

Lecture 1

Objectives: Students will be able to:

1. Describe the terms, classical thermodynamics, quantum mechanics, statistical mechanics.
2. Define the terms “intensive” and “extensive” variables.
3. Identify different notational conventions.
4. Derive the Gibbs phase rule.
5. Define the four laws of thermodynamics.

1 Overview

In this class we will be concerned with three mechanics, namely classical thermodynamics (continuum mechanics), quantum mechanics, and statistical mechanics. We can briefly describe these as follows:

1. Classical thermodynamics:

This is the observational science dealing with heat and work. It was developed based on empirical observations without assumptions about the make up of matter. It describes *macroscopic* quantities, such as heat, work, internal energy, enthalpy, entropy, Gibbs free energy, etc. It does not contain any information about the state or even existence of molecules! Classical thermodynamics tacitly assumes that the world is made up of a continuum.

2. Quantum mechanics:

Quantum mechanics lies on the other end of the spectrum from classical thermodynamics. It deals with *nanoscopic* properties, i.e., length scales on the order of 10^{-9} m. Quantum mechanics gives rise to concepts such as the particle-wave duality, which states that all energy and all matter behaves both like a wave and like a particle. It tells us that energy and other quantities are not continuous, but discrete. The governing equation is the Schrödinger equation. The state of any system is described by the wave function, which is the solution of the Schrödinger equation. Quantum chemistry typically deals with solving the Schrödinger equation for single molecules, giving information on the electronic structure (how atoms are bonded together, how electrons are shared to make up chemical bonds) and the geometrical structure. Recent experiments have now been able to image individual molecules identifying the same sorts of information through atomic force microscopy (AFM) as one can compute from quantum chemistry. See Figure 1 as an example the bonds in the pentacene molecule. In principle one could solve the Schrödinger equation for a macroscopic system, such as the state of a polymer mixture inside an extrusion reactor, but in practice these systems are *much* too difficult to solve. Therefore, quantum mechanics is limited to isolated molecules or perfect crystals, usually at absolute zero temperature. Hence, quantum mechanics does not tell us anything about the thermodynamics of a *macroscopic* system.

3. Statistical mechanics:

Many of the methods of statistical mechanics were developed by arguably the greatest American scientist, J. Willard Gibbs (1839-1903). Gibbs even coined the term statistical mechanics. The basic idea is that one can take the properties, energy levels, probabilities of *individual molecules* from quantum mechanics and average these in an appropriate way to obtain the

properties of a *macroscopic* collection of molecules. For example, if you know the probable states of a single isolated polymer then you can predict the thermodynamic properties of 10 kg of the polymer in an extruder by applying the techniques of statistical mechanics. An example of the liquid-liquid phase equilibrium between a polymer and a model protein calculated from statistical mechanics is given in Figure 2

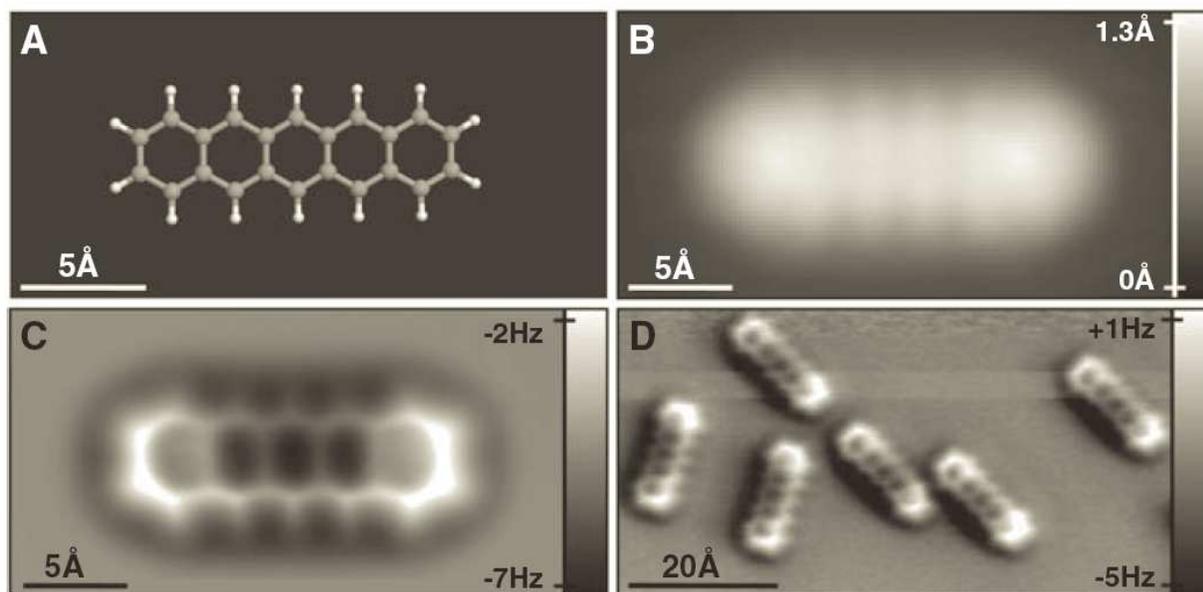


Fig. 1. STM and AFM imaging of pentacene on Cu(111). **(A)** Ball-and-stick model of the pentacene molecule. **(B)** Constant-current STM and **(C and D)** constant-height AFM images of pentacene acquired with a CO-modified tip. Imaging parameters are as follows: **(B)** set point $I = 110$ pA, $V = 170$ mV; **(C)** tip height $z = -0.1$ Å [with respect to the STM set point above Cu(111)], oscillation amplitude $A = 0.2$ Å; and **(D)** $z = 0.0$ Å, $A = 0.8$ Å. The asymmetry in the molecular imaging in **(D)** (showing a “shadow” only on the left side of the molecules) is probably caused by asymmetric adsorption geometry of the CO molecule at the tip apex.

Figure 1: AFM image of pentacene on Cu(111). From Gross et al., *Science*, **325**, 1110–1114 (2009).

Hence, statistical mechanics is the bridge between quantum mechanics (single molecules) and thermodynamics (continuum mechanics).

2 Basics of Thermodynamics

1. Difference between intensive and extensive variables. The difference between intensive and extensive properties is like the difference between “quality” and “quantity”. As an example, would you be excited if I said I was going to give you 1 kg of gold? If I said that the gold was contained in 10^8 m³ of sea water you would probably be much less excited. The concentration in sea water is the “quality”, while the 1 kg is the “quantity”. For example, temperature is intensive, if one block of ice is at -10° C then adding another identical block does not make the temperature -20° C, but it does mean that melting the two blocks of ice will take twice as much energy.

- Name some other intensive and extensive variables

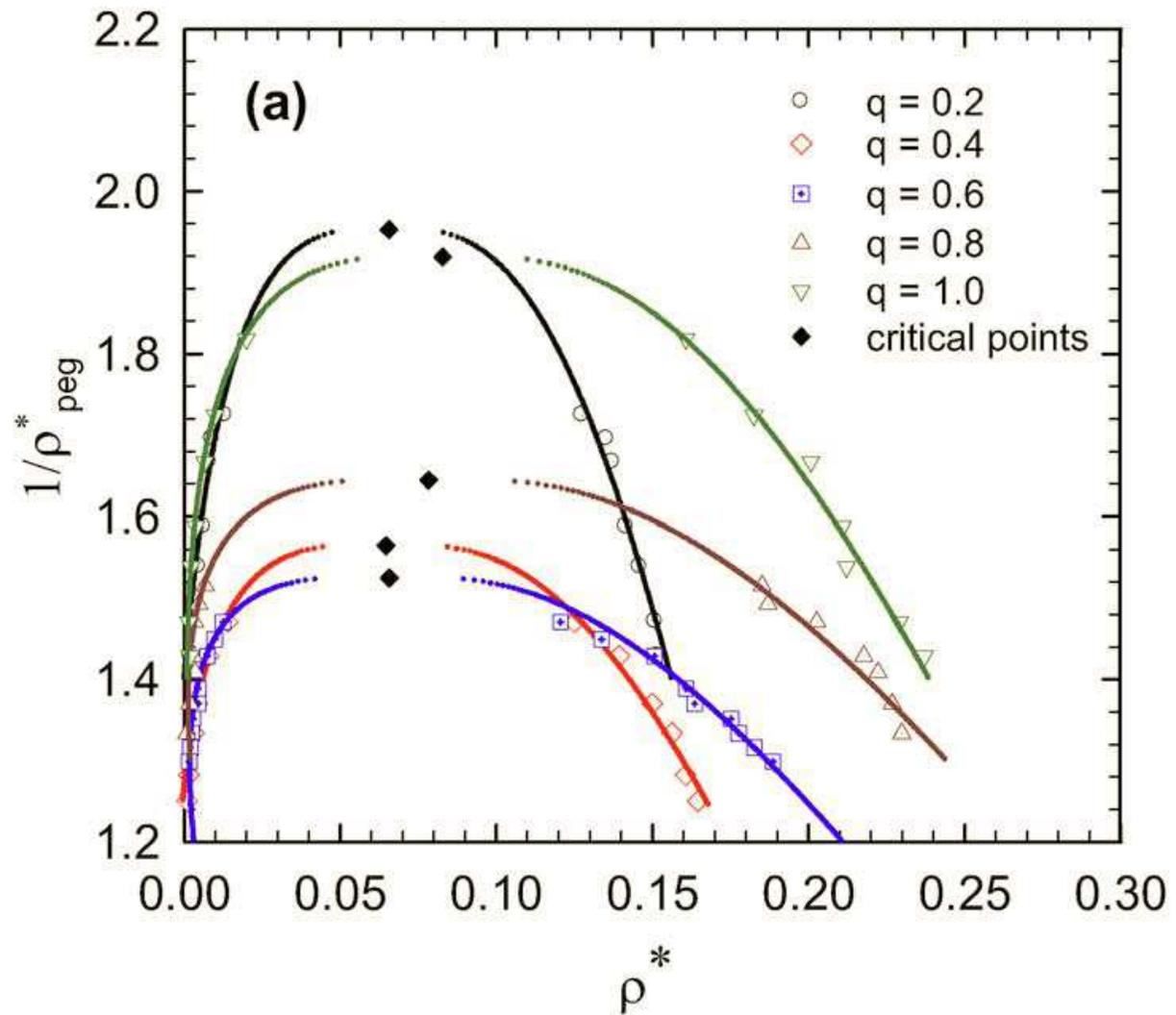


Figure 2: Computed liquid-liquid equilibrium phase diagrams for a model of a polymer (PEG) and a protein as a function of the ratio of the PEG to protein size ratio, q . Figure taken from Li et al. *J. Chem. Phys.*, **128**, 205105 (2008).

Note that any extensive property can be made into an intensive property by dividing by another extensive property. Example: $V \rightarrow V/N$.

2. Notation. Inconsistent notation has plagued thermodynamics perhaps since the beginning. The key in reading any text is to find out what the notation means before you read. There are basically four types of variables:
 - (a) Extensive: e.g. V , U , N , or \underline{V} (Tester & Modell) (Walas), V^t (Van Ness & Abbott).
 - (b) Molar: e.g. V/N , U/N sometimes denoted \underline{V} (Sandler), v (Denbigh), V (Van Ness & Abbott, Walas; note that this is the same as other author's extensive) and \tilde{V} .
 - (c) Specific: e.g. V/M where M is the total mass, sometimes denoted \hat{V}
 - (d) Partial molar: e.g., V_i (Denbigh), \bar{V}_i (Van Ness & Abbott, Walas, Sandler),

Pure component and partial molar notation occur when we are talking about mixtures. Partial molar properties are defined as

$$V = \sum_i N_i \bar{V}_i$$

Example: If you mix 1 liter of CCl_4 and 1 liter C_6H_6 you actually get *more* than 2 liters of the mixture. The partial molar properties tell you how each component behaves in the mixture.

We will use V for extensive, \tilde{V} for molar, \hat{V} for specific, and \bar{V}_i for partial molar.

3. Gibbs Phase Rule.

We observe that there are many variables for a given system, e.g., pressure, density, internal energy, viscosity, thermal conductivity, composition, volume, etc. How many of these properties do we have to specify to fix the system? (i.e., put it in a definite state of being) For example, you are designing a system to pump some fluid up a hill. You want to make sure that the fluid is in a liquid state, not a two-phase or a vapor state because that would make it much more difficult to pump. How many variables do you have to specify?

Consider a fluid of C independent components and \mathcal{P} coexisting phases. How many variables do we have? It is sufficient to specify a quantity for each component and the temperature and pressure in each phase, i.e., $T^\alpha, P^\alpha, n_1^\alpha, \dots, n_C^\alpha$. Note that specifying $n_1^\alpha, \dots, n_C^\alpha$ is the same as specifying $x_1^\alpha, \dots, x_{C-1}^\alpha, N^\alpha$, where N is the total number of moles in that phase. Now, one does not need to specify the total number of moles, or the extent of the system, in order to specify the state of the system. Therefore, specifying $T^\alpha, P^\alpha, x_1^\alpha, \dots, x_{C-1}^\alpha$ intensive properties is sufficient. This gives us $C + 1$ variables for each phase.

$$\text{Num. variables} = (C + 1)\mathcal{P}$$

How many constraints do we have for equilibrium? Thermal equilibrium requires that T is the same in each phase. Mechanical equilibrium requires that P is the same in each phase. Chemical equilibrium means that the chemical potential of each component must have the same value in each phase.

$$\begin{aligned} T^\alpha &= T^\beta = \dots = T^\mathcal{P} \text{ thermal equilibrium} \\ P^\alpha &= P^\beta = \dots = P^\mathcal{P} \text{ mechanical equilibrium} \\ \mu_1^\alpha &= \mu_1^\beta = \dots = \mu_1^\mathcal{P} \\ &\vdots \\ \mu_C^\alpha &= \mu_C^\beta = \dots = \mu_C^\mathcal{P} \text{ chemical equilibrium} \end{aligned}$$

$$\Rightarrow (\mathcal{P} - 1)(C + 2) = \text{num. constraints}$$

Then the number of *intensive* degrees of freedom left to specify is

$$\mathcal{F} = (C + 1)\mathcal{P} - (\mathcal{P} - 1)(C + 2)$$

$$\mathcal{F} = C - \mathcal{P} + 2$$

What does it mean?

- (a) If you specify \mathcal{F} *intensive* properties then you can calculate all others (if you are clever enough).
- (b) Total differentials for changes in state: (pure components)

$$P = P(\tilde{V}, T) \Rightarrow dP = \left(\frac{\partial P}{\partial \tilde{V}} \right)_T d\tilde{V} + \left(\frac{\partial P}{\partial T} \right)_{\tilde{V}} dT$$

Example: Suppose you want to separate a mixture of *ortho*-, *meta*-, and *para*-, xylene by vapor-liquid equilibrium. Can I specify the temperature and pressure of the system and guarantee that the system is in the two phase region?

3 The Four Laws of Thermodynamics

The “Laws” of thermodynamics are not laws, but principles derived from observation that have never known to have been violated. There are theoretical underpinnings, but no rigorous proof of these laws. All four laws give rise to distinct concepts. Additionally, each of the first three laws of thermodynamics give rise to a certain thermodynamic function. What are these functions?

1. The Zeroth law of thermodynamics.

If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C.

Importance: This gives rise to the idea of temperature. A, B, C are at the same temperature.

Hence, the zeroth law gives rise to the concept of: _____

2. The First law of thermodynamics.

The first law deals with work and heat. Recall from physics that work is the integral of some force over some distance

$$W = \int_S \vec{F} \cdot d\vec{r}$$

where S is some path. This means that work is dependent on the path taken. For example, what is the work required to carry a book from the first floor to the 12th floor of BEH? That depends on how you get there. In contrast, what is the increase in potential energy is independent of the path, and so is an *exact* differential. δW is inexact, but dU (internal energy) is exact. An exact differential of two variables is one which can be written

$$F = F(X, Y)$$

$$dF = \left(\frac{\partial F}{\partial X} \right)_Y dX + \left(\frac{\partial F}{\partial Y} \right)_X dY$$

The next concept is heat. Consider a container with rigid walls.

Rigid walls means no work can be done on (or by) the system. The system initially has ice and a liquid water. Time goes by and the system now has only liquid water. What happened? The internal energy of the system (stuff inside the container) changed. The change in internal energy must have been due solely to heat interactions.

$$dU = \delta Q$$

Now consider the same system, but with adiabatic walls. Result? No change in internal energy, therefore only heat and work can change internal energy of a closed system.

Now consider a gas inside a cylinder with adiabatic walls and fitted with a massless, frictionless piston. Now compress the gas (perform work on the system) and look at the energy change:

$$dU = \delta W$$

Consider performing work by heating a cylinder of gas fitted with a piston. You put heat into the system and get work out. The amount of heat and work depend on factors such as friction, etc. The change in energy is an exact differential:

$$dU = \delta W + \delta Q$$

dU is exact, but δW and δQ are inexact differentials. Therefore the “inexactness” must cancel.

Note also that you can turn work into heat with this device. If you compress the gas the gas will give up heat to the surroundings. The first law states that the energy in these processes is conserved, and that heat can be converted into work and work into heat. You can't get more work out than heat you put in, and you can't get more heat out than work you put in.

Here are other statements of the first law:

- The energy of a closed system can only be changed through heat and work interactions.
- Heat and work are equal.
- (Due to Clausius) Die Energie der Welt ist konstant. (The energy in the universe is constant.)

The first law of thermodynamics give rise to the concept of: _____

3. The Second law of thermodynamics. Consider two blocks of copper, block 1 at T_1 and block 2 at T_2 , where $T_1 > T_2$. We put the blocks in thermal contact. The final temperature of the system is T_f where $T_1 > T_f > T_2$. What about the inverse event? We have two blocks of copper at T_f , we bring them together and their final temperatures are $T_1 > T_2$. The first law says this is fine because the total energy of the system is constant. Why doesn't this happen?

Statements of the second law include:

- Spontaneous processes always increase the entropy of the universe.

$$dS \geq 0$$

where S is the entropy, the measure of disorder in the universe.

- Heat and work are equal, but work is more equal than heat (with apologies to George Orwell).
- (Due to Clausius) Die Entropie der Welt strebt einem Maximum zu. (The entropy in the universe tends to a maximum.)

Consider a container with rigid walls. Only thermal interactions change the energy. If the system initially contains two phases, ice and water, then after some passage of time the ice will melt as heat is transferred into the system. The ice is more ordered, so that the final state has a higher entropy than the initial state. From this we see that the entropy is related to the heat interactions.

$$\delta Q_{\text{rev}} = TdS = dU$$

Only for a reversible process.

Now consider a massless frictionless piston, adiabatic.

$$\delta W_{\text{rev}} = -PdV = dU$$

Putting these together we have

$$dU = \delta Q + \delta W = TdS - PdV$$

and

$$\delta Q_{\text{rev}} = TdS$$

$$\delta W_{\text{rev}} = -PdV$$

Note that from the Gibbs phase rule we know that we only need two intensive variables to specify the state of a pure substance. Hence,

$$\tilde{U} = \tilde{U}(\tilde{S}, \tilde{V})$$

therefore,

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Comparing, we get

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

Significance: These equations can be used to find changes of state (temperature, pressure, energy).

The second law gives rise to the concept of: _____

4. Third law of thermodynamics. The Third law has to do with an absolute value of the last function, entropy. In simple terms the Third law states that the absolute entropy is zero for any perfect crystalline substance at a temperature of absolute zero. This is only true when the crystalline phase does not have any energetic degeneracies. The third law also defines the concept of the zero of temperature. Hence, the Kelvin scale comes about because of the third law of thermodynamics. Without it, all temperature scales would be arbitrary.