MSE421
Exercise Session 1

07.03.2024

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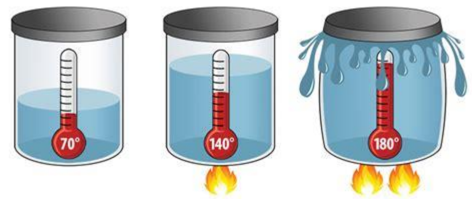
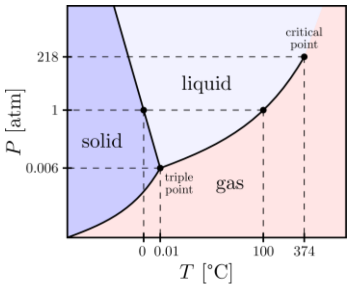
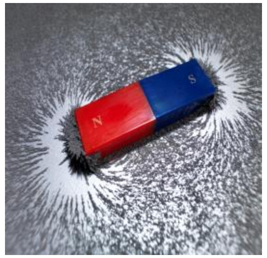
1. What is the most central concept in thermodynamics?
2. What have been the most important ideas during Monday’s lecture?

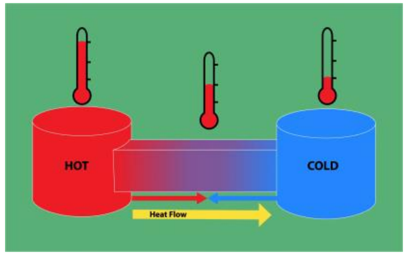
Goal of Statistical Mechanics

Macroscopic World









Entropy and Free energies:

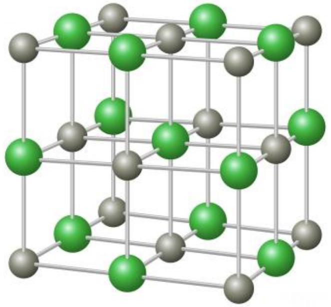
$G = H - TS$

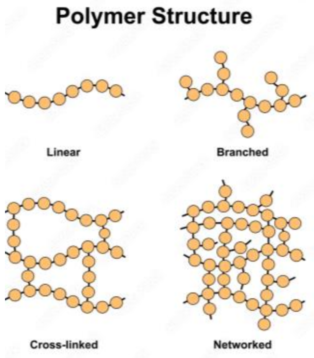
$A = E - TS$

Thermo-dynamics

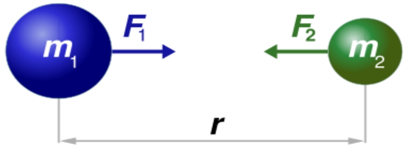
StatMech

Microscopic World

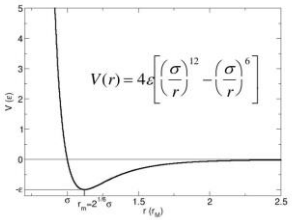




Atoms, potentials, forces



Lennard-Jones potential



Mechanics

Structure of this Course

Preparation
Weeks 1-2

- Thermodynamics
- Probability Theory

Foundations
Weeks 3-6

Applications
Weeks 7-14

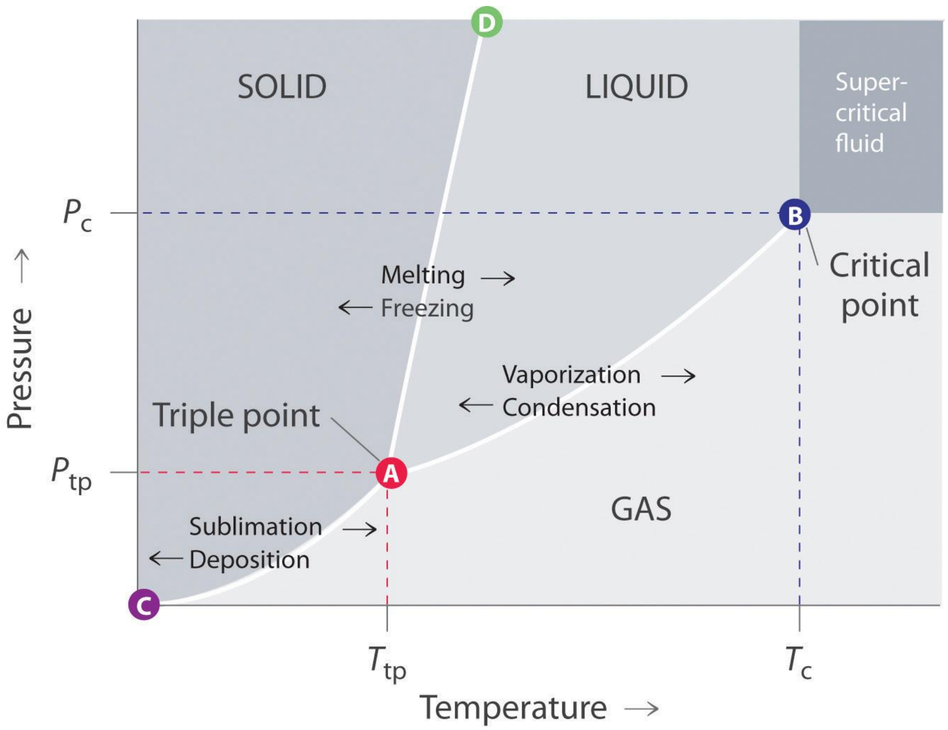
- Solids (Phonons and Electrons)
- Phase Transitions and Magnetism
- Liquids
- Polymers

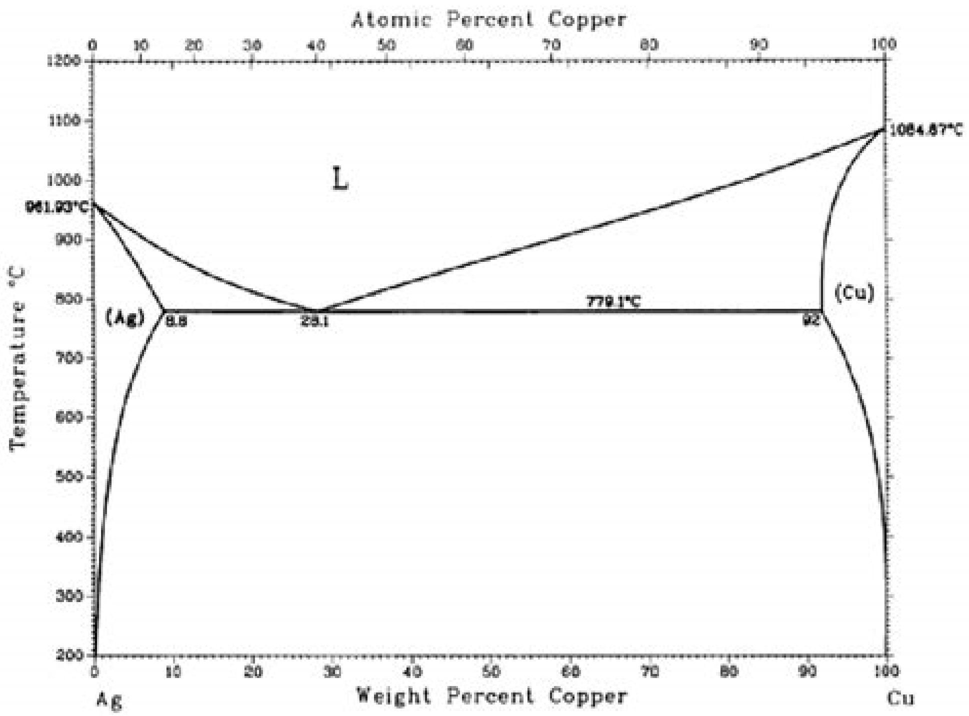
What is the most fundamental concept in thermodynamics?

Some Questions that can be answered by (equilibrium) thermodynamics:

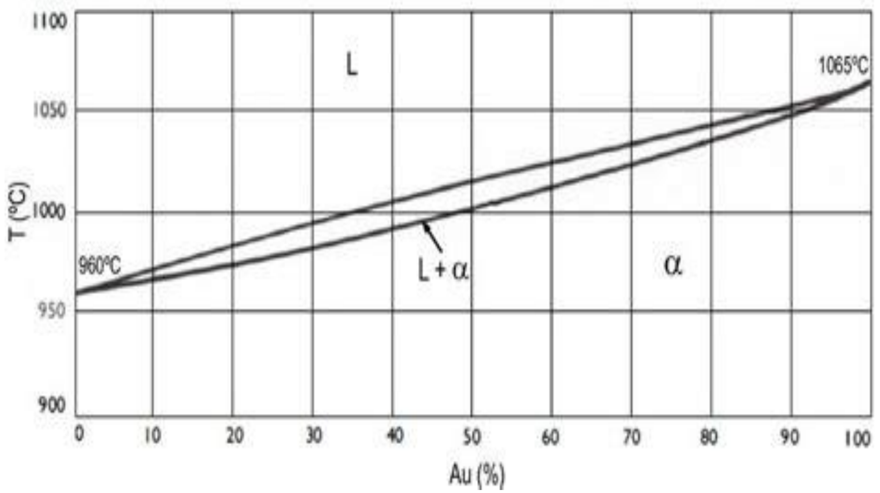
- Phase transitions:
  - Why and at which temperature does a material melt?
  - Which compositions of the binary Ag-Au system can exist?
- Reactions:
  - For a chemical reaction A+B=C, what is the reaction constant?
  - Why is material A more corrosion resistant than material B?
- Material constants:
  - How does the volume of a material depend on temperature and pressure?
  - Why are some materials magnetic, while others aren’t?

Phase Diagrams



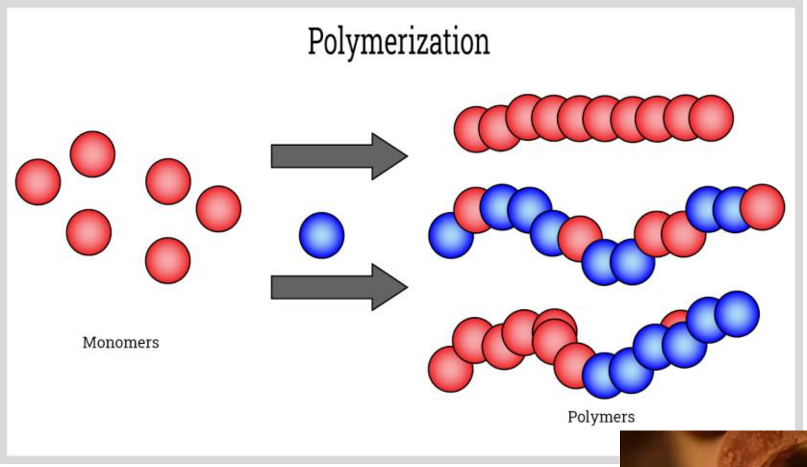


Ag-Cu (top) vs Ag-Au (bottom)

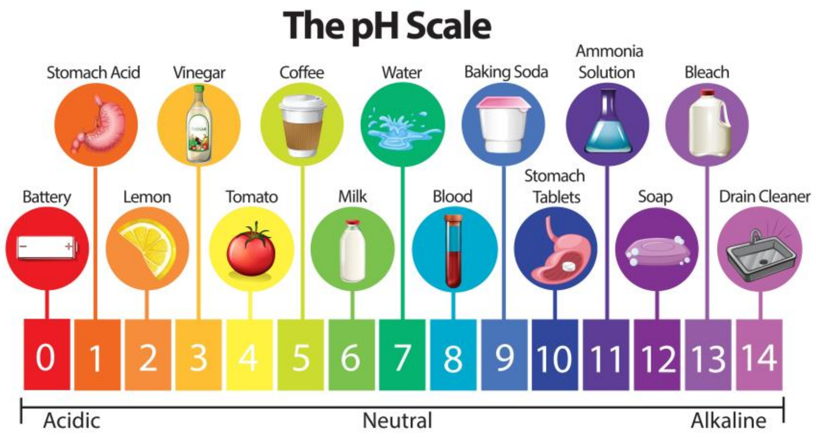


Reactions

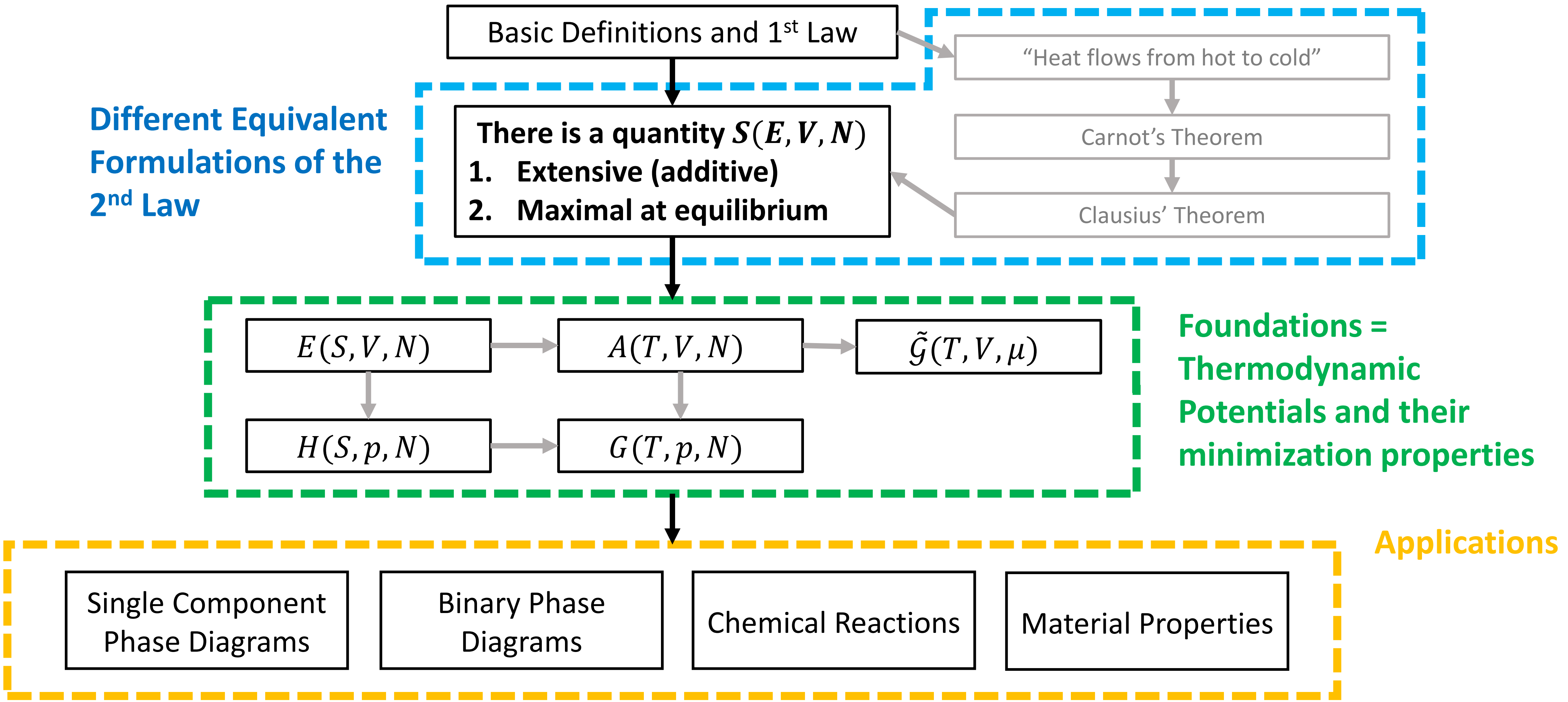

A + B A B
A B A + B
A B + C A C + B
A B + C D A D + C B


Polymerization
Monomers
Polymers


CORROSION


The pH Scale
Stomach Acid
Vinegar
Coffee
Water
Baking Soda
Ammonia Solution
Bleach
Battery
Lemon
Tomato
Milk
Blood
Stomach Tablets
Soap
Drain Cleaner
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Acidic
Neutral
Alkaline

Mathematical Structure of Thermodynamics



Entropy in Statistical Mechanics

Main result

$$S(E, V, N) = k_B \log \Omega(E, V, N)$$

where Ω is the number of possible microstates of the system for a given total energy E.

The entropy is an extensive quantity that is maximal at equilibrium.

Why do we work with G instead of S?

Ideal gas law

$$pV = Nk_BT$$

If T, V, N are the primary variables: $p = \frac{Nk_BT}{V}$

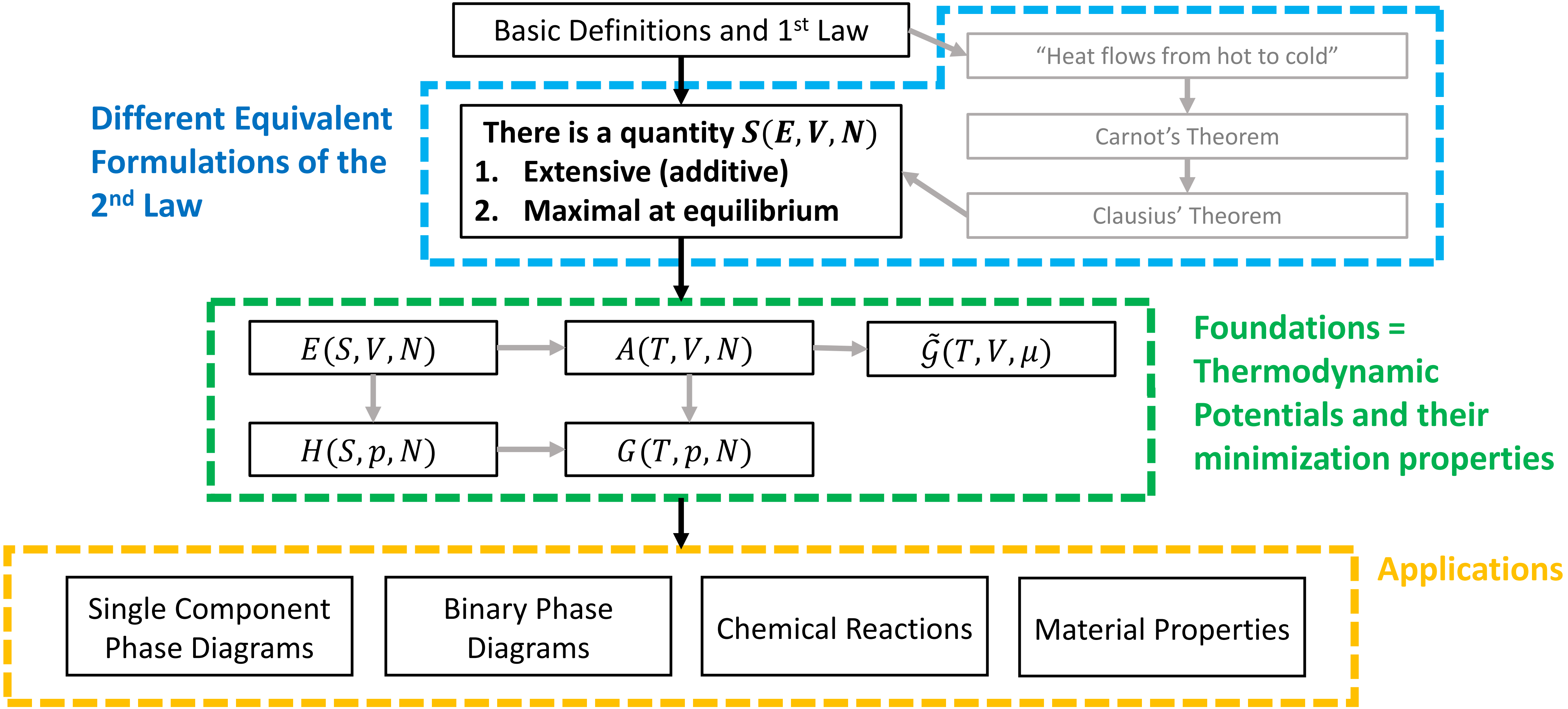
If T, p, N are the primary variables: $\mathrm{V} = \frac{Nk_BT}{p}$

Why do we work with G instead of S?

Minimization / maximization theorems depend on primary variables!

- If E, V, N are fixed (isolated system): S is maximal
- If T, V, N are fixed: Helmholtz free energy $A = E - TS$ is minimal
- If T, p, N are fixed: Gibbs free energy $G = E - TS + pV$ is minimal
- If S, V, N are fixed: internal energy E is minimal
- If S, p, N are fixed: enthalpy H is minimal
- If $\mathrm{T}, \mathrm{V}, \mu$ are fixed: grand canonical potential Ξ is minimal

Mathematical Structure of Thermodynamics



Problem Set 1

Exercise	Topic	Exam Questions
1	Stirling formula Visualization	3
2	Stirling formula applied to Combinatorics	3
3	Microcanonical Ensemble	2 and 5

Stirling formula

Usual form $\log n! \approx n \log n - n$

Common form in statistical mechanics: $\binom{n}{k} = \frac{n!}{k!(n-k)!}$

And hence

$$\log \binom{n}{k} = \log \left(\frac{n!}{k!(n-k)!} \right) = \log n! - \log k! - \log(n-k)!$$

Applying Stirling gives

$$\log \binom{n}{k} \approx n \log n - k \log k - (n-k) \log(n-k)$$

Recipe for Microcanonical Ensemble

Step 1: Calculate $\Omega(E, N, V)$

Step 2: Calculate $S(E, N, V) = k_B \log \Omega(E, N, V)$

Step 3: To get the temperature, use (hint: second version is nicer)

$$\frac{1}{T} = \frac{\partial S}{\partial E} \qquad \beta = \frac{1}{k_B T} = \frac{\partial \log \Omega}{\partial E}$$

Step 4: Solve the equation for the energy E to get $E(T, N, V)$

Step 5: Calculate other quantities of interest, such as $C_V = \frac{\partial E}{\partial T}$ etc.