Lecture 1: 09.09.05 Introduction to fundamental concepts

Today:

Reading: Engel and Reid: 1.1, 1.2

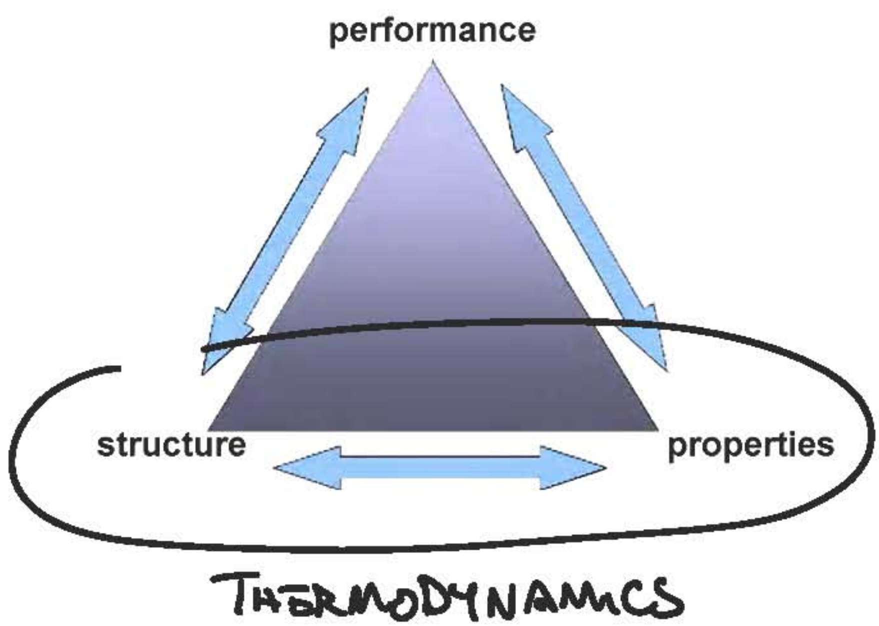
Supplementary Reading: H.A. Bent, *The Second Law*, pp. 1-5

ANNOUNCEMENTS: PROBLEM SET 1 POSTED TODAY
DUE: 09.20.05 (WEEK FROM MONDAY)

Thermodynamics as a basic tool for materials science & engineering

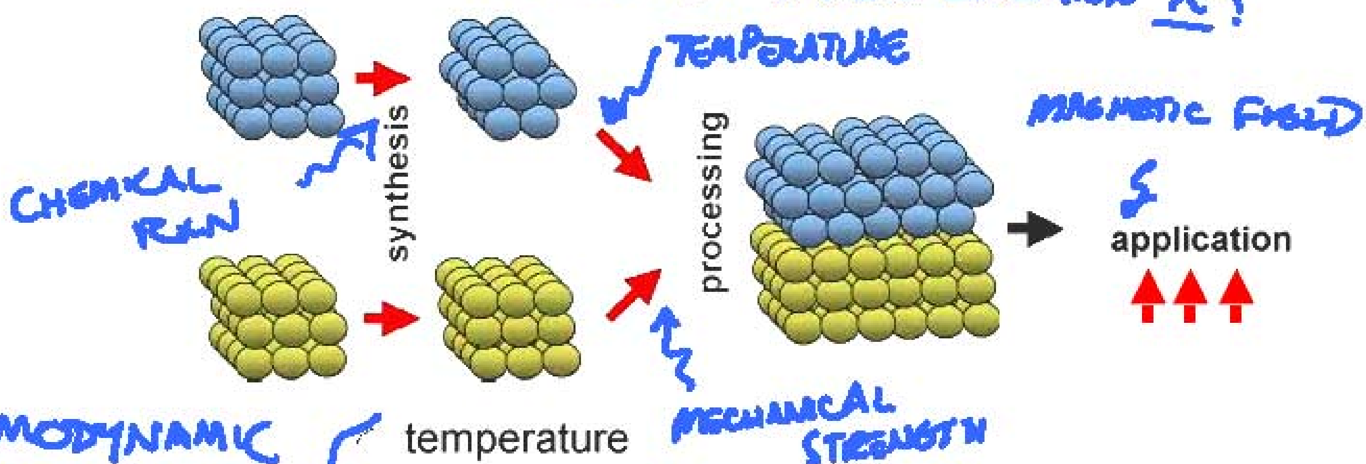
Thermodynamic forces and materials

- Materials scientists seek to tune the structure and synthesize materials with properties that provide optimum performance in every type of materials application – the structure-properties-performance triangle



- In order to design materials with optimum performance in various applications, we need to know how properties change in response to their environment
    - These responses determine how we can synthesize/fabricate materials, build devices from materials, and how the devices will operate in a given application:
        - Raw materials –(synthesis, processing, fabrication)-> final devices
        - Materials are exposed to a variety of forces (mechanical, chemical, electrical, magnetic, etc.) during synthesis, processing, and in their final applications

2 QUESTIONS: (1) HOW DO I ACHIEVE A CERTAIN STRUCTURE THROUGH PROCESSING?
(2) WHAT WILL HAPPEN UNDER CONDITION X?



THERMODYNAMIC FORCES 'INPUTS' →

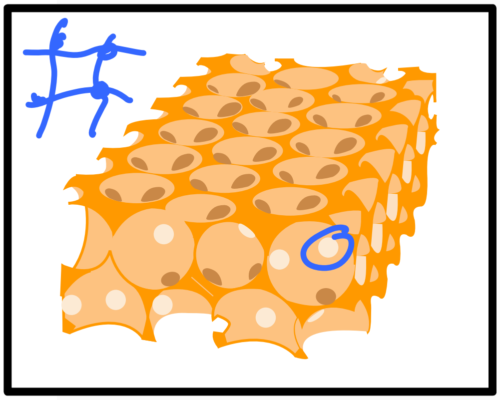
temperature	
Mechanical stress	concentration gradients
Chemical reaction	intermolecular forces
Electric fields	surface forces
Magnetic fields	etc.

RESPONSE?

CHANGES IN STRUCTURE (PHASE)
VOLUME
CHEMICAL SPECIES PRESENT
⋮

An example: Drug delivery materials that respond to pH:

- The images below show optical micrographs of pH-responsive microporous hydrogels which were fabricated in the Irvine laboratory to have the 3D structure illustrated at left:



COLLAPSE SWELLS

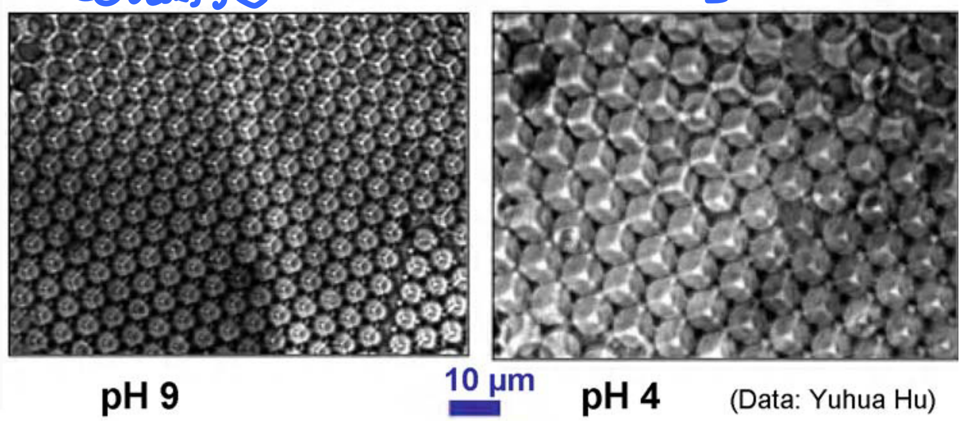


Figure by MIT OCW.

- The gels contain pH-sensitive amine groups that protonate at reduced pH. How does charging of the gel control swelling? What controls the swelling/collapse of these materials? These are questions we can answer qualitatively and quantitatively using thermodynamics.
    - A thermodynamic driving force called the ***chemical potential*** (which will be a major player in our studies this term) drives water into/out of the gel: μ

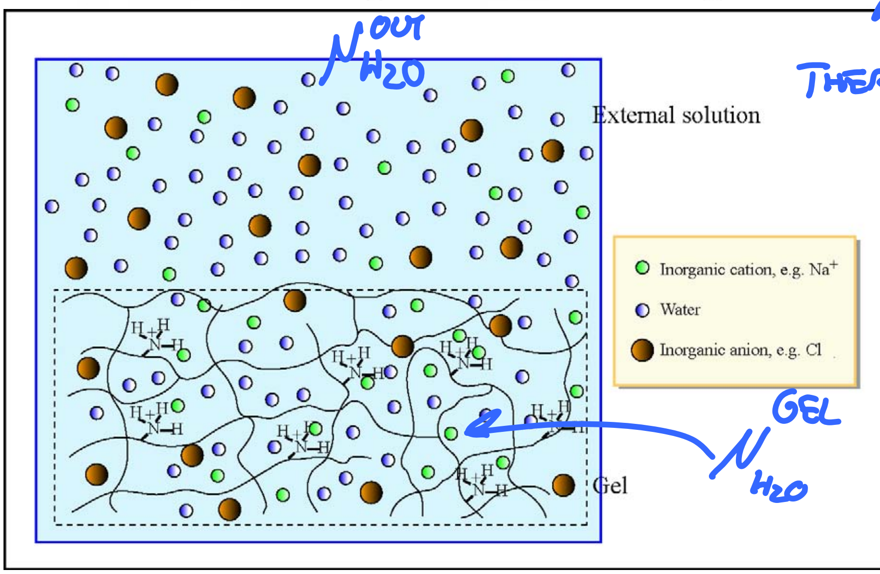


Figure by MIT OCW.

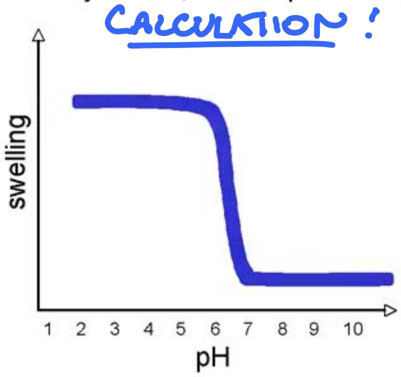
THERMODYNAMIC FORCES

$\mu_{H_2O}^{GEL} < \mu_{H_2O}^{OUT}$

... H_2O DRIVEN INTO GEL → SWELLING!

- Using thermodynamics, we can predict how these gels should swell:

CALCULATION!



- This is a qualitative sketch of a theory developed by Nicholas Peppas[1]- who was a graduate student at MIT! (This is an advanced calculation, but one which you will have the basic tools to understand by the end of the term.)

What is thermodynamics?

2 points of view

- Thermodynamics provides the theory to understand how materials respond to all types of forces in their environment- including some forces you may have not thought about or recognized as 'forces'. We will introduce two different points of view during this term:

Classical thermodynamics

- *Classical Thermodynamics* is the theoretical framework to understand and predict how materials will tend to change *internally* in response to forces of many types on a **macroscopic** level.

– 4 LAWS DICTATE RESPONSES

– DOES NOT RELY ON A MOLECULAR-LEVEL UNDERSTANDING OF A MATERIAL

"[Thermodynamics] is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never be overthrown." — Albert Einstein

Statistical mechanics

- Statistical mechanics (or statistical thermodynamics) is the calculation of thermodynamic properties starting from molecular models of materials- either simple lattice models or quantum mechanical models.

– QUANTUM MECH. (OR COARSE-GRAINED) MOLECULAR MODELS AND MAKE PREDICTIONS OF THERMODYNAMIC PROPERTIES

– (STILL OBEY 4 LAWS!)

- **Why 2 approaches?**
  - Useful in different applications

CLASSICAL: GENERALLY APPLICABLE TO ALL MATERIALS, BUT OFFERS NO MOLECULAR-LEVEL INSIGHT

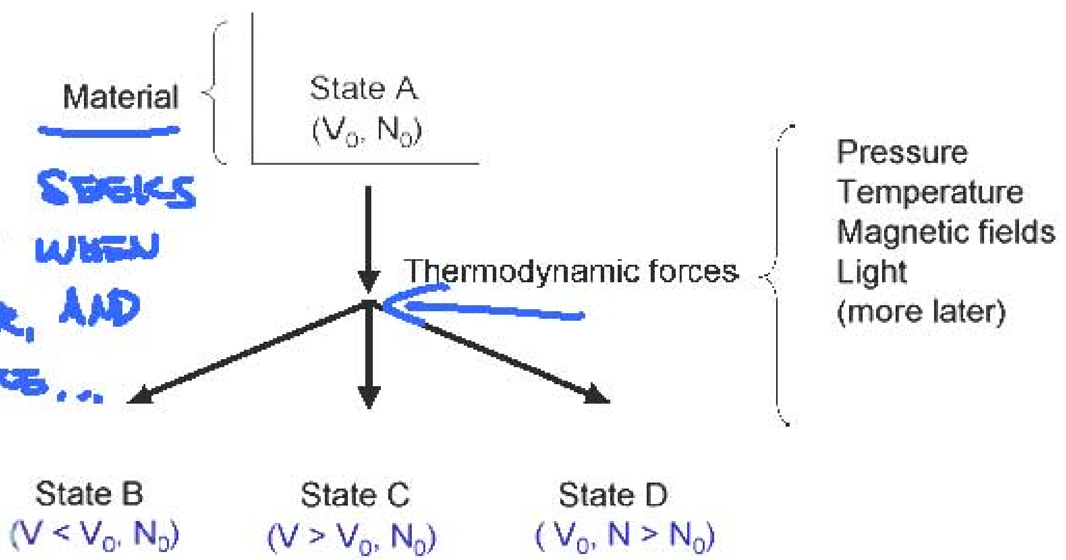
STAT MECH: UNDERSTAND THE ROLE OF MOLECULAR DETAILS, BUT LIMITED TO SIMPLE PROBLEMS, AND APPROXIMATIONS

Changes of state and equilibrium

A sentence of new concepts

- Thermodynamics is concerned with predicting the ***state*** of materials at **equilibrium** using thermodynamic functions, particularly **internal energy**, **entropy**, and **free energy**.

  - **State**
    - A unique set of values for the variables that describe a material on the macroscopic level.
      - For example:
    - The molecules in materials heat up, react, rearrange, change shape, form and break bonds with one another, and undergo myriad other changes in response to changes in their environment. ***The changes in macroscopic properties that occur due to these internal molecular interactions are changes in the state of the material.***



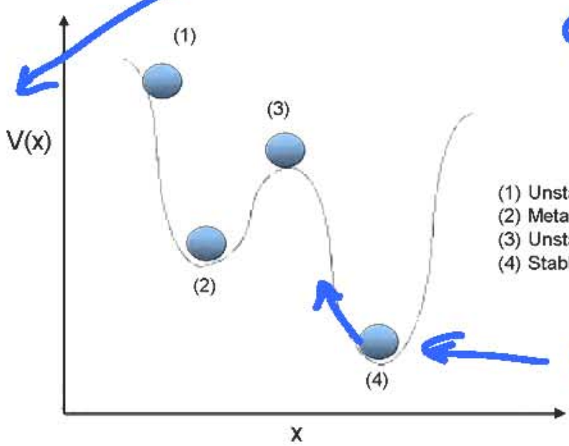
- Let's continue to define a few key terms, as a brief introduction to the concepts we will focus on for much of the term:

Equilibrium

- Equilibrium is defined as ***a state from which a material has no tendency to undergo a change.***
- Analogy to potential energy: a ball rolling on hills and valleys:

U INTERNAL ENERGY

G FREE ENERGY



(1) Unstable state - system is actively tending toward a new equlibrium state
(2) Metastable equilibrium state - system can change to a lower total energy state
(3) Unstable equilibrium state - any perturbation will cause the material to change to a new equilibrium state
(4) Stable equilibrium state - material does not change its state in response to small perturbations

STABLE EQUILIBRIUM STATE

- We will return to define the different types of equilibrium states in mathematical terms later in the term.
- In physics, you learn that stable mechanical equilibrium is achieved when the potential energy is at its lowest level- when the potential energy is minimized. Similar ***extremum principles*** will come into play in reaching internal equilibrium in materials- we may look for the maximum or minimum of a thermodynamic function to identify equilibrium states.

Internal energy (U)

- ***Internal energy is a quantity that measures the capacity to induce a change which would not otherwise occur.***
- In freshman physics you learned:

$$E_{TOTAL} = V + KE + U$$

V: POTENTIAL ENERGY OF POSITION; KE: KINETIC ENERGY; U: INTERNAL ENERGY

U ⇒ ENERGY STORED WITHIN A MATERIAL: IN BONDS, VIBRATIONS, IN MAGNETIC MOMENTS, IN POLARIZATION

- Internal energy in a material is 'stored energy'- energy is transferred to a material via all the possible forces that act on it- pressures, thermal energy, chemical energy, magnetic energy, etc.- and is stored within the random thermal motions of the molecules, their bonds, vibrations, rotations, and excitations.

TYPICAL THERMO CALC: $\Delta E_{TOTAL} = \Delta V + \Delta KE + \Delta U$ ($\Delta V \to 0$, $\Delta KE \to 0$)

$\Delta E = E_{FINAL} - E_{INITIAL}$

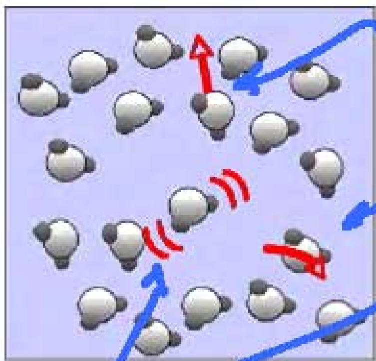
Entropy (S)

- Entropy is a non-intuitive but absolutely critical parameter of materials- along with the more common extensive parameters like volume and number of molecules. We will introduce a rigorous thermodynamic definition for entropy in the coming lectures, but let's start with a conceptual interpretation of entropy to aid in our grasp of what entropy is:

ENTROPY IS AN INDEX OF # WAYS A MATERIAL HAS TO STORE ENERGY

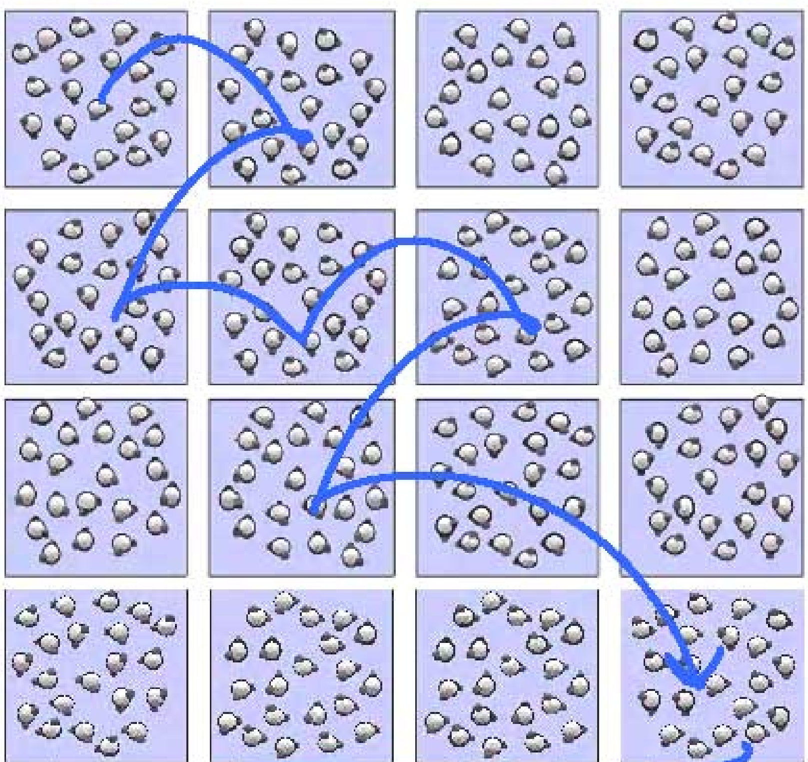
- Suppose we consider a glass of water:

A snapshot of the molecules in our glass of water at one instant:



The ~10^{23} individual ***molecular*** details (position, velocities, states of vibration) of each water molecule together give rise to a ***macroscopically*** observed (T, P, V)

...AT FINITE TEMPERATURE: MANY SNAPSHOTS (MICROSTATES) ARE EVOLVING IN TIME



$\Omega\uparrow$ THEN $S\uparrow$

The 2nd law of thermodynamics:
The system is equally likely to be in any of the ***possible*** microstates (consistent with the macroscopic (T,V,P).

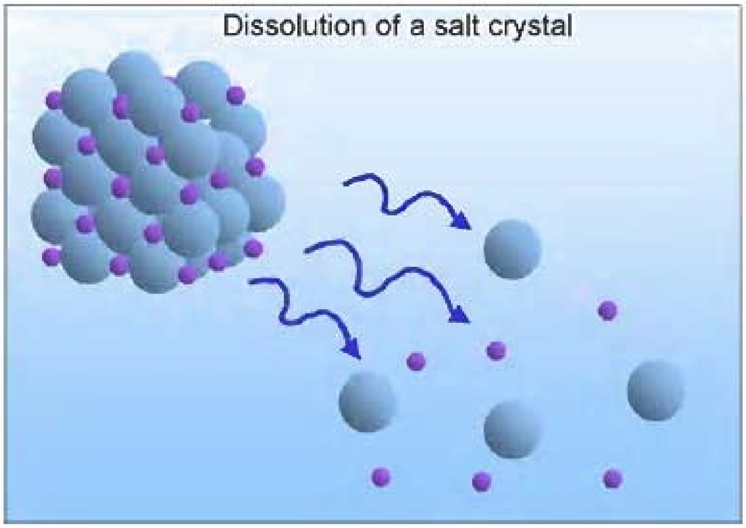
$$S = k_b \ln \Omega$$

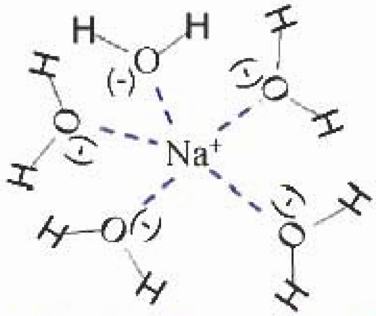
(k_b: BOLTZMANN CONSTANT)

The balance between internal energy and entropy determines the behavior of real systems

- If I drop a crystal of table salt (NaCl) into a beaker of pure water, the salt will dissolve quite rapidly. It is equally common experience that once dissolved, the salt crystal will never spontaneously re-form- even though the bonding energy between ions in the crystal would be quite strong. This is common knowledge, but why should it happen?

BONDING ENERGY: ~787 kJ/mole

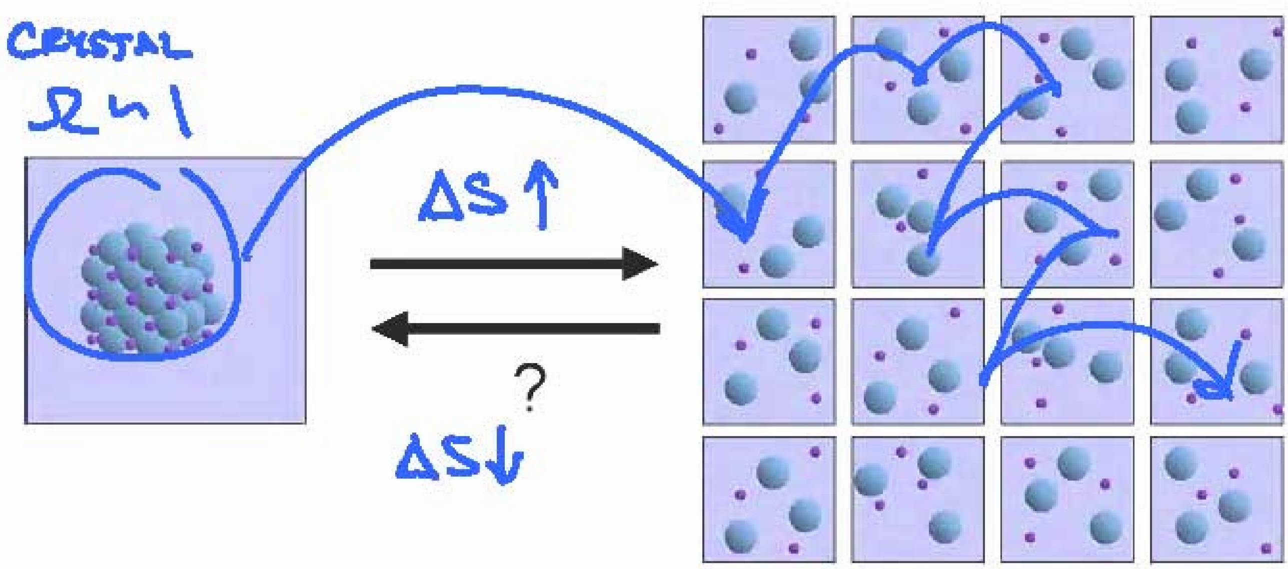




ENERGY ~342 kJ/mole DISSOLVED IONS

- So what drives the dissolution and non-resolidification of this crystal in water? The answer is that dissolution increases the entropy of the system, while resolidification would decrease the entropy:

Ω = A VERY VERY VERY VERY BIG #



- There are many cases when the increase in entropy occurring for a given process is not obvious, but for any spontaneous process ever analyzed, entropy increases have been found.

- On a molecular level, once the atoms are released from the crystal, their thermal energy will scramble them thoroughly (and randomly) through the solution- and because this thermally-driven process is random, it *extremely* unlikely that it will ever randomly reverse. **Finding the balance between energies (like bonding between molecules, or forces induced by an electric field) and entropy (random thermally-induced disorder) is what defines equilibrium states.**

The connection between energies, entropy, and equilibrium: thermodynamics is governed by thermodynamic laws.

- There are **4** thermodynamic laws in total, but the 2 most practically important laws, which will use thoughout the term, can be summarized as follows:

FIRST LAW: ΔU = (work in/out) + (heat in/out)

SECOND LAW: The entropy of the universe increases in any spontaneous process.

- THE LAWS HAVE NEVER BEEN PROVEN, ONLY NEVER DISPROVEN
- THE LAWS PROVIDE A DESCRIPTION OF HOW UNIVERSE WORKS, NOT AN EXPLANATION

So what's fundamental about it?

- Thermodynamics has many practical uses. It provides the theory to answer the following sorts of practical materials questions:[2]

Thermodynamics in Materials *Science*

- Thermodynamics explains many phenomena in the natural world:

  - HOW DO I FORMULATE PREDICTIONS FOR A MATERIAL'S BEHAVIOR?
  - WHAT PROCESSES MAKE A MATERIAL UNSTABLE?
  - WHAT'S THE MAX VALUE A PROPERTY CAN TAKE?

- …and it continues to be a fundamental part of new materials discoveries.

Thermodynamics in Materials *Engineering*

- The interpretation of a material's response to the forces in its environment is the basis of many technologies. Some examples:

Thermodynamic Driving Force:	Technology Based Upon It:
Temperature	internal combustion engines, phase change materials
Electrostatic potential	batteries, dielectrics
Mechanical stress	All materials for load-bearing and structural applications
concentration gradients	dialysis systems
Chemical reactions	corrosion-resistant materials, batteries
Electric fields	piezoelectric materials
surface forces	engineered crystals and composites
Magnetic fields	disk drives and magnetic storage materials

A conceptual roadmap

- Road map of the thermodynamics component:

Lectures	Topic	What are we after?
1-2	Basic concepts for thermodynamics	DEFINITIONS, HOW DO WE DESCRIBE MATERIALS
3-7	The first law, work, and heat	ΔU = (WORK) + (HEAT) HEAT ⟷ T ⟷ ENTROPY
8-14	The second law and free energy at equilibrium	HOW DO PREDICT SPONTANEOUS CHANGES?
15-20	Phase diagrams and thermodynamics of solutions	DETERMINING STABLE FORMS OF MATERIALS
21-24	Introduction to statistical mechanics, microscopic models of materials	HEAT ⟷ T ⟷ ENTROPY MICROSCOPIC VIEWPOINT!

Thermodynamic variables, systems, and functions

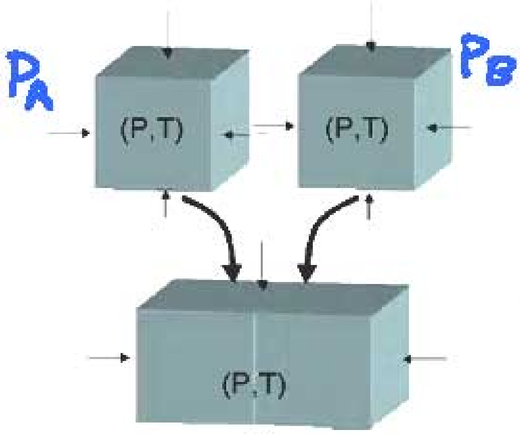
Thermodynamic Variables

- Remember that classical thermodynamics is concerned with macroscopic properties

  MACROSCOPIC VARIABLES: P, V, T, n ...

- 2 types of variables
  - **intensive** → MAGNITUDE DOES VARY W/ THE SIZE OF SYSTEM

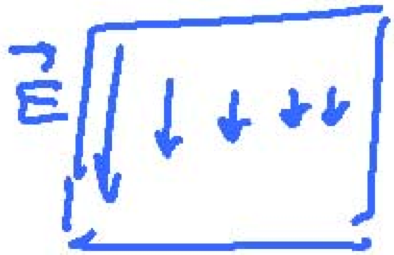
Intensive variables:



$P_{final} = P_A = P_B$

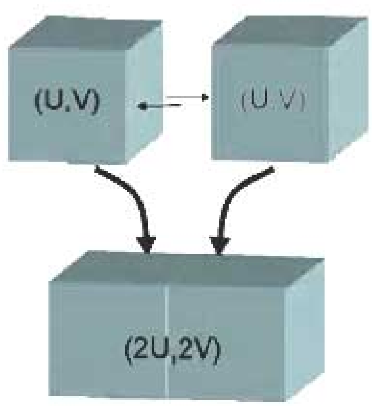
...BUT CAN VARY IN SPACE FROM POINT TO POINT:

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



  - **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***

References

1. Peppas, N. A. & Brannon-Peppas, L. Equilibrium swelling of pH-sensitive hydrogels. Chem. Eng. Sci., 715-722 (1989).
2. Carter, W. C. (2002).