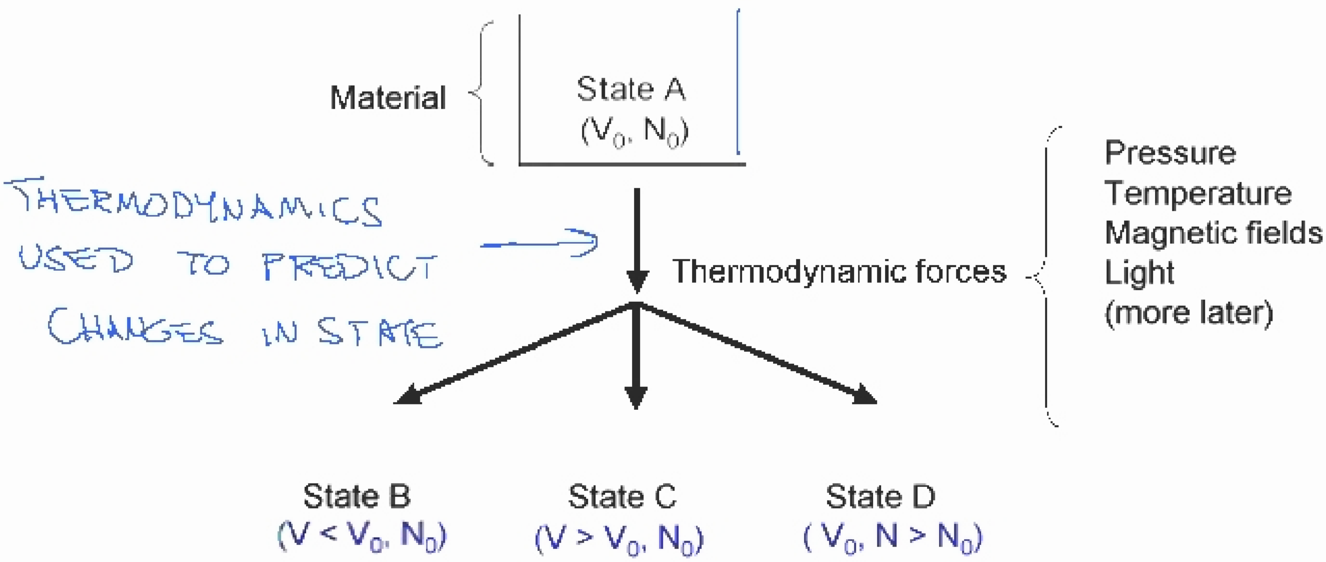
Lecture 2: 09.12.05 Fundamental concepts continued

Today:

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

ANNOUNCEMENTS: – PS 1 POSTED: DUE NEXT TUES. 9/20
(REMINDERS) – 3.014: ONLINE SAFETY TRAINING

Last Time


Material
State A
(V_0, N_0)
THERMODYNAMICS USED TO PREDICT CHANGES IN STATE
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

MACROSCOPIC THERMO VARIABLES: P, V, T, N or n, ...

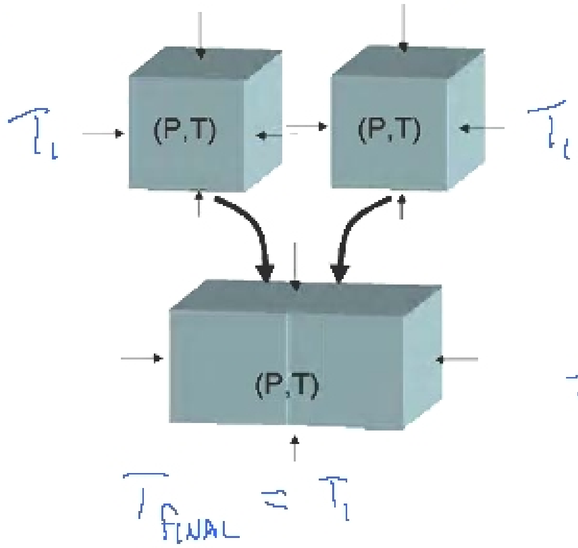
SIMPLE SYSTEM

- 2 types of variables
  - **intensive**

MAGNITUDE DOES NOT VARY W/ THE SIZE (# MOLES OF MATERIAL) OF SYSTEM

Intensive variables:

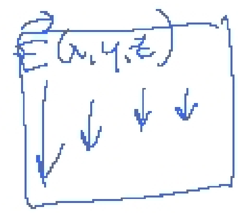
e.g., P, T:



CAN VARY POINT-TO-POINT IN SPACE:

ELECTRIC FIELDS:

$\vec{E} = \vec{E}(x,y,z)$



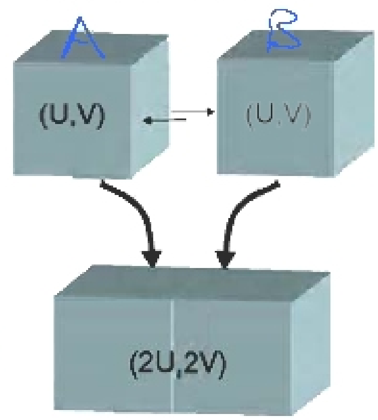
$T_{FINAL} = T_1$

  - **Extensive**

→ MAGNITUDE SCALES LINEARLY W/ THE SIZE OF THE SYSTEM

VOLUME, INTERNAL ENERGY, ENTROPY (S)

extensive variables:



$U_{TOTAL} = U_A + U_B = 2U$

- intensive and extensive variables form coupled pairs:

PHYSICS: INCREMENT OF WORK $= dW =$ [ENERGY] $= F \cdot dx$

'FORCE' (F) 'RESPONSE' (dx)

HYDROSTATIC WORK: $-PdV =$ [ENERGY]

  - 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

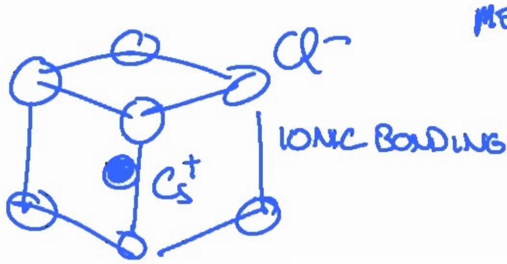
Components

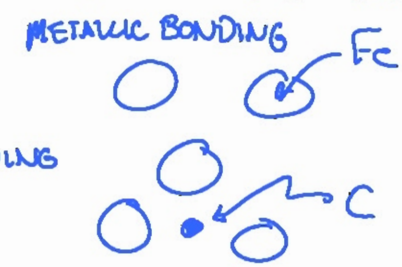
- The **components** are the irreducible molecules, compounds, or atoms that make up a system:

COMPONENTS MAY OR MAY NOT = ATOMS!

Example system	Class of material	Components	Class of components
STAINLESS STEEL	METAL ALLOY	Fe, Cr, C	ATOMS
CESIUM CHLORIDE	IONIC SOLID	CsCl	STOICHIOMETRIC COMPOUND
POLY (VINYL CHLORIDE)	POLYMER	POLYMER CHAINS	MACROMOLECULE
DIAMOND	COVALENT SOLID	C	ATOM

ASK: WHAT CAN I REMOVE FROM THE SYSTEM?





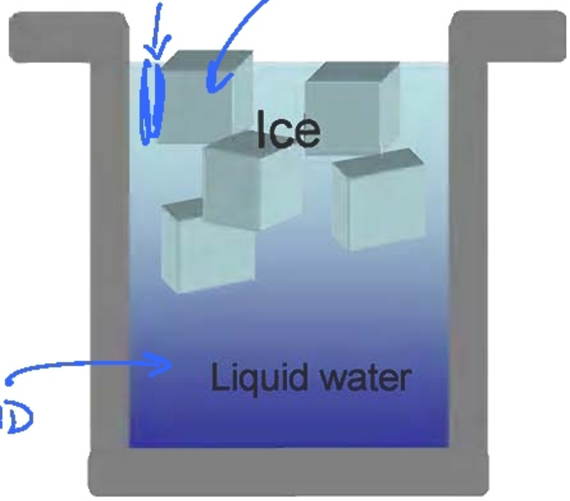
phases

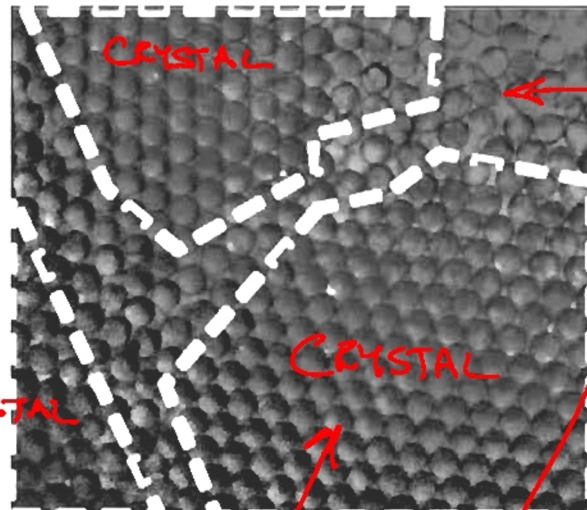
- **Phase:** A UNIQUELY IDENTIFIABLE FORM OF A MATERIAL, SEPARATED FROM OTHER FORMS OF THE MATERIAL BY AN IDENTIFIABLE INTERFACE

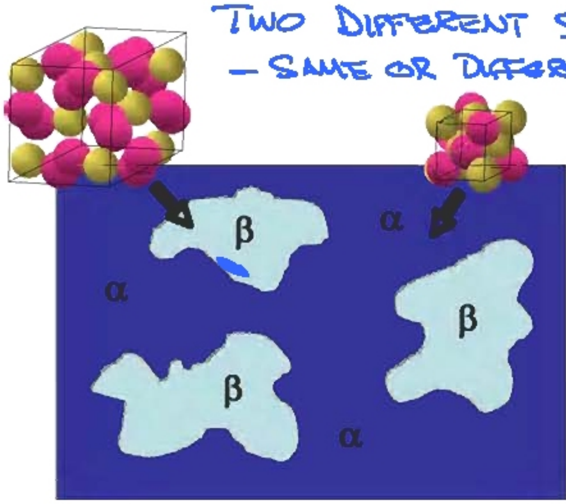
CRYSTALLINE : LONG-RANGE PERIODIC ORDER

AMORPHOUS : DISORDERED

  - examples:







TWO DIFFERENT STRUCTURES
– SAME OR DIFFERENT COMPOSITIONS → STRUCTURE ALONE CAN DEFINE A PHASE

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

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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.

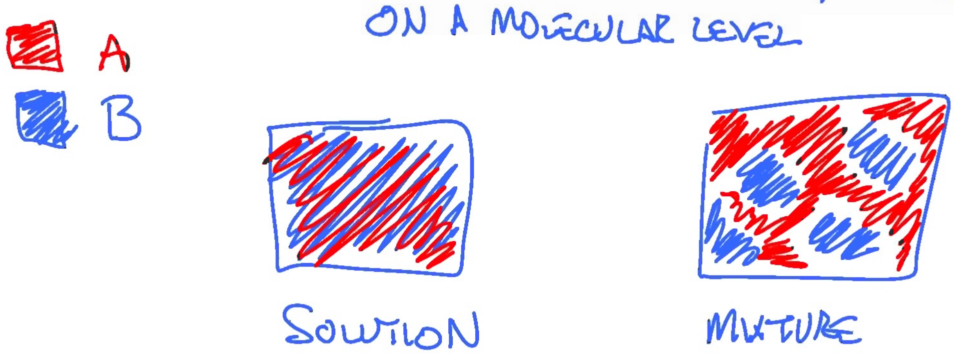
Figure removed for copyright reasons.

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

(Prof. Thomas' group: Bockstaller et al., *J. Amer. Chem. Soc.*, **125** (18): 5276-5277 2003)

(Mann[3]) calcium carbonate crystals stacked with interleaving protein layers

- A few other useful definitions:
  - **Mixture**: INHOMOGENEOUS MULTI-PHASE SYSTEM WHERE THE COMPONENTS ARE NOT MIXED ON A MOLECULAR LEVEL
  - **Solution**: HOMOGENEOUS SYSTEM; COMPONENTS ARE MIXED ON A MOLECULAR LEVEL

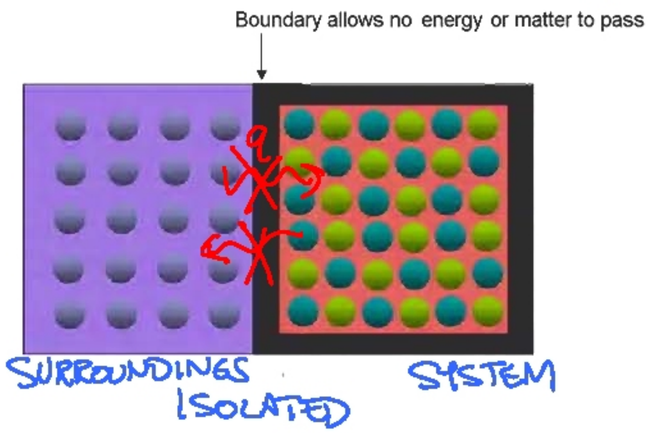


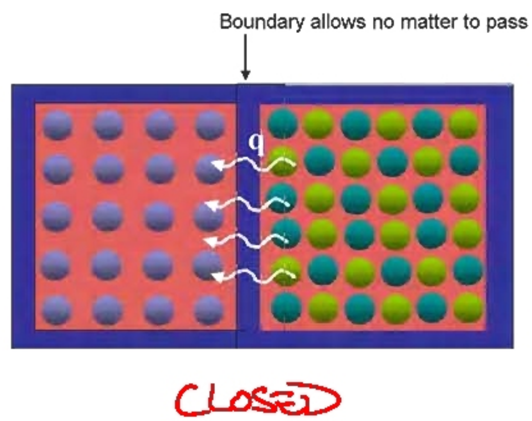
Thermodynamic systems

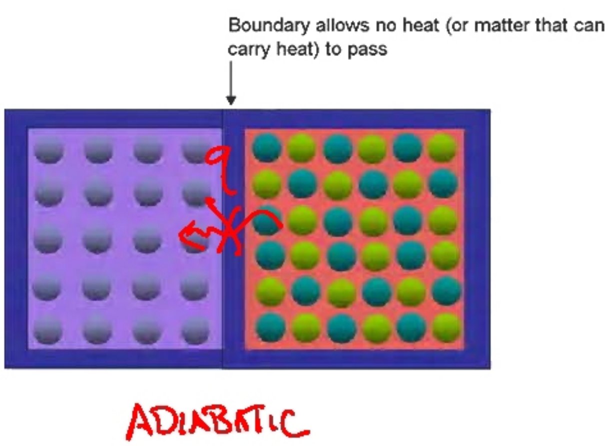
- Thermodynamic systems can have boundary conditions that limit the exchange of energy or atoms/molecules with their surroundings. Some of the types of systems one may be interested in for materials science and engineering problems include:

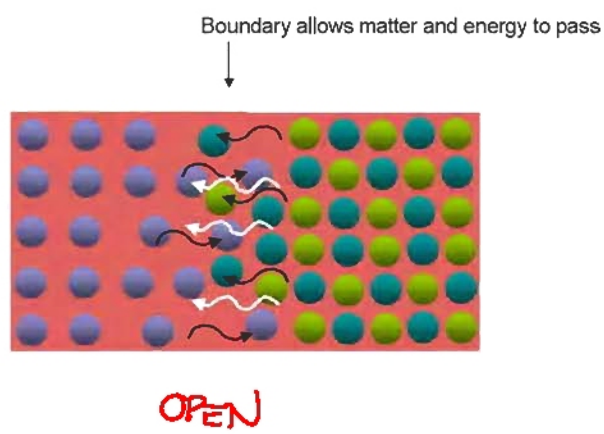
System	Boundary condition:
Isolated	NO ENERGY OR MOLECULES IN/OUT OF THE SYSTEM
Closed	NO MOLECULES IN/OUT
Adiabatic	NO HEAT IN/OUT
Open	MOLECULES OR ENERGY CAN PASS IN/OUT OF SYSTEM

ENERGY: 2 FORMS: HEAT = q WORK = W

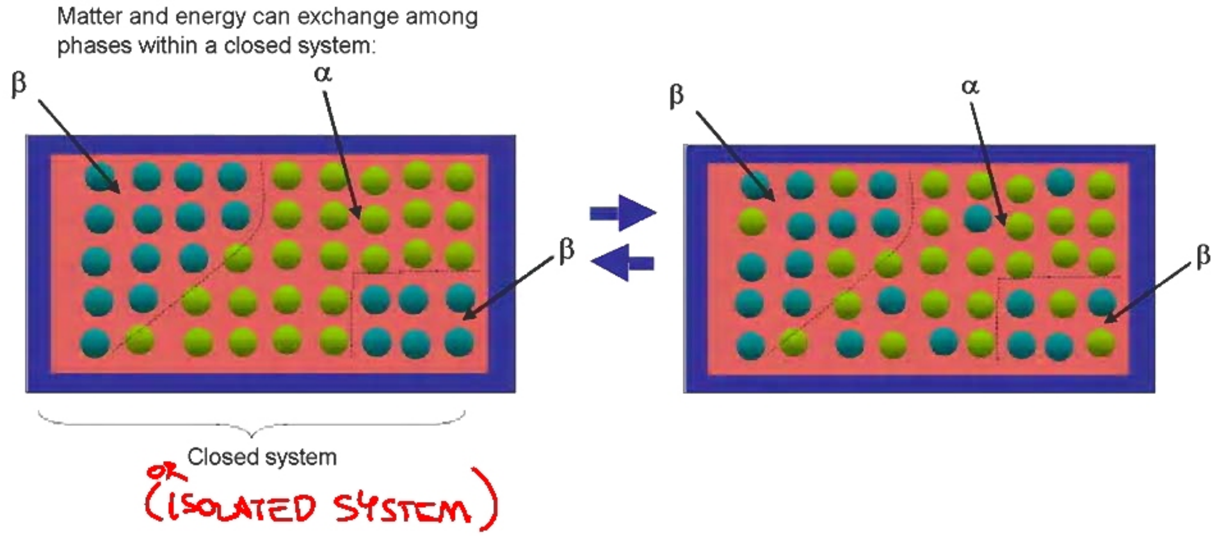








- In closed multi-phase systems, molecules and energy ***can*** be exchanged ***among phases within the system***:



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	PROCESS WHERE NO HEAT PASSES BOUNDARIES OF SYSTEM
Isochoric	PROCESS WITH NO VOLUME CHANGE
Isothermal	PROCESS WITH NO TEMPERATURE CHANGE
Isobaric	PROCESS AT CONSTANT P
Isobarothermal	PROCESSS AT CONSTANT T, P

→ CORRECT IDENTIFICATION OF PROCESS ALLOWS SIMPLIFICATION OF THERMODYNAMIC EQUATIONS

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: CLOSED

   Process: ISOBAROTHERMAL

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

   Type of System: OPEN

   Process: ISOBARIC

Reversible and Irreversible Processes

Reversible Processes

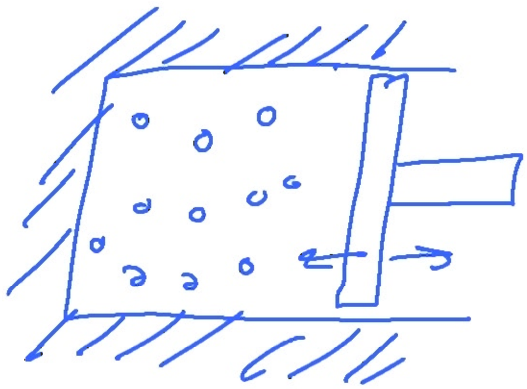
- Reversible processes are idealized processes that:

FRICTION
VISCOSITY
ELECTRICAL RESISTANCE
↑ ⋮

① SYSTEM IS ALWAYS IN EQUILIBRIUM
② HAVE NO DISSIPATIVE PROCESSES
(PROCESSES WHERE ENERGY AS HEAT TO SURROUNDINGS!)

occur "forward" or "backward" ***with no change in the surroundings***

- Examples:



FRICTIONLESS PISTON
↓
MOVING ∞-SLOWLY SO THAT GAS IS ALWAYS IN EQUILIBRIUM

Irreversible processes

- Natural processes typically occur in only 1 direction spontaneously

  ESSENTIALLY ALL REAL PROCESSES

  - These are *irreversible* processes

Experiment	Process	Observation of irreversibility
Add a drop of food coloring to a glass of water	• DIFFUSION	DROPLET NEVER REFORMS
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

2ND LAW: ENTROPY OF UNIVERSE MUST INCREASE:

↓

REVERSAL OF THESE PROCESSES WOULD LOWER ENTROPY!

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* (2002).