

### 4.3: Probability Density Functions from the Energies of Classical-mechanical Models

Guided by our development of the Maxwell-Boltzmann probability density function for molecular velocities, we could postulate that similar probability density functions apply to other energies derived from classical-mechanical models for molecular motion. We will see that this can indeed be done. The results correspond to the results that we get from the Boltzmann equation, where we assume for both derivations that many energy levels satisfy  $\epsilon \ll kT$ . The essential point is that, at a sufficiently high temperature, the behavior predicted by the quantum mechanical model and that predicted from classical mechanics converge. This high-temperature approximation is a good one for translational motions but a very poor one for vibrational motions. These results further illuminate the differences between the classical-mechanical and the quantum-mechanical models for the behavior of molecules.

Let us look at how we can generate probability density functions based on the energies of classical-mechanical models for molecular motions. In the classical mechanical model, a particle moving in one dimension with velocity  $v$  has kinetic energy  $mv^2/2$ . From the discussion above, if many velocities satisfy  $kT \gg mv^2/2$ , we can postulate a probability density function of the form

$$\frac{df}{dv} = B_{\text{trans}} \exp\left(\frac{-mv^2}{2kT}\right)$$

where  $B_{\text{trans}}$  is fixed by the condition

$$\int_{-\infty}^{\infty} \left(\frac{df}{dv}\right) dv = B_{\text{trans}} \int_{-\infty}^{\infty} \exp\left(\frac{-mv^2}{2kT}\right) dv = 1$$

Evidently, this postulate assumes that each velocity constitutes a quantum state and that the degeneracy is the same for all velocities. This assumption is successful for one-dimensional translation, but not for translational motion in two or three dimensions. The definite integral is given in Appendix D. We find

$$B_{\text{trans}} = (m/2\pi kT)^{1/2}$$

and

$$\frac{df}{dv} = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(\frac{-mv^2}{2kT}\right)$$

With  $m/kT = \lambda$ , this is the same as the result that we obtain in [Section 4.4](#). With  $B_{\text{trans}}$  in hand, we can calculate the average energy associated with the motion of a gas molecule in one dimension

$$\langle \epsilon \rangle = \int_{-\infty}^{\infty} \left(\frac{mv^2}{2}\right) \left(\frac{df}{dv}\right) dv = \left(\frac{m^3}{8\pi kT}\right)^{1/2} \int_{-\infty}^{\infty} v^2 \exp\left(\frac{-mv^2}{2kT}\right) dv$$

This definite integral is also given in Appendix D. We find

$$\langle \epsilon_{\text{trans}} \rangle = \frac{kT}{2}$$

We see that we can obtain the average kinetic energy for one degree of translational motion by a simple argument that uses classical-mechanical energies in the Boltzmann equation. We can make the same argument for each of the other two degrees of translational motion. We conclude that each degree of translational freedom contributes  $kT/2$  to the average energy of a gas molecule. For three degrees of translational freedom, the total contribution is  $3kT/2$ , which is the result that we first obtained in [Section 2.10](#).

Now let us consider a classical-mechanical model for a rigid molecule rotating in a plane. The classical kinetic energy is  $\epsilon_{\text{rot}} = I\omega^2/2$ , where  $I$  is the molecule's moment of inertia about the axis of rotation, and  $\omega$  is the angular rotation rate. This has the same form as the translational kinetic energy, so if we assume  $kT \gg I\omega^2/2$  and a probability density function of the form

$$\frac{df}{d\omega} = B_{\text{rot}} \exp\left(\frac{-I\omega^2}{2kT}\right)$$

finding  $B_{\text{rot}}$  and  $\langle \epsilon_{\text{rot}} \rangle$  follows exactly as before, and the average rotational kinetic energy is

$$\langle \epsilon_{\text{rot}} \rangle = kT/2$$

for a molecule with one degree of rotational freedom.

For a classical harmonic oscillator, the vibrational energy has both kinetic and potential energy components. They are  $mv^2/2$  and  $kx^2/2$  where  $v$  is the oscillator's instantaneous velocity,  $x$  is its instantaneous location, and  $k$  is the force constant. Both of these have the same form as the translational kinetic energy equation. If we can assume that  $kT \gg mv^2/2$ , that  $kT \gg kx^2/2$ , and that the probability density functions are

$$\frac{df}{dv} = B_{\text{vib}}^{\text{kinetic}} \exp\left(\frac{-mv^2}{2kT}\right)$$

and

$$\frac{df}{dx} = B_{\text{vib}}^{\text{potential}} \exp\left(\frac{-kx^2}{2kT}\right)$$

the same arguments show that the average kinetic energy and the average potential energy are both  $kT/2$ :

$$\langle \epsilon_{\text{vib}}^{\text{kinetic}} \rangle = kT/2$$

and

$$\langle \epsilon_{\text{vib}}^{\text{potential}} \rangle = kT/2$$

so that the average total vibrational energy is

$$\langle \epsilon_{\text{vib}}^{\text{total}} \rangle = kT$$

In summary, because the energy for translational motion in one dimension, the energy for rotational motion about one axis, the energy for vibrational kinetic energy in one dimension, and the energy for vibrational potential energy in one dimension all have the same form ( $\epsilon = Xu^2$ ) each of these modes can contribute  $kT/2$  to the average energy of a molecule. For translation and rotation, the total is  $kT/2$  for each degree of translational or rotational freedom. For vibration, because there is both a kinetic and a potential energy contribution, the total is  $kT$  per degree of vibrational freedom.

Let us illustrate this for the particular case of a non-linear, triatomic molecule. From our discussion in [Section 18.4](#), we see that there are three degrees of translational freedom, three degrees of rotational freedom, and three degrees of vibrational freedom. The contributions to the average molecular energy are

- $3(kT/2)$  from translation
- $+3(kT/2)$  from rotation
- $+3kT$  from vibration
- $= 6kT$  in total

Since the heat capacity is

$$C_V = \left( \frac{\partial \epsilon}{\partial T} \right)_v$$

each translational degree of freedom can contribute  $k/2$  to the heat capacity. Each rotational degree of freedom can also contribute  $k/2$  to the heat capacity. Each vibrational degree of freedom can contribute  $k$  to the heat capacity. It is important to remember that these results represent upper limits for real molecules. These limits are realized at high temperatures, or more precisely, at temperatures where many energy levels,  $\epsilon_i$ , satisfy  $\epsilon_i \ll kT$

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