PhaseBook-Introduction to structure, symmetry, EOS & Phase Diagrams

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Pure substance approximation

- Chemical composition is "same" in the system under study

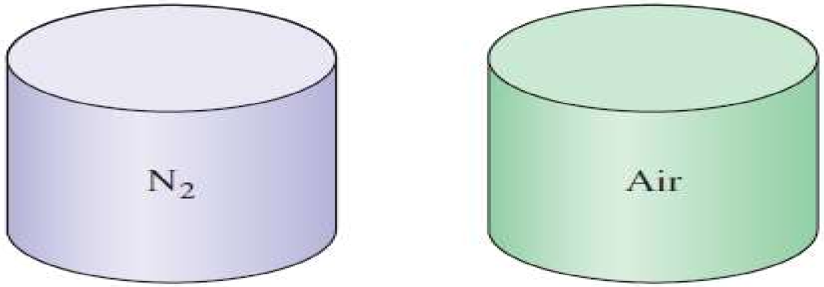


FIGURE 3–1
Nitrogen and gaseous air are pure substances.

Figs: Cengel & Boles

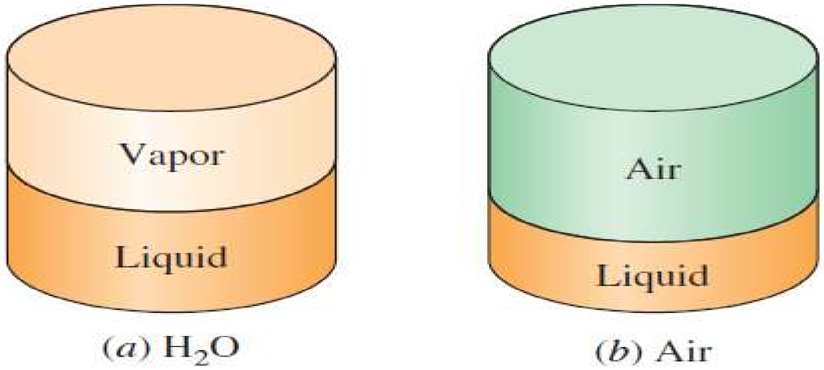


FIGURE 3–2
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

- In practice, "pure" depends on properties & processes that are studied
- Gas separation (for e.g. CO_2 separation) by liquefaction: Is air pure?
- Compositions can be different at the surface, but if bulk properties are only important…Radiation Thermodynamics & Nuclear isotopes…

"Structure"-property correlations

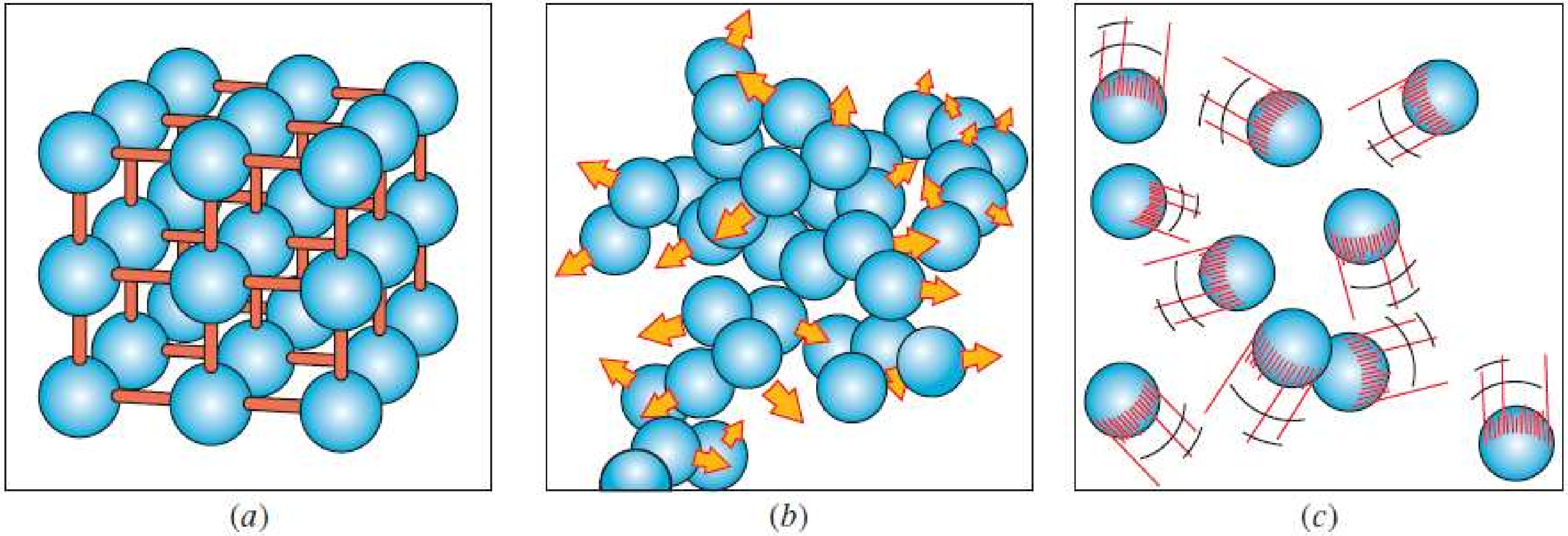
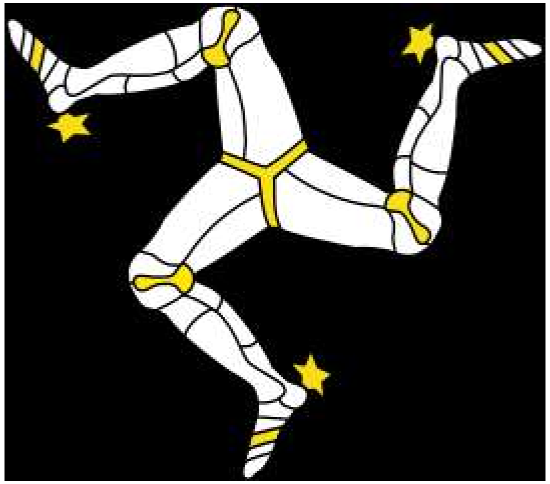
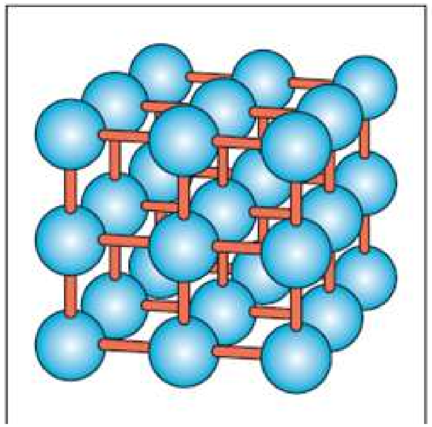
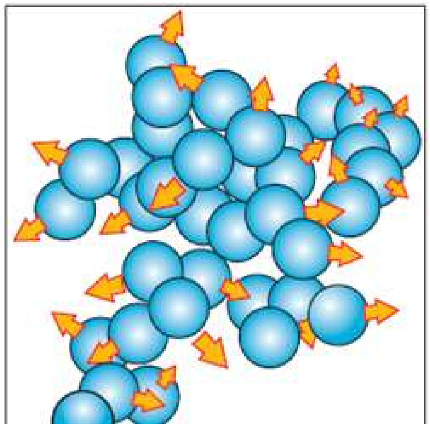
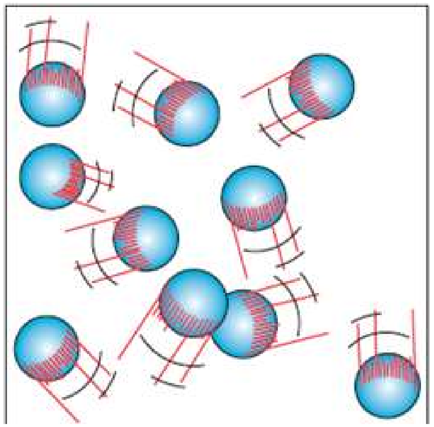


FIGURE 3–4
The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

- What makes gases ideal?
- "Ideal solids", not just ideal gases
- What can make solids ideal?
- Despite strong interactions, solids can be discussed via an "unit cell"
- There are no "ideal liquids"; Why?

Structure & “Symmetry”

- How do we describe structure beyond a high-school description?
- Which is more symmetric: Crystalline solid or gas?
- Solid (fluids) has discrete (continuous) translational symmetry
- Continuous translational symmetry is “broken” to discrete in solids
- Greater the number of symmetry operations=Greater symmetry

Figs: ebook- https://en.wikipedia.org/wiki/Symmetry; Cengel & Boles

Structure, Symmetry and the EOS

- Symmetry & structure determines Equation of State (EOS)
- Ideal gas EOS: PV=RT (no structure)
- Van der waals EOS for non-ideal gas incorporates finite atomic "size":

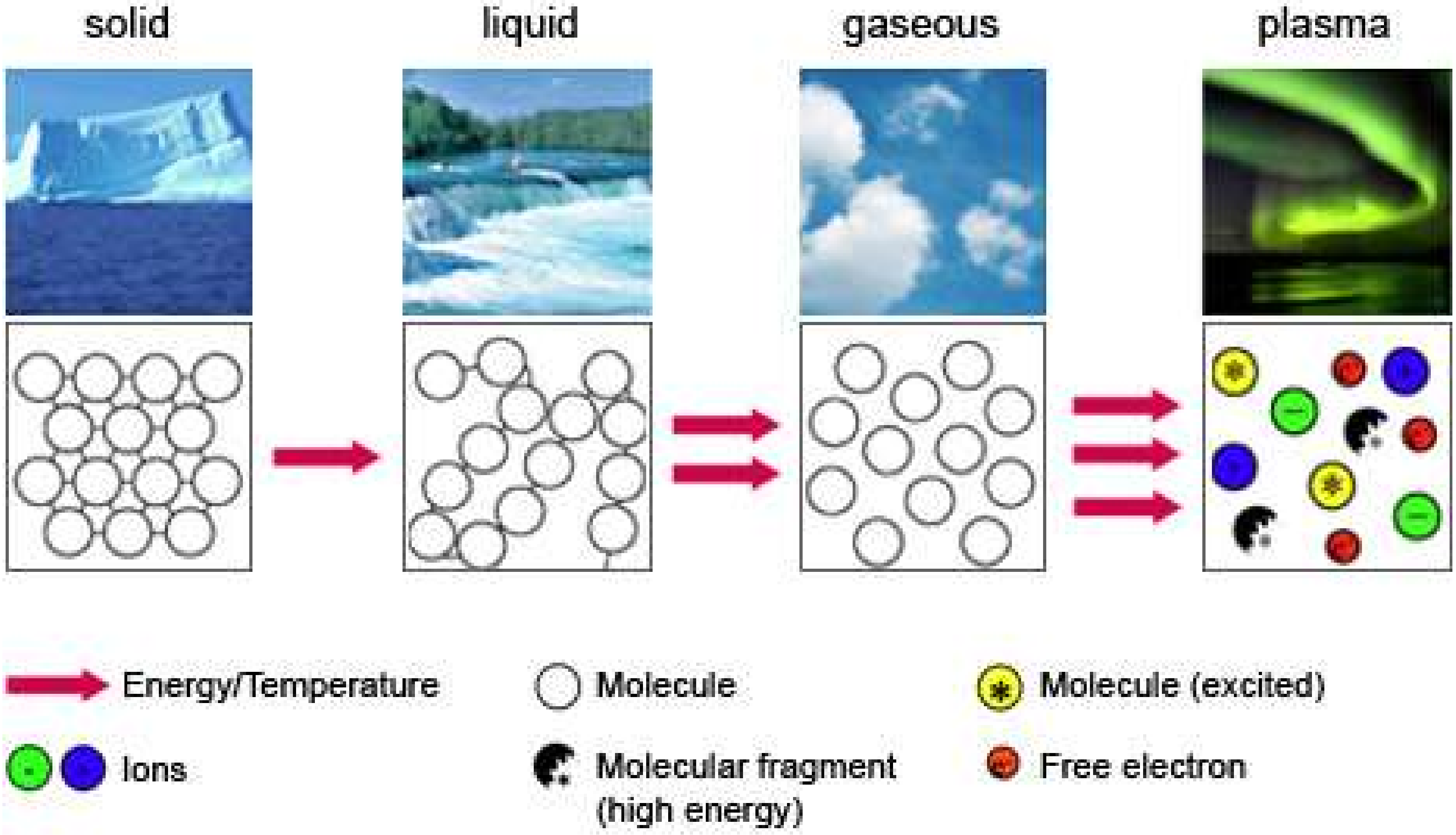
$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

- EOS (Murnaghan) for condensed matter: $\boldsymbol{P(V) = \frac{K}{K_0}\left[\left(\frac{V}{V_0}\right)^{K_0} - 1\right]}$

$\boldsymbol{K_0}$=Modulus of incompressibility at ambient pressure

- More symmetric structures(like fluids) have more isotropic material properties; Isotropic =No directional dependence
- Beyond descriptive/qualitative words from high school, symmetry can be quantified by mathematical theory of point & space groups
- EOS determines material's thermodynamic properties & processes

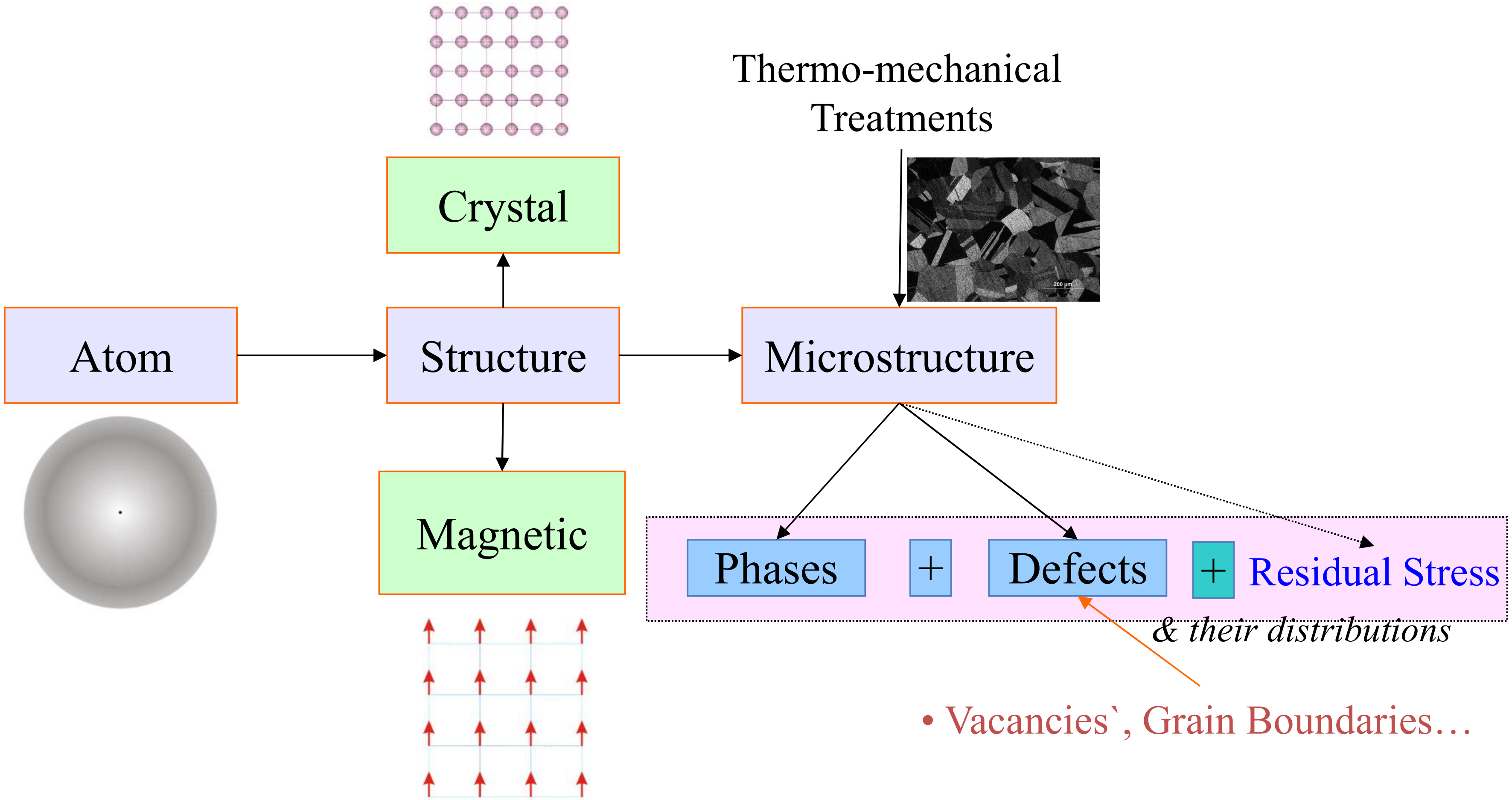
Energetic interactions & T are the primary determinant of "Structure"



Ref: https://physics.stackexchange.com/questions/79426/is-a-plasma-a-distinct-phase-of-matter

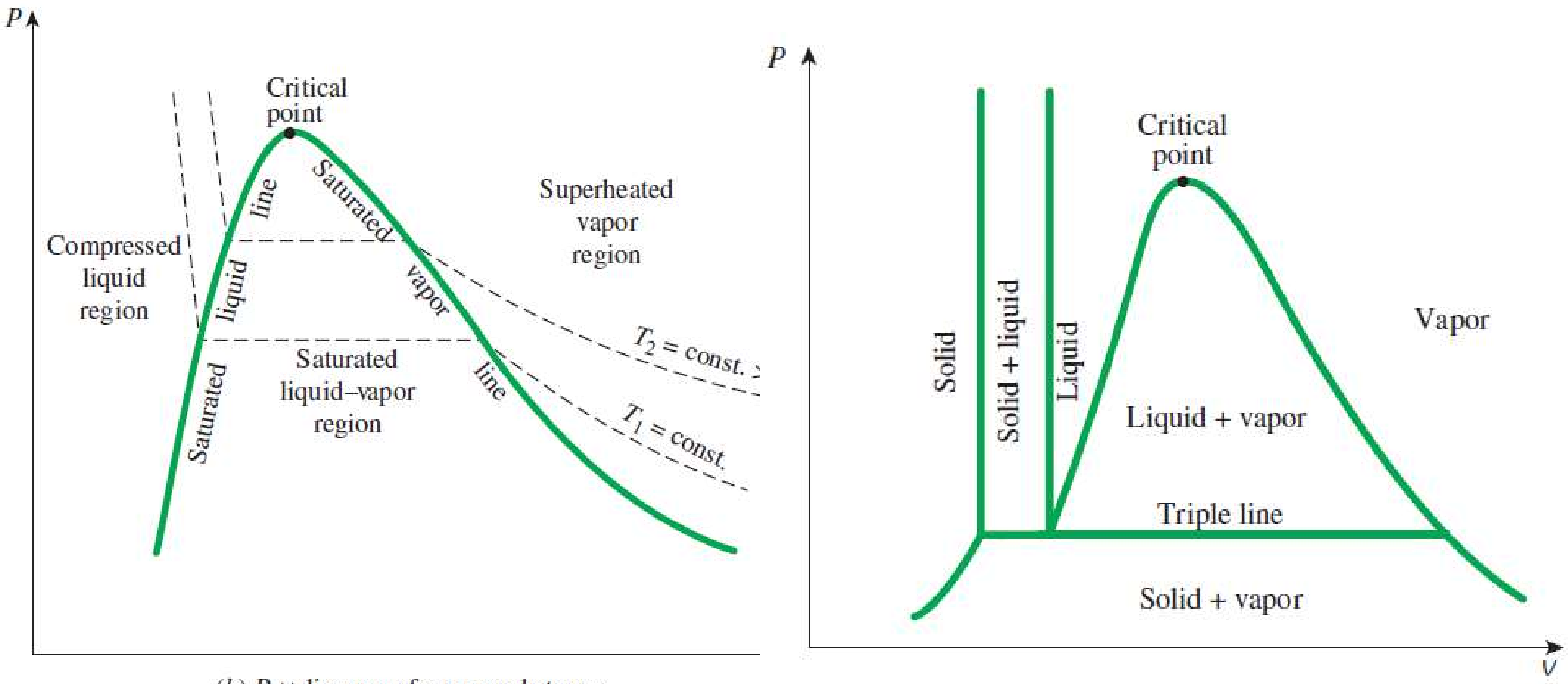
TD in practice: "Structure" is multiscale

- "Structure" can be characterized at many levels: Microstructure (very important for engineering applications), atomic structure, electronic structure, nuclear structure…(am not consideration "large" length scales)
- Relevant structure depends on application at under consideration



Ref: ebook-MSE, Anandh Subramaniam

Greater structure → More complex EOS & phase diagram

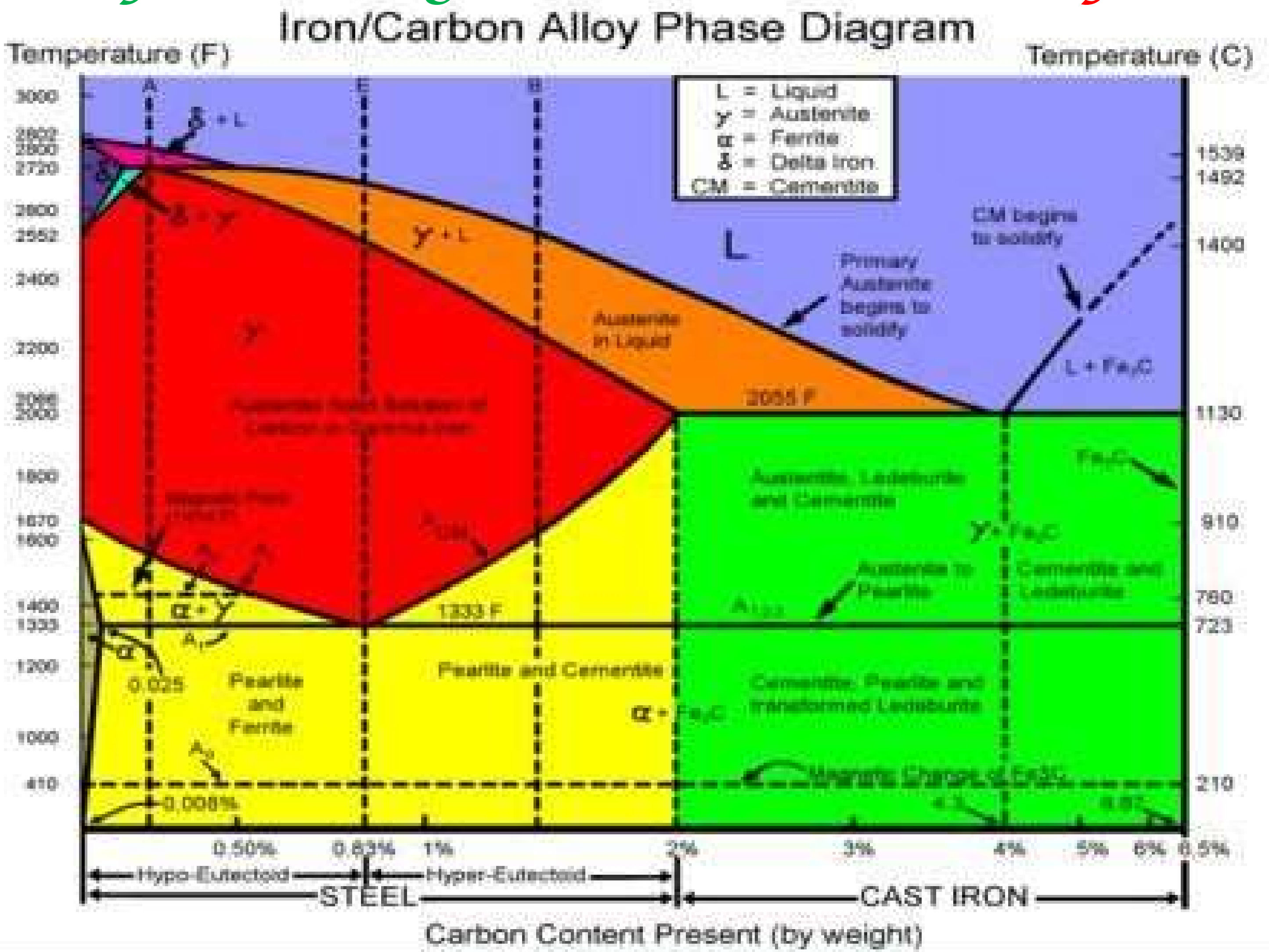


(*b*) *P*-*v* diagram of a pure substance

(*a*) *P*-*v* diagram of a substance that contracts on freezing

Figs: Cengel & Boles; http://www.engineersgallery.com/iron-carbon-equilibrium-diagram/

Greater structure → More complex EOS & phase diagram + chemical complexity



- Second most important phase diagram of in human civilization!
- Which is the first?

http://www.engineersgallery.com/iron-carbon-equilibrium-diagram/