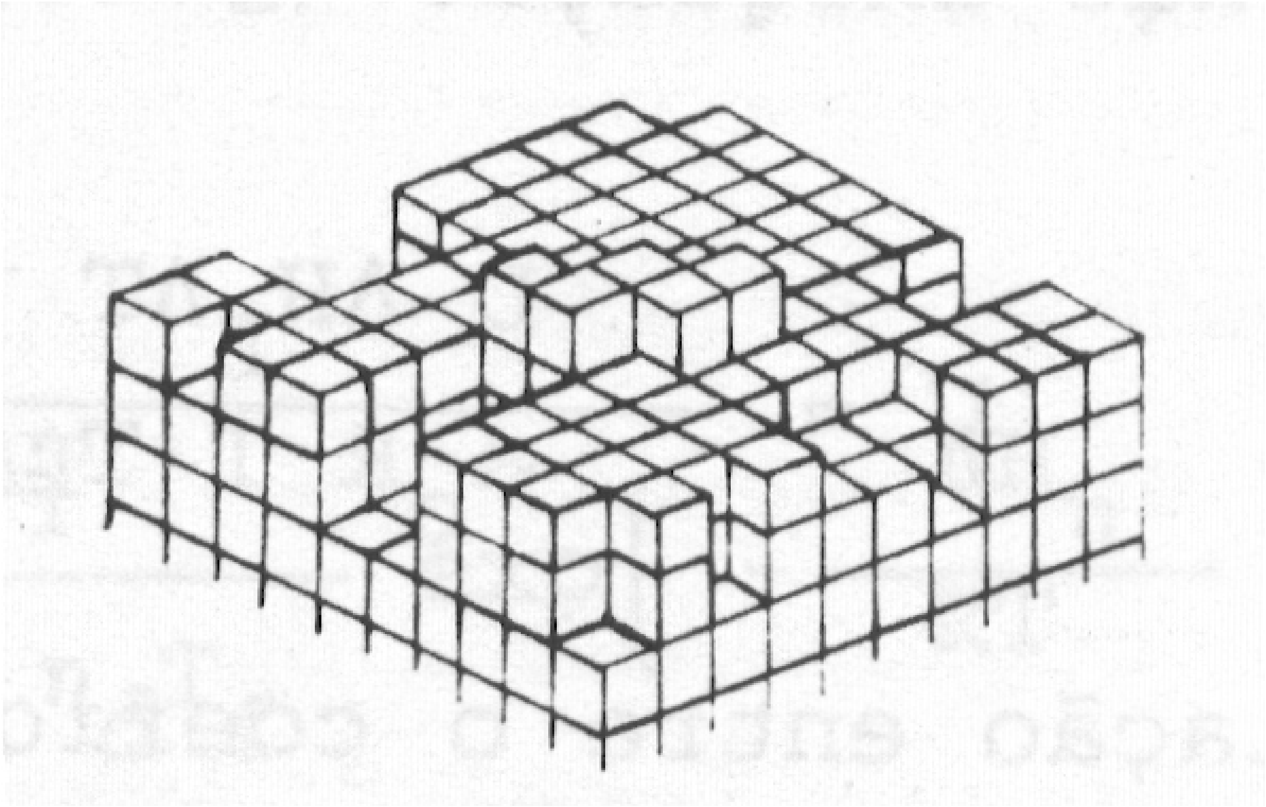


$Na_2O{\cdot}2SiO_2$

α-phase growth on NS2 at 780°C / 1 min intervals

How Crystals Grow?

Three Classical Mechanisms



i) **NORMAL**

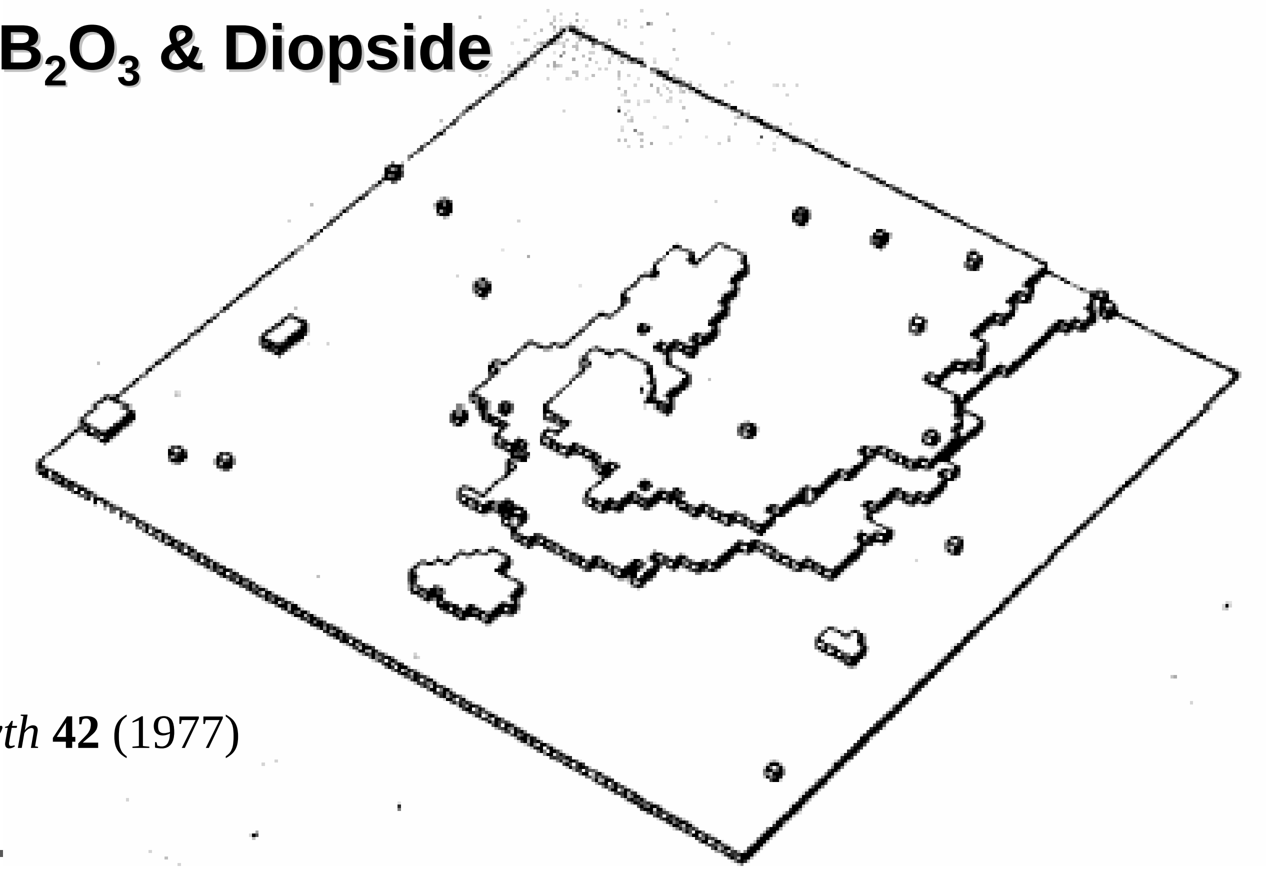
SiO_2 & GeO_2

George Gilmer

How Crystals Grow?

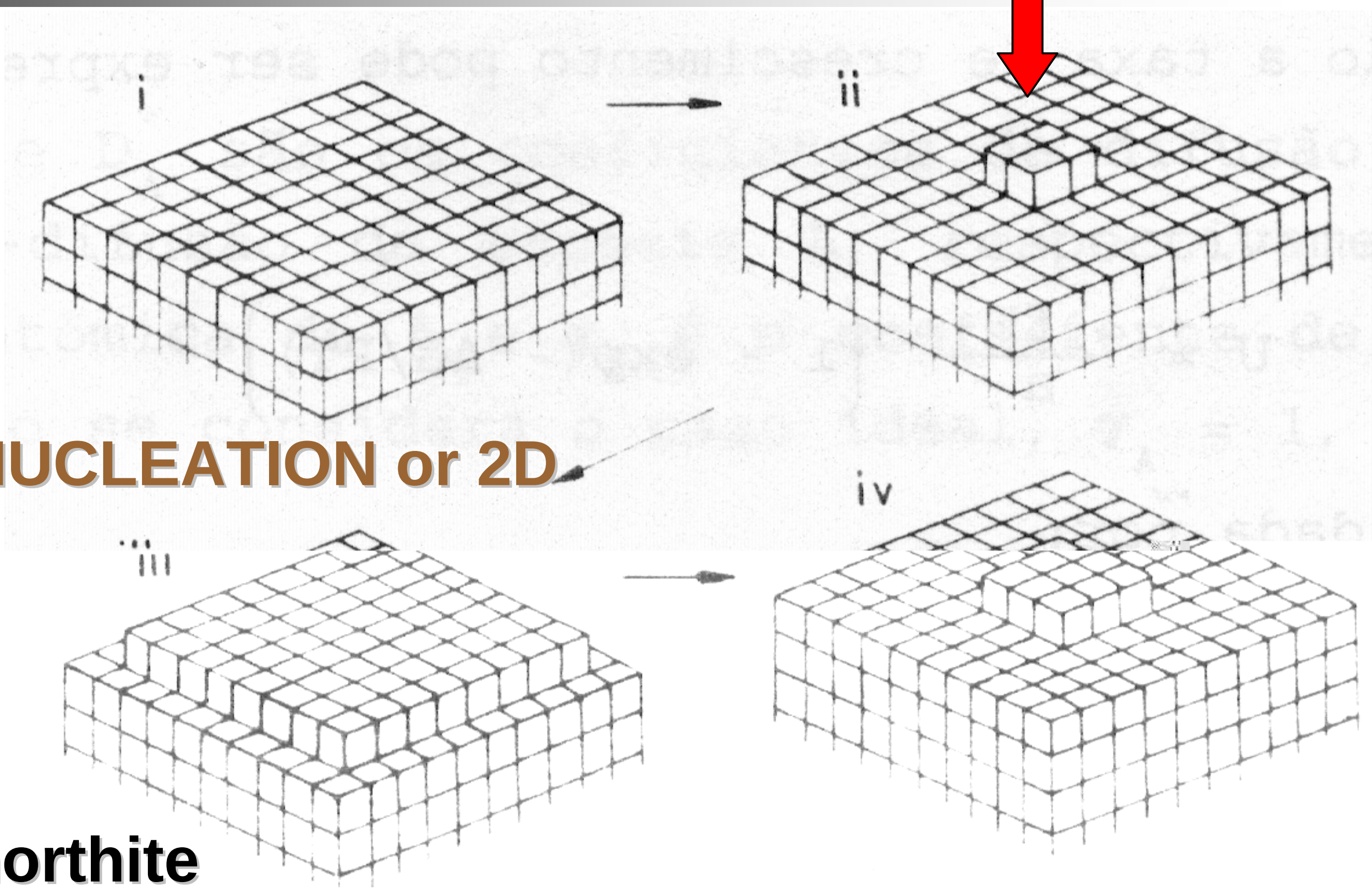
ii) SCREW DISLOCATION MODEL

$Na_2O{\cdot}2SiO_2$, $Na_2O{\cdot}4B_2O_3$ & Diopside



G. H. Gilmer, *J. Crystal Growth* **42** (1977)

How Crystals Grow?



iii) **SURFACE NUCLEATION or 2D**

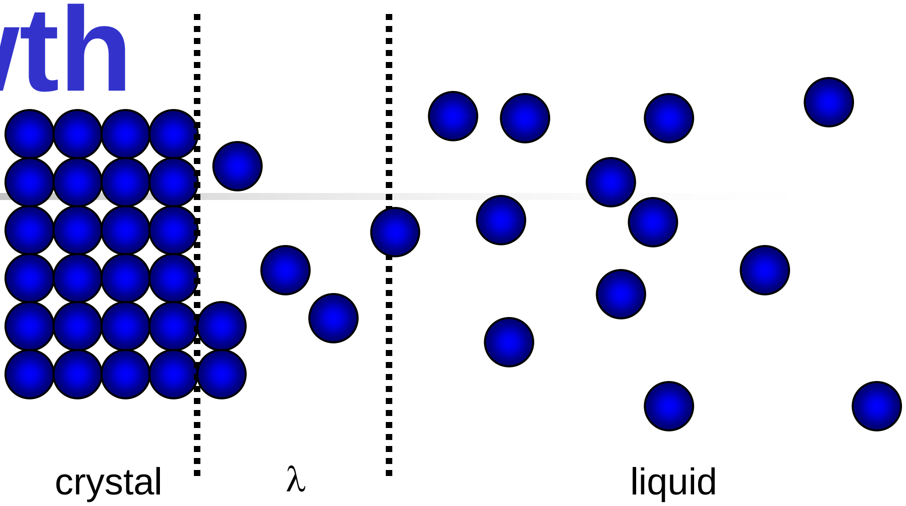
$PbO \cdot SiO_2$ & Anorthite

NORMAL GROWTH

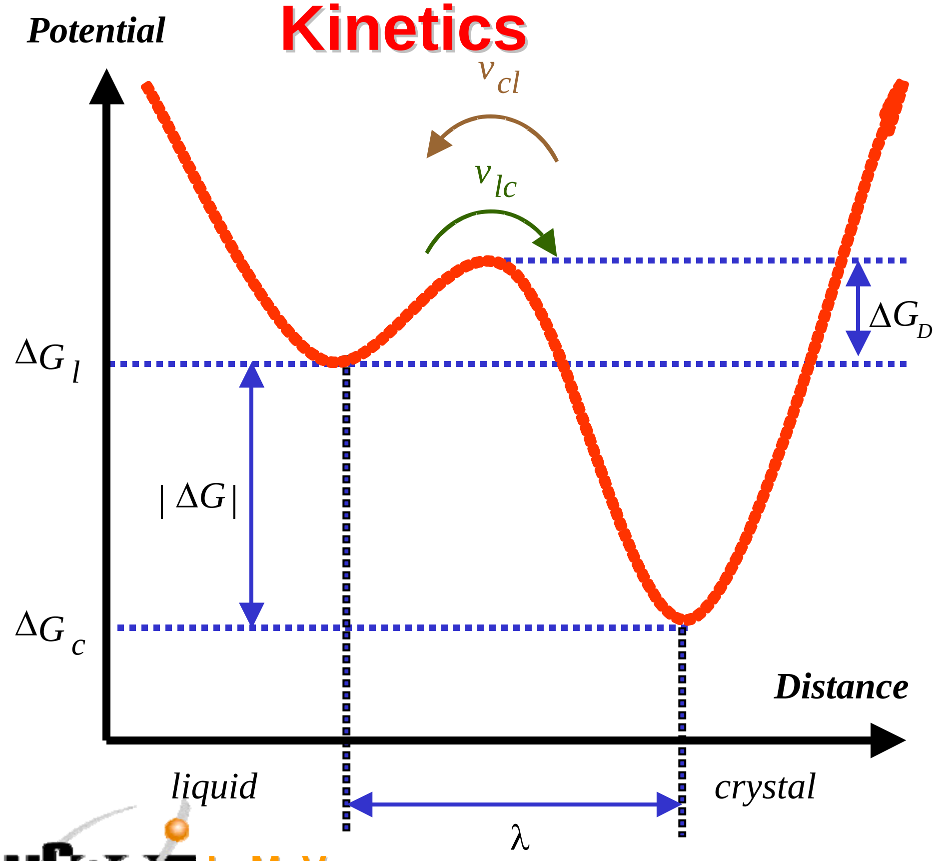
S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Processes* (1941)

Normal Growth

crystal-liquid interface



Kinetics



$$v_{lc} = v_0 \exp\left(-\frac{\Delta G_D}{RT}\right)$$

$$v_{cl} = v_0 \exp\left(-\frac{|\Delta G| + \Delta G_D}{RT}\right)$$

$$u = \lambda\left(v_{lc} - v_{cl}\right)$$

$$\boxed{u(T) = \lambda v_0 \exp\left(-\frac{\Delta G_D}{RT}\right)\left[1 - \exp\left(-\frac{|\Delta G|}{RT}\right)\right]}$$

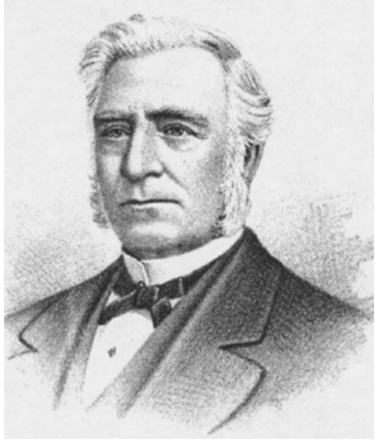
H. A. Wilson, *Philos. Mag.* **50** (1900)
Ya. Frenkel, *Phys. Z. Sowjetunion* **1** (1932)

Normal Growth

$$\boxed{u(T) = f\lambda\nu_0 \,\mathbf{exp}\left(-\frac{\Delta G_D}{RT}\right)\left[1 - \mathbf{exp}\left(-\frac{|\Delta G|}{RT}\right)\right]}$$

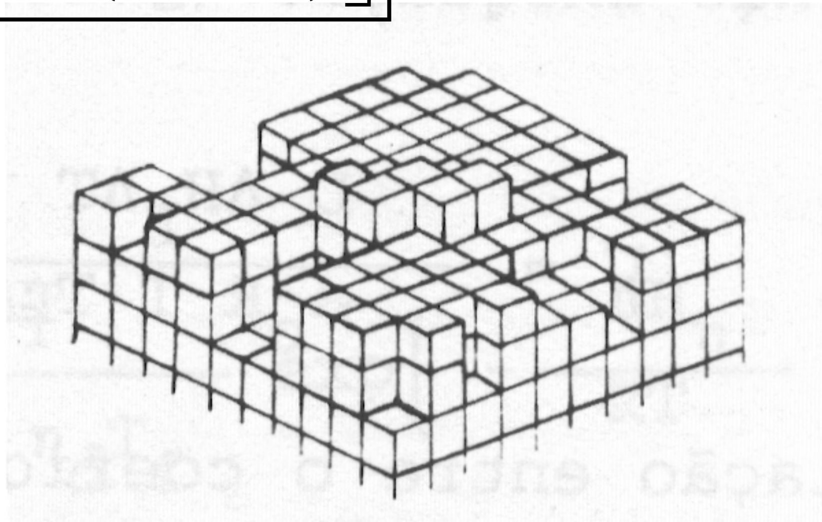
Fraction of prefered growth sites f

$f \approx$ constant ≈ 1



Harold A. Wilson

Yakov Frenkel



Main supposition: crystal growth front has a high concentration of growth sites f ~1

SCREW DISLOCATION GROWTH

W. K. Burton, N. Cabrera, F. C. Frank, *Trans. Roy. Soc. London* **A243** (1951)

Screw Dislocation

- The screw dislocation mechanism was proposed by Burton, Cabrera & Frank.

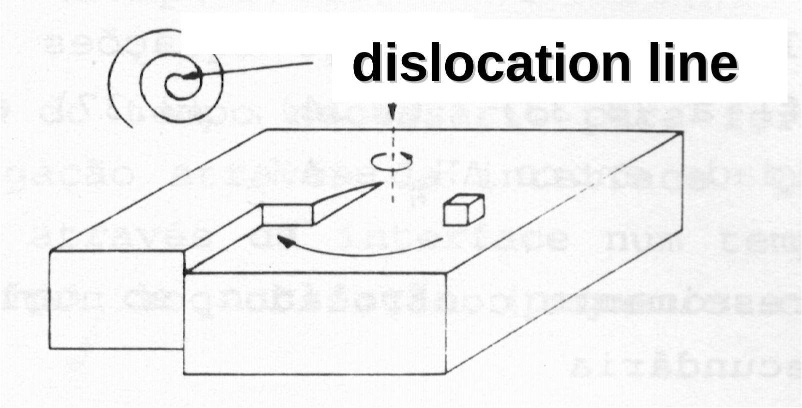

Frederick Frank


Nicolás Cabrera

Surface is smooth but imperfect at atomic level

Screw Dislocation

$$u(T) = f\lambda v\left[1-\mathbf{exp}\left(-\frac{|\Delta G|}{RT}\right)\right]$$



$$f \approx \frac{T_m - T}{2\pi T_m}$$

$$v = \frac{k_B T}{\lambda^3 \eta}$$

SE

$$u(T) = f(T)\lambda\frac{k_B T}{\lambda^3 \eta}\left[1-\mathbf{exp}\left(-\frac{|\Delta G|}{RT}\right)\right]$$

Transport

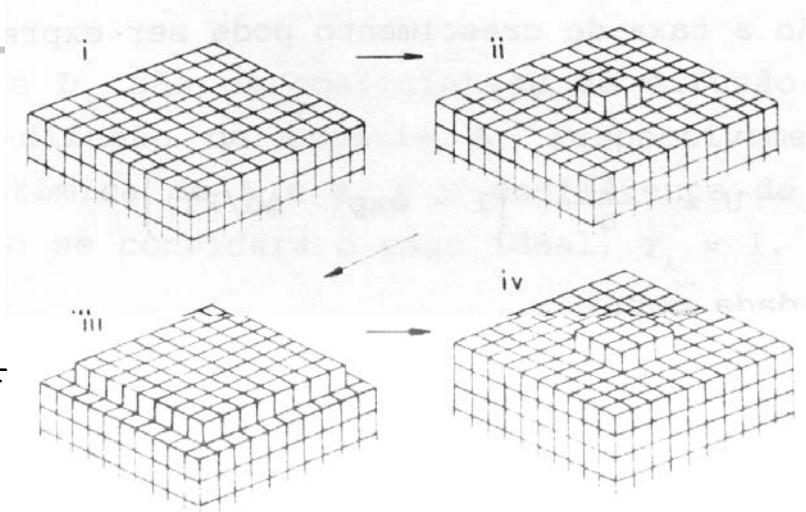
Thermodynamic

SECONDARY SURFACE NUCLEATION
2D-GROWTH

Surface is smooth but also imperfect at atomic level, but free of intersecting screw dislocations

Surface Growth: 2*D*

$$u = C\frac{b}{\eta}\mathbf{exp}\left(-\frac{B}{T\Delta G}\right)$$



where:

$$b = \frac{k_B T}{\lambda^3} \qquad \sigma = \alpha\frac{\Delta H_m}{\sqrt[3]{N_A V_m^2}}$$

(*small* crystal case)

$$B = \frac{\pi\lambda V_m \sigma^2}{k_B}$$

$$C \approx \lambda N_S A_0$$

(*large* crystal case)

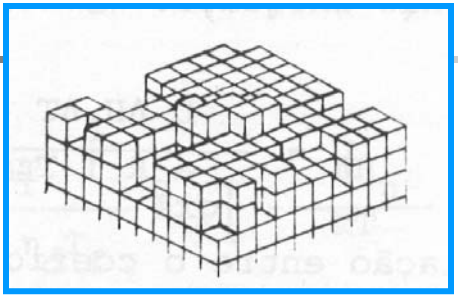
$$B = \frac{\pi\lambda V_m \sigma^2}{3k_B}$$

$$C = \frac{\sqrt[3]{\pi N_S \lambda^5 / 3}}{\Gamma(4/3)}\left[1 - \mathbf{exp}(-\Delta G / RT)^{2/3}\right]$$

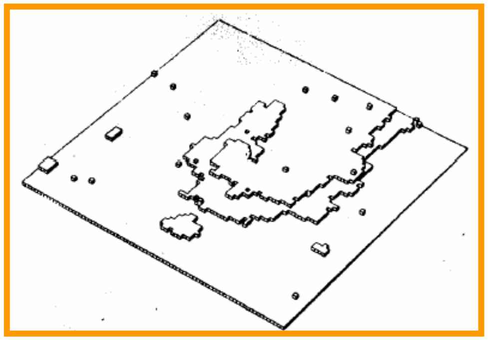
ufscar LaMaV

Summary: Growth Mechanisms

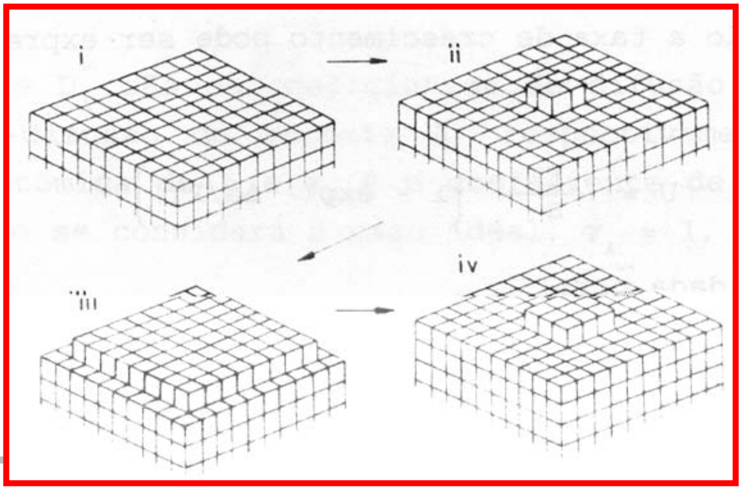
i) Normal (N) →



ii) Screw Dislocations (SD) →



iii) Surface Nucleation (2D) →



Summary: Growth Mechanisms

i) Normal (N) →

$$u(T) = \frac{D_u}{\lambda}\left[1 - \mathbf{exp}\left(-\frac{\Delta G}{RT}\right)\right]$$

ii) Screw Dislocations (SD) →

$$u(T) = f\,\frac{D_u}{\lambda}\left[1 - \mathbf{exp}\left(-\frac{\Delta G}{RT}\right)\right]$$

iii) Surface Nucleation (2D) →

$$u(T) = C\,\frac{D_u}{\lambda^2}\,\mathbf{exp}\left(-\frac{B}{T\Delta G}\right)$$

if $D_u \approx D_\eta$

$$D_u = \frac{k_B T}{\lambda^3 \eta}$$

LaMaV

EXAMPLES OF

CRYSTAL GROWTH CURVES

Properties required to test models
or calculate growth rates

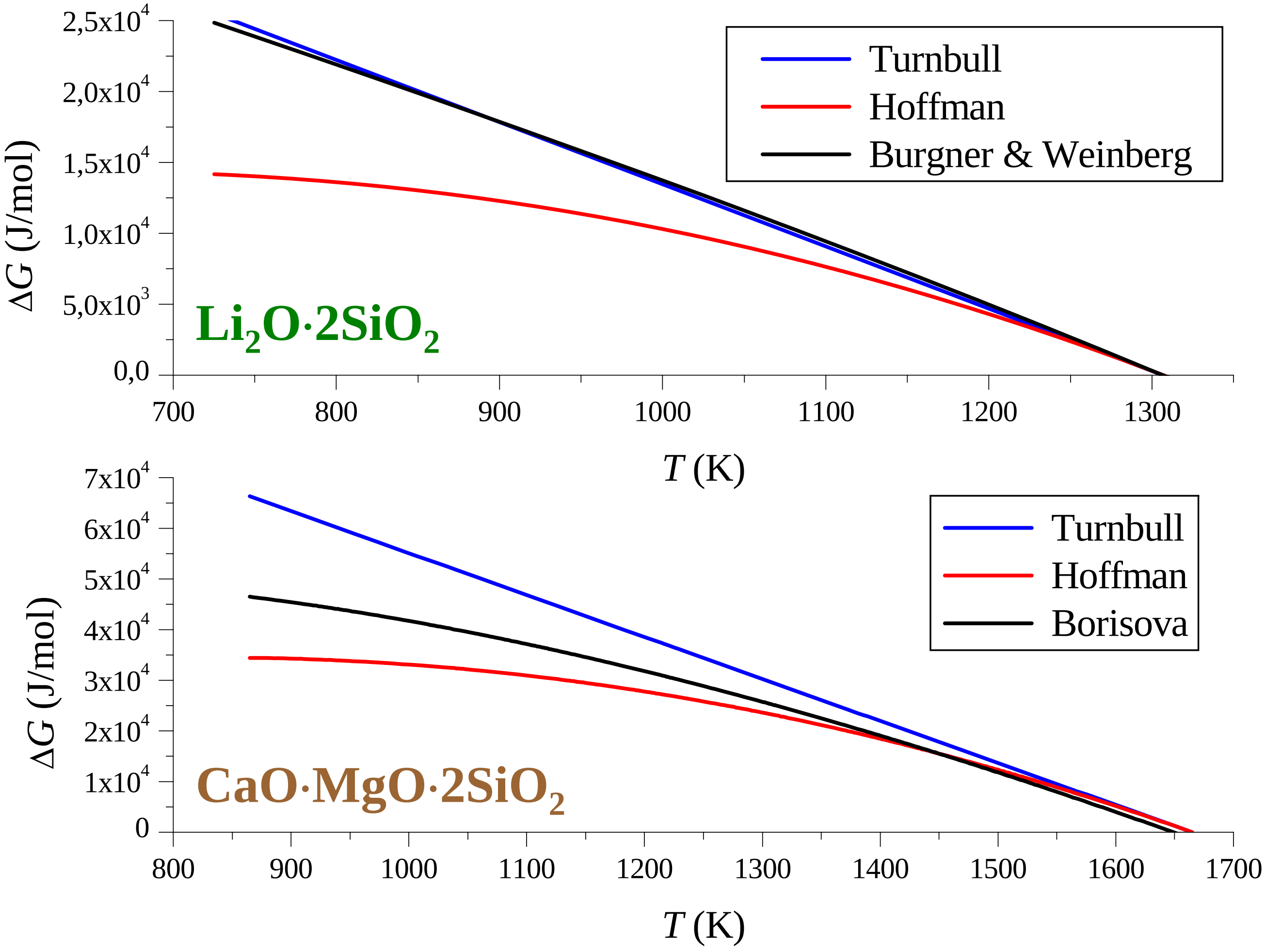
i) Diffusivity (or viscosity) *vs.* T;
ii) Crystal-glass free energy *vs.* T

M. L. F. Nascimento, *Thesis, Federal University of São Carlos* (2004)

Gibbs Free Energy

Comparison of measured and calculated Gibbs free energies ΔG for LS$_2$ and diopside in wide range of temperatures.

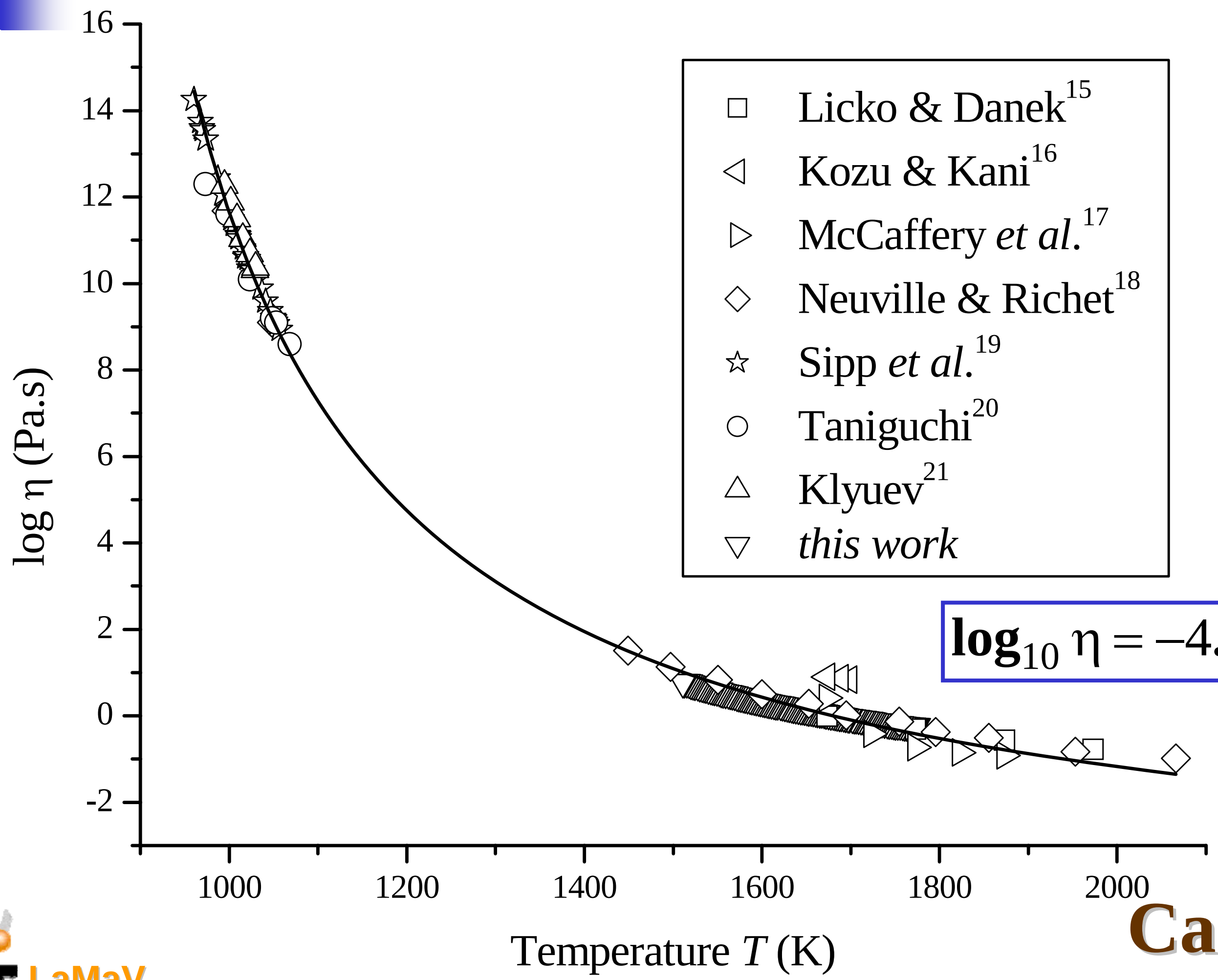
Both approximations are valid near T_m. For **normal** and **screw dislocation** growth ΔG does <u>not</u> have a strong influence on U compared to the transport term.



M. L. F. Nascimento, E. B. Ferreira, E. D. Zanotto, *J. Chem. Phys.* **121** (2004)

Viscosity: Diopside

Eduardo Ferreira



$$\mathbf{log}_{10}\,\eta = -4.27 + 3961/(T - 751)$$

$CaO{\cdot}MgO{\cdot}2SiO_2$


Svante Arrhenius


Gordon Fulcher

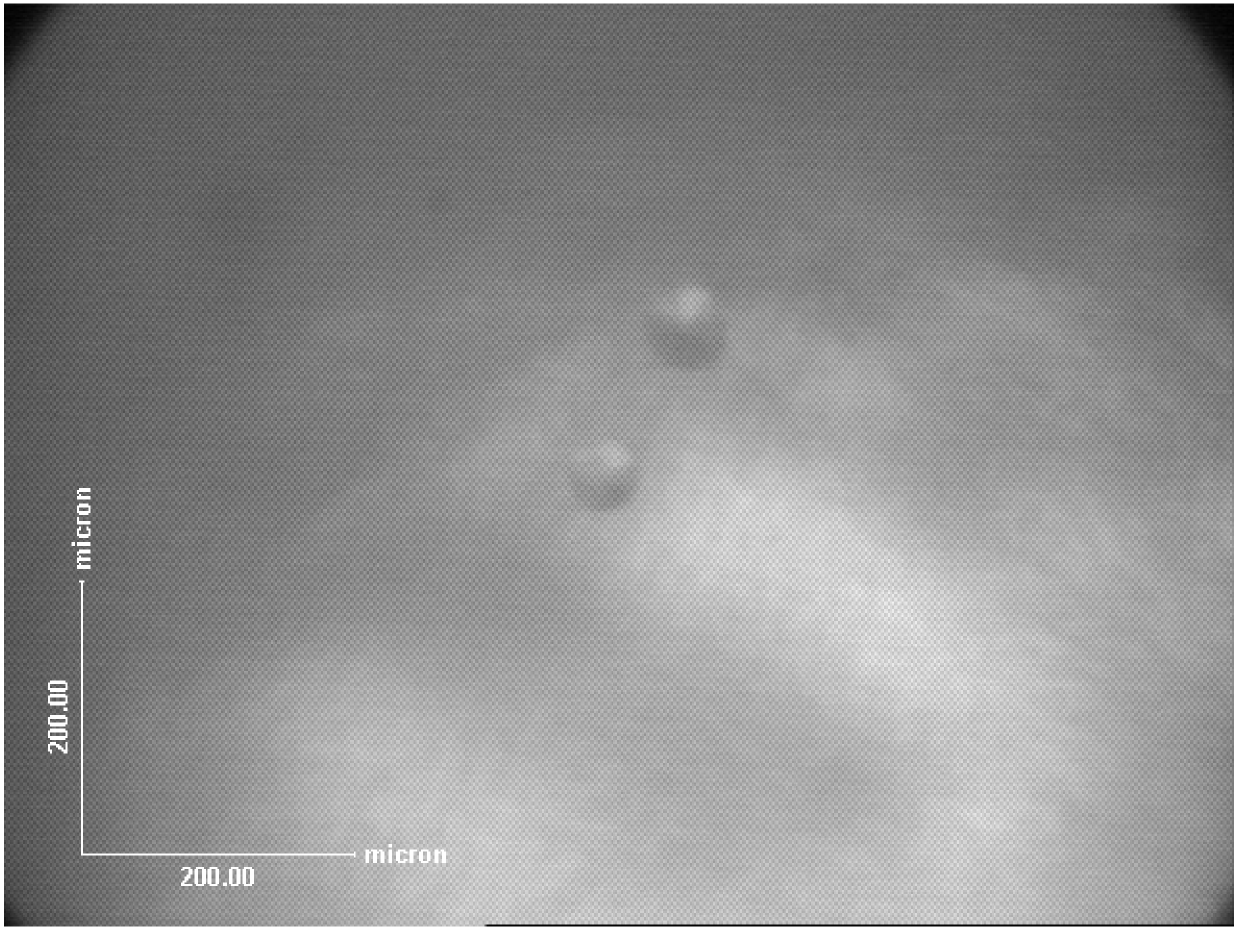

Gustav Tammann

- **Arrhenius or Vogel-Fulcher-Tammann-Hesse (VFTH) equations describe viscosity data between T_g and T_m for many systems; but is the Stokes-Einstein/Eyring equation adequate to describe the rearrangements on the crystal growth front?**

Growth *in situ*: Diopside

950°C

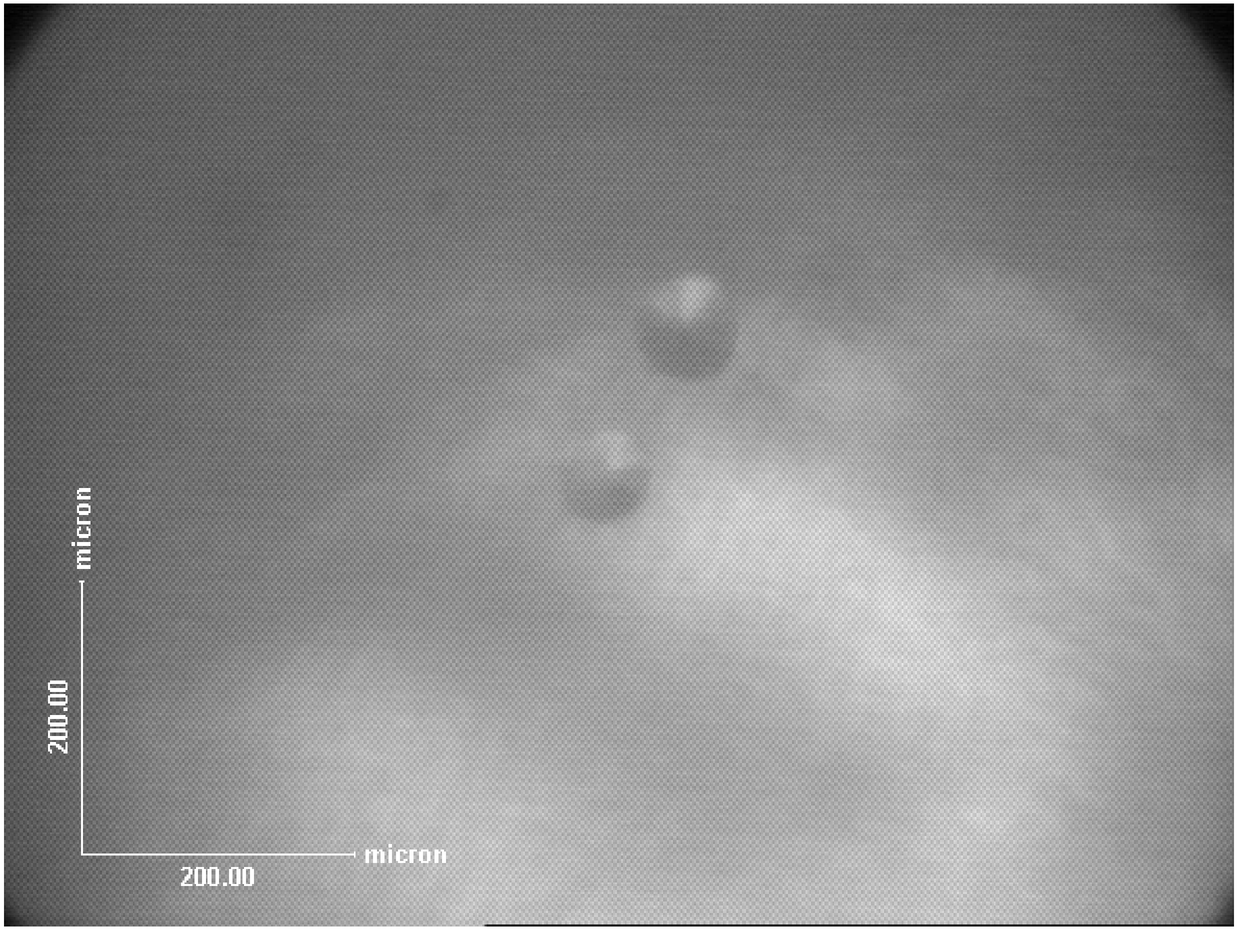
2min 00s



Growth *in situ*: Diopside

950°C

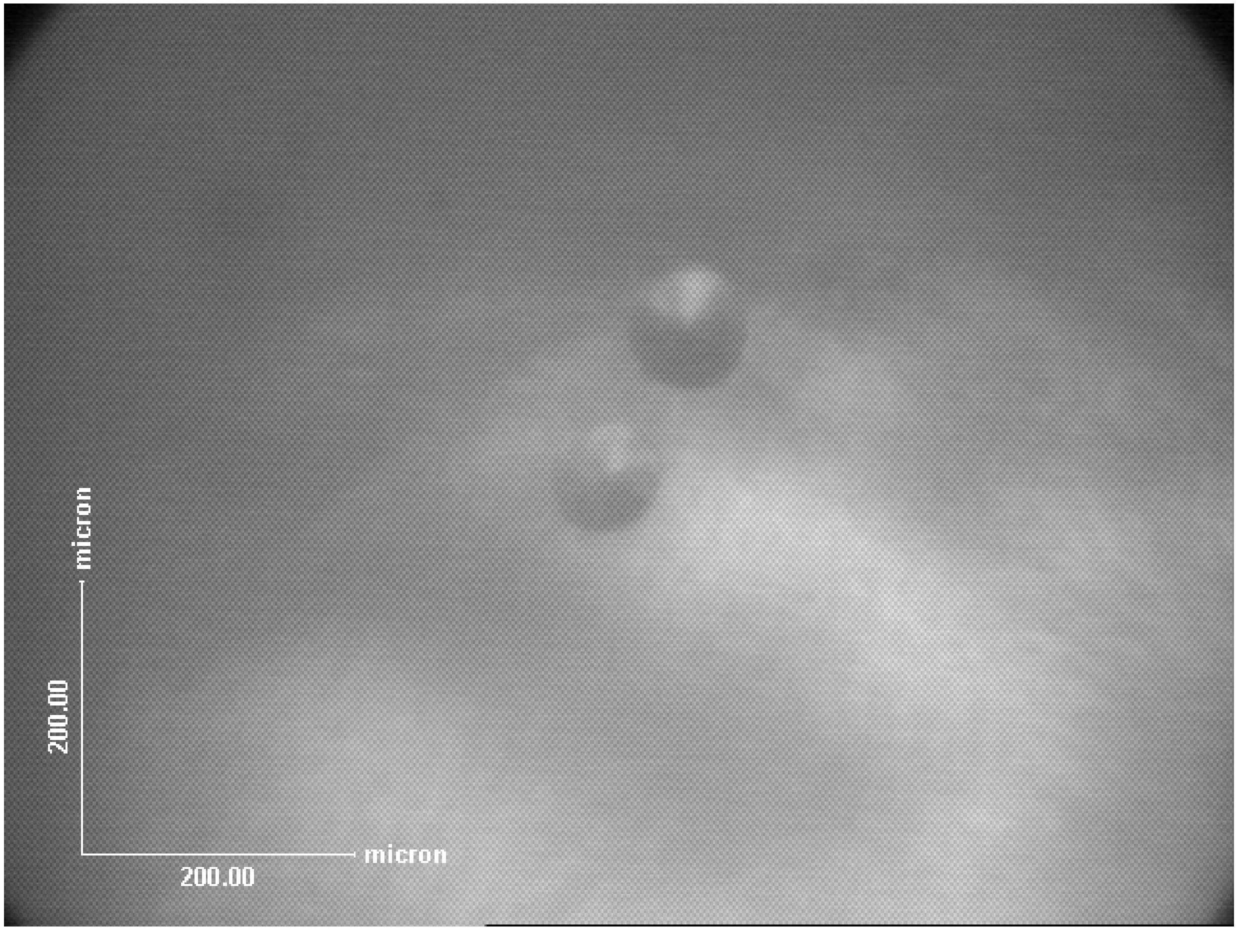
2min 30s



Growth *in situ*: Diopside

950°C

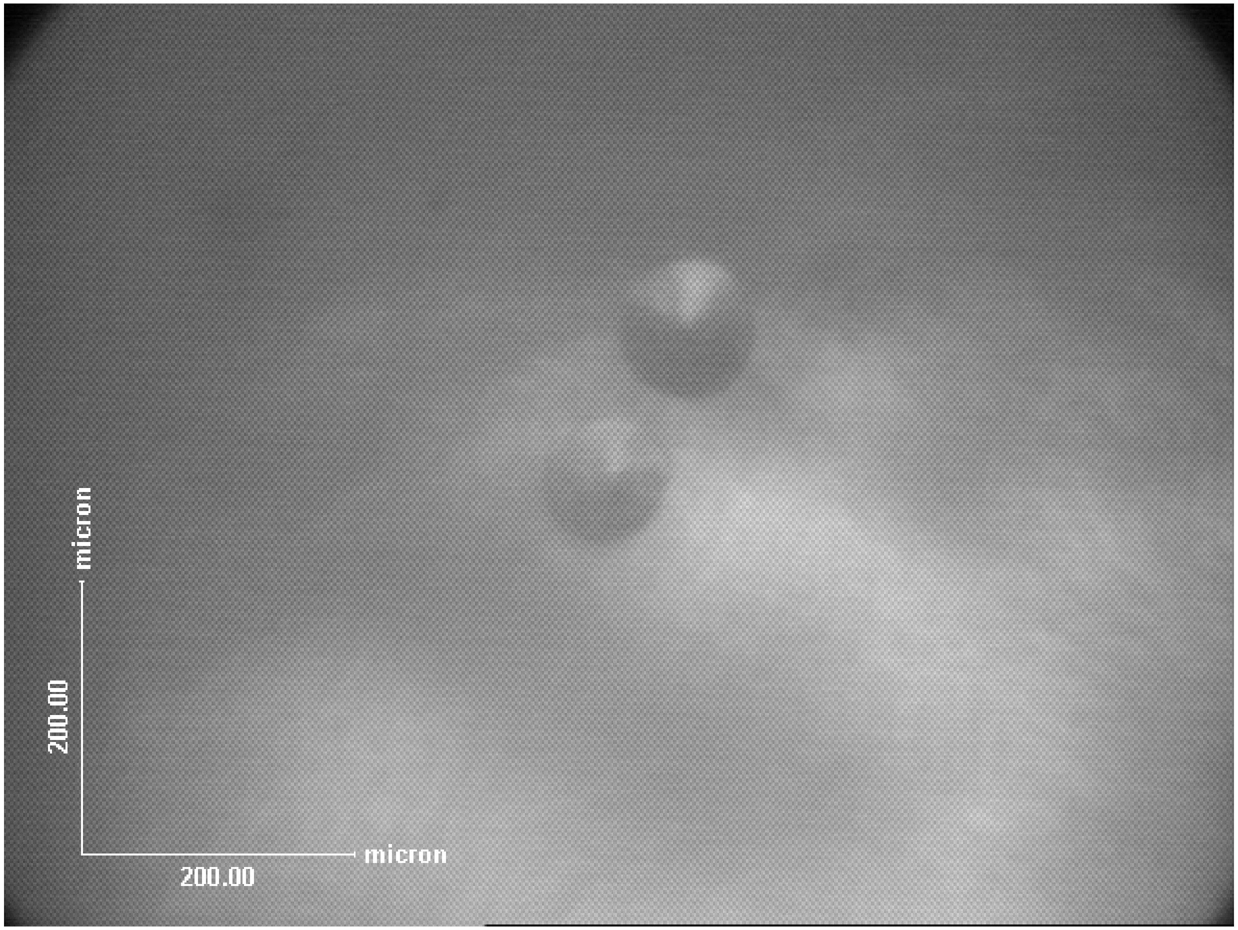
3min 00s



Growth *in situ*: Diopside

950°C

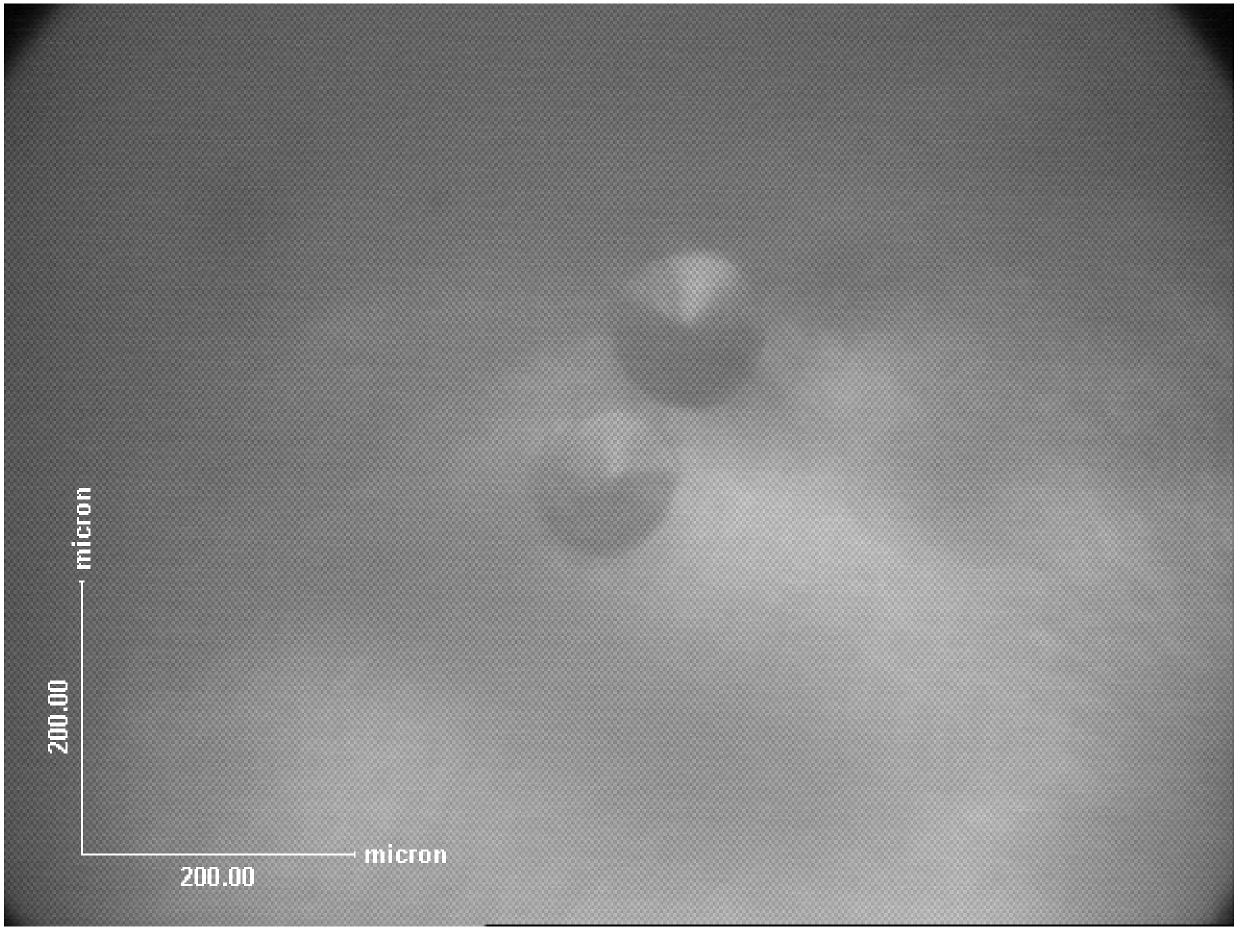
3min 30s



Growth *in situ*: Diopside

950°C

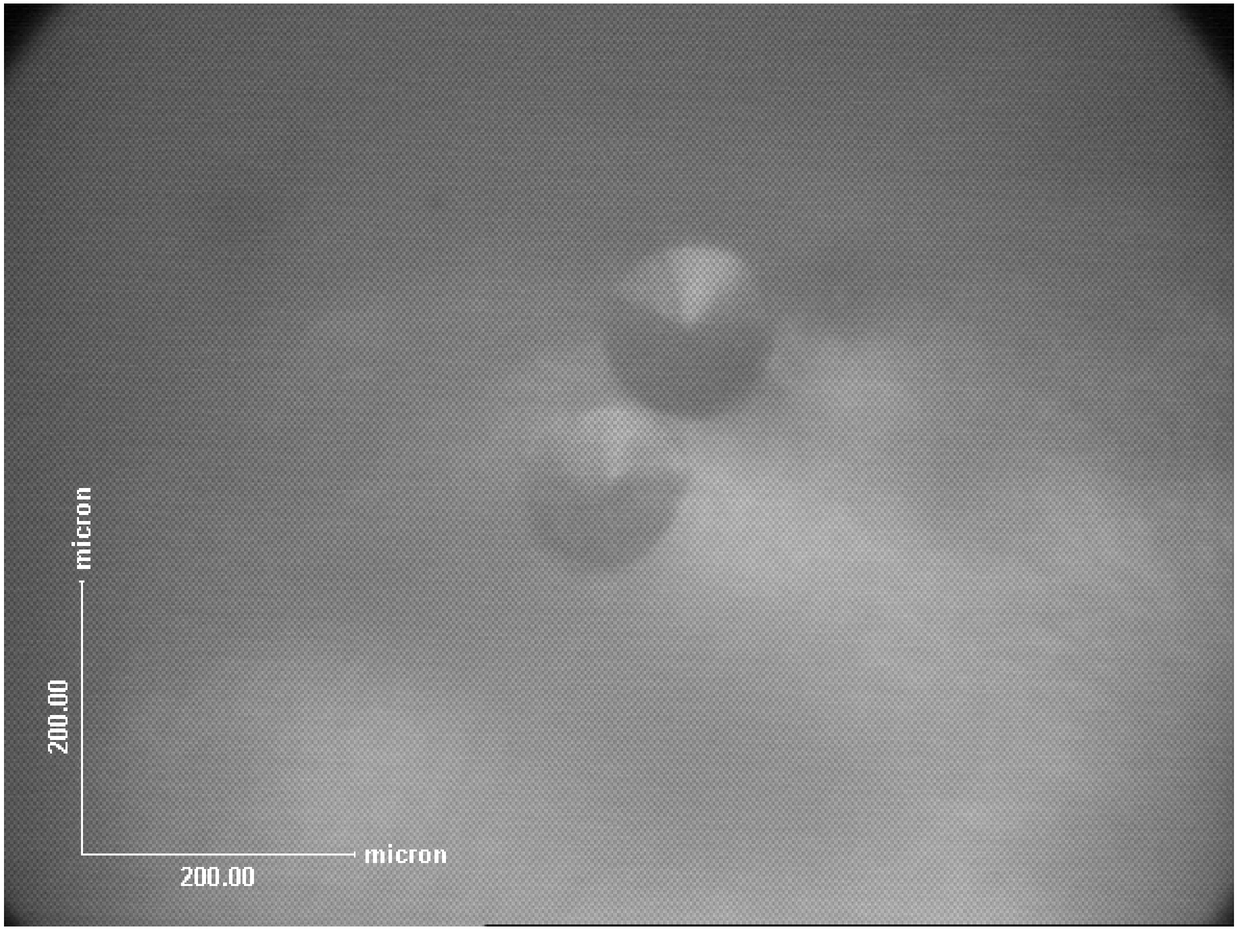
4min 00s



Growth *in situ*: Diopside

950°C

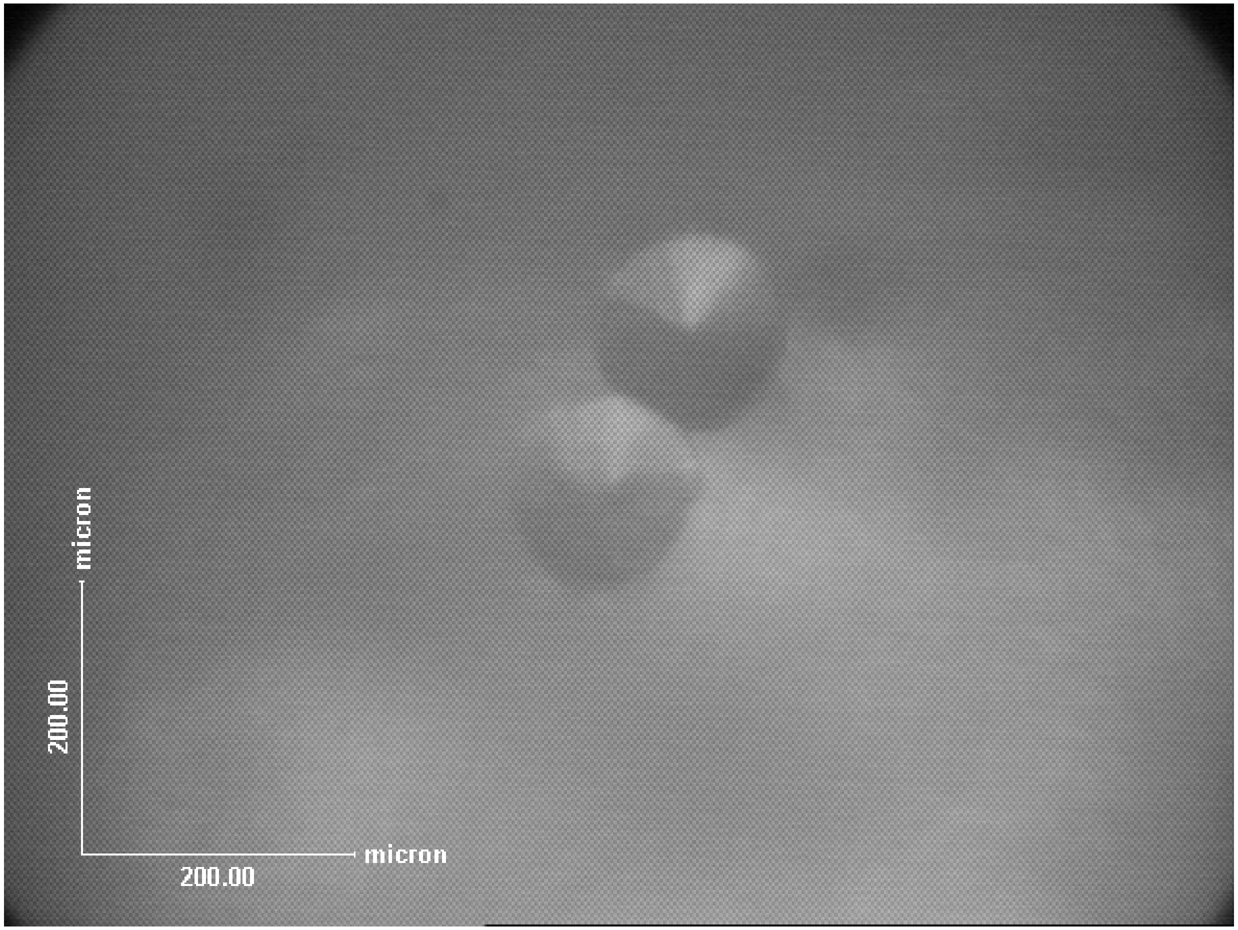
4min 30s



Growth *in situ*: Diopside

950°C

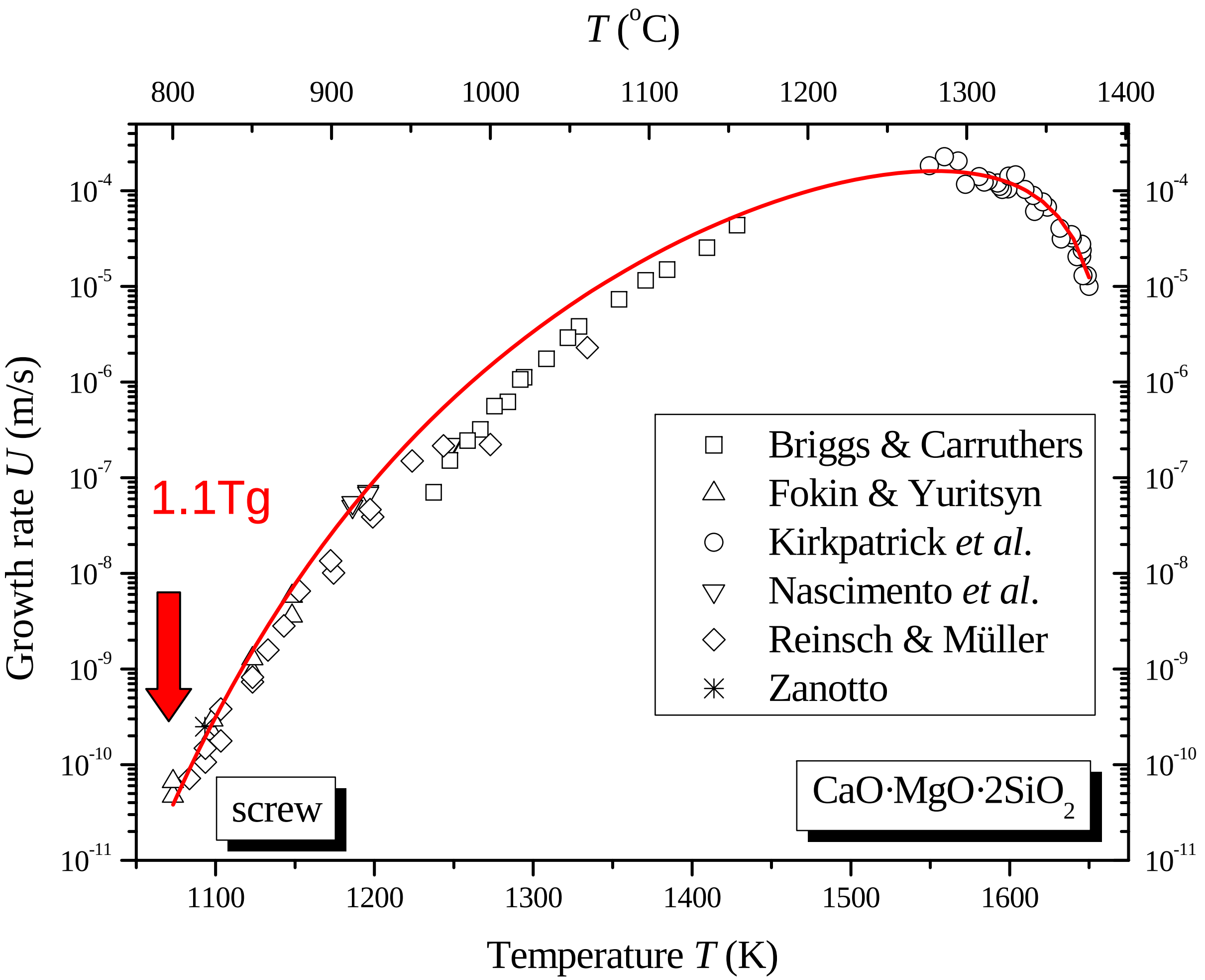
5min 00s



Growth rates: Diopside

$$u(T) = f\,\frac{D_u}{\lambda}\left[1-\mathbf{exp}\left(-\frac{\Delta G}{RT}\right)\right]$$

SD λ ~ 1.5 A



S. Reinsch, M. L. F. Nascimento, R. Muller, E. D. Zanotto, *sub. JACS*

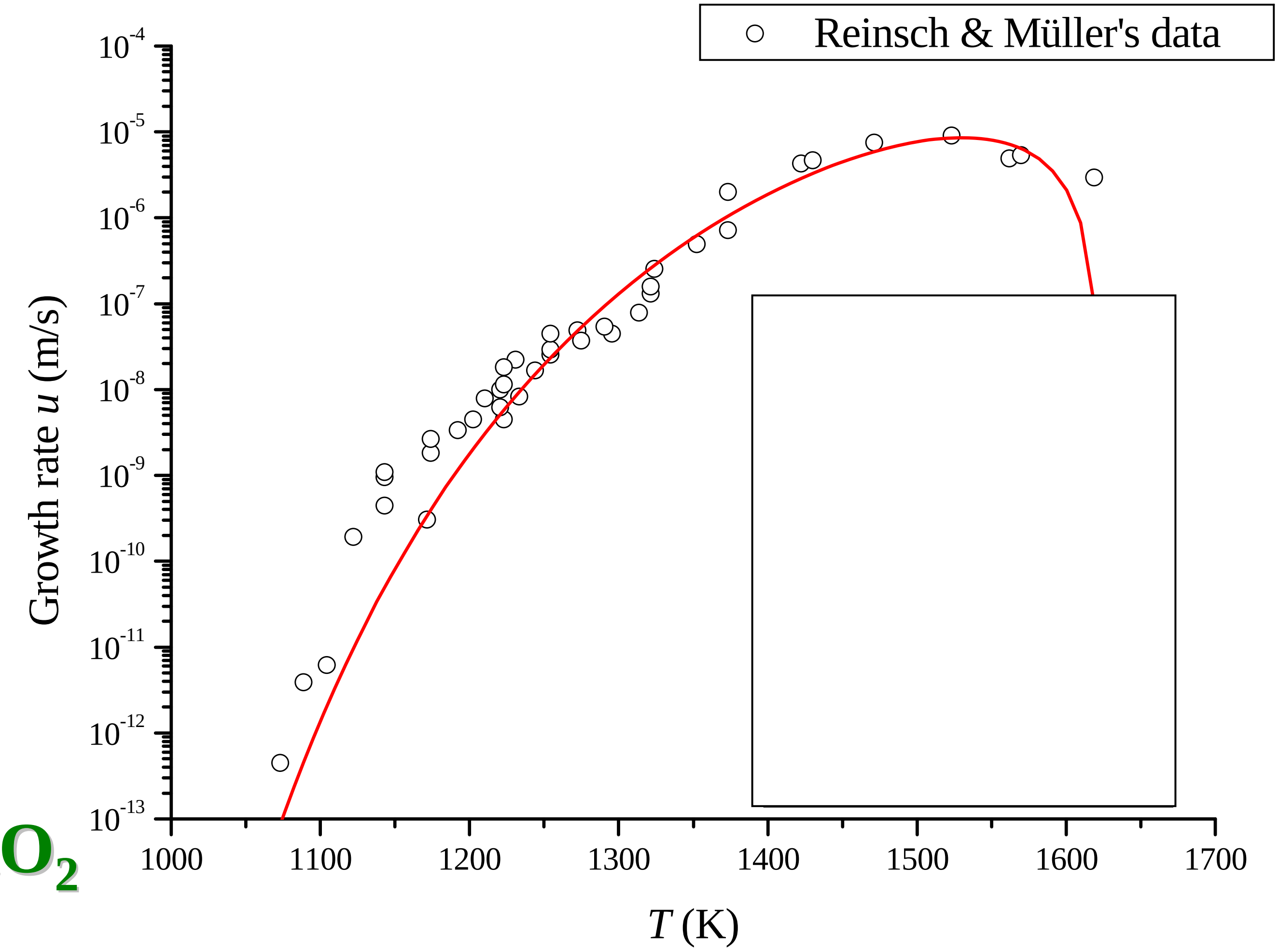
Cordierite

The mechanism depends on the T_m of μ–cordierite, a metastable phase...

If T_m = 1350°C ⇒ SD

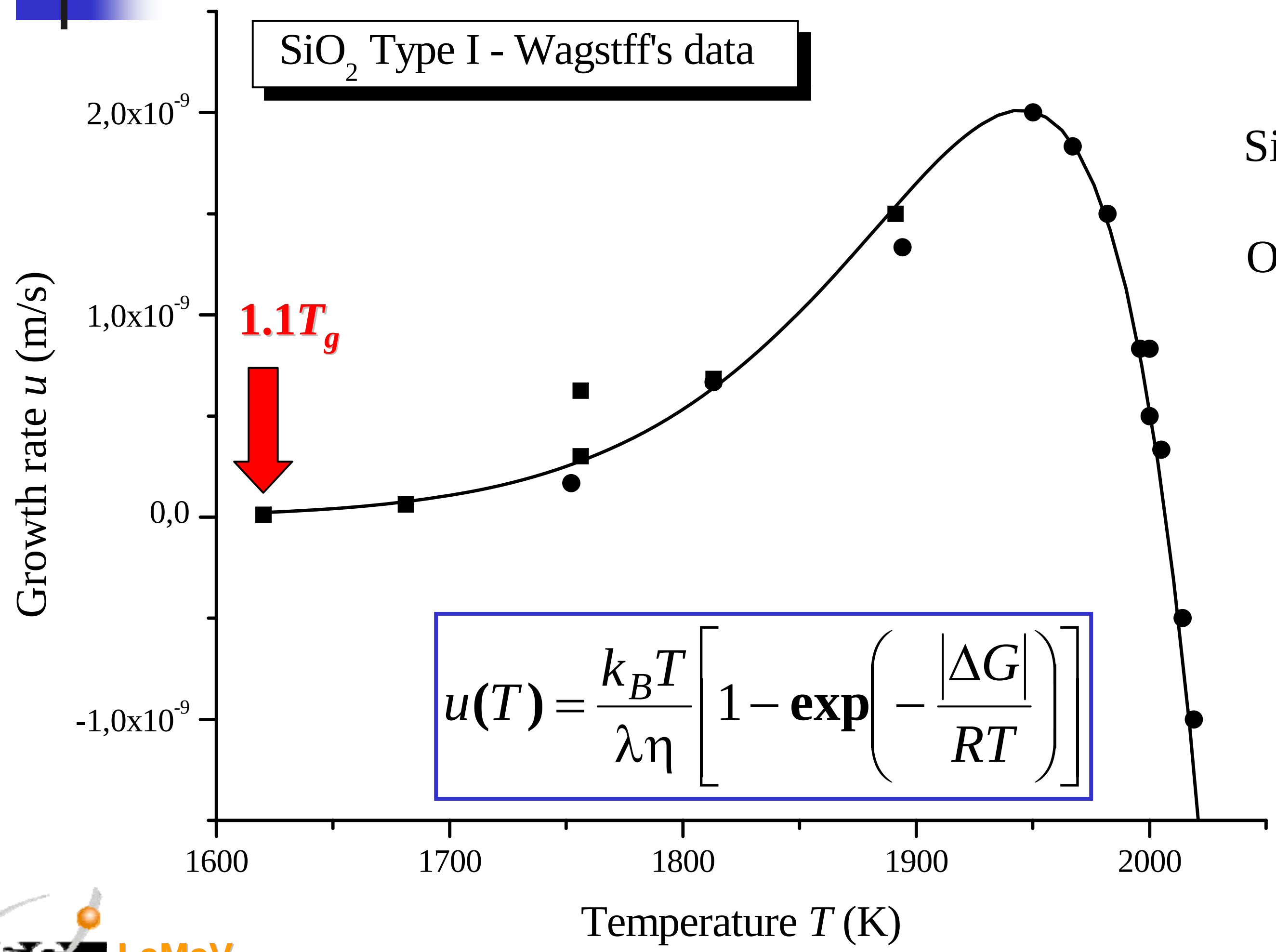
If T_m = 1467°C ⇒ 2D

$2MgO\cdot 2Al_2O_3\cdot 5SiO_2$



Nascimento & Zanotto, PRB (2006)

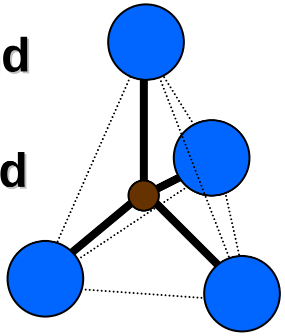
Silica Type I



$$u(T)=\frac{k_B T}{\lambda\eta}\left[1-\mathbf{exp}\left(-\frac{|\Delta G|}{RT}\right)\right]$$

SiO_2 glass

Si–O **bond**
1.62Å
O–O **bond**
2.64Å



λ ~ **1 A**

Normal growth

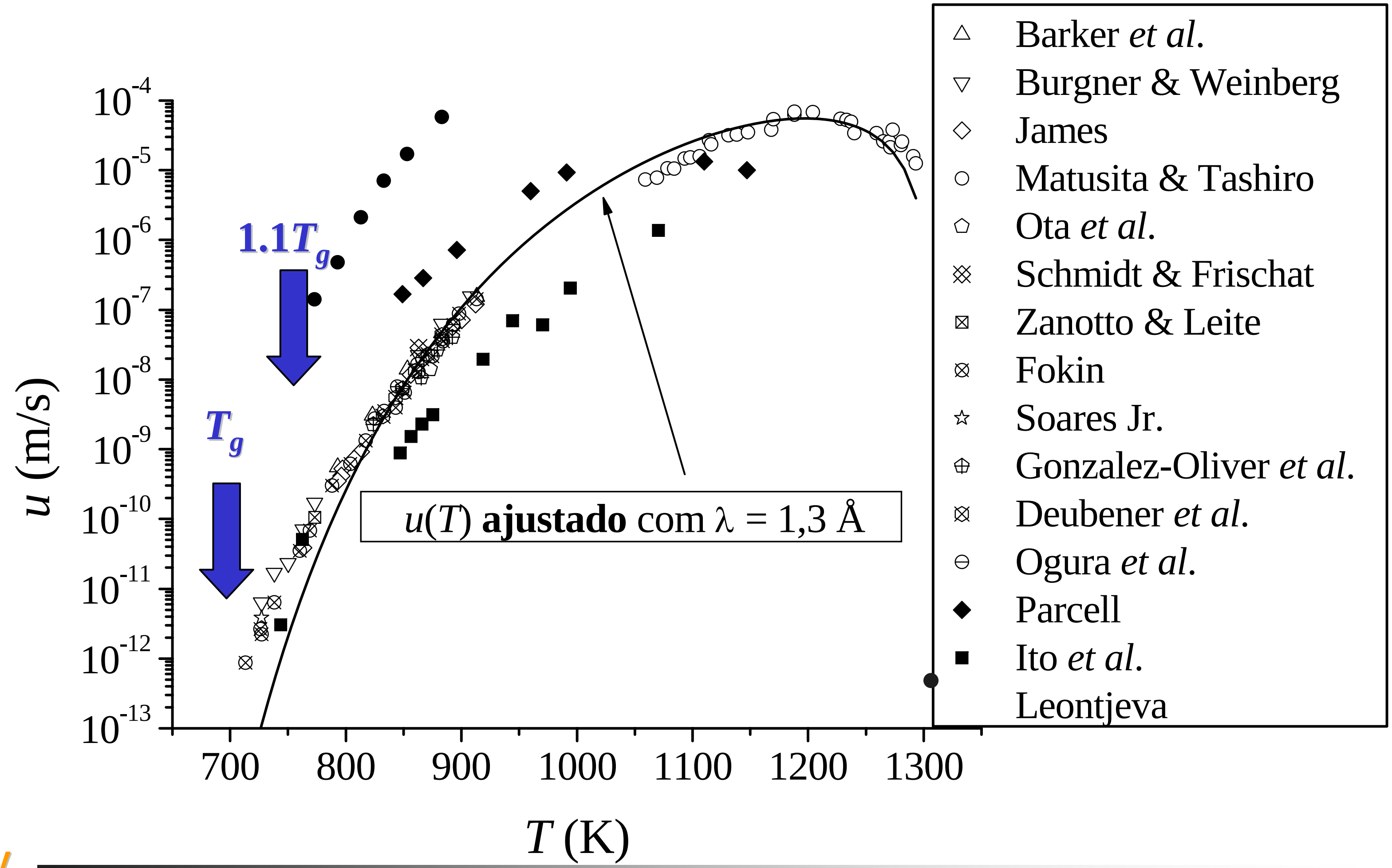
LS_2

$Li_2O \cdot 2SiO_2$

2D

$$B = \frac{\pi \lambda V_m \sigma^2}{3 k_B}$$

$$u(T) = C \frac{D_u}{\lambda^2} \mathbf{exp}\left(- \frac{B}{T \Delta G} \right)$$



Summary

Three classical types: normal, screw & 2D

ΔG = Turnbull or Hoffmann

ΔG_D = via Stokes-Einstein / Eyring

ΔH_m = melting enthalpy

η = viscosity

Validity of crystal growth models & Stokes-Einstein / Eyring equation in a wide temperature range