

**University of Washington**  
**Department of Chemistry**  
**Chemistry 453**  
**Winter Quarter 2015**

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Lecture 1. 1/05/15

“There are three kinds of lies: lies, damned lies, and statistics”  
From “Chapters from my Autobiography”, Mark Twain 1906.

**A. Microscopic vs. Macroscopic Properties of Physical Systems**

- Any large scale system contains an enormous number of molecules.  
Example: A liter of oxygen contains at STP about  $1.82 \times 10^{22}$  molecules.
- In Chemistry 452 we learned about the thermodynamic properties of large scale systems: P, V, T, S, U, G, etc. Individual molecules however are characterized by their physical coordinates, velocities, and the kinetic and potential energies that are functions of these quantities.
- One of the important goals of Chemistry 453 is to show you how to relate properties of individual molecules to macroscopic properties observed for large scale systems.
- As the diagram below shows, because of the “big data” sets associated with large scale systems, we cannot keep track of all the microscopic properties and deduce directly from them the macroscopic properties.
- We require therefore statistical techniques to relate the properties of individual molecules to the properties of large scale systems, including in particular thermodynamic properties. This field is called Statistical Mechanics.

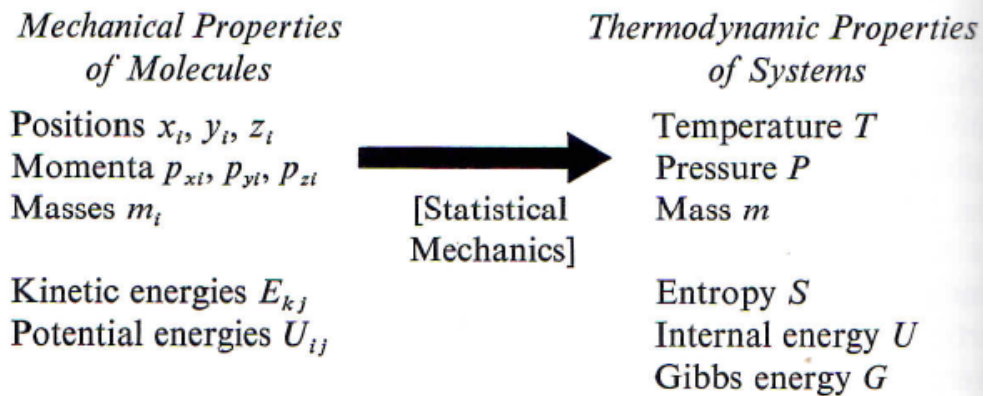
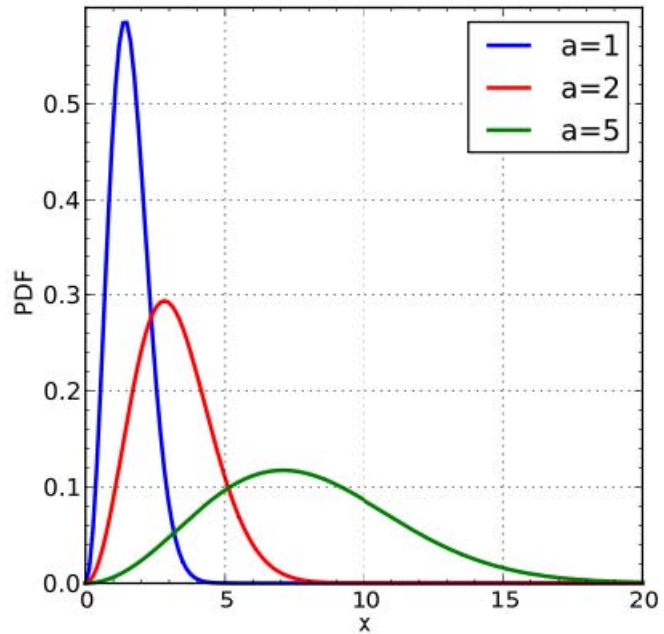


Figure 1.1: Statistical Mechanics relates molecular properties to thermodynamic properties

**B. Basic Statistical Mechanical Concept: Kinetic Energy vs. Internal Energy**

- In Chemistry 452 we learned for an ideal gas of monatomic particles the internal energy  $U$  is  $U = \frac{3RT}{2}$ . We have also learned that for an individual gas molecule the kinetic energy is  $E = \frac{mv^2}{2}$ . Temperature  $T$  appears only in  $U$  while velocity  $v$  appears in  $E$ . How are these two types of energy related?
- From the Kinetic Theory of Gases we know that in a mole of gas there exists a distribution of velocities. The distribution changes with temperature. See Figure 1.2

Figure 1.2: Distribution of molecular velocities  $u^2 f(u)$  (arbitrary units) as a function of temperature  $a$  (arbitrary units).



- From the Kinetic theory of Gases, the internal energy per molecule is equal to the average of  $E$ . In equation form this is

$$\frac{U}{N_A} = \frac{3RT}{2N_A} = \frac{3k_B T}{2} = \langle E \rangle = \frac{m}{2} \langle v^2 \rangle = \frac{m}{2} \sum_n f(v_n, T) v_n^2 \quad (1.1)$$

- $N_A$  is Avagadro's number and  $R$  is the universal gas constant
- Boltzmann's constant is the ratio of  $R$  and  $N_A$ :

$$k_B = \frac{R}{N_A} = \frac{8.31 JK^{-1} mol^{-1}}{6.02 \times 10^{23} mol^{-1}} = 1.38 \times 10^{-23} JK^{-1}$$

- The notation  $\langle O \rangle$  indicates the average of property  $O$
- $f(v_n, T)$  is the fraction of molecules that have velocity  $v_n$  at temperature  $T$ .  $f(v_n, T)$  is called a velocity distribution function. It is equivalent to the probability of selecting from an ensemble of molecules at a given  $T$ , a molecule with velocity  $v_n$ .
- The curves shown in Figure 1.2 are velocity distribution functions.

### C. Form for the Velocity Distribution Function: Simple Kinetic Derivation

- Distribution functions are used to calculate many types of averages, but the velocity distribution function is especially easy to calculate and can be derived from a simple physical model.
- Consider a dilute ideal gas. The gas is so dilute that only pairs of gas molecules have any chance of colliding. Such a collision is shown in Figure 1.3.

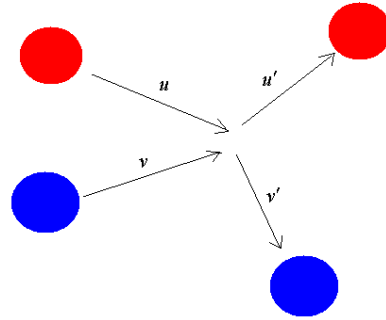


Figure 1.3: A bimolecular collision. Prior to the collision the red and blue coded molecules have velocities  $u$  and  $v$ , respectively. After the collision the velocities are  $u'$  and  $v'$ .

- Assuming the two molecules have the same masses, suppose this collision has the following properties,
  - Momentum is conserved:  $m\bar{u} + m\bar{v} = m\bar{u}' + m\bar{v}'$
  - Kinetic energy is conserved;  $\frac{mu^2}{2} + \frac{mv^2}{2} = \frac{mu'^2}{2} + \frac{mv'^2}{2}$
  - The probability of two molecules colliding with velocities  $u$  and  $v$  is equal to the probability of two molecules colliding with velocities  $u'$  and  $v'$ . This means that occurrence of the reverse collision has equal probability to occurrence of the forward collision. Mathematically this “time reversal symmetry” is expressed as  $f(u)f(v) = f(u')f(v')$
- Suppose we take the logarithm of the time reversal conditional so that

$$\ln f(u) + \ln f(v) = \ln f(u') + \ln f(v') \quad (1.2)$$

- We can make a very educated guess about the form of the distribution function that will satisfy equation 1.2 and the conservation of energy condition:

$$f(u) = \alpha \exp\left(-\beta \frac{mu^2}{2}\right) \quad (1.3)$$

where  $\alpha$  and  $\beta$  are constants to be determined. You should satisfy yourself that equation 1.2 leads to the conservation of energy. The exponent has a negative sign in its argument because the probability must diminish as the velocity increases, see Figure 1.2.

- The constant  $\alpha$  is called a normalization constant and must be determined from the properties of  $f(u)$  as a probability.
- Now  $u$  is a velocity vector in three dimensions so that from the Pythagorean theorem:  $u^2 = u_x^2 + u_y^2 + u_z^2$ . The  $x$ ,  $y$ , and  $z$  components of  $u$  may assume any values between  $-\infty$  and  $+\infty$

- Because  $f(u)$  has the meaning of a probability, if we sum (i.e. integrate) over all possible values of the  $u_x$ ,  $u_y$ , and  $u_z$ , the result must be 1. In equation form this means:

$$\int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z f(u) = 1 \quad (1.4)$$

- Evaluating the integral in (1.4) requires some thought. First, substitute the expression for  $f(u)$  into (1.4)

$$\int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z f(u) = \int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z \alpha \exp\left(-\beta \frac{mu^2}{2}\right) = 1 \quad (1.5)$$

- We now put the relationship  $u^2 = u_x^2 + u_y^2 + u_z^2$  into (1.5)

$$\int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z \alpha \exp\left(-\beta \frac{mu^2}{2}\right) = \int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z \alpha \exp\left(-\beta \frac{m(u_x^2 + u_y^2 + u_z^2)}{2}\right) = 1 \quad (1.6)$$

- We now use the property of exponentials to produce of product of three integrals:

$$\begin{aligned} & \int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z \alpha \exp\left(-\beta \frac{m(u_x^2 + u_y^2 + u_z^2)}{2}\right) \\ &= \alpha \int_{-\infty}^{+\infty} du_x \exp\left(-\beta \frac{mu_x^2}{2}\right) \int_{-\infty}^{+\infty} du_y \exp\left(-\beta \frac{mu_y^2}{2}\right) \int_{-\infty}^{+\infty} du_z \exp\left(-\beta \frac{mu_z^2}{2}\right) = 1 \end{aligned} \quad (1.7)$$

- Except for the x, y, and z subscripts these integrals are equal. We can use the symmetry property for the integral of an even function and the standard integral expression :

$$\int_{-\infty}^{+\infty} dx e^{-ax^2} = 2 \int_0^{+\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad (1.8)$$

- Using (1.8) we can solve for the normalization constant  $\alpha$  in (1.7):

$$\begin{aligned} \frac{1}{\alpha} &= \int_{-\infty}^{+\infty} du_x \exp\left(-\beta \frac{mu_x^2}{2}\right) \int_{-\infty}^{+\infty} du_y \exp\left(-\beta \frac{mu_y^2}{2}\right) \int_{-\infty}^{+\infty} du_z \exp\left(-\beta \frac{mu_z^2}{2}\right) \\ &= \left(\sqrt{\frac{2\pi}{m\beta}}\right)^3 \end{aligned} \quad (1.9)$$

or

$$\alpha = \left(\frac{m\beta}{2\pi}\right)^{3/2} \quad (1.10)$$

so that the velocity distribution function is:

$$f(u) = \left(\frac{m\beta}{2\pi}\right)^{3/2} \exp\left(-\beta \frac{mu^2}{2}\right) \quad (1.11)$$

- The parameter  $\beta$  can be determined from the expression for the average translational energy of an ideal monatomic gas molecule:

$$\langle E \rangle = \frac{3k_B T}{2} = \int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z \frac{mu^2}{2} f(u) = \int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z \frac{mu^2}{2} \left( \frac{m\beta}{2\pi} \right)^{3/2} \exp\left(-\beta \frac{mu^2}{2}\right) \quad (1.12)$$

- The integral in (1.12) is best evaluated in a spherical coordinate system. We use the relationship between the unit volumes in Cartesian and spherical coordinates:

$$du_x du_y du_z = d\varphi \sin \theta d\theta u^2 du \quad (1.13)$$

$$u_x = u \sin \theta \cos \varphi$$

$$u_y = u \sin \theta \sin \varphi$$

$$u_z = u \cos \theta$$

$$u = \sqrt{u_x^2 + u_y^2 + u_z^2}$$

$$\varphi = \tan^{-1} \left( \frac{u_y}{u_x} \right)$$

$$\theta = \cos^{-1} \left( \frac{u_z}{u} \right)$$

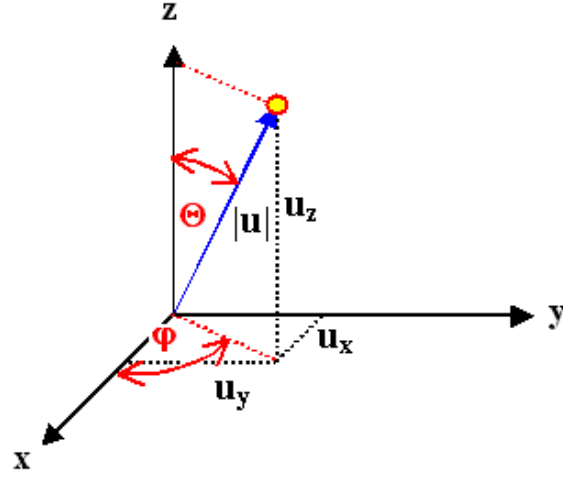


Figure 1.4: Relationships between velocities in Cartesian and spherical coordinates

- Using the relationship (1.13) and standard integral ranges we obtain

$$\int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y \int_{-\infty}^{+\infty} du_z \frac{mu^2}{2} \left( \frac{m\beta}{2\pi} \right)^{3/2} \exp\left(-\beta \frac{mu^2}{2}\right) = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta \int_0^{+\infty} du \frac{mu^2}{2} \left( \frac{m\beta}{2\pi} \right)^{3/2} \exp\left(-\beta \frac{mu^2}{2}\right) \\ = 4\pi \left( \frac{m\beta}{2\pi} \right)^{3/2} \frac{m}{2} \int_0^{\infty} u^4 \exp\left(-\beta \frac{mu^2}{2}\right) du = \frac{3k_B T}{2} \quad (1.14)$$

- Solving the integral we find that  $\beta = \frac{1}{k_B T}$  and the velocity distribution function is:

$$f(u) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp\left[-\frac{mu^2}{2k_B T}\right] \quad (1.15)$$

- When the distribution of molecular velocities is shown as in Figure 1.2, the function

$$u^2 f(u) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 \exp\left[-\frac{mu^2}{2k_B T}\right] \quad (1.16)$$

is plotted. The factor of  $u^2$  causes the distribution to be zero at  $u=0$  and skews the distribution curve to higher velocities.

- Equation (1.15) is called the Maxwell-Boltzmann velocity distribution function. It is the fundamental tool of the Kinetic Theory of Gases.



Figure 1.5: James Clerk Maxwell (1831-1879, left) was a Scottish physicist, considered by many to be one of the greatest physicists of all time, after Newton and Einstein. His crowning achievement was development of electromagnetic theory. He also developed independent of Ludwig Boltzmann, the kinetic theory of gases. Ludwig Boltzmann (1844,-1906, right) was an Austrian physicist who developed independently the kinetic theory of gases, statistical mechanics, and promoted in the late 19<sup>th</sup>-early 20<sup>th</sup> century, against considerable opposition, atomistic physics.