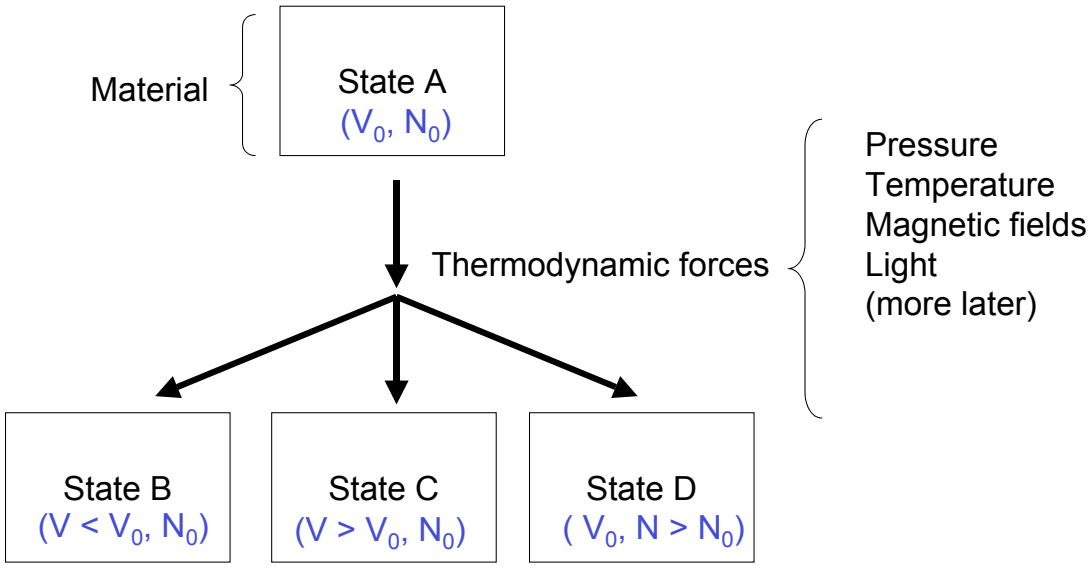
Lecture 2: 09.12.05 Fundamental concepts continued

Today:

Reading: Engel and Reid: 1.4, 2.1, 2.2, 2.3

Last Time


Material
State A
(V_0, N_0)
Thermodynamic forces
Pressure
Temperature
Magnetic fields
Light
(more later)
State B
($V < V_0$, N_0)
State C
($V > V_0$, N_0)
State D
(V_0, $N > N_0$)

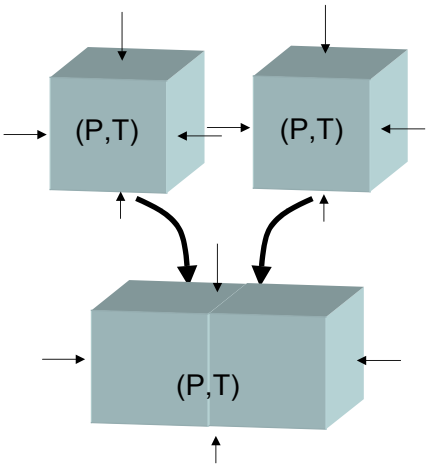
Thermodynamic variables, systems, and functions

Thermodynamic Variables

- Remember that classical thermodynamics is concerned with macroscopic properties

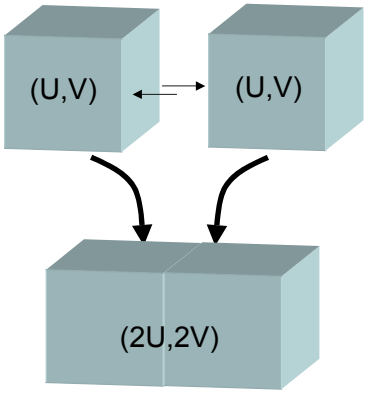
- 2 types of variables
  - **intensive**

Intensive variables:



  - **Extensive**

extensive variables:



- intensive and extensive variables form coupled pairs:

  - e.g. pressure and volume P <-> V
  - the product of one intensive variables multiplied by its coupled extensive variables is ***work***

The constituents of materials: components and phases

Components

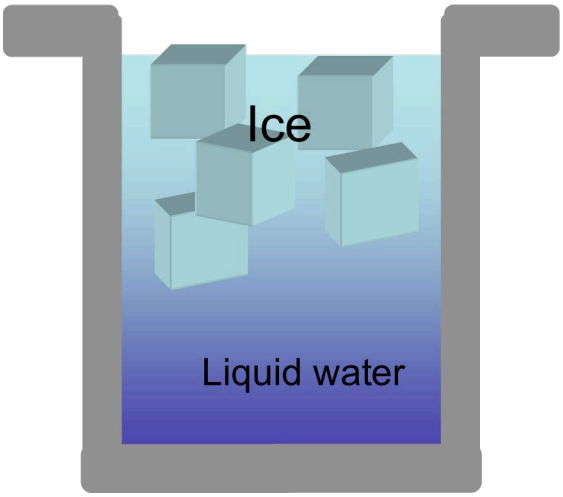
- The **components** are the irreducible molecules, compounds, or atoms that make up a system:

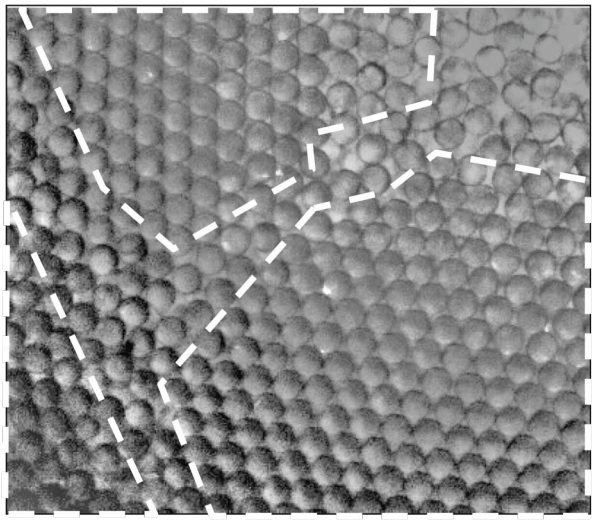
Example system	Class of material	Components	Class of components

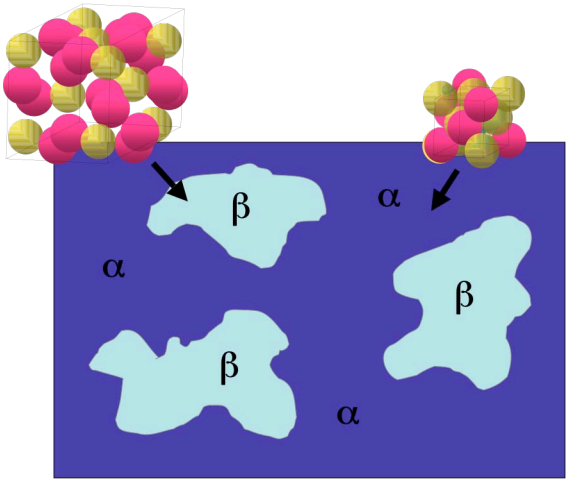
phases

- **Phase**:

  - examples:







Stable phases of Fe[1]

Stable temperature range (K)	Form of matter	Phase	Identification symbol of phase
> 3013	Gas	Gas	Gas
1812-3013	Liquid	Liquid	Liquid
1673-1812	Solid	Body-centered cubic	δ
1183-1673	Solid	Face-centered cubic	γ
< 1183	Solid	Body-centered cubic	α

- *Phases may have multiple components*, and different phases may have the *same* components (though in different *relative amounts*). Phases, particularly solid phases, are often identified using Greek letters (as seen above for Fe- the solid phases are denoted δ, γ, and α).

- A multiphase system is one where the components of the system exist in multiple unique forms (structure or composition) within the system.

- **Phases can have dimensions from macroscopic down to a few molecules:**

Figure removed for copyright reasons.

See Fig. 6.18(a) on p. 370 of Allen, S., and E. L. Thomas. *The Structure of Materials*. New York, NY: Wiley, 1999.

Figure removed for copyright reasons.

See Fig. 2 in Bockstaller et al. "Size-selective Organization of Enthalpic Compatibilized Nanocrystals in Ternary Block Copolymer/Particle Mixtures." *J. Amer. Chem. Soc.* 125 (2003): 5276-5277.

Figure removed for copyright reasons.

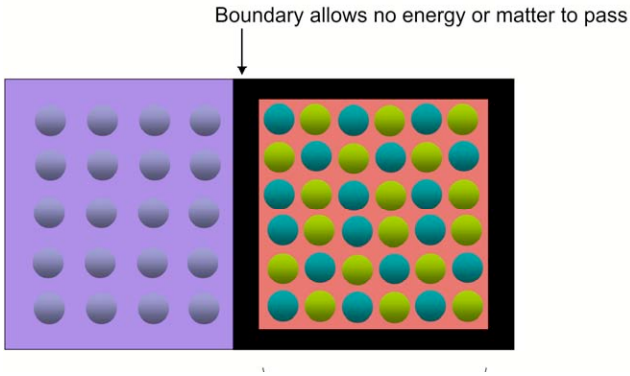
See p. 198 in Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. New York, NY: Oxford University Press, 2001.

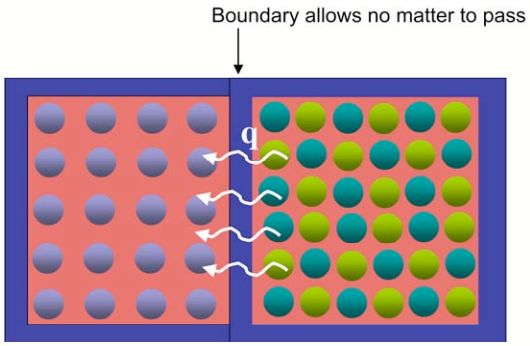
- A few other useful definitions:
  - **Mixture**:
  - **Solution**:

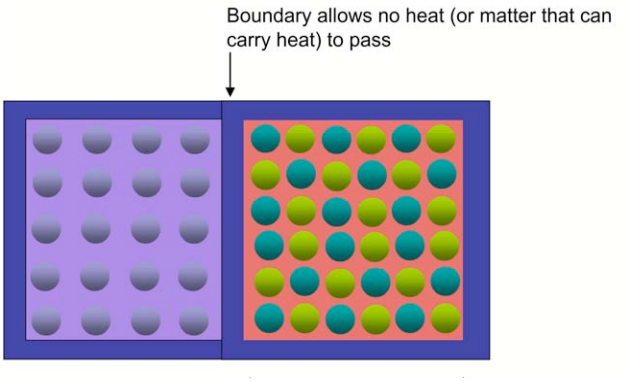
Thermodynamic systems

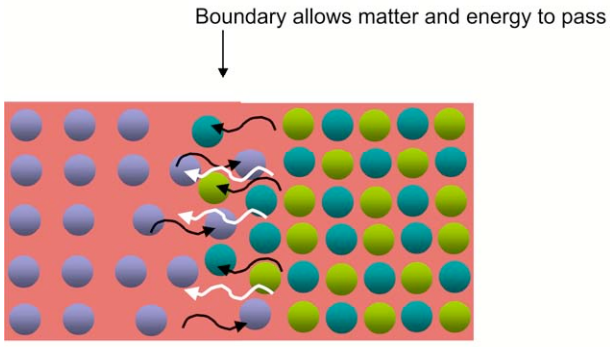
- Thermodynamic systems can have boundary conditions that limit the exchange of energy or atoms/molecules with their surroundings. Some of the types of systems one may be interested in for materials science and engineering problems include:

System	Boundary condition:
Isolated	
Closed	
Adiabatic	
Open	

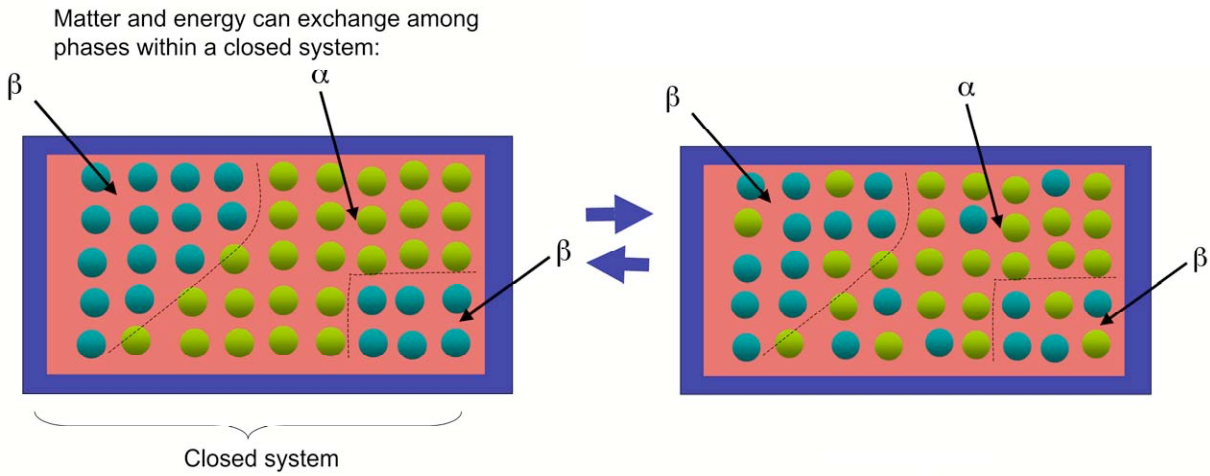








- In closed multi-phase systems, molecules and energy ***can*** be exchanged ***among phases within the system***:



Identification of processes

Types of processes

- We've stated that thermodynamics is a theory for predicting what changes will happen to a material/system. A key part of making correct predictions is identifying what processes can happen within the system.
  - Several common processes include:[4]

Process type	Conditions
Adiabatic	
Isochoric	
Isothermal	
Isobaric	
Isobarothermal	

Examples of classifying a system and process:

1. You place a thin metal film (your system) in an oven to *anneal* (equilibrate at elevated temperature).

   Type of System:

   Process:

2. Your system is a cold glass of water, and you place it on your porch on a sunny day.

   Type of System:

   Process:

Reversible and Irreversible Processes

Reversible Processes

- Reversible processes are idealized processes that:

occur “forward” or “backward” ***with no change in the surroundings***

- Examples:

Irreversible processes

- Natural processes typically occur in only 1 direction spontaneously

  - These are *irreversible* processes

Experiment	Process	Observation of irreversibility
Add a drop of food coloring to a glass of water	•	
Expansion of a gas into a vacuum	•	
Cooling of a hot object placed in a cold room	•	
Melting of a solid at T = Tm + 100°	•	

Thus irreversible processes are driven in the one allowed direction by the second law

References

1. Reed-Hill, R. E. & Abbaschian, R. *Physical Metallurgy Principles* (PWS Publishing, Boston, 1994) 926 pp,
2. Allen, S. & Thomas, E. L. *The Structure of Materials* pp,
3. Mann, S. *Biomineralization: Principles and concepts in Bioinorganic Materials Chemistry* (Oxford University Press, New York, 2001) 198 pp,
4. Carter, W. C. *3.00 Thermodynamics of Materials Lecture Notes* http://pruffle.mit.edu/3.00/ (2002).