

# **MSE 3050: Thermodynamics and Kinetics of Materials**

**Monday and Wednesday, 2:00 – 3:15 pm**

**Mechanical Engineering Building 339**

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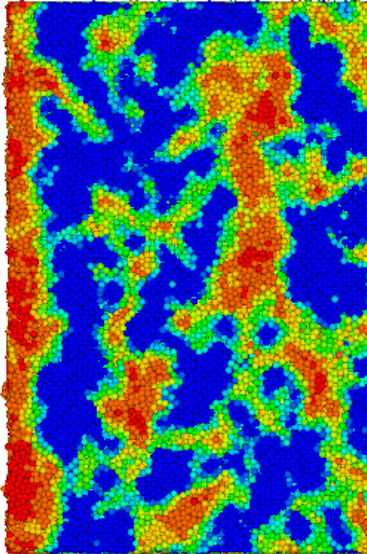
**Class web page:**

<http://www.people.virginia.edu/~lz2n/mse305/>

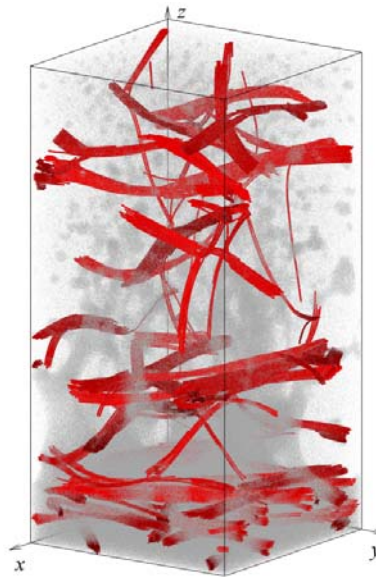
**Class e-mail list:** 12sp-mse-3050@collab.itc.virginia.edu

# Research in Computational Materials Group:

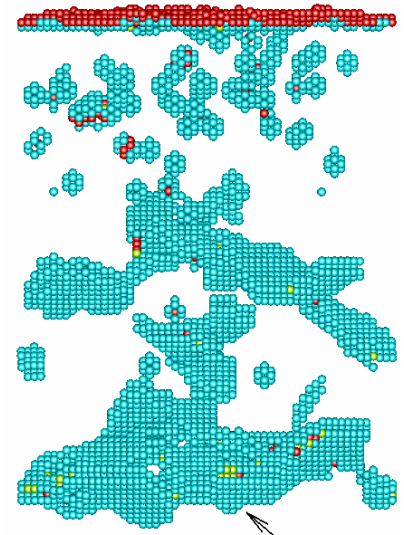
## laser-materials interactions:



laser melting

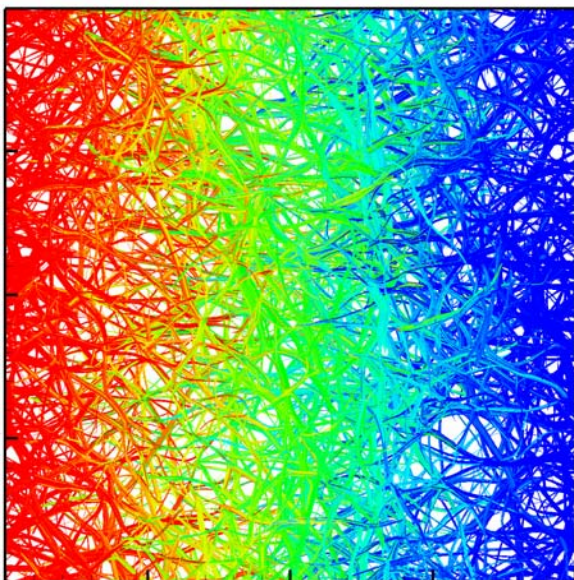


laser ablation

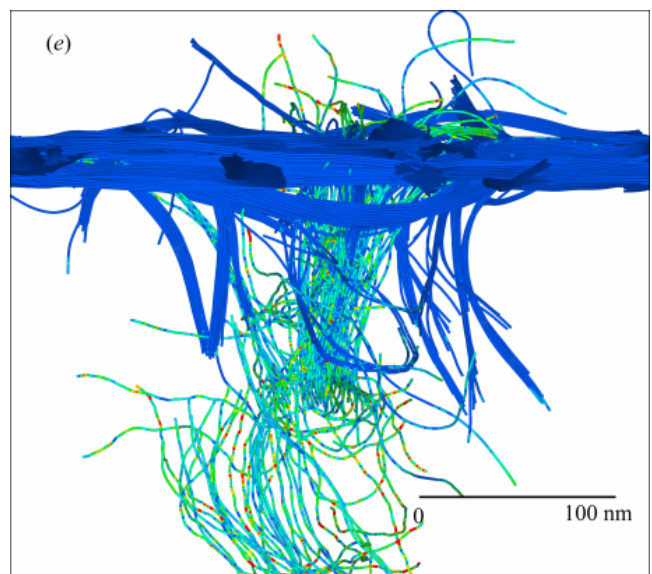


generation of  
crystal defects

## nano-structured materials:



Simulation of heat transfer in  
carbon nanotube material



Simulation of impact resistance  
of carbon nanotube materials

## Grading:

- **Homework 25%**
- **Mid-Term tests 30%**
- **The final exam: 45%**

**Homework** will be due at the beginning of class on the due date. Homework solutions should be neat and stapled. *Late homework is not accepted.*

*Discussions among students through the class mailing list and discussion forum are permitted/encouraged at the conceptual level, but comparing the results and discussing/copying solutions is **not** allowed.*

**Mid-term tests and the final exam:** pledged, closed-book and closed-notes

## **Textbooks:**

**Main (optional) text:** D. A. Porter and K. E. Easterling, Phase Transformations in Metals and Alloys, 2<sup>nd</sup> edition, Chapman & Hall, London, UK, 1992 (TN690 .P597)

(reserve circulate at Science and Engineering Library).

Reprinted by CRC Press in 2003 & 2009 (3<sup>rd</sup> edition)

can be bought at [www.crcpress.com](http://www.crcpress.com) or [www.amazon.com](http://www.amazon.com)

**Lecture notes** will appear at the class web page (<http://www.people.virginia.edu/~lz2n/mse305>) as course progresses.

**Optional textbooks** (placed on reserve circulate):

D. R. Gaskell, Introduction to the Thermodynamics of Materials, 4<sup>th</sup> Ed., New York: Taylor & Francis, 2003 (TN673 .G33 2003)

can be bought at [www.amazon.com](http://www.amazon.com)

## Syllabus:

1. Review of classical thermodynamics needed for understanding of phase diagrams.
2. Application of the thermodynamic concepts to the analysis of phase equilibria, phase transformations, and phase diagrams in one-component and multi-component systems.
3. Basic concepts of kinetic phenomena in materials. Mechanisms of diffusion in materials, analytical and numerical methods to describe diffusion. Kinetics of phase transformations. Effect of kinetics on microstructure.

**thermodynamic driving forces**  
+  
**kinetics of mass and heat transfer**  
=  
**complex microstructure of real materials**

# MSE 3050: Thermodynamics – Phase Diagrams – Kinetics

## Review of classical thermodynamics

- **First Law - Energy Balance**
  - Thermodynamic functions of state
  - Internal energy, heat and work
  - Types of paths (isobaric, isochoric, isothermal, adiabatic)
  - Enthalpy, heat capacity, heat of formation, phase transformations
  - Calculation of enthalpy as a function of temperature
  - Heats of reactions and the Hess's law
- **Theoretical calculation of the heat capacity**
  - Principle of equipartition of energy
  - Heat capacity of ideal and real gases
  - Heat capacity of solids: Dulong-Petit, Einstein, Debye models
  - Heat capacity of metals – electronic contribution
- **Entropy and the Second Law**
  - Concept of equilibrium
  - Reversible and irreversible processes
  - The direction of spontaneous change
  - Entropy and spontaneous/irreversible processes
  - Calculation of entropy in isochoric and isobaric processes
  - Calculation of entropy in reversible and irreversible processes

# MSE 3050: Thermodynamics – Phase Diagrams – Kinetics

- **The Statistical Interpretation of Entropy**

- Physical meaning of entropy
- Microstates and macrostates
- Statistical interpretation of entropy and Boltzmann equation
- Configurational entropy and thermal entropy
- Calculation of the equilibrium vacancy concentration

- **Fundamental equations**

- The Helmholtz Free Energy
- The Gibbs Free energy
- Changes in composition
- Chemical potential
- Thermodynamic relations and Maxwell equations

## Phase Transitions and Phase Diagrams

- **One-component systems**

- Enthalpy and entropy dependence on P and T
- Gibbs free energy dependence on P and T
- Clapeyron equation
- Understanding phase diagrams for one-component systems
- Polymorphic phase transitions
- Driving force for a phase transition
- First order and second-order phase transitions

# MSE 3050: Thermodynamics – Phase Diagrams – Kinetics

- **Introduction to Solution Thermodynamics**

- Ideal solution: Entropy of formation and Gibbs free energy
- Chemical potential of an ideal solution
- Regular solutions: Heat of formation of a solution
- Activity of a component
- Real solutions: interstitial solid solutions, ordered phases, intermediate phases, compounds
- Equilibrium in heterogeneous systems

- **Binary phase diagrams**

- Binary phase diagrams and Gibbs free energy curves
- Binary solutions with unlimited solubility
- Relative proportion of phases (tie lines and the lever principle)
- Development of microstructure in isomorphous alloys
- Binary eutectic systems (limited solid solubility)
- Solid state reactions (eutectoid, peritectoid reactions)
- Binary systems with intermediate phases/compounds
- The iron-carbon system (steel and cast iron)
- Gibbs phase rule
- Temperature dependence of solubility
- Multi-component (ternary) phase diagrams

# MSE 3050: Thermodynamics – Phase Diagrams – Kinetics

## Kinetics

- **Basic concepts in kinetics**
  - Kinetics of phase transformations
  - Activation free energy barrier
  - Arrhenius rate equation
- **Diffusion in solids - phenomenological description**
  - Driving force for diffusion in ideal solutions
  - Flux, steady-state diffusion, Fick's first law
  - Diffusion coefficient, Einstein relation
  - Nonsteady-state diffusion, Fick's second law
- **Thermodynamics of diffusion**
  - Driving force for diffusion revisited
  - Diffusion in ideal and real solutions
  - Thermodynamic factor
  - Diffusion against the concentration gradient
  - Spinodal decomposition
- **Solutions to the diffusion equation**
  - Numerical integration
  - Analytical solution
  - Applications
    - Chemical homogenization
    - Carburization of steel

# MSE 3050: Thermodynamics – Phase Diagrams – Kinetics

- **Atomic mechanisms of diffusion**

- Substitutional diffusion
- Interstitial diffusion
- Temperature dependence
- High diffusivity paths (grain boundaries, surfaces, dislocations)

- **Kinetics of phase transformations**

- Supercooling and superheating
- Driving force for phase transformation
- Homogeneous nucleation
- Critical radius, nucleation rate
- Heterogeneous nucleation
- Nucleation in melting and boiling
- Growth mechanisms
- Rate of phase transformations
- Solidification and growth morphologies
- Kinetics of solid-state transformations

# Application of thermodynamics and kinetics to materials

## Definitions: Components and Phases

**Component** - chemically recognizable species (Fe and C in carbon steel, H<sub>2</sub>O and Sucrose in sugar solution in water). A binary alloy contains two components, a ternary alloy - three, etc.

Materials consist of phases or mixtures of phases. A **phase** is a portion of a system that has uniform properties and composition. The phase may or may not be in an equilibrium state.

Two distinct phases in a system have distinct chemical **or** physical characteristics (e.g. liquid water and ice) and are separated from each other by definite **phase boundaries**. A phase may contain one or more components.

A single-phase system is called **homogeneous**, systems with two or more phases are **mixtures** or **heterogeneous** systems.

**Equilibrium** – the state in which the system parameters no longer evolve (there are no fluxes of matter or energy, small disturbances decay, ...).

The phases that are **not in equilibrium** can undergo a **spontaneous** phase transformation to an equilibrium phase or mixture of phases.

# Application of thermodynamics and kinetics to materials

## Thermodynamics of phase stability and phase transitions

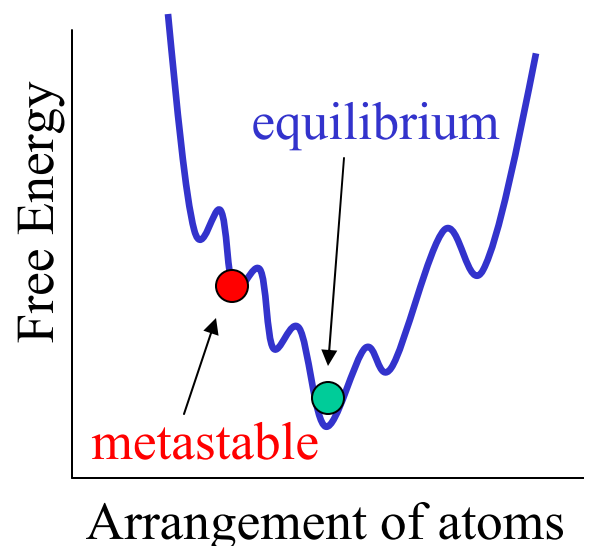
**Thermodynamics** can be used to predict whether the system is in equilibrium and to analyze the **phase stability and phase transformations**.

Questions thermodynamics can answer: Is a particular process possible? Is a spontaneous evolution in a particular direction possible? What is the final/equilibrium state of the system?

**Equilibrium** is the state that is achieved given *sufficient* time. But the time to achieve equilibrium may be very long (the kinetics can be slow) and a state along the path to the equilibrium may *appear* to be stable. This is called a **metastable state**.

In thermodynamics, the equilibrium is described as a state of a system that corresponds to the minimum of thermodynamic function called the **free energy**. Thermodynamics tells us that:

- Under conditions of a constant  $T$ ,  $P$ , and composition, the direction of any spontaneous change is toward a lower Gibbs free energy.
- The state of stable thermodynamic equilibrium is the one with minimum free energy.
- A system at a metastable state is trapped in a local minimum of free energy that is not the global one.



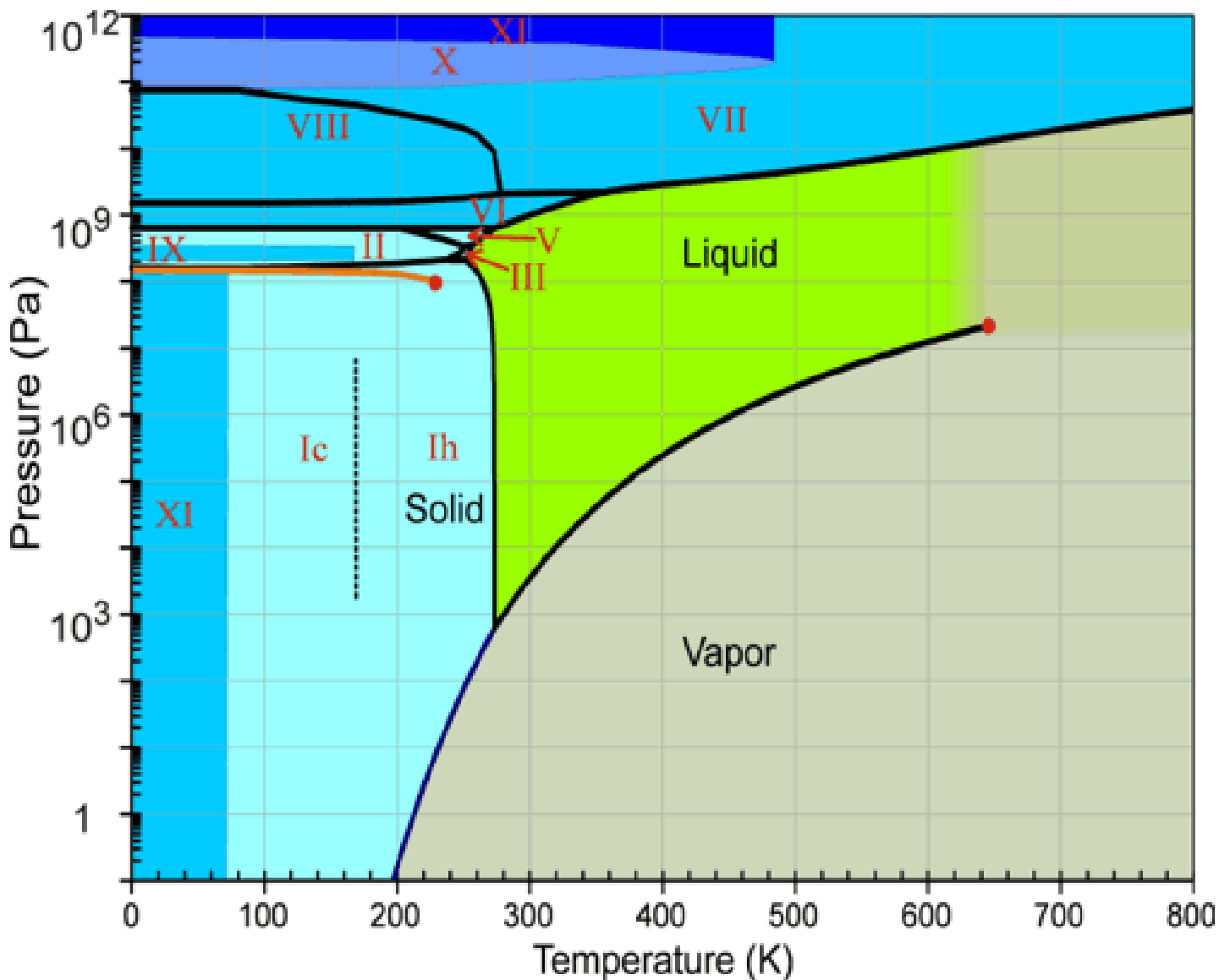
# Application of thermodynamics and kinetics to materials

## Phase diagrams

A **phase diagram** is a graphical representation of all the **equilibrium** phases as a function of temperature, pressure, and composition.

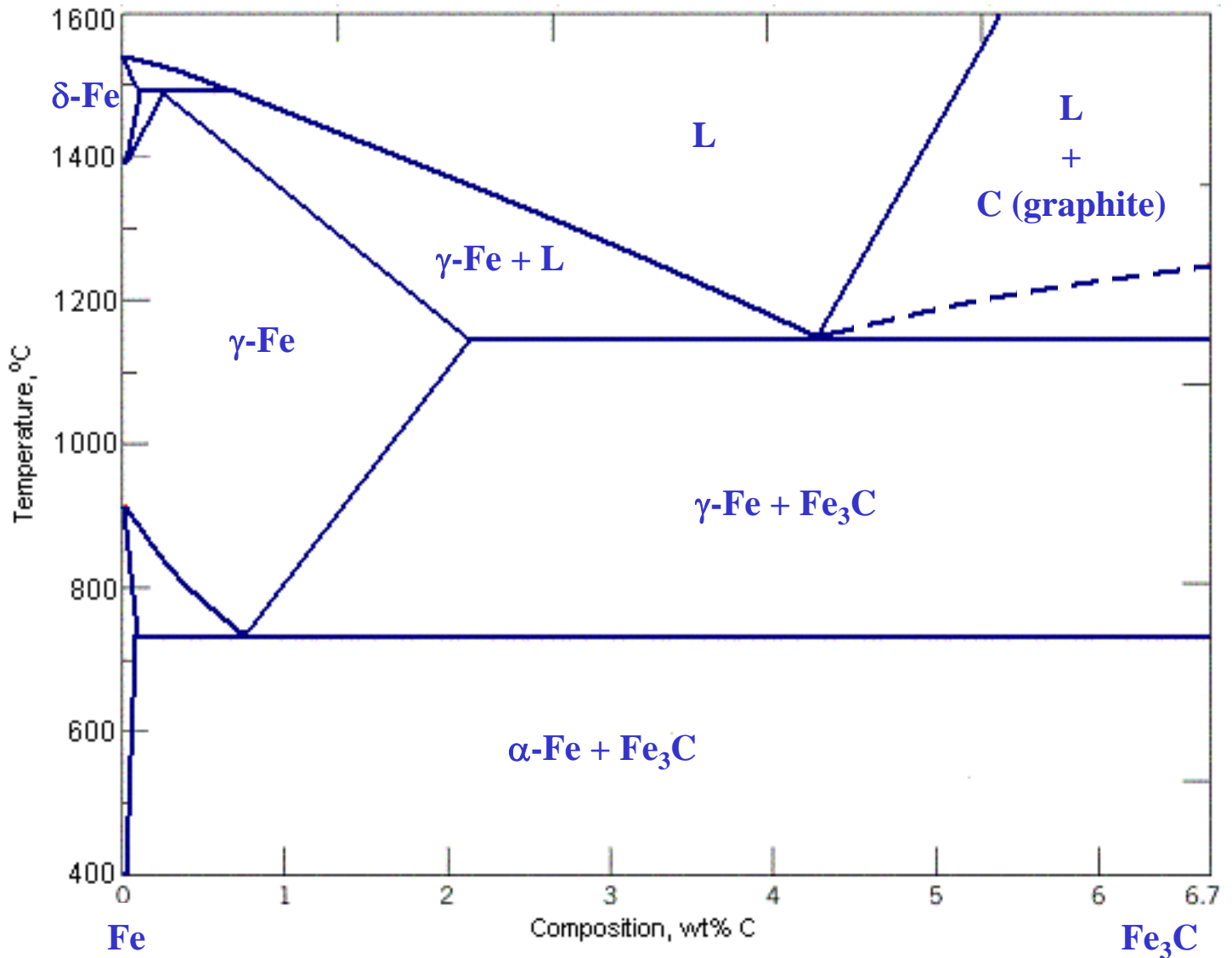
**Phase diagrams can be predicted (calculated) through analysis of free energies of phase and their mixtures.** They can be used to describe gas - liquid - solid transitions, polymorphic solid-to-solid transitions, stable phases in alloys of different composition, etc.

Pressure-temperature phase diagram for H<sub>2</sub>O:



# Application of thermodynamics and kinetics to materials

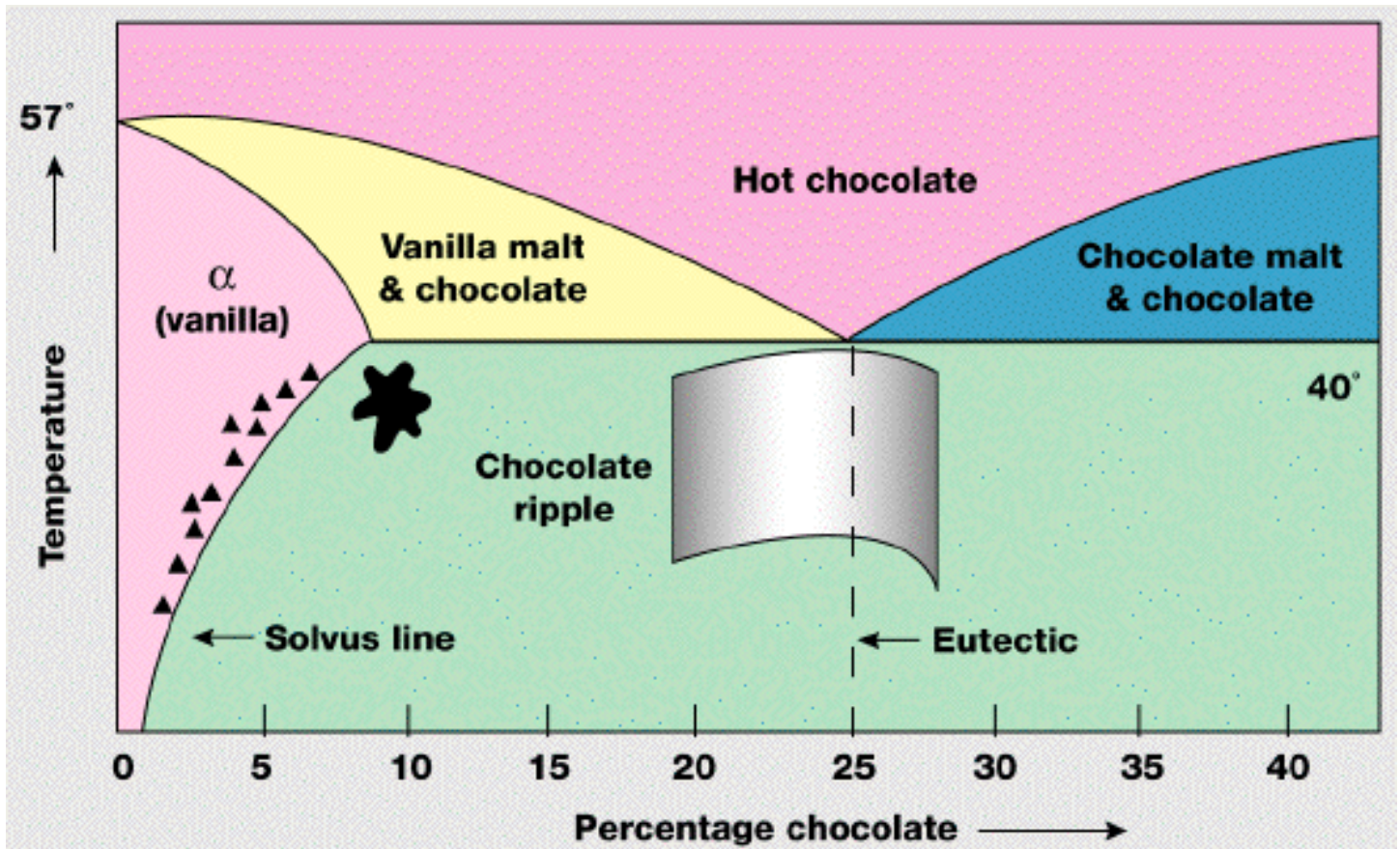
## Example of a binary phase diagram: steel iron–iron carbide (Fe–Fe<sub>3</sub>C)



In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The Fe-C phase diagram is a fairly complex one, here we are only looking at the steel part of the diagram, up to ~7 wt.% Carbon.

# Application of thermodynamics and kinetics to materials

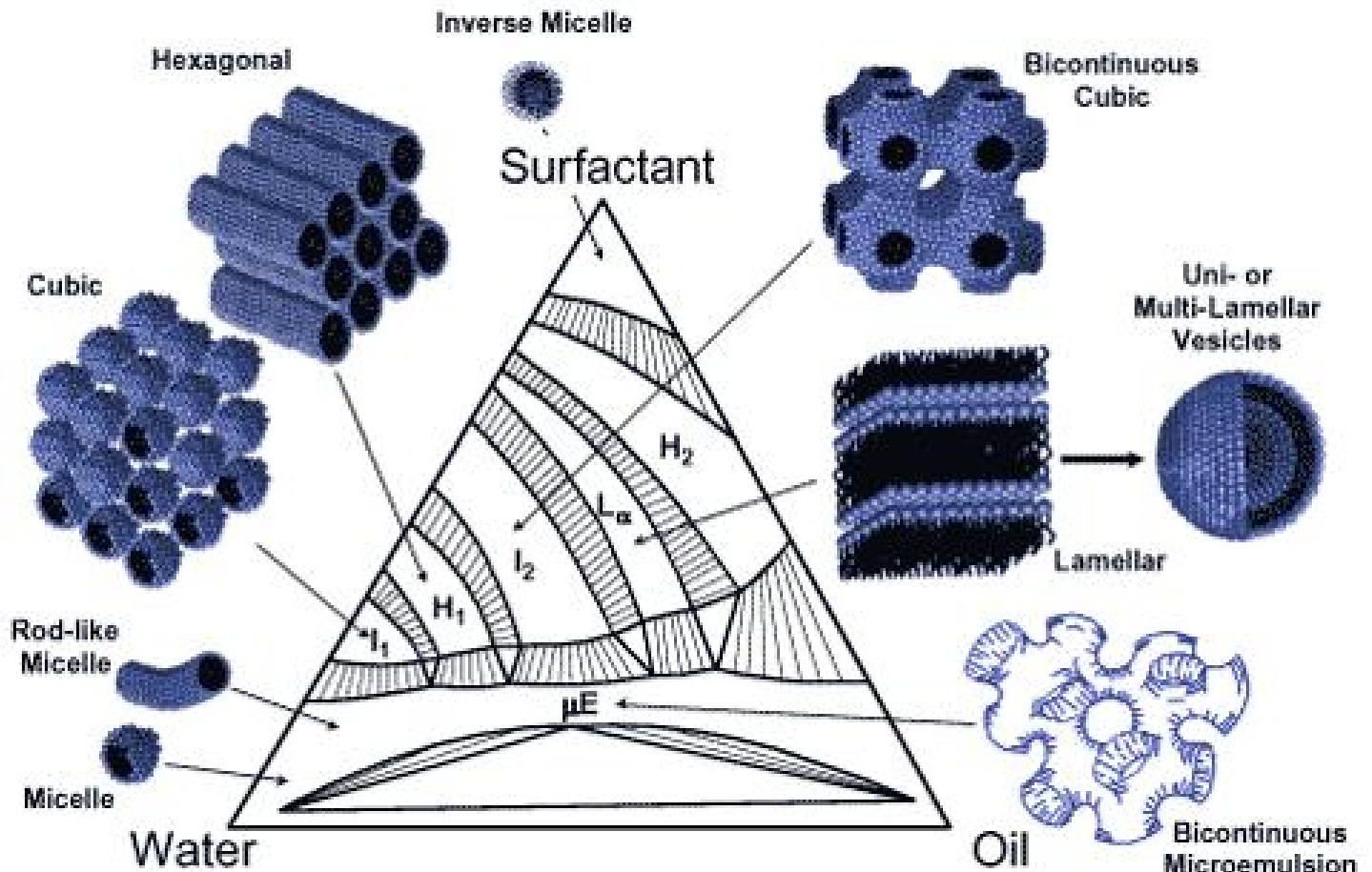
## Another example: phase diagram for chocolate and vanilla



Credit: Kenneth A. Jackson, University of Arizona.

# Application of thermodynamics and kinetics to materials

## Example of ternary phase diagram: oil – water – surfactant system



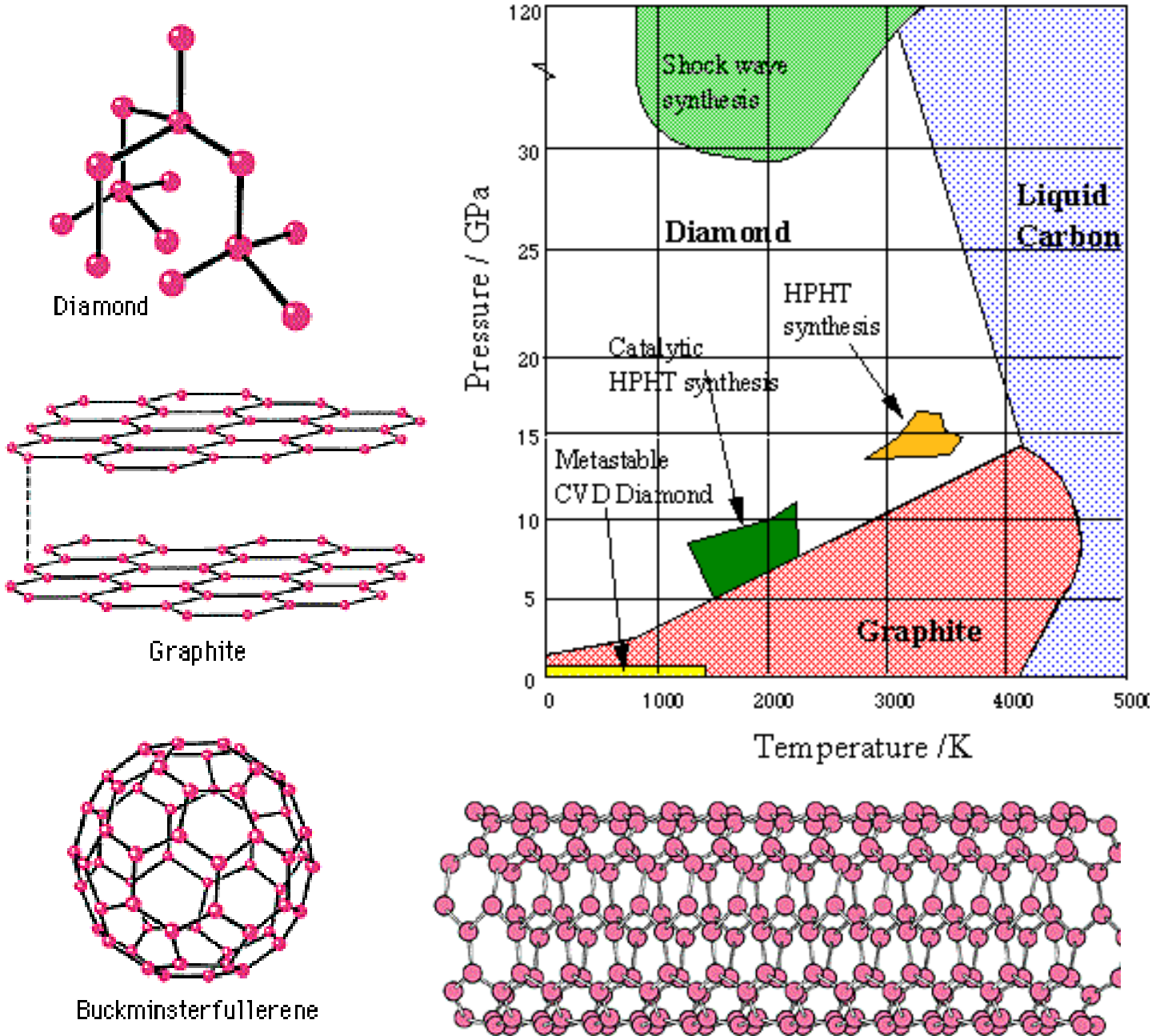
Drawing by Carlos Co, University of Cincinnati

Surfactants are surface-active molecules that can form interfaces between immiscible fluids (such as oil and water). A large number of structurally different phases can be formed, such as droplet, rod-like, and bicontinuous microemulsions, along with hexagonal, lamellar, and cubic liquid crystalline phases. Ternary phase diagram shows compositional ranges for different phases.

# Application of thermodynamics and kinetics to materials

## Phase diagrams do not predict all the possible structures

Pressure-temperature phase diagram for carbon:



We can see graphite, diamond, liquid carbon on the phase diagram... but where are fullerenes and nanotubes?

# Application of thermodynamics and kinetics to materials

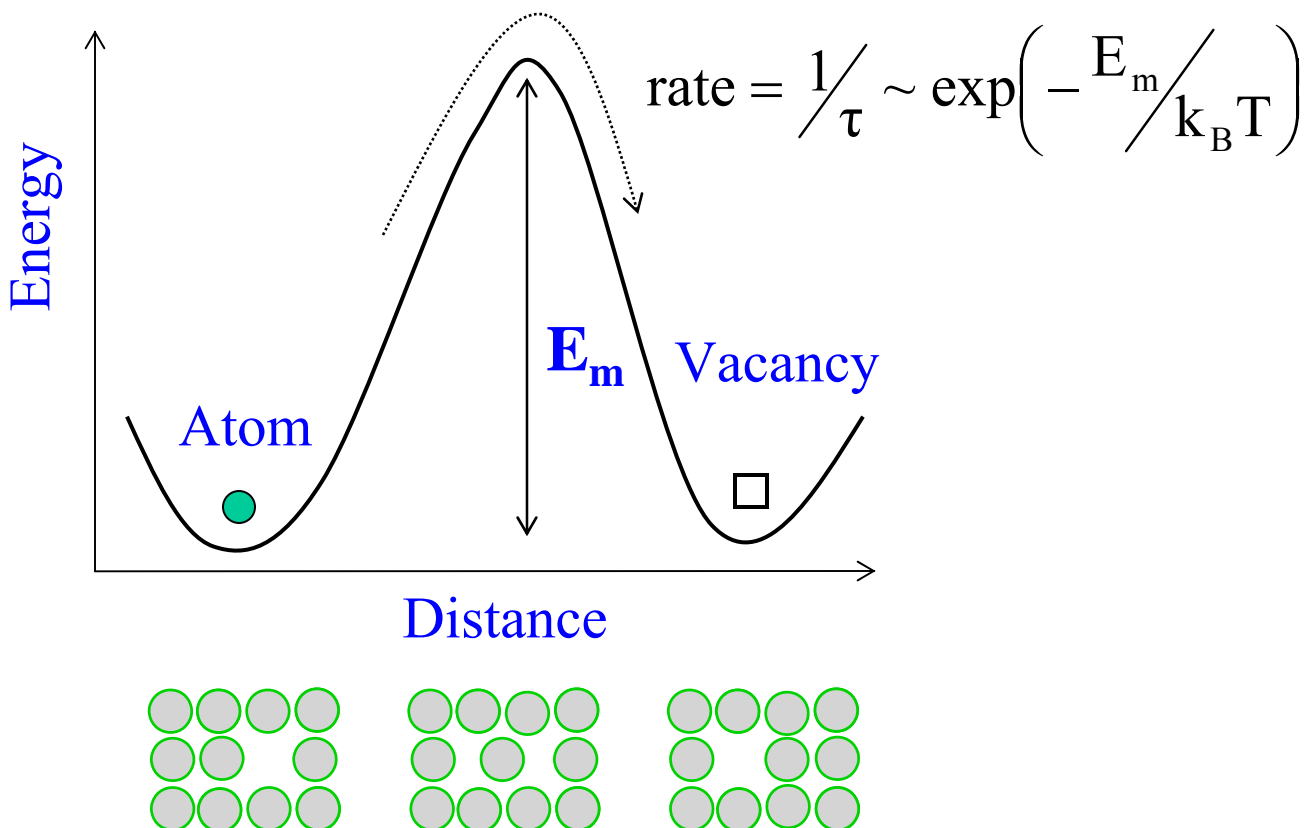
## Kinetics

Thermodynamics can be used to predict the equilibrium phases for different conditions as well as the phase transformations that **can occur**.

“When or how fast does a phase transformation occur?” is not a right question for classical thermodynamics.

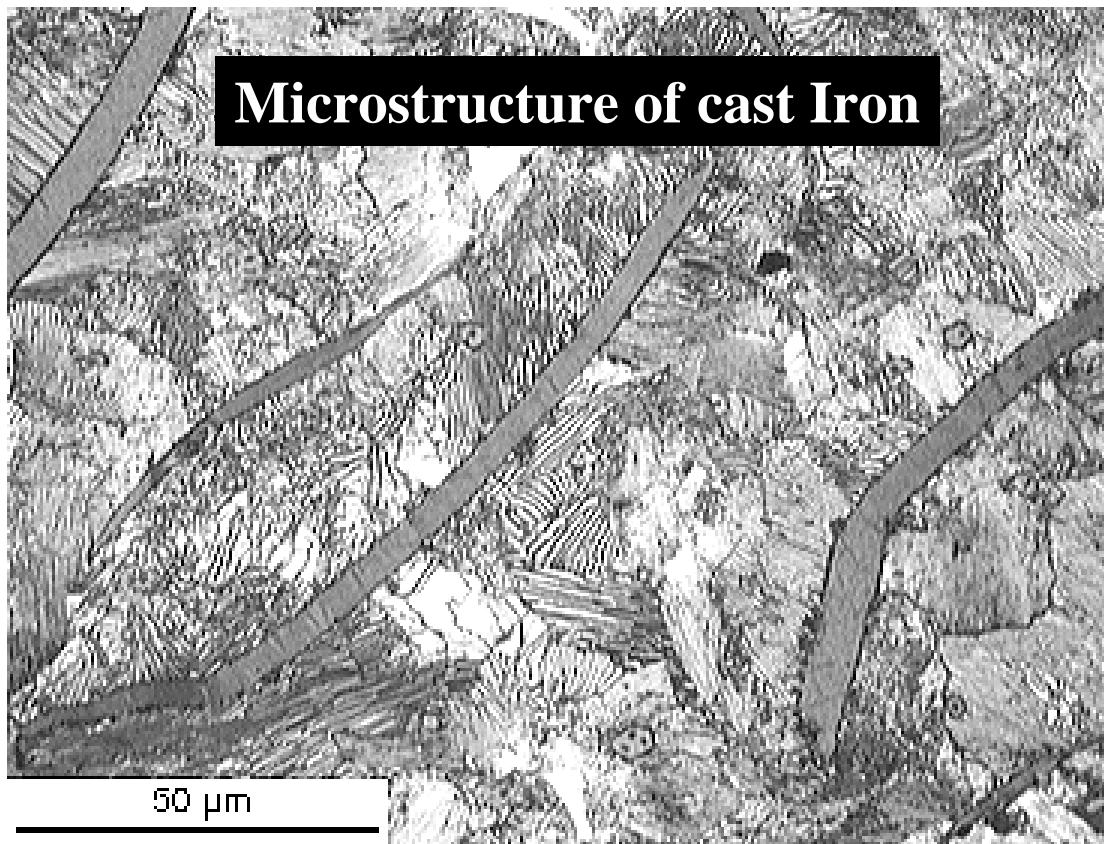
Thermodynamics tells us what should happen - not how fast it will happen . “How fast?” is the question addressed by **kinetics**.

Most kinetic phenomena in materials involve **diffusion**. Therefore we will consider mechanisms of diffusion in materials before discussing kinetics of the nucleation and growth of a new phase.



## Application of thermodynamics and kinetics to materials

Analysis of both the equilibrium phase diagrams and the kinetics of phase transformations will help us to understand and predict complex microstructures like the one shown below



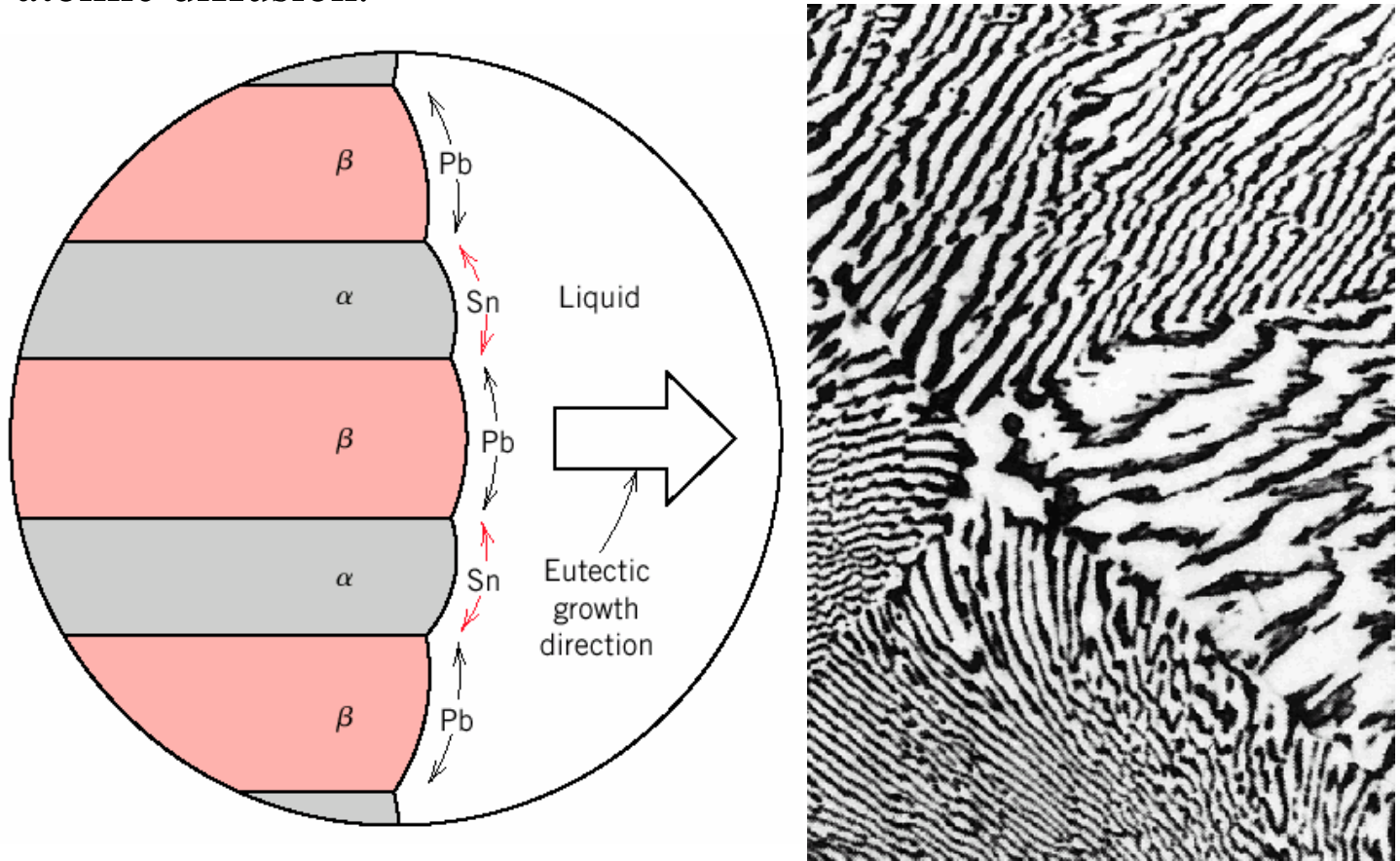
<http://www2.umist.ac.uk/material/research/intmic/>

The long gray regions are flakes of graphite.

The matrix is a fine mixture of BCC Fe and Fe<sub>3</sub>C compound.

## Application of thermodynamics and kinetics to materials

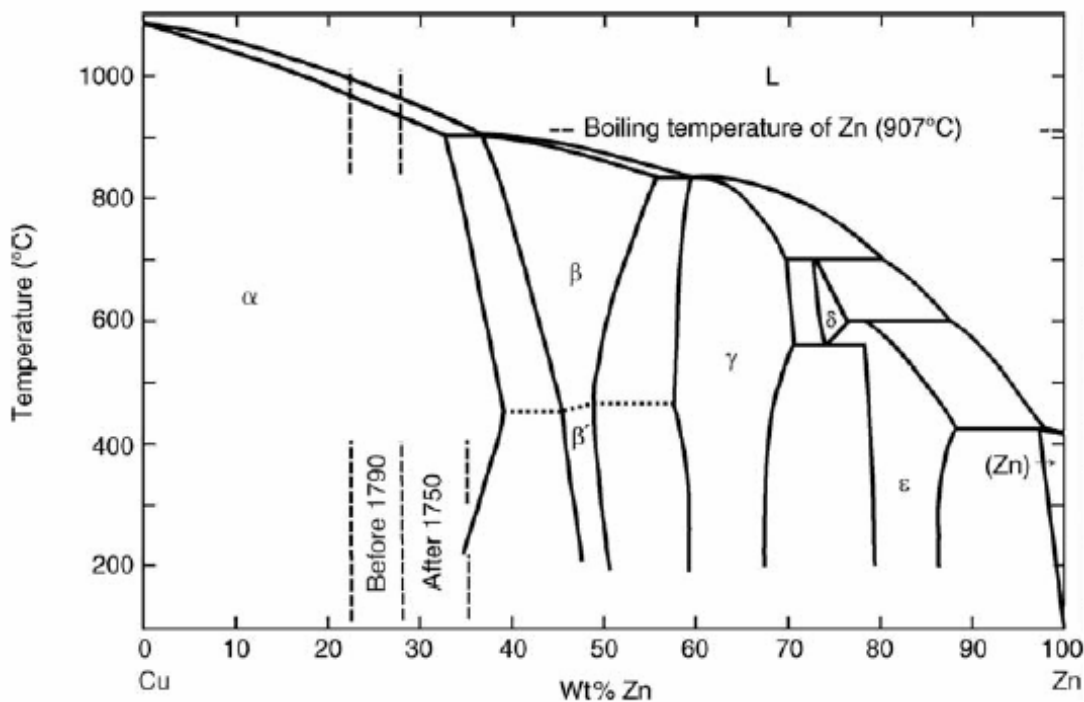
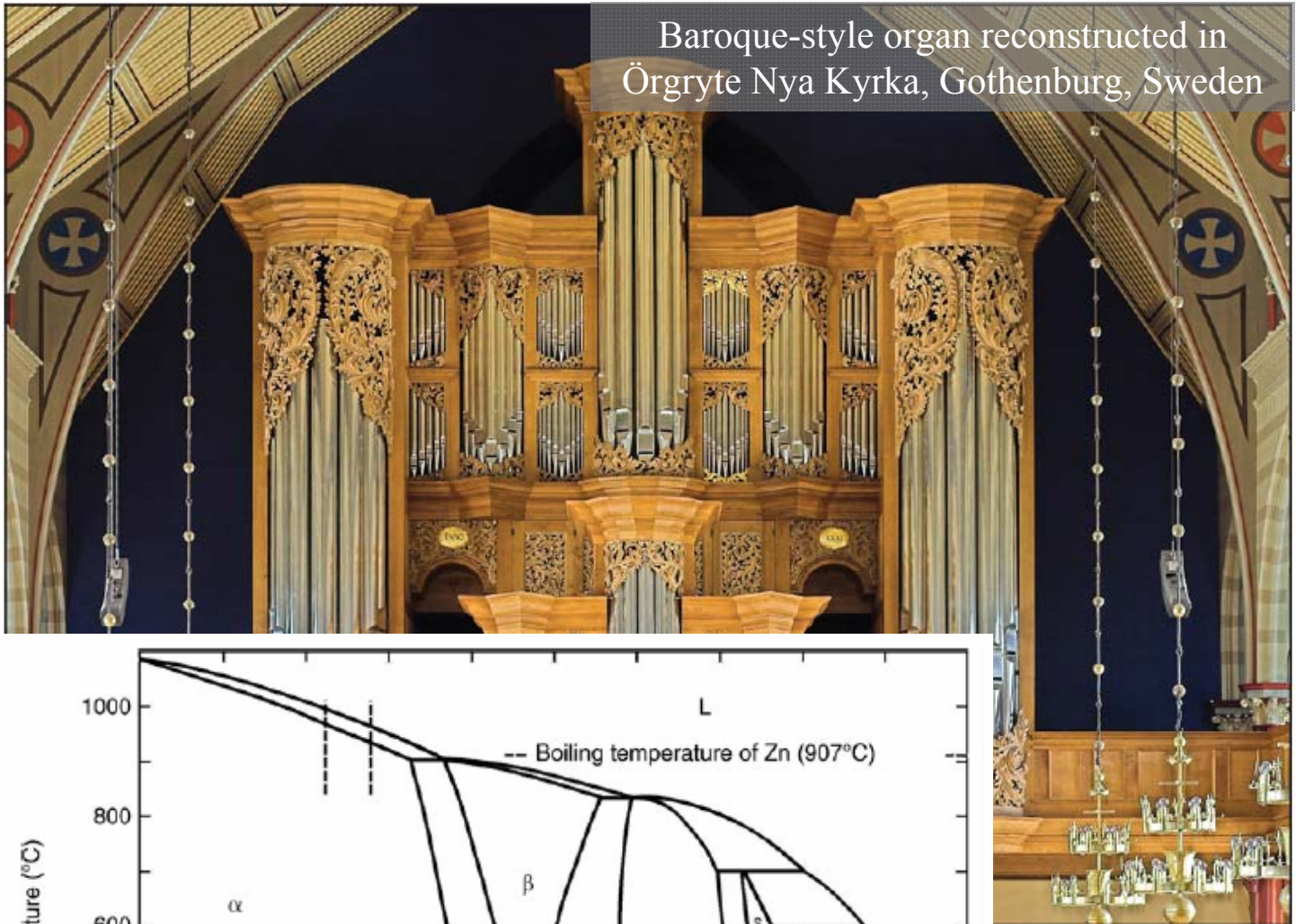
Formation of eutectic layered microstructure in the lead-tin system during solidification **at the eutectic composition**. Compositions of  $\alpha$  and  $\beta$  phases are very different  $\rightarrow$  solidification involves redistribution of Pb and Sn atoms by atomic diffusion.



In the micrograph, the dark layers are lead-rich  $\alpha$  phase, the light layers are the tin-rich  $\beta$  phase.

Compositions of  $\alpha$  and  $\beta$  phases are defined by **thermodynamics** and can be determined from the **phase diagram**, the size and arrangement of the layers in the microstructure is defined by the **kinetics** of solidification.

# Application of thermodynamics and kinetics to materials

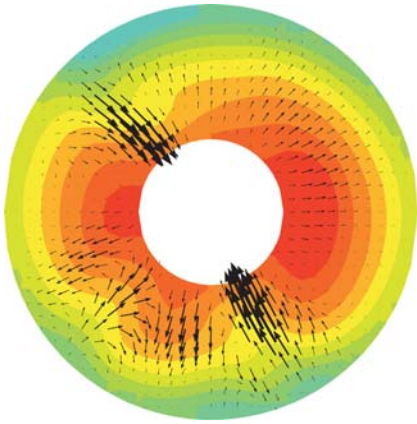


MRS Bulletin  
Vol 32, March  
2007, 249-255

Analysis of phase diagrams for brass helps to understand the connections between the evolution of the brass production methods and changes in composition of brass pipes used in historical organs.

# Application of thermodynamics and kinetics to materials

## Melting at the inner-core boundary



Buffett, Nature **473**, 292, 2011  
Gubbins et al., Nature **473**, 361, 2011

