2 Energy and temperature

The purpose of this chapter is to explore how we describe heat energy and its spontaneous flow. We don't really have a principle to explain **why** energy flows from hot to cold yet. For that we'll need entropy, which will be covered in the later chapters.

Summary of concepts:

- If two objects are placed into thermal contact, heat flows from high temperature to low temperature until the temperatures are the same.

- Heat conduction – how fast heat flows.

- Heat capacity – how much heat energy it takes to change the temperature.

- Equipartition – gives us a way to estimate heat capacity for a wide class of materials.

2.1 Temperature

Temperature is the propensity for an object to give up its heat energy. Heat spontaneously flows from higher temperature to lower temperature. In this course, it is almost always measured in Kelvin. It is recommended to always convert to Kelvin before performing any thermodynamic calculations.

2.2 Heat capacity

Heat capacity is a measure of how much heat it takes to change the temperature.

$$C = \frac{\partial Q}{\partial T} \tag{1}$$

You can imagine an experiment as follows: you put a small amount of heat into an object, and measure how much the temperature changed. If the temperature changes a lot, then the object has small heat capacity, while if it changes a little, the object has large heat capacity. The units in SI are J/K.

Specific heat capacity Particularly in chemistry it is useful to know the heat capacity *per mass* of a substance. To measure the specific heat of a substance, you just divide the heat capacity by the mass of the substance. The units in SI are J/K kg.

Molar specific heat capacity As it turns out, the heat capacity per atom is often fairly universal–at high temperatures most solids have the same heat capacity per atom. Typically, though, we work with moles of atoms. One mol is N_A atoms, where N_A is Avagadro's number. To measure the molar specific heat, you just divide the heat capacity by the number of moles in the object. If you know the atomic mass of the atoms, you can get that from the mass. For example, if an atom has an atomic mass of 40, then that means that its mass is 40 g/mol.

Heat capacity at constant volume If the volume is constant, that means that $dV = 0$, so all changes in the internal energy are due to heat. Therefore

$$C_V = \frac{dQ}{dT} = \frac{dU + pdV}{dT} = \frac{dU}{dT} \tag{2}$$

where the V subscript means constant volume.

Heat capacity at constant pressure If the pressure is constant, then

$$C_p = \frac{dQ}{dT} = \frac{dU + pdV}{dT} = \frac{dU}{dT} + p\frac{dV}{dT}, \tag{3}$$

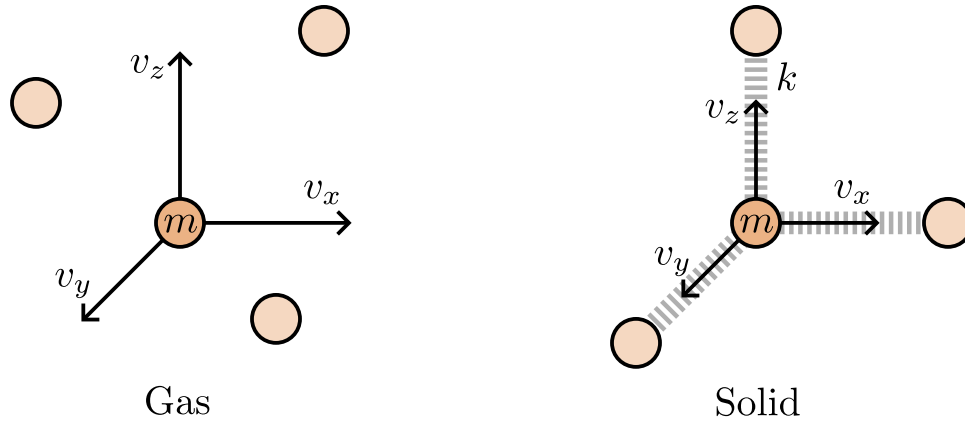where the p subscript means constant pressure. To compute this, one needs to know $V(T)$.

Figure 1: An atom of gas has a total energy equal to its kinetic energy $E_g = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$. An atom in the solid has kinetic energy *and* potential energy from its bonds with other atoms, for a total energy $E_s = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}k(x^2 + y^2 + z^2)$. The gas's energy is proportional to 3 squared quantities, while the solid's energy is proportional to 6 squared quantities. Each quadratic degree of freedom corresponds to one squared quantity.

2.3   Equipartition hypothesis

The equipartition hypothesis is not always true, but later in the class we will learn some more about why it works as well as it does. The statement is the following: for every **quadratic** degree of freedom, the internal energy per atom is $\frac{1}{2}k_B T + C$, where k_B is the Boltzmann constant and C is an unknown constant (remember that a constant offset of energy doesn't change physics). Each direction of travel or rotational mode counts as one degree of freedom from the kinetic energy, and each direction of vibration counts as two degrees of freedom from the kinetic and potential energy.

Example: monatomic gases Consider a monatomic gas (for example, He) in which the atoms are free to whiz around. Each atom can go in three directions, and the kinetic energy is given by $\frac{1}{2}mv^2$, which is quadratic. Therefore, the internal energy of a gas of N He atoms is $\frac{3}{2}Nk_B T + C$. Alternatively, the total internal energy of a gas of n moles of He atoms is $\frac{3}{2}nRT + C$, where R is the ideal gas constant. So the molar heat capacity at constant volume of a monatomic gas is very simply $\frac{3}{2}R$

Example: diatomic gases In this case, we have two-atom molecules in the gas. This applies to air, which is mostly N_2 and O_2. In this case ,the number of degrees of freedom is 5, because the molecules now have two extra rotational degrees of freedom. It is two because rotation around axis of the molecule requires a lot of energy due to quantum mechanics. So the internal energy is $\frac{5}{2}Nk_B T + C$.

Example: solids In solids the atoms cannot move freely, but can vibrate against one another. Each atom has three directions in can vibrate (x,y,z), so that is a total of 6 degrees of freedom per atom. So the molar heat capacity at constant volume of a solid is $3R$.

The equipartition hypothesis is very useful since it allows us to estimate the heat capacity for many diverse objects! We should note that it becomes inaccurate at very low temperatures due to quantum mechanical effects; however, for room temperatures it is often very good.

2.4   Heat conduction

For the most part, this course deals with equilibrium, and not so much in how systems come into equilibrium. However, there is a simple model for heat conduction that is worth including. Conduction of heat can be approximately described using *heat conductivity*, which is very much like electrical conductivity. In this analogy, potential difference (voltage) corresponds to the difference in temperature and current is heat. Usually the symbol κ is used for the conductivity of a given material and the the SI units are W/m K.
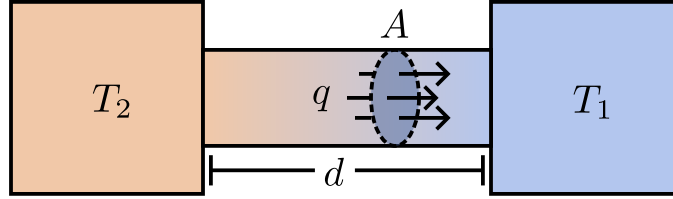
Figure 2: Heat flows from an object at a higher temperature T_2 to an object at a lower temperature T_1. The heat flux q through an area A depends on the difference in temperature and the distance between the two objects according to Equation 4.

The total heat transport per second Q (W) is given by

$$q = -\frac{\kappa A}{d}(T_2 - T_1) \tag{4}$$

where d is the length of the connection, and κ is the thermal conductivity of the material. It is useful to define the conductance of a given object with cross-sectional area A and length d as $k = \frac{\kappa A}{d}$

If there are multiple paths with conductance k_1 and k_2, then they combine very much like electrical conductivity. For example, for two objects in series,

$$k_{tot} = \frac{1}{k_1} + \frac{1}{k_2}. \tag{5}$$

And for parallel:

$$k_{tot} = k_1 + k_2. \tag{6}$$

Sometimes the thermal resistance is used $R = 1/k$, which helps as a mnemonic for the serial and parallel formulae: in serial the resistance is summed, while in parallel the conductance is summed.

2.5 Managing all the variables in thermodynamics.

In thermodynamics, we have many macrostate variables to keep track of. Already in this course, we've seen T, p, V, C, U, W_{on}, Q, N. You may have noticed that we often don't indicate that each of these variables can actually also be dependent on each of the others. For example, pressure can be written as a function of number, volume, and temperature $p(N, V, T)$. Indeed, that is precisely what the comforting ideal gas law does for us; for an ideal gas, $p = Nk_BT/V$. Other systems might have different relations between the macrostate variables. At the same time, one can write volume V as a function of N, p, T. The equipartition hypothesis allows us to write internal energy as a function of T: $U = \frac{N_{DOF}}{2}Nk_BT + C$.

For these problems a general strategy is to:

- Identify what is constant and what is changing. (example: constant volume, but temperature is changing as in the blocks example)

- Find the equilibrium condition (example: $T_1 = T_2$)

- Use the first law to compute changes in internal energy. This will require integration; make sure that all integrals are written in terms of constants and the integration variable.

- Do all integrals to find changes in the macrostate variables.

This strategy works for almost all problems in this course.