Lecture 20: 11.28.05 Spinodals and Binodals; Continuous Phase Transitions; Introduction to Statistical Mechanics

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Reading: Engel and Reid 13.1, 13.2

Supplementary Reading: Zallen, The Physics of Amorphous Solids, Ch. 1.4 ‘The Glass Transition,’ pp. 16-23
Engel and Reid Ch. 12 – review of basic probability concepts

ANNOUNCEMENT: LAST PS POSTED TODAY
Conditions for stability as a function of composition

- For closed systems at constant temperature and pressure, the Gibbs free energy is minimized with respect to fluctuations in its other extensive variables. Thus, if we allow the composition of a binary system to vary, the system will move toward the minimum in the free energy vs. \( X_B \) curve:

\[
\text{d}G = G(X_B = X^*) - G(X_B = X_0) \geq 0
\]

If the system is at the minimum in \( G \), then we can write:

\[
\text{d}G = G(X_B = X^*) - G(X_B = X_0) = 0
\]

- We can perform a Taylor expansion for a fluctuation in Gibbs free energy, assuming the only variable that can vary is composition \( (X_B) \):

\[
\text{d}G = \left( \frac{\partial^2 G}{\partial X_B^2} \right)_{X_P, n} (X_B - X_0) + \frac{1}{2} \left( \frac{\partial^2 G}{\partial X_B^2} \right)_{X_P, n} (X_B - X_0)^2 + \frac{1}{3!} \left( \frac{\partial^2 G}{\partial X_B^2} \right)_{X_P, n} (X_B - X_0)^3 + \cdots \geq 0
\]

\[
\left( \frac{\partial^2 G}{\partial X_B^2} \right)_{X_P, n} \geq 0 \quad \text{for stable equilibrium}
\]
**Regular Solution**

\[ \frac{\partial G}{\partial x_b} = 0 \]

\[ \frac{\partial^2 G}{\partial x_b^2} < 0 \]

Phase boundaries (BINODALS)

**Binodals**

\[ \frac{\partial G}{\partial x_b} > 0 \]

Outside spinodal: System stable to small composition fluctuations

(Metastability!)

Small fluctuation in composition

\[ \Delta G > 0 \]

Not spontaneous!

Spinodal

\[ \Delta G < 0 \]

Large fluctuation

Spinodal

Binodal

**Binodal**: Points of common tangent

Lecture 20 – Regions of stability on phase diagrams; Continuous phase transitions

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Phase transformations occurring in unstable and metastable regions of the phase diagram result in very different microstructures:

- Nucleation and growth occurs from discrete points in a system, while spinodal decomposition occurs simultaneously throughout a system. You can view a computer simulation of the composition evolution during spinodal decomposition of a binary system of two metals at: [http://math.gmu.edu/~sander/movies/spinum.html](http://math.gmu.edu/~sander/movies/spinum.html).
First-order vs. second-order phase transitions

- The phase transitions we have focused on thus far - melting of a crystalline solid, boiling of a liquid, or structural transformations of allotropes from one crystal structure to another - are known as first-order transitions. The 'order' is noted by whether the transition is accompanied by a discontinuity in a first-, second-, or higher-order derivative of the Gibbs free energy. In addition to first-order transitions, there are continuous phase transitions, including second-order transitions and lambda transitions. As you will expect, the second-order phase transitions occur with a discontinuity in a thermodynamic quantity that is a second derivative of the Gibbs free energy. Two of the most important continuous phase transitions are the glass transition and order-disorder transitions.

\[
C_p = T \left( \frac{\partial G}{\partial T} \right)_{p,n} = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{p,n}
\]

Continuous transitions

First-order

Second-order

Lambda

Ordering in metal alloys. Two different atom types are interspersed: (a) ordered at low temperature, and (b) disordered at high temperature.

Figure by MIT OCW.

(order-disorder figure- Dill and Bromberg)

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Examples of order-disorder transitions

- Order-disorder transitions are found in many classes of materials:

Metallic solutions:

![Copper-Zinc Phase Diagram](image)

The copper-zinc phase diagram.

Figure by MIT OCW.

Organic-inorganic co-crystals:

![Organic-Inorganic Co-Crystals](image)

Projection of the low-temperature structure of (CH$_3$)$_4$NBF$_4$ on the ab plane. In the high-temperature phase, the orientations of the BF$_4$ groups are randomly distributed among the four orientations obtained by successive 90$^\circ$ rotations around the B-F axis perpendicular to the drawing.

Figure by MIT OCW.
Experimental heat-capacity points from the step measurements and from the thermograms in the transition region.

Ferroelectric materials:

The temperature dependence of the molar heat capacity for two individual DNP monomer single crystals. The full curve shows a Debye fit.
Block copolymers:

Figure by MIT OCW.
Heat and the microscopic state of materials

- We have so far utilized macroscopic thermodynamics (what is usually referred to as ‘classical’ thermodynamics) to understand the behavior of materials as a function of their environment (T, P, composition, reactions, etc.). Classical thermodynamics does not rely on a theory of the molecular behavior of matter- it explains macroscopic phenomena (involving ~Avogadro’s numbers of atoms) based on the laws of thermodynamics- which were formulated without knowledge of molecular details.

- The functional form of free energies/chemical potentials, entropies, and enthalpies is not predicted by classical thermodynamics, because these depend on the molecular details of materials- their atomic structure and bonding. In a practical sense, this doesn’t limit the power of classical thermodynamics, since all of these thermodynamic functions can be empirically measured- using calorimetry, electrochemistry, and other experimental methods.

In some cases we may wish to understand how the molecular structure of a material influences its thermodynamic properties, or predict how new materials may behave thermodynamically. One way to proceed is to develop molecular scale models for the thermodynamic behavior of materials- such models are the realm of statistical mechanics. We will now change gears for a few lectures and examine the fundamentals of statistical mechanics, how entropy relates to the microstates available to the system at a molecular level, and how simple models of materials are formulated, which can predict the macroscopic properties of materials.

- We have shown in our discussions of bonding that the energies (internal energy) of electrons in atoms and molecules are quantized. In addition, you learned that molecules themselves may have quantum mechanical vibrations in crystals, which are likewise quantized in their allowed energies:

A reminder from lecture 12 in your bonding notes:

Images removed due to copyright reasons.
A fundamental goal of statistical mechanics

- Thermal energy (heat) transferred to a molecule does not change the nature of the available energy levels, but it does change which energy levels are occupied:

- At finite temperature, molecules (or in some cases, electrons within a molecule) are excited to some distribution among the available energy levels; with increasing thermal energy in the system, they are able to access higher and higher energy levels. **One of the main objectives of statistical mechanics is to predict how the energy levels are occupied for a given total quantity of thermal energy. This occupation of states in turn dictates macroscopic thermodynamic properties.**
A simple model to introduce the concept of microstates: the Einstein solid

- Our introduction to the connection of thermodynamic quantities to microscopic behavior begins by considering a simple model of a monatomic crystalline solid—models of materials are the starting point for statistical mechanics calculations.

- Suppose for definiteness we have a diamond, where each carbon atoms is tetrahedrally bonded (covalently) to its neighbors. As a model for how this material behaves in response to temperature, we propose that the most important degree of freedom available to the atoms to respond to thermal energy is vibration of the atoms about their at-rest positions.

  - The bonding between atoms creates a potential energy well in which the atoms are centered at their at-rest position. Oscillations of the atoms about the at-rest position can be induced by thermal energy in the material. The potential is called a harmonic potential because of its shape—similar to the potential of a spring in classical mechanics. Because the oscillation of the atoms is constrained by bonding to center about their at-rest positions in the crystal lattice, the energy of vibration for each atom is quantized:

  Model for a 3-atom solid as 1D harmonic oscillators

... where \( h \) is Planck’s constant \( (h = 6.62 \times 10^{-27} \text{ gm cm}^2 \text{ sec}^{-2}) \) and \( \nu \) is the frequency of the atomic vibrations. The total energy of the solid is the sum of the individual energies of each oscillator:

Let \( E_{\text{total}} = (7/2)\epsilon \):

6 possible microstates

Figure by MIT OCW.
The total number of allowed microstates is a parameter we will refer to again and again; we give it the symbol $\Omega$. For the system above, $\Omega = 6$. The collection of all $\Omega$ microstates for a given system is called its ensemble. (For the case of a system with fixed $(E,V,N)$ it is referred to as the microcanonical ensemble).

**Distinguishable vs. indistinguishable atoms/particles**

- Two cases arise in modeling real systems: one where we can identify each atom uniquely, and the case of atoms being identical and indistinguishable.

- If we had indistinguishable atoms, then we would only be able to observe the unique microstates, whose number is given the symbol $W$:

\[
W = 2
\]

Unique states:

- $j=1$
- $j=2$

Energy

- $j=1$
- $j=2$

$\Omega_1 = 3$

$\Omega_2 = 3$

\[
\Omega = \Omega_1 + \Omega_2 = 6 \text{ total microstates}
\]

- We have collected the individual microstates now into 2 groups characterized by the number of atoms in each energy level ($n_0$, $n_1$, and $n_2$). We will call the set of microstates that has a given set of occupation numbers a state (as opposed to microstate). The total number of distinguishable states is $W$.

- For our overly-simplified 3-atom model with a low total energy of $E_{\text{total}} = \langle 7/2 \rangle$, the number of distinct arrangements is small. However, for a material containing a mole of atoms at room temperature, the number of possible ways to occupy the available energy levels is enormous. Thus, rather than writing diagrams of all the possible microstates, we become concerned with the probability of finding a certain set of microstates $j$ in the ensemble that have a given distribution of the atoms among the energy levels.
The first postulate of statistical mechanics

- The first postulate of statistical mechanics tells us the probability of each of these arrangements being found in the ensemble:

- Question: what kind of thermodynamic system is this ensemble?

- This postulate is often called the principle of equal a priori probabilities. It says that if the microstates have the same energy, volume, and number of particles, then they occur with equal frequency in the ensemble.

  - This postulate tells us what the $p_i$'s for the two states in our 3-atom $E_{\text{total}}=2$ system are:
    - We have a total of $L = 2$ states, (3 microstates in each of the two unique states $j=1, j=2$). Thus the probability for each state is:

- Each state has a frequency of 50% in the ensemble.
References

2. Allen, S. & Thomas, E. L.