Field Method of Simulation of Phase Transformations in Materials

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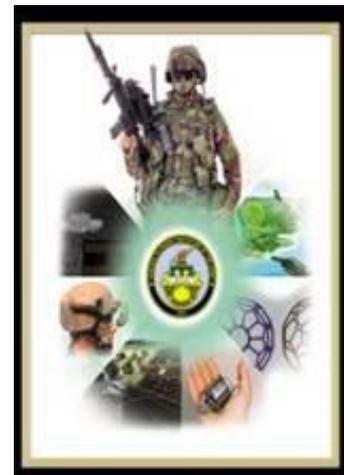
What do we need to account for?

Multi-phase states: thermodynamic systems may have multiple stable phase 'coexisting' at the same conditions.

Heterogeneous states: phase transformations may go along very complicated paths.

Dynamic structures: rate of transformation can make a difference for the final structure and properties

Nucleation: phase transformations are initiated through the process of overcoming of some kind of a potential barrier.

Pillar 1: Order Parameter: Symmetries of the System

Order-disorder transformation in β-brass (Cu-Zn alloy)

Coarse-graining procedure
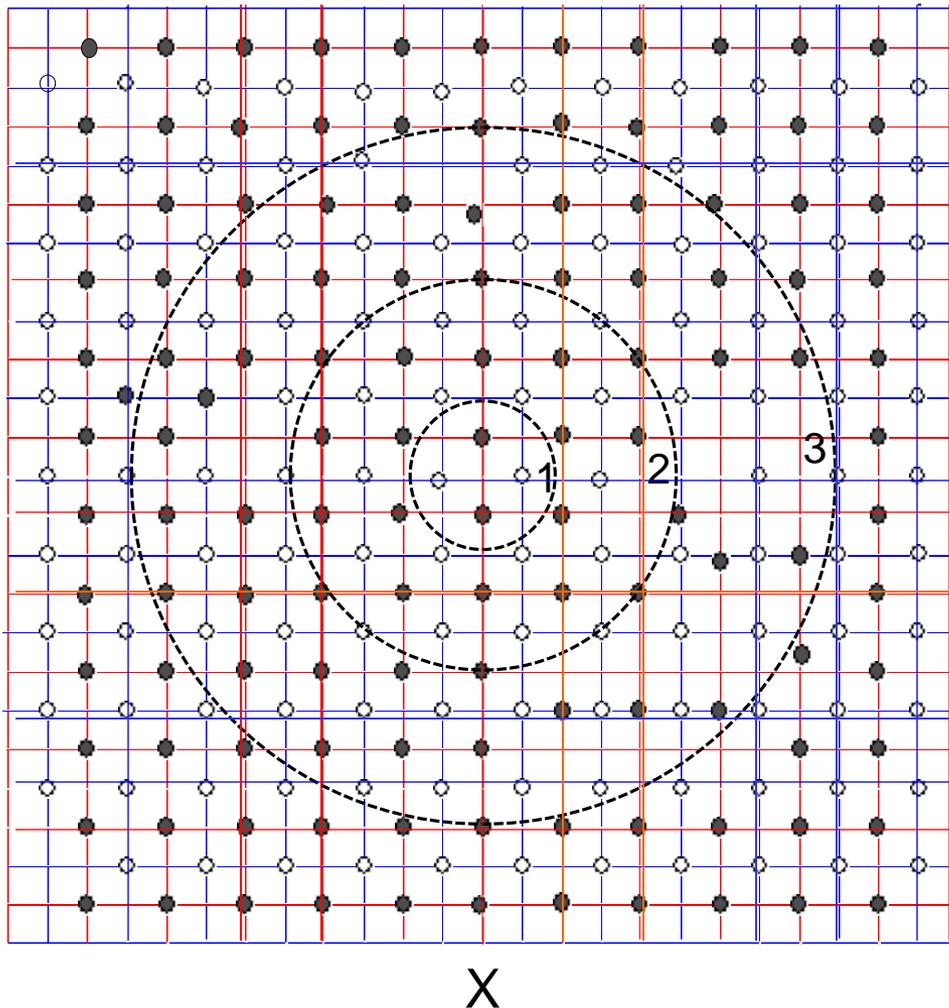
○ --Zn atom
● --Cu atom

$$concentration$$

$$C = \frac{N_{Cu}}{N_{Cu} + N_{Zn}}$$

$$order\ parameter$$

$$\eta = 1 + \frac{N_{Cu/red} - N_{Zn/blue}}{N_{Cu} + N_{Zn}}$$

	C	η
R1	0.500	1.000
R2	0.486	0.971
R3	0.487	0.920

Pillar 2: Free Energy

$$g(T,\eta) = g_0(T) + \frac{1}{2}W\eta^2 + \frac{1}{3}(\Delta\mu)\eta^3 + \frac{1}{4}\eta^4 \longleftarrow \text{Landau potential}$$
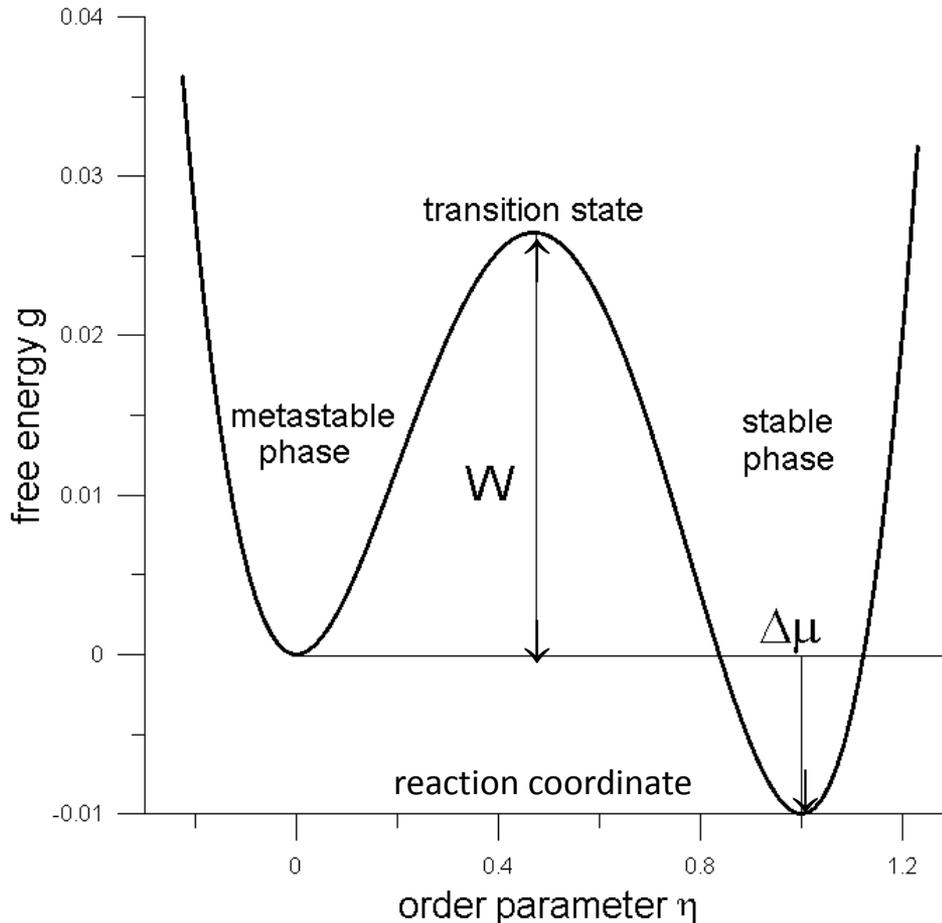
stable phase: 'crystal'

metastable phase: 'liquid'

W—potential barrier—energy scale

$\Delta\mu$-chemical potential difference

$\Delta \equiv \Delta\mu/W$-driving force

Pillar 3: Heterogeneous Systems: Gradient Energy

$$G = \int [g(W,\eta) + \frac{1}{2}\kappa(\nabla\eta)^2]dv$$

Length scale:

$$Correlation\ length: \xi = \sqrt{\frac{\kappa/W}{1-\Delta}} - \text{interface thickness}$$

$$Interfacial\ energy: \sigma = \sqrt{\kappa W}$$
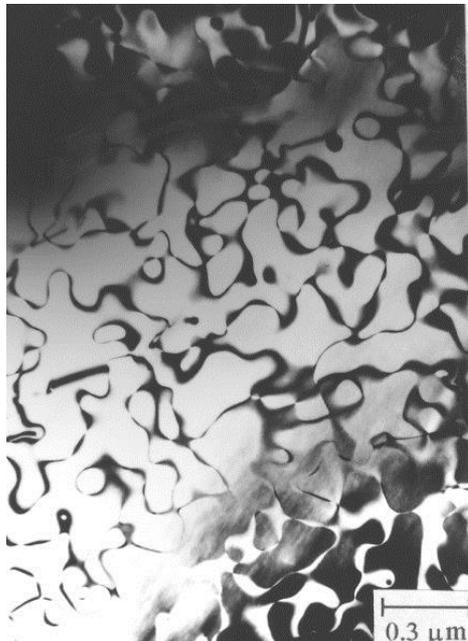
Order-Disorder Fe-Al Allen, Cahn Circa'82

0.3 μm

0.3 μm
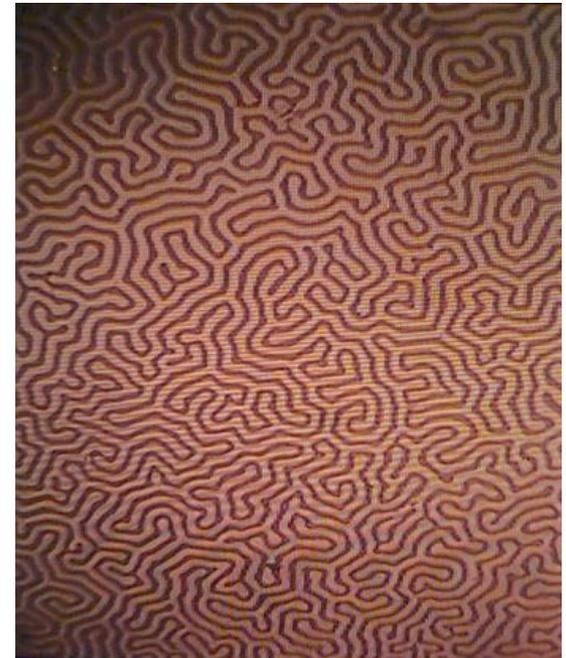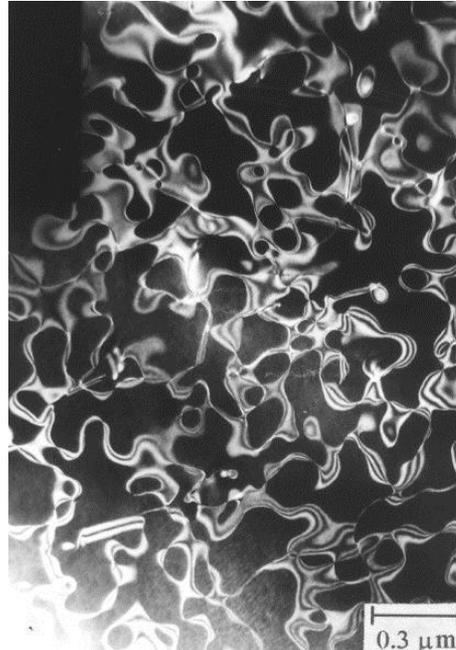
# Pillar 4: Kinetics

The Gradient Flow Equation:

$$\frac{d\eta}{dt} = -\gamma \frac{\delta G}{\delta \eta}$$

$$Time\ scale: \tau = \frac{1}{\gamma W}$$

$$V_{int} = \frac{\xi}{\tau}\Delta$$

- transition state
- metastable phase
- W
- Δ
- stable phase
- order parameter
- Gibbs free energy G

M.I. Mendelev, J. Schmalian, C.Z. Wang, J.R. Morris, and K.M. Ho,
Phys. Rev. B, **74**, 104206 (2006).
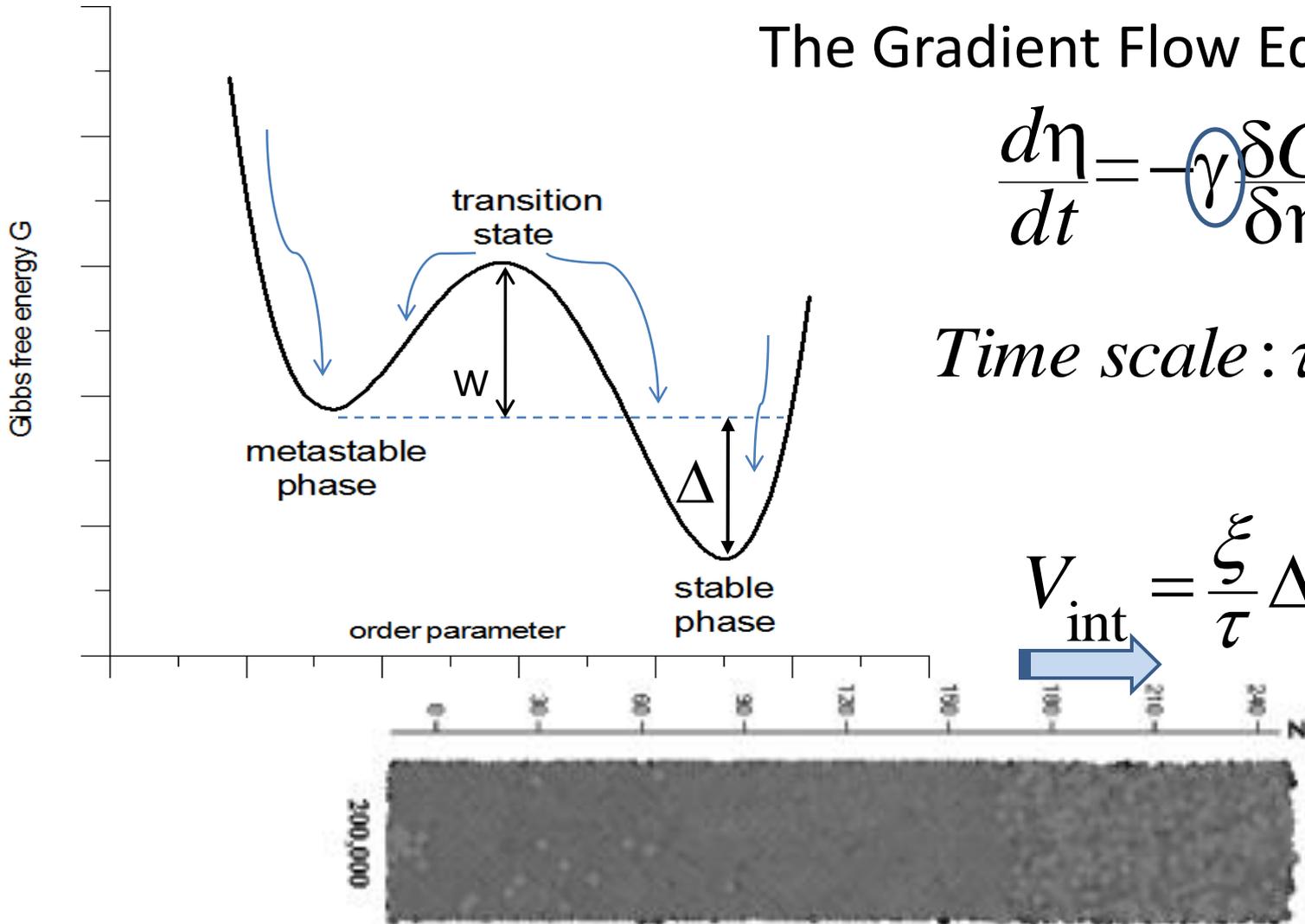
Pillar 5: Internal fluctuations: Langevin force

$$\frac{d\eta}{dt} = -\gamma(\frac{\delta G}{\delta \eta})_{T,P} + \zeta(x,t)$$

$$<\zeta(x,t)> = 0$$

$$<\zeta(x,t)\zeta(x',t')> = \Gamma\delta(x'-x)\delta(t'-t)$$

$$\Gamma = 2\gamma k_B T$$

$\zeta(\mathbf{x}, t)$—noise:
Gaussian, white, additive

One more energy scale:
thermal fluctuations-$k_B T$

0.5 μm
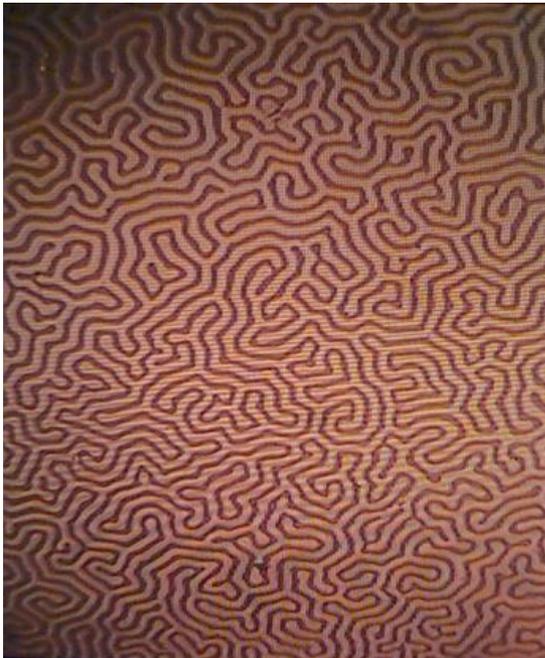
Pillar 6: 'Hydrodynamic Modes':

Momentum Flow (Pressure or Stress)
Diffusion (Concentration of species)
Electromagnetic Field Variation (Waves)
Heat Flow (Temperature Variation):

Conservation Laws

'Thermodynamically consistent heat equation'
A. Umantsev and A. Roytburd. Sov. Phys. Solid State **30**(4), 651-655, (1988)

General Heat-Equation →
$$C\frac{dT}{dt} = \nabla(\lambda \nabla T) + Q(\mathbf{x},t)$$

Heat Source →
$$Q(\mathbf{x},t) = -[(\frac{\partial e}{\partial \eta})_{V,T} - \kappa_E \nabla^2 \eta]\frac{d\eta}{dt}$$

↑ Latent Heat L

Length Scales

$$l_I = \sqrt{\frac{\kappa}{W}}$$ – interfacial thickness

$$l_C = \frac{CT_E\sigma}{L^2}$$ – capillary length

$$l_\mu = \frac{\lambda}{\mu L}$$ – kinetic length

$$l_T = \frac{\lambda}{CV_n}$$ – thermal length

$$K^{-1}$$ – radius of curvature
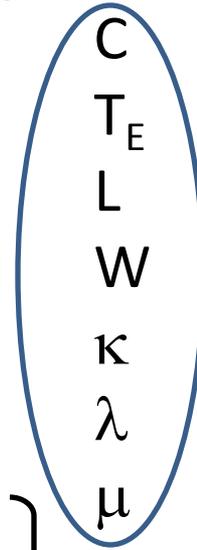
$\left.\begin{array}{c}\\\\\end{array}\right\}$ dynamic

Time scales

$$\tau = \frac{1}{\gamma W}$$

relaxation time

$$\tau_\mu = \frac{\lambda C}{(\mu L)^2}$$

kinetic time

C
T_E
L
W
κ
λ
μ

$$U = \frac{l_C}{l_I} = \frac{CT_E W}{L^2}$$

$$R = \frac{l_\mu}{l_C} = \frac{\lambda}{C\gamma\kappa}$$

Truly Multi-Scale Method

D. Danilov

temperature

-----melting temp-----   ------solid phase

------transition state

order parameter

liquid phase

distance into the sample

τ_μ

τ

Time scale

Å   nm   μm   Length scales   mm

ξ l_C l_μ l_T X
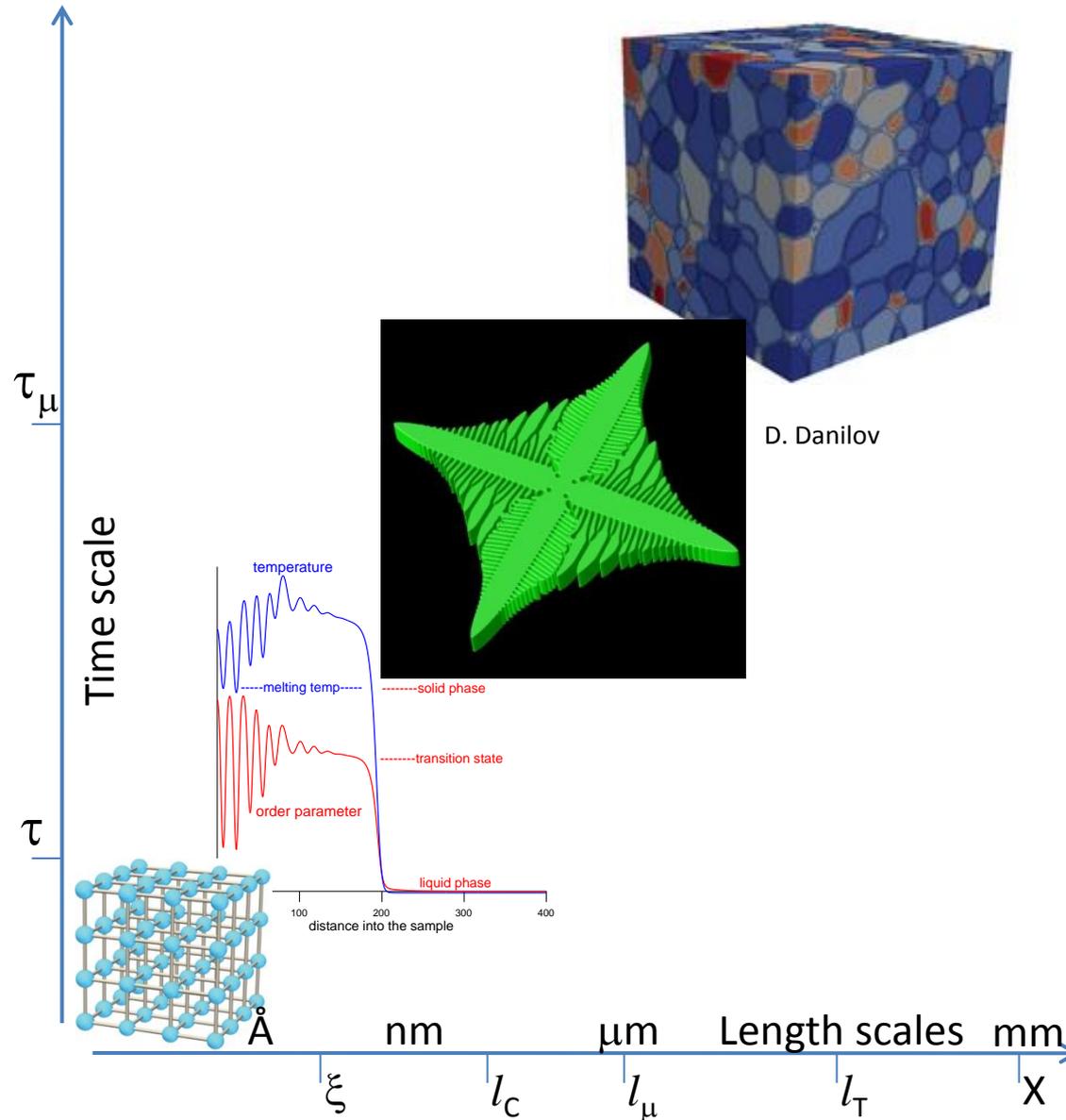
Real Material Modeling

Problem A: Convert thermodynamic functions of two or more phases into a continuous Landau-Gibbs Free Energy

$G\{\eta_i; T, P, C\}$

Solution 1: LTPT: Symmetry expansion
Solution 2: Speculate

$\{\eta_i\}$

CALPHAD $\quad \{T, P, C\}$
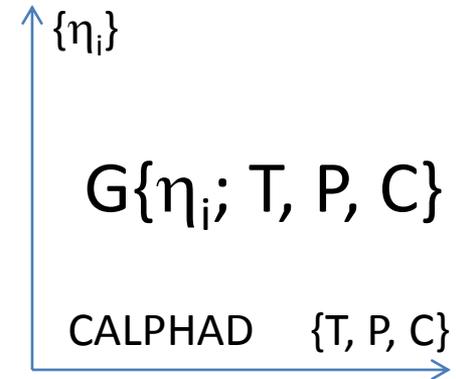
Problem B: Find the PFM parameters: $\{W_i, \kappa_i, \gamma_i\}$

Solution 1: Calculate from First Principles
Solution 2: Calibrate from experiments or MD/MC simulations

Landau-Gibbs Free Energy of Au-Sn Alloy
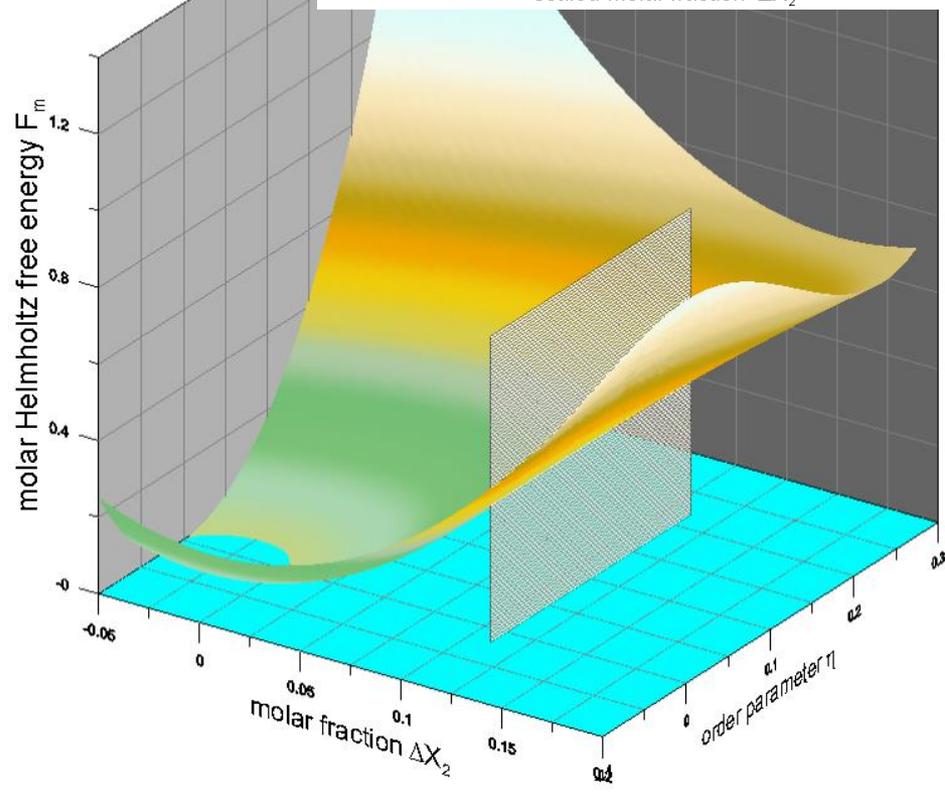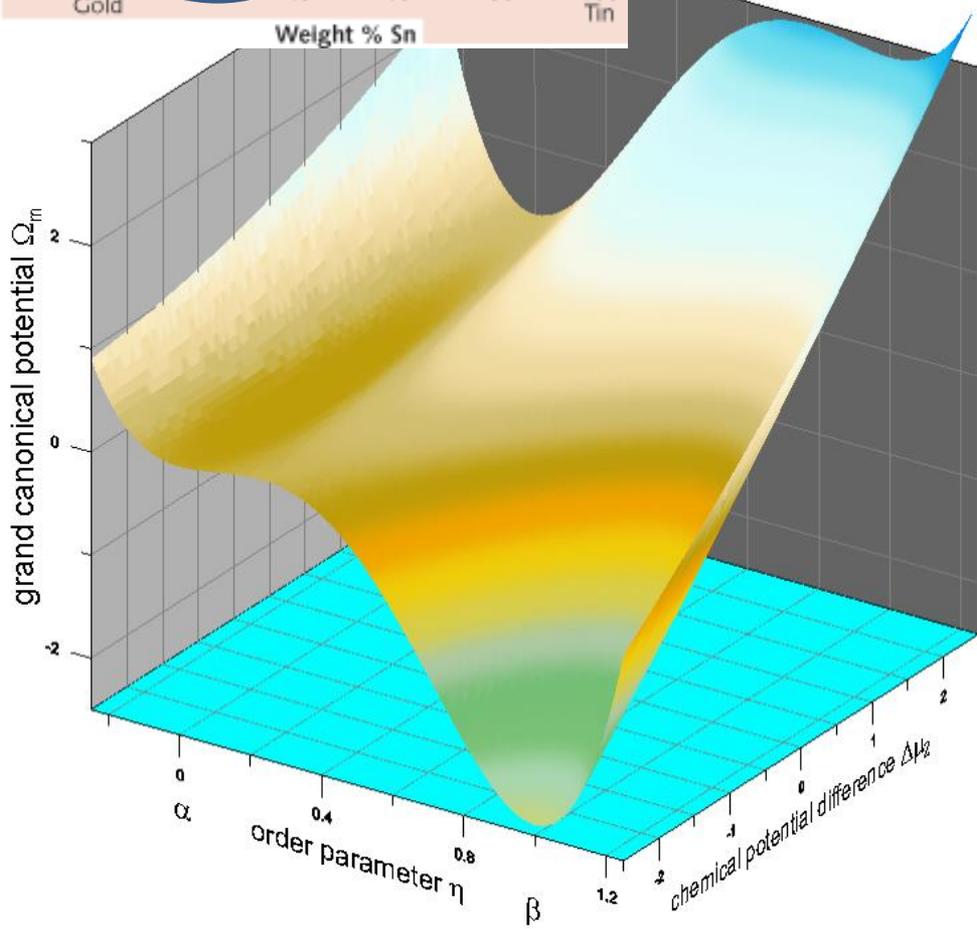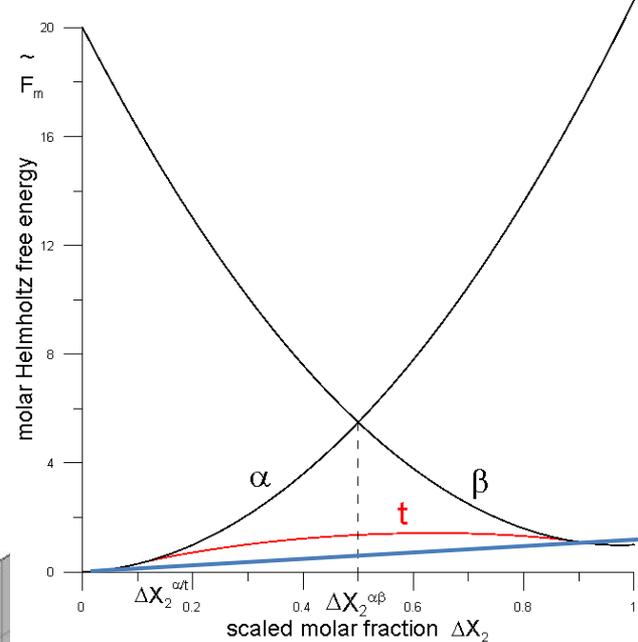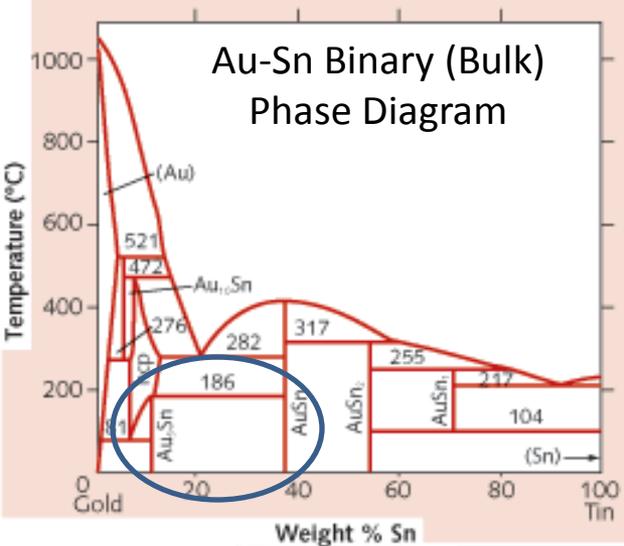
Landau-Gibbs Free Energy of Carbon
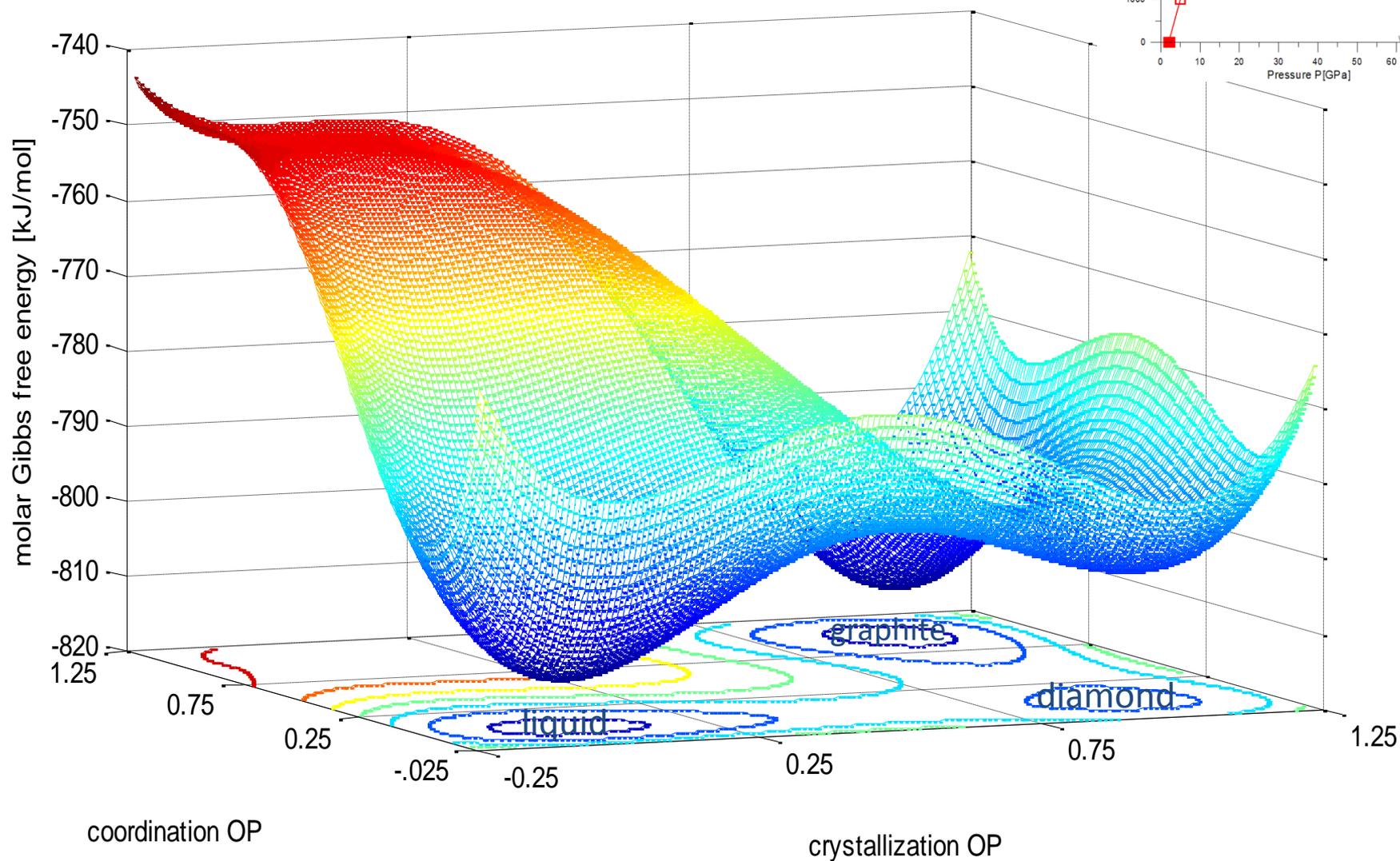
Measurable Quantities

Interface thickness: $l_I \sim \sqrt{\dfrac{\kappa}{W}}$

Interface energy: $\dfrac{free\ energy}{unit\ area} \equiv \sigma \sim \sqrt{\kappa W}$

Kinetic coefficient: $\dfrac{interface\ velocity}{1K\ of\ supercooling} \equiv \mu = \gamma \sqrt{\dfrac{\kappa}{W}} \dfrac{L}{T_E}$

Equilibrium Fluctuations of OP

$$\langle |\widehat{\Delta\eta}_V(\mathbf{k})|^2 \rangle = \dfrac{k_B T}{V\left[\dfrac{\partial^2 g}{\partial \eta^2}(\bar{\eta}) + \kappa |\mathbf{k}|^2\right]}$$

Non-Equilibrium Fluctuations of OP

γ Dynamic structure factor

time

Materials Genome
Database of Interfacial Properties

CHiMaD — Center for Hierarchical Materials Design
About   News & Events   Research   Outreach   People   Contact
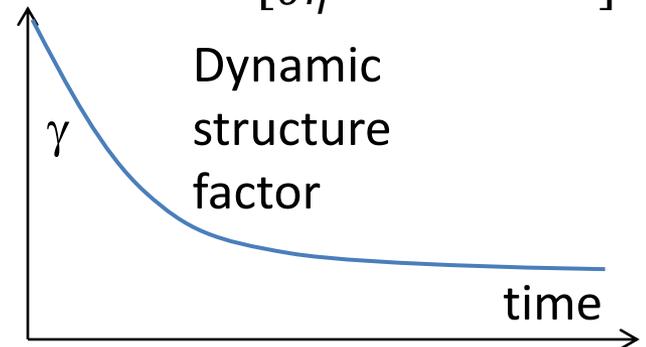
RESEARCH

RESEARCH
DATABASES
PUBLICATIONS
OPEN POSITIONS

AFLOW — High-throughput Calculations for Materials Properties
CALPHAD — Computer Coupling of Phase Diagrams and Thermochemistry

Crystallization database for pure substances.

Quantity	Te	L	C	ρ	λ	σ	μ	δ	B=3σ/(16δ)	Ta=L/C	α=λ/(ρC)	m=Teμσ/(Lρ)	X=σ/(Lρ)	/c=TeCσ/(ρL^2)	/μ=λ/(μρL)		Q=L/CTe=T	E=16B/3L	U=TeCB/(ρL^2)	R=/μ/δ	RU	γ
Units	K	J/kg	J/kg*K	kg/m³	J/K*m*s	J/m²	m/s*K	m	J/m³	K	m²/s	m²/s	m	m	m				≈/c/δ			m³/Js
Elements																						
Aluminum	933.52	3.87E+05	900.00	2699	210	1.15E-01	10	1.00E-09	2.16E+07	4.30E+02	8.65E-05	1.03E-06	1.10E-10	2.39E-10	2.0111E-08		4.61E-01	1.10E-01	4.48E-02	20.111005	9.02E-01	
Aluminum	939.30	3.71E+05	1252.00	2332	0.777	1.02E-01	0.65	1.00E-09	1.92E+07	296.33387	2.66127E-07	7.23E-08	1.18355E-10	3.75153E-10	1.3816E-09		0.3154837	1.18E-01	0.070341253	1.3816356		9.72E-02
Cobalt	1765.15	2.59E+05	799.10	8900	25.08	4.00E-02	1.88	1.00E-09	7.50E+06	3.24E+02	3.53E-06	5.75E-08	1.73E-11	9.44E-11	5.78E-09		1.84E-01	1.73E-02	1.77E-02	5.78E+00		1.02E-01
Copper	1356.15	2.05E+05	493.70	8930	170.5	1.36E-01	1.58	1.00E-09	2.55E+07	4.15E+02	3.87E-05	1.59E-07	7.43E-11	2.43E-10	5.90E-08		3.06E-01	7.43E-02	4.55E-02	5.90E+01		2.68E+00
Helium	35.04	6.60E+04	2975.00	410.3	0.117	1.70E-04	0.2	1.00E-09	3.19E+04	2.22E+01	9.59E-08	4.40E-11	6.28E-12	9.92E-12	2.16E-08		6.33E-01	6.28E-03	1.86E-03	2.16E+01		4.02E-02
Hydrogen					8.74E-04				#DIV/0!			#DIV/0!	#DIV/0!		#DIV/0!		#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!
Nickel	1725.15	2.92E+05	735.00	8900	40.96	4.64E-01	0.39	1.00E-09	8.70E+07	3.98E+02	6.26E-06	1.20E-07	1.78E-10	7.74E-10	4.04E-08		2.30E-01	1.78E-01	1.45E-02	4.04E+01		5.86E+00
Nickel	1728.00	2.64E+05	540.00	8900	90.9	3.70E-01	2	5.00E-10	1.39E+08													4.90E+02
Lead	600.65	2.30E+04	129.00	10660	34.4	2.99E-02	0.28	1.00E-09	5.61E+06	1.78E+02	2.50E-05	2.05E-08	1.22E-10	4.11E-10	5.01E-07		2.97E-01	1.22E-01	7.70E-02	5.01E+02		3.86E+01
Phosphoru	317.10	8.47E+04	3310.16	1745	0.1881	8.00E-03	0.177	1.00E-09	1.50E+06	25.6	3.26E-08	3.04E-09	5.41E-11	6.70E-10	7.19E-09		8.07E-02	5.41E-02	1.26E-01	7.19E+00		9.03E-01
Silver	1234.15	1.05E+05	284.50	10500	204.5	1.11E-01	1.65	1.00E-09	2.08E+07	3.67E+02	6.85E-05	2.06E-07	1.01E-10	3.40E-10	1.13E-07		2.98E-01	1.01E-01	6.37E-02	1.13E+02		7.20E+00
									#DIV/0!			#DIV/0!	#DIV/0!		#DIV/0!		#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!
Xenon	161.39	1.75E+04	339.68	2963	0.0734	9.43E-03		1.00E-09	1.77E+06	5.15E+01	7.29E-08	0.00E+00	1.82E-10	5.69E-10	#DIV/0!		3.19E-01	1.82E-01	1.07E-01	#DIV/0!		#DIV/0!
												#DIV/0!										0.00E+00
Substances																						0.00E+00
Cyclohexa	298.61							1.00E-09	0.00E+00	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!		#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	
Succinonit	331.24	4.62E+04	1998.00	970	0.2226	8.95E-03	0.2	1.00E-09	1.68E+06	2.31E+01	1.15E-07	1.32E-08	2.00E-10	2.86E-09	2.48E-08		6.99E-02	2.00E-01	5.36E-01	2.48E+01		1.33E+01
Water	273.15	3.33E+05	4184.00	1000	0.5607	3.19E-02		1.00E-09	5.98E+06	7.96E+01	1.34E-07	0.00E+00	9.57E-11	3.28E-10	#DIV/0!		2.92E-01	9.57E-02	6.16E-02	#DIV/0!		#DIV/0!

Copper-Nickel alloy system

Quantity	Te measur	Te simulat	δT	σ measure	σ simulate	σ	XsolidCu	ρsolid	G"solid	g"solid	XliquidCu	ρliquid	G"liquid	g"liquid	ΔXCu	L	C	λ	μ
Units	K	K		J/m²	J/m²	eV/nm²	mol. frac.	(atoms/nm^	J/mol×mol.fra	J/m³×mol.frac.	mol. frac.	(atoms/nm^	J/mol×mol.fra	J/m³×mol.frac.	mol. frac.	J/kg	J/kg*K	J/K*m*s	m/s*K
pure Ni	1728	1820		0.255	0.31	1.935081	0							0	0				
															0				
		1750	0.82134		0.287	1.791511	0.05	83.2	3.0616E+05	4.2313E+10	0.104	77.1	1.5606E+05	1.9987E+10	-0.054				
															0				
pure Cu	1356	1428.194		0.177	0.215176	1.343174	1				1				0				

Soldering: InterMetallic Phase Growth

Soldering 101

Cross-section

Solder

IMP

Cu

100μm

Sn-Solder

IMP

Cu-Plate

5μm
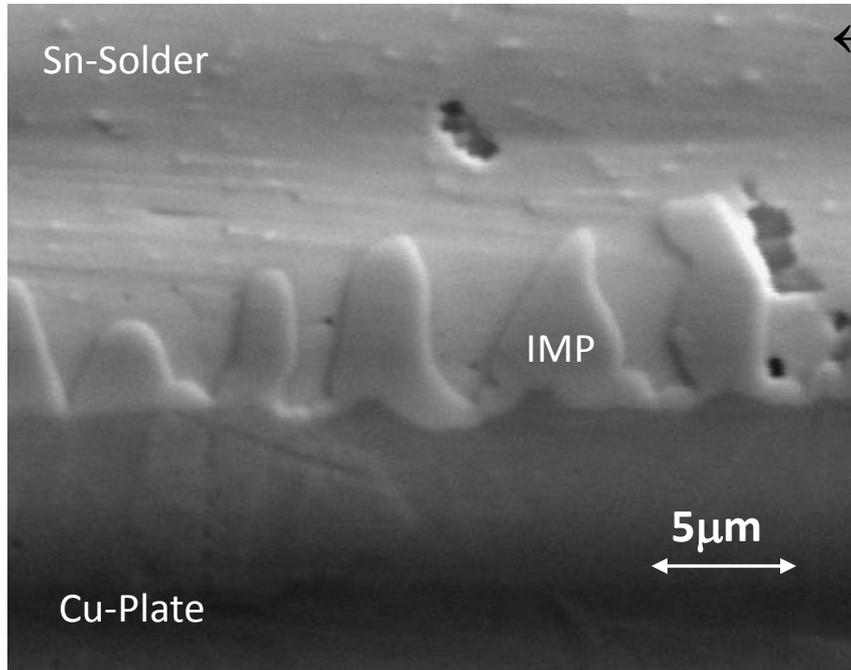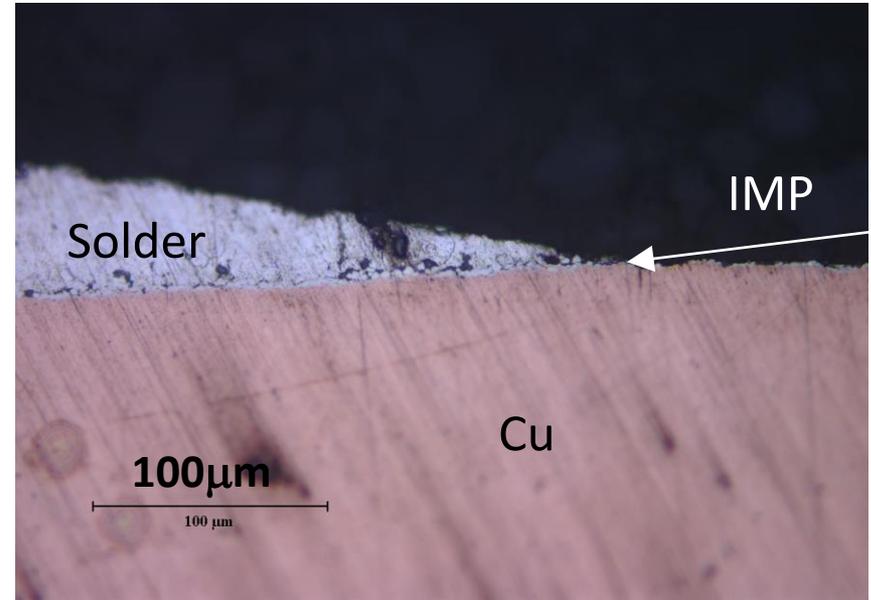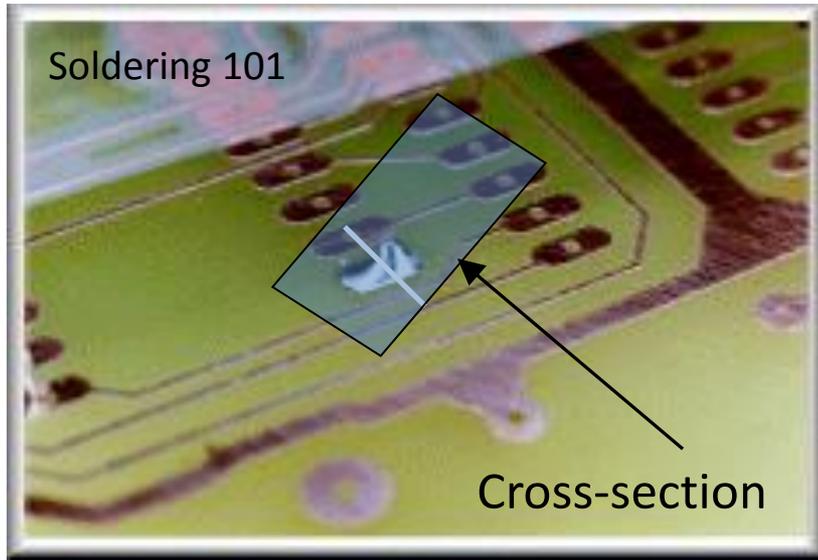
← Liquid-state solder

Solid-state solder →

Where was the original interface between the tin and copper?

Sn-Solder

Cu-Plate

20 μ
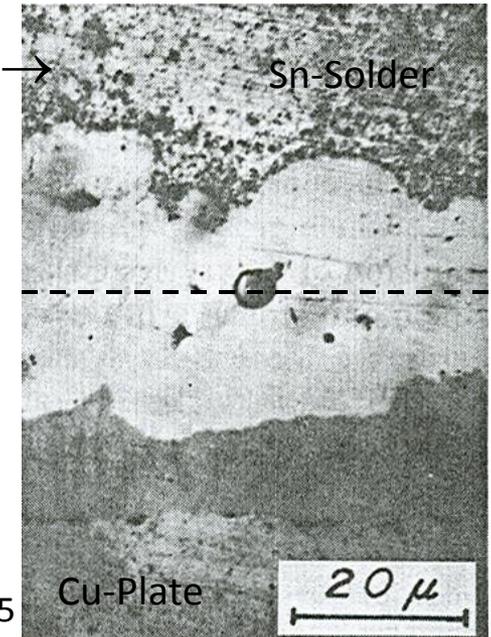
Gagliano and Fine'00

Onishi and Fujibuchi'75

Experimental results

Lord & Umantsev, J. Appl. Phys. **98**, 063525 (2005)
(Centennial Campus, 2004)
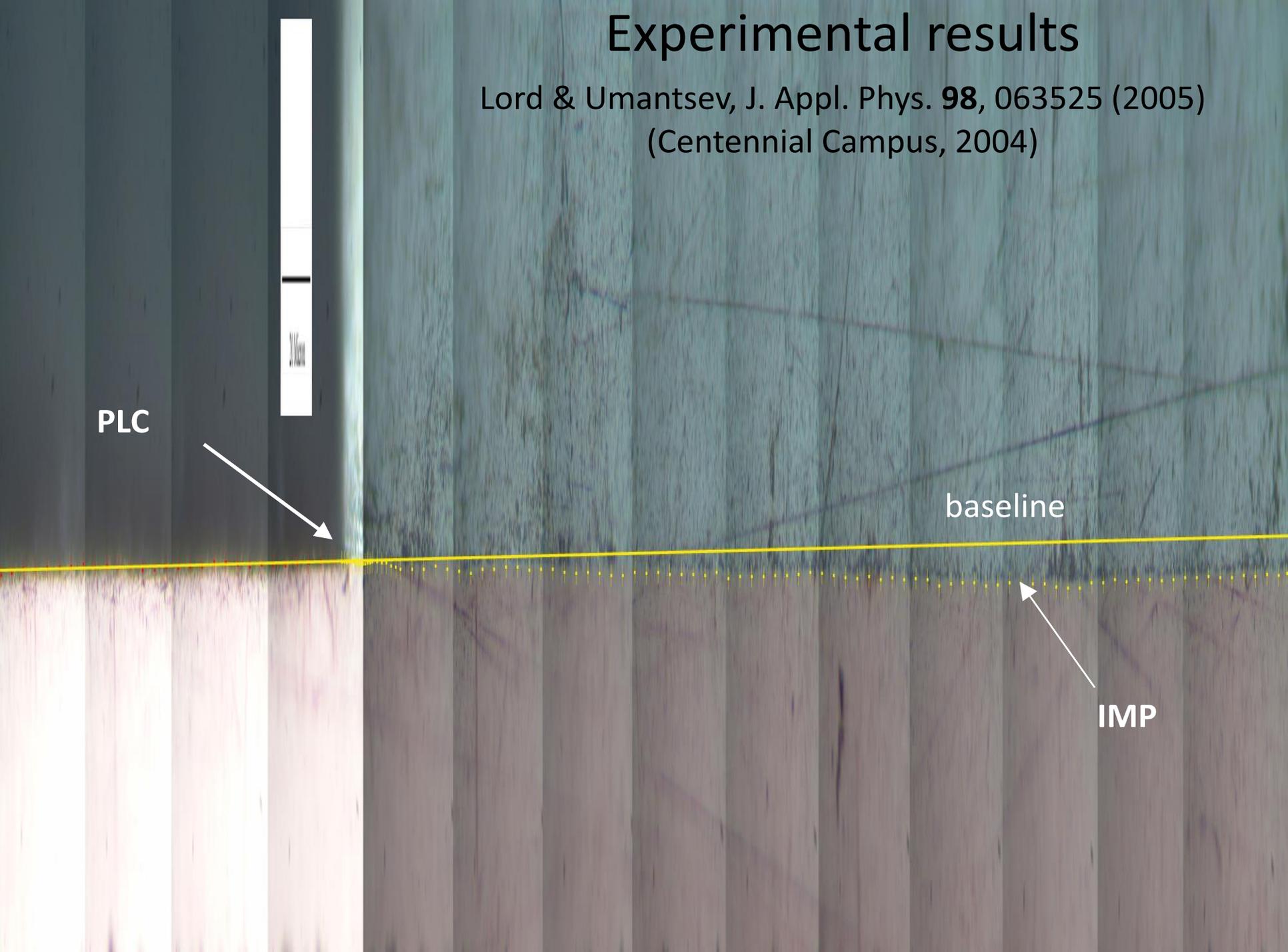
PLC

baseline

IMP

Total Free Energy

Umantsev, JAP '07

$$F = \int d\mathbf{r}[f(\xi,\eta,c) + \kappa_\xi(\nabla\xi)^2 + \kappa_\eta(\nabla\eta)^2]$$

Homogeneous part

$$f(\xi,\eta,c) = f_{liquid}(c) +$$

$$Aw(\xi) + [f_{solid}(c) - f_{liquid}(c)]s(\xi) +$$

$$Bw(\eta) + [f_{intermet}(c) - f_{solid}(c)]s(\eta)$$

molecular liquid

inter metallic

ordering η

normal liquid

disordered solid

ξ

crystallization

Thermocalc® G. Ghosh

free energy J/mol

molecular liquid

atomic liquid solution

fcc solid solution

intermetallic compound

concentration Cu
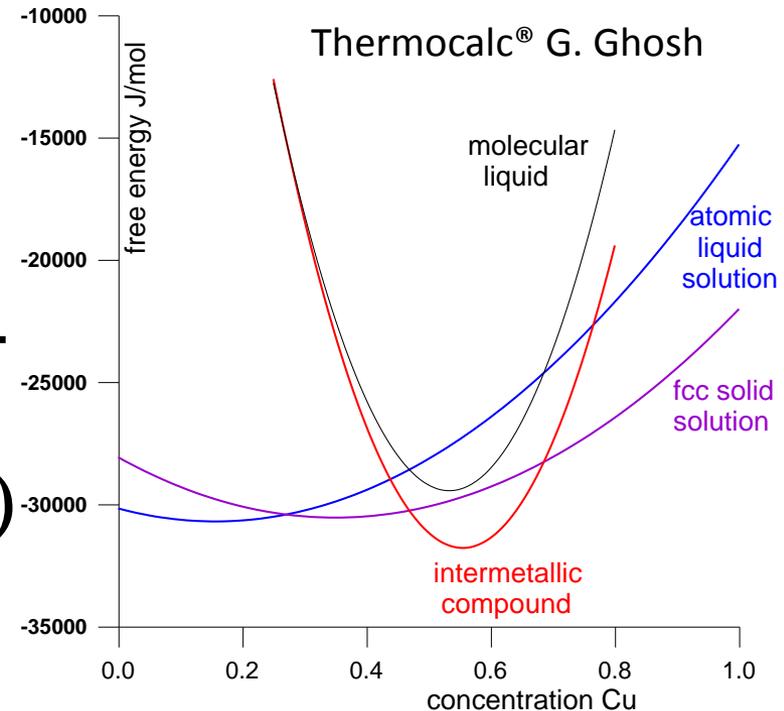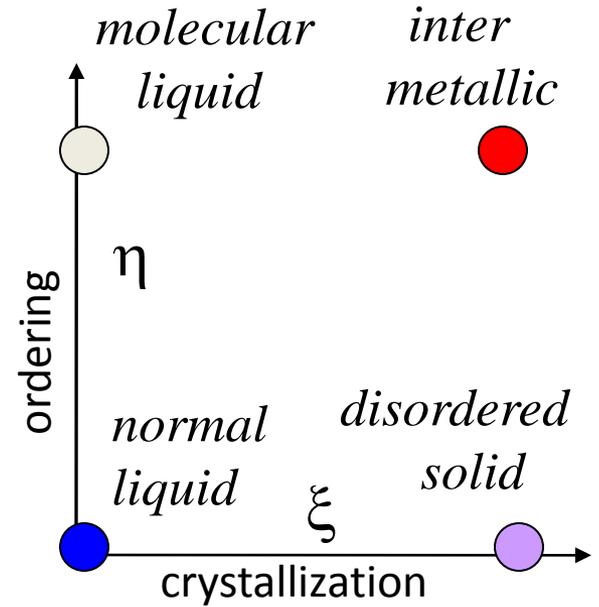
Grain Boundary Contribution to Free Energy

1. $f_{ori}=f(\theta)$—not invariant against rotation of the reference frame

2. $f_{ori}=f(\theta_1,\theta_2,\theta_3,\dots)$—orientation $\equiv$order parameter

3. $f_{ori}=f(|\nabla\theta|)= s|\nabla\theta|+ q|\nabla\theta|^2$ —Kobayashi, Warren, Carter

$f=\dots+[1-s(\xi)]f_{liquid}(c)+[s(\xi)-s(\eta)]f_{solid}(c)+ s(\eta)f_{intermet}(c)$
$+\varphi(\xi,\eta)\, f_{ori}$

Dynamics

$$\frac{\partial\theta}{\partial t}=-\gamma_{\theta(\xi,\eta)}\frac{\delta F}{\delta\theta}$$

Grain-boundary diffusion:
Mobility: $M=M(\xi,\eta,|\nabla\theta|)$
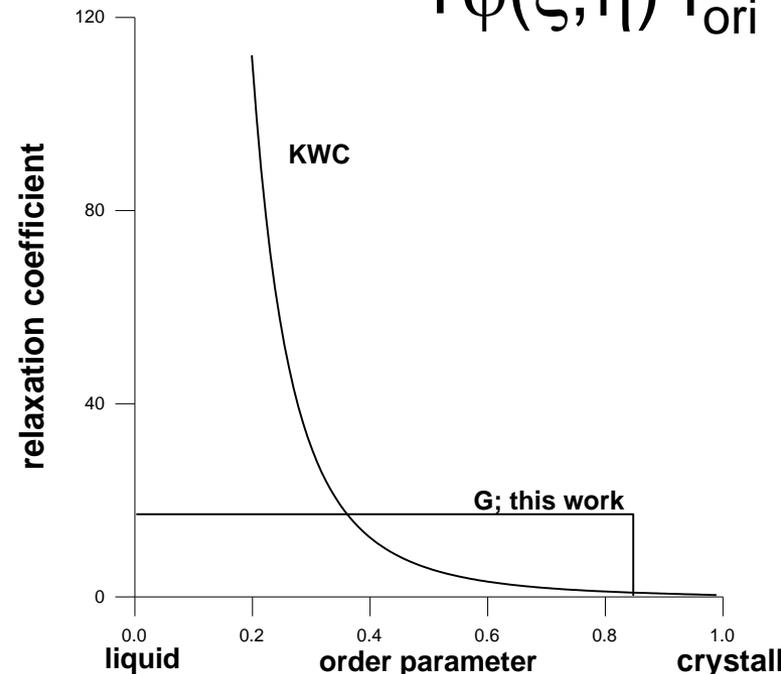
Evolution Equations

Crystallization

$$\frac{\partial \xi}{\partial t} = -\gamma_\xi \frac{\delta F}{\delta \xi}$$

Ordering

$$\frac{\partial \eta}{\partial t} = -\gamma_\eta \frac{\delta F}{\delta \eta}$$

GB orientation

$$\frac{\partial \theta}{\partial t} = -\gamma_{\theta(\xi,\eta)} \frac{\delta F}{\delta \theta}$$

Diffusion

$$\frac{\partial c}{\partial t} = \nabla [M(\xi,\eta,c) \nabla \frac{\delta F}{\delta c}]$$

$$M = M_{liq} + (M_{sol} - M_{liq})\xi + (M_{int} - M_{sol})\eta$$

Initial Conditions: slab, no nucleation

Parameters:
3 Diffusion coefficients: solder intermetallic substrate
+
9 interfacial parameters (interface energies thicknesses, and mobilities)

Scales:
Length=0.25nm
Time=0.25μs

2D Modeling

molecular liquid

inter metallic

C-concentration

η

$|\nabla\theta|$-grad angle orient

ordering

solder ξ *disordered solid*

crystallization

Liquid state soldering

Copper

Tin

Solid State Soldering

Copper
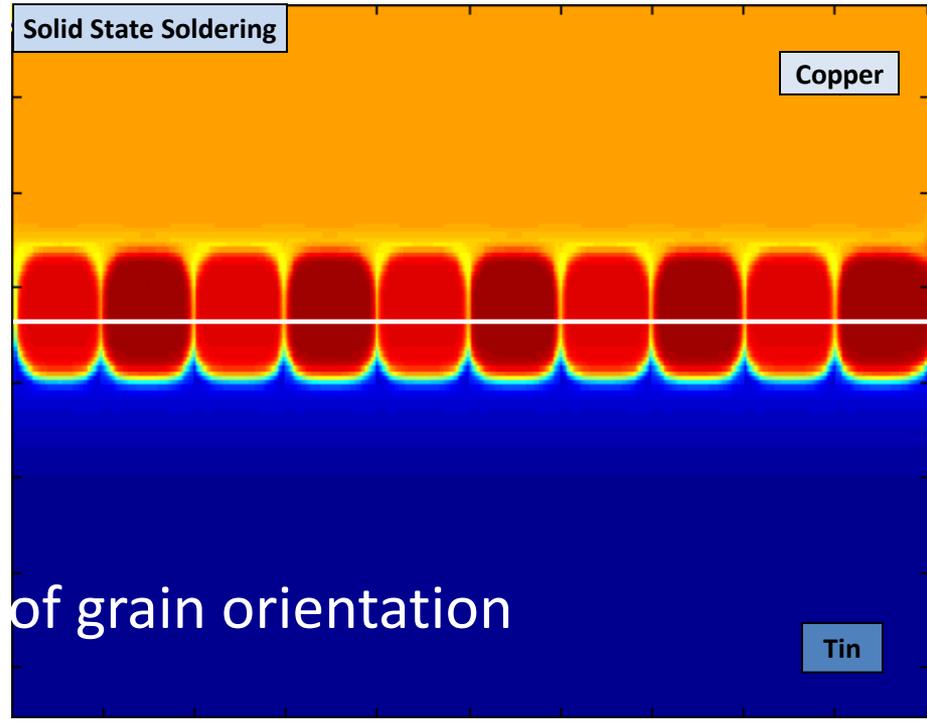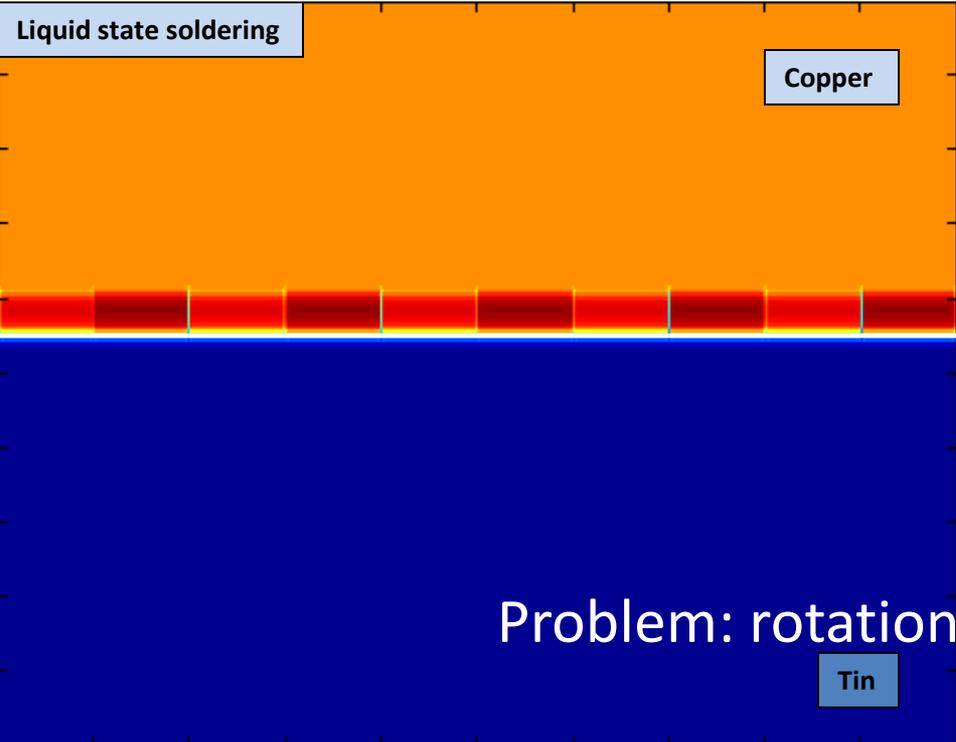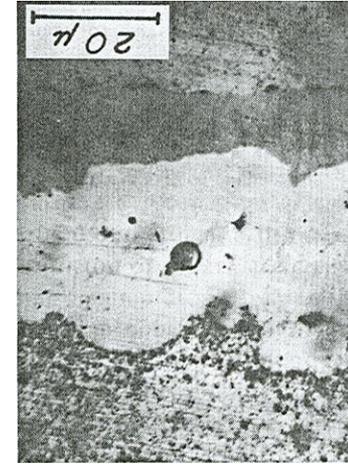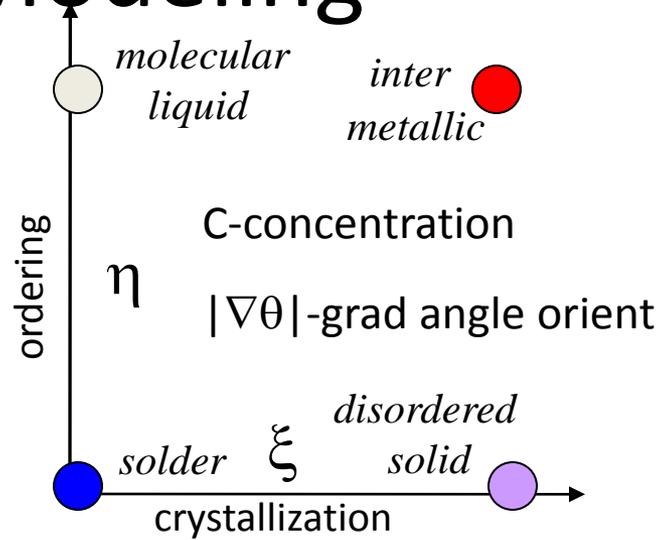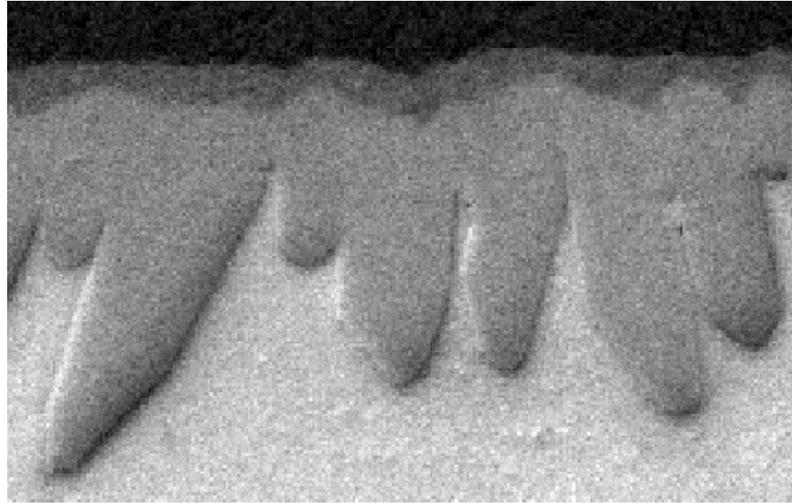
Problem: rotation of grain orientation

Tin

Phase Field Simulation of Nucleation at Large Driving Forces

Lifetime: time for a supercritical nucleus to appear in the system.
Advantages:1. more reliable theory
2. free-energy landscape

3D as opposed to 2D

Correlation properties of the fluctuations are very different.

Numerical simulations

Δx, Δt are not just grid parameters. They are physical quantities–the noise correlation length and time.

Supercritical Nucleus

X-Y plane

Y-Z plane

plane Z-X
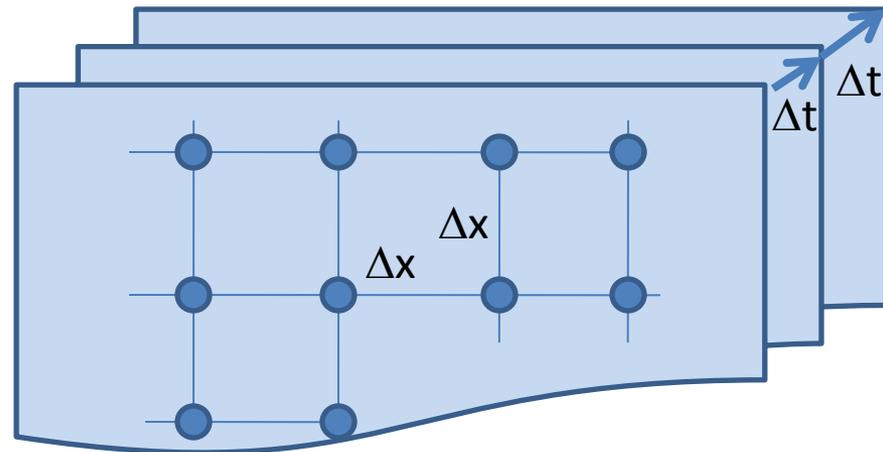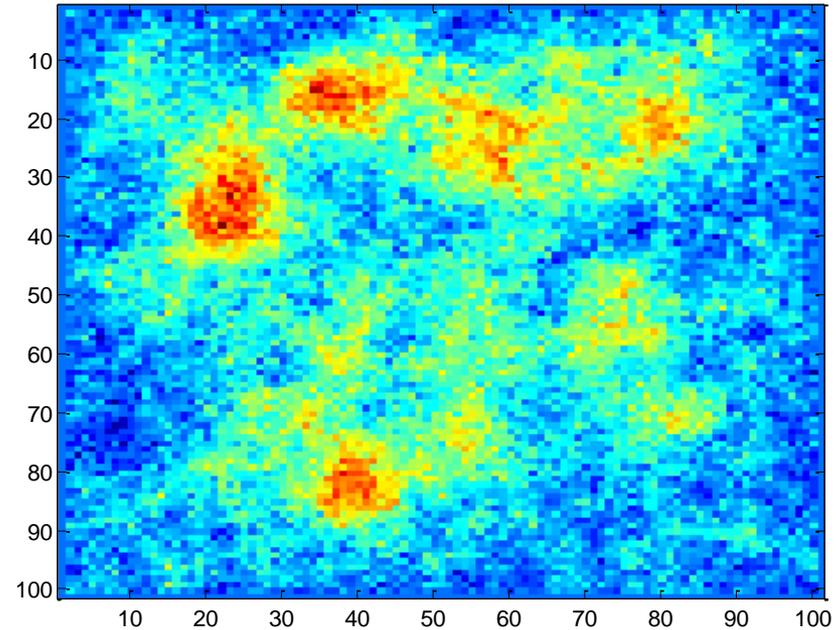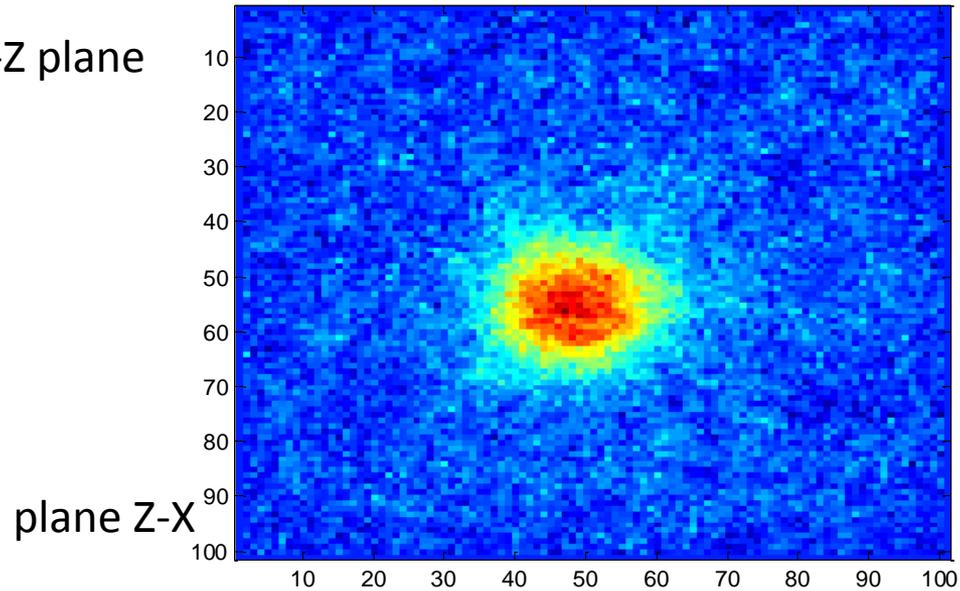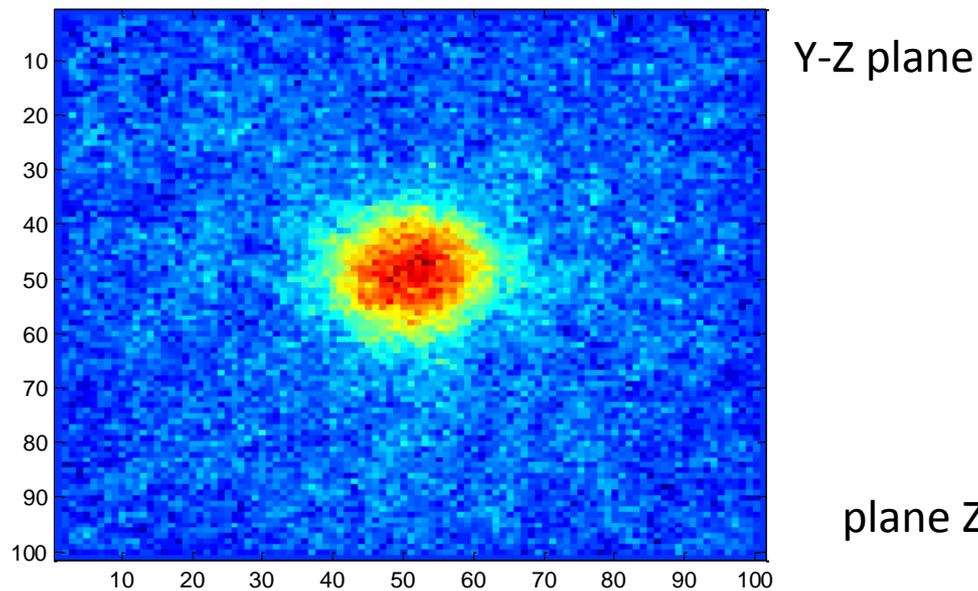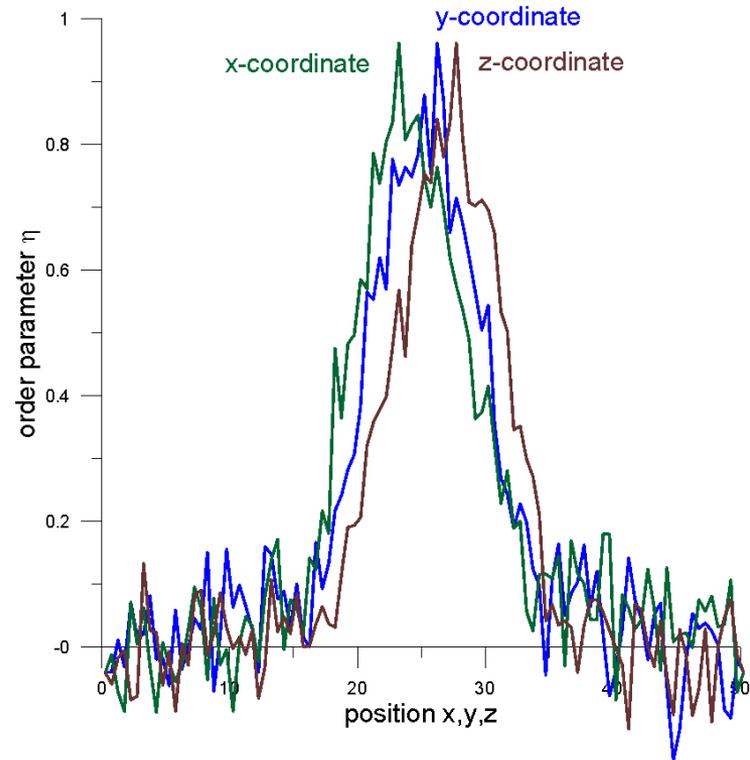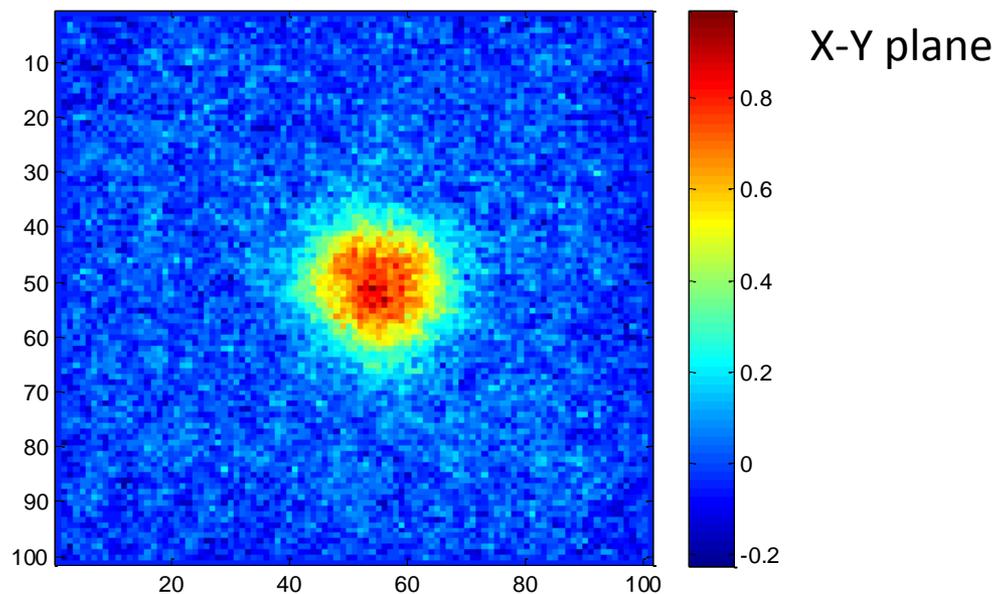
Time Evolution of the System

free energy density g

-0.002   0   0.002   0.004

$$\eta_V(t) = \frac{1}{V}\int \eta(\mathbf{x}, t)\, d\mathbf{x}$$

←transition state

equilibrium fluctuations

←rectification of fluctuations

escape ↑

perturbation theory

theory (uniform modes only)

←α-phase

0   100   200   300   400

time t

volume averaged order parameter η_V
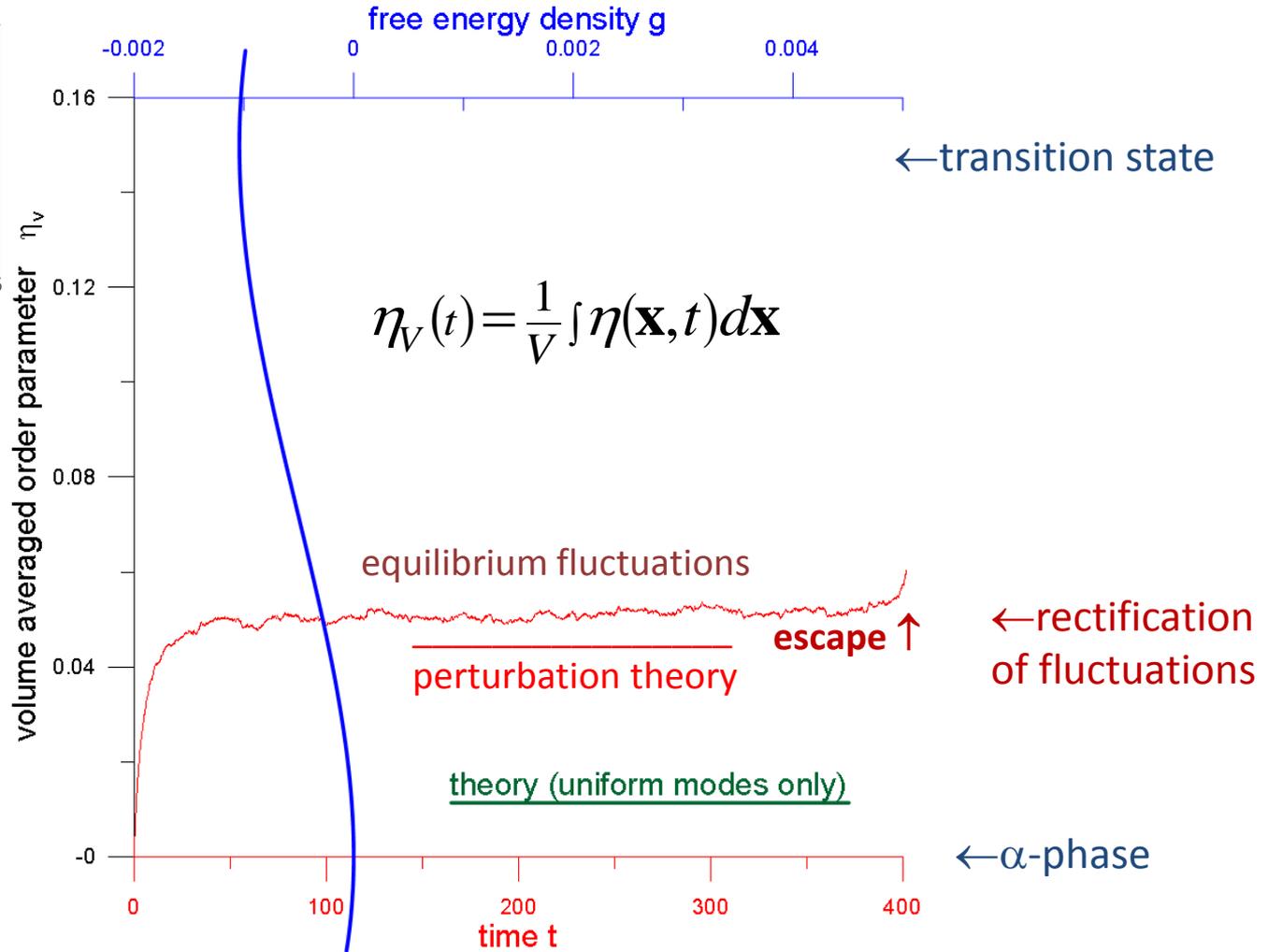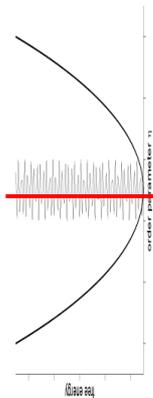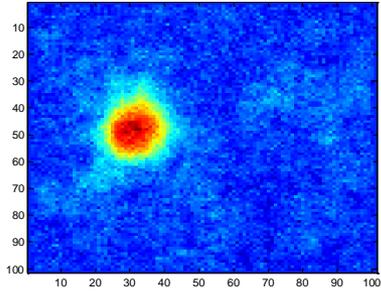
Free Energy Barrier
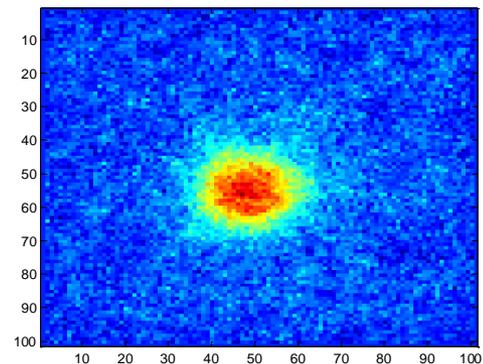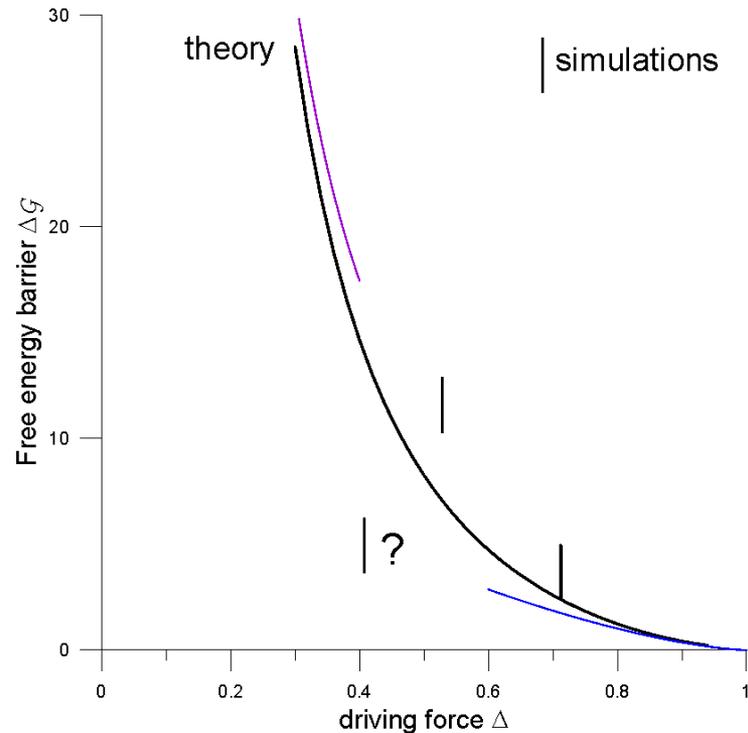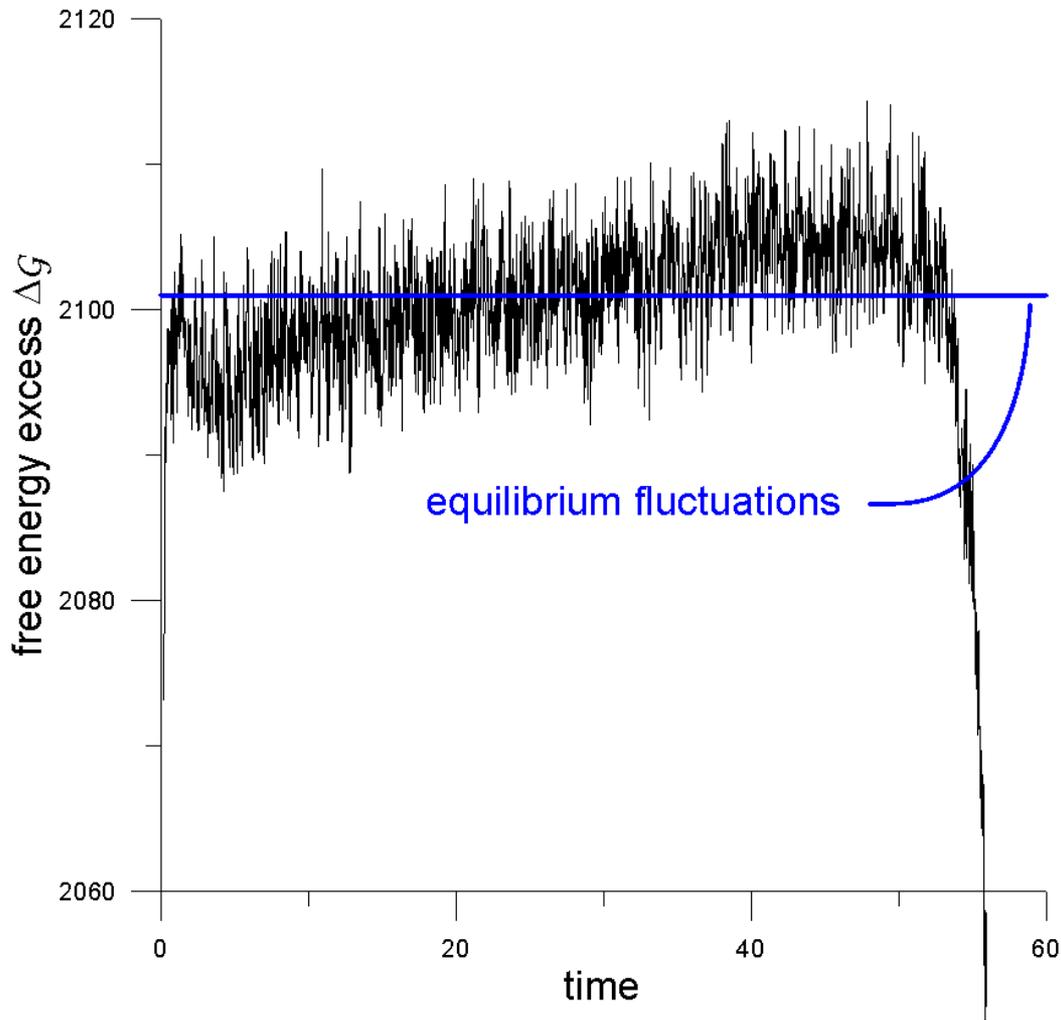
3D Structure of Supercritical Nucleus
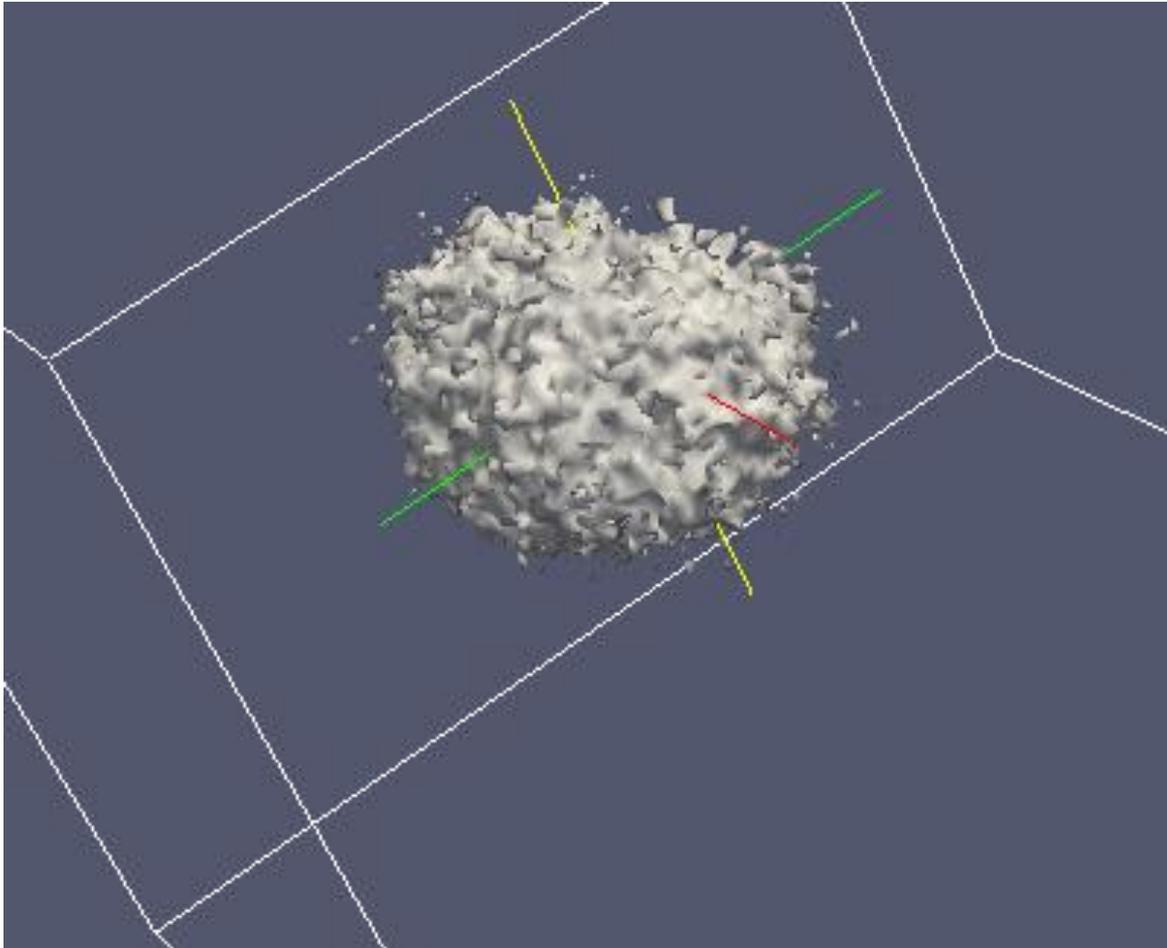
Shape characterization

1. Volumetric content
2. Eccentricity
3. Roughness
4. Probability distribution