

## *Reading assignment*

Schroeder, sections 1.5 and 1.6. This is the last of the material from chapter 1 that we will cover.

## *Recap of lecture 1*

- Equilibrium states of macroscopic amounts of matter are characterized by a small number of macroscopic properties, such as energy, entropy, volume, number of particles, temperature, and pressure.
- Thermodynamics deals purely with the macroscopic aspects of systems in equilibrium states. Entropy is mysterious.
- Statistical mechanics applies statistical methods to the microscopic aspects of systems to derive their macroscopic properties. It provides a clear definition of entropy and a foundation for thermodynamics.
- Toy system: ideal gas—noninteracting particles.  
 $PV = NkT$ .

## *Recap of lecture 1*

- Using a kinetic model for pressure in a monatomic ideal gas, we found that  $PV$  and the mean kinetic energy are related; this leads, via the ideal gas law, to a relation between the mean kinetic energy and the temperature:

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT.$$

## *Equipartition theorem*

We found that for the monatomic ideal gas

$$\frac{1}{2}m\overline{v_i^2} = \frac{1}{3} \times \frac{1}{2}m\overline{v^2} = \frac{1}{2}kT,$$

where  $i = x, y,$  or  $z$ .

The total energy is then

$$U = N \times \frac{1}{2}m\overline{v^2} = 3N\frac{1}{2}kT.$$

That is, each direction of motion of each particle contributes, on average,  $\frac{1}{2}kT$  to the total energy of the system.

This turns out to be an instance of a more general feature of all classical mechanical systems:

## *Equipartition theorem*

### *Theorem*

*In a classical system, each quadratic degree of freedom contributes  $\frac{1}{2}kT$  to the total energy.*

In other words, every generalized coordinate *or momentum* that appears quadratically in the Hamiltonian function of the system contributes  $\frac{1}{2}kT$  to the total energy.

The proof requires some machinery that we haven't developed yet, so we'll defer the proof until later in the semester.

## Identifying quadratic degrees of freedom

Some examples of Hamiltonians with quadratic coordinates or momenta:

- Free point particle:

$$H = \sum_{i=1}^3 \frac{1}{2} m v_i^2 = \sum_{i=1}^3 \frac{p_i^2}{2m} \quad (3 \text{ degrees of freedom})$$

- Simple harmonic oscillator:

$$H = \frac{p^2}{2m} + \frac{1}{2} k x^2 \quad (2 \text{ degrees of freedom})$$

- Dumbbell (or any rigid body):

$$H = \sum_{i=1}^3 \frac{P_i^2}{2M} + \sum_{i=1}^3 \frac{L_i^2}{2I_i} \quad (6 \text{ degrees of freedom})$$

## Quantum effects

The equipartition theorem applies to classical systems, for which the separation between energies is zero—there's a continuous range of allowed energies of the system.

In quantum systems that isn't true. Suppose the energy required to excite a particular degree of freedom (viewed as a subsystem) from the ground state is  $\Delta E$ . Then:

- If  $kT \ll \Delta E$ , there is very low probability of excitation, since very few of the other subsystems have sufficient energy to donate for the excitation. Thus, that degree of freedom is *frozen out*—it doesn't store a significant portion of the energy of the whole system.
- If  $kT \gg \Delta E$ , the equipartition theorem can be applied safely.

## *Diatomic gases*

A diatomic molecule is similar to a dumbbell with a spring instead of a rigid connecting rod. Since the atoms can vibrate in and out like a simple oscillator, there should be **2** vibrational degrees of freedom of the oscillator plus the **6** translational and rotational degrees of freedom of the dumbbell, for a total of **8**.

Experimentally, one finds that the total energy of a diatomic gas is less than  $8N \times \frac{1}{2}kT$ , and the reason is quantum freeze-out of some degrees of freedom.

Rotational degrees of freedom contribute terms to the Hamiltonian that are of the form

$$\frac{L^2}{2I},$$

for which the quantized eigenenergies are

$$\frac{\hbar^2 l(l+1)}{2I}.$$



## *Diatomic gases*

The excitation energy from the ground state with  $l = 0$  to the  $l = 1$  state is:

$$\Delta E = \frac{\hbar^2}{I},$$

which becomes large when the moment of inertia is small. That is always the case for rotation about the bond axis, so that rotational degree of freedom is never observed.

The other two principal axes of inertia, perpendicular to the bond, have much larger moments, so they are excited thermally. For common diatomic gases such as  $O_2$  and  $Cl_2$ ,

$$\frac{\hbar^2}{Ik} = O(2 \text{ K}),$$

well below the temperatures at which they become gaseous.

## *Diatomic gases*

The energy of a quantum harmonic oscillator is

$$\left(n + \frac{1}{2}\right) \hbar\omega ,$$

so the excitation energy is

$$\Delta E = \hbar\omega .$$

For common gases  $\text{O}_2$  and  $\text{Cl}_2$ ,

$$\frac{\hbar\omega}{k} = O(\text{few thousand K}).$$

So their vibrational degrees of freedom are frozen out at room temperature.

Thus, each molecule of a gas of identical diatomic molecules has just 5 degrees of freedom at room temperature, each of which holds an average of  $\frac{1}{2}kT$  of energy.

## *The first law of thermodynamics*

$$\Delta U = Q + W$$

That is, the change in energy of a system is the sum of the heat transferred into it and the work done on it. This is just a statement of the law of conservation of energy.

Thus *heat* is defined as the energy transferred to a system by means that are neither mechanical nor electromagnetic.

Once the energy has been changed by either means, there is no way to discover by examining the state of the system whether the energy change was due to heat transfer or work. Neither heat nor work is a characteristic of the state of the system—they merely describe mechanisms by which the energy, which is a characteristic of the system, can be altered.

# *Homework*

## *HW Problem*

Schroeder problem 1.26, p. 19.

## *HW Problem*

Schroeder problem 1.28, p. 20.