

# 10.40 Lecture 21

## Fundamental Principles of Quantum and Classical Statistical Mechanics

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(In preparation for Lecture 21, also read T&M, beginning of Ch. 10 through 10.1.3).

Now, we turn to the microscopic: atoms and molecules. Why do we need to use the theory of atoms and molecules and how do we know that they really exist?

(Think about these issues for class discussion.)

Concurrent with the development of the atomic theory is the concept of statistical averaging. Thermodynamic properties, here known as *macroscopic properties*, such as  $T, P, \underline{U}$ , etc. are the result of averaging the properties of many different atoms and molecules. This is useful, because the important property, the *microscopic property*, of each atom or molecule is its energy. Averaging the energies of a large number of atoms and/or molecules in the proper way will yield the *macroscopic properties* of the *system*. Thus, the need to average introduces the need for *statistics* and for *probability*.

### 21.1 Objectives of 10.40 Part II

The objectives of this part of the course is to give you an appreciation of the tools of statistical thermodynamics and statistical mechanics and how they can be used **(1) to compute thermodynamic quantities** for specific systems and **(2) to better understand thermodynamic quantities** in general. It is not expected that you will have a full understanding of statistical thermodynamics and statistical mechanics. You should, however, be able to solve simple problems and understand enough to know how to increase your understanding, if so needed for your research.

### 21.2 Quantum mechanics yields the energy levels of a *system*

The main equation of quantum mechanics, the Schrödinger equation, gives the possible energy levels of a system:

$$H|\psi_\nu\rangle = \underline{E}_\nu|\psi_\nu\rangle,$$

where  $\nu = 0, 1, \dots$   $\psi_\nu$  is the *state of the system* and  $\underline{E}_\nu$  is the energy of state  $\nu$ .  $\psi_0$  is the *ground state* of the system,  $\psi_1$  is the first *excited state*, etc. An example can be seen in Figure 1.



Figure 1: Example of different energy levels coming from the solution to Schrödinger's equation. Note that it does not matter if we write  $E$  in intensive or extensive form. Only the units will change, e.g. kJ versus kJ/mol.

The thermal energy is in units of  $kT$  ( $k$  is Boltzmann's constant =  $1.381021 \times 10^{-23}$  J K $^{-1}$ ;  $R = kN_A$ ), where  $1 \text{ kcal mol}^{-1} = 505 \text{ K} = 351 \text{ cm}^{-1}$ .

If one were to solve Schrödinger's equation, for example, for you in 66-110, and treating you as a particle in a box, if you weigh 60 kg, then for you,  $E_1 - E_0 \approx 1 \times 10^{-50}$  kJ mol $^{-1}$ .

Note that quantum mechanics does not in itself tell which energy levels are occupied and the degree of occupancy. Those are in the realm of *statistical mechanics*. In this sense, the solutions to the Schrödinger equation are only the possible energy levels.

### 21.3 Probabilities and averaging

An observable property,  $B_{obs}$ , is some *mechanical, measured property*, that is an average over many measurements of short time:

$$B_{obs} = \frac{1}{N_m} \sum_{j=1}^{N_m} B_j,$$

where  $N_m$  is the number of measurements.

Examples of mechanical properties:  $V, P, N, \underline{E}, M$  ( $M$  is the *magnetization*.)

Examples of non-mechanical properties:  $T, \underline{S}, A, \mu$

If  $p_j$  is the *probability* that the system is in state  $j$ , then

$$B_{obs} = \sum_j p_j B_j = \langle B \rangle,$$

where  $\langle B \rangle$  is called the *ensemble average*, and an *ensemble* is a collection of microstates (see below). Also note, that

$$\sum_j p_j = 1.$$

In systems at equilibrium, it turns out, as we shall show later,

$$p_j = \frac{e^{-\beta \underline{E}_j}}{Q},$$

where  $\underline{E}_j$  is the energy of state  $j$ ,  $\beta = 1/kT$ , and

$$Q = \sum_j e^{-\beta \underline{E}_j},$$

where  $Q$  is the *partition function*. It is merely the normalization factor, so that  $\sum_j p_j = 1$ .

$e^{-\beta \underline{E}_j}$  is called the *Boltzmann factor*.

### 21.4 Example of application of the Boltzmann factor

Let us analyze a two-state system, where  $E_1 - E_0 = 1.0 \text{ kcal mol}^{-1}$ . At any given time, what is the probability to find the system in the ground state at 300 K and at 1000 K.

At 300 K,  $kT = 0.6 \text{ kcal mol}^{-1}$ , and at 1000 K,  $kT = 2.0 \text{ kcal mol}^{-1}$ .

At 300 K,

$$p_0 = \frac{e^{-E_0/0.6}}{e^{-E_1/0.6} + e^{-E_0/0.6}} = \frac{e^{-E_0/0.6}}{e^{-E_0/0.6} e^{-(E_1-E_0)/0.6} + e^{-E_0/0.6}} = \frac{1}{e^{-(E_1-E_0)/0.6} + 1} = 0.84.$$

Similarly, at 1000 K,

$$p_0 = \frac{1}{e^{-(E_1 - E_0)/2.0} + 1} = 0.62.$$

$$\lim_{T \rightarrow \infty} p_0 = ?$$

$$\lim_{T \rightarrow 0} p_0 = ?$$