Lecture 2.1

Temperature

Today we shall finally move outside of the domain of classical mechanics and address thermal properties of macroscopic systems. By macroscopic we mean a continuous systems consisting of large number of particles. We have already discussed some examples of such systems when we talked about fluids. We have introduced several variables to describe fluids. The variables were density $\rho$, and pressure $p$. Introducing these variables we were not concerned with microscopic structure of fluid. Both pressure and density can be measured experimentally as a result of a certain averaging over system's volume without looking into their local behavior. This type of the system’s description is known as macroscopic description. The part of physics, which uses this method, is called classical thermodynamics. We shall continue developing this method for now, while later we shall also study some microscopic approaches.

Even though we have introduced pressure and density as fundamental variables, the description of the system is still not complete. We have only considered the case of the constant temperature, even though we have not made this explicit. So, essentially we have left out of our consideration the entire area of physics which has to do with heat and thermal energy. However, you may remember that when you were talking about energy conservation you found that some part of mechanical energy of a system can be lost due to friction and it is spent to increase system's thermal (or internal energy). We have never considered this subject in details. Now it is the right time to do so. We shall start by introducing the new physical quantity, known as temperature.

1. Temperature

Temperature as well as mass, length and time is one of the fundamental dimensions which forms the basis for SI (International System of Units). The SI uses Kelvin scale to measure temperature (SI unit of temperature is Kelvin). The main difference of the Kelvin scale from all other temperature scales, such as British Fahrenheit scale or European Celsius scale, is that Kelvin scale starts from absolute zero. Even though there is no upper limit for temperature of a physical body, but there is a low limit. In no case temperature can be below this value. In fact, even this value itself can not be reached, because the process of cooling will stop working at such low temperatures. It is natural to count temperature from this lowest value (as the Kelvin scale does), without having negative values of temperature as it occurs in Fahrenheit or Celsius scales.
Temperature is the measure of the internal energy of a system. As soon as this energy changes, so do the properties of the body. For instance, if one heats a body, it may change its size (thermal expansion), pressure, density and other properties. This fact should help us to measure temperature by watching other properties of the body. Let us see how we can do that.

If we have three bodies $A$, $B$ and $C$, we can bring body $A$ and $C$ in contact and wait for some time. During this time we can observe properties of the bodies, for instance volumes. These properties will change at first, but eventually all the changes will stop. In this case we say that bodies $A$ and $C$ have reached their *thermal equilibrium* and have the same temperature. We can also bring bodies $B$ and $C$ in contact. If it so happens that there are no changes to their properties then they are already in thermal equilibrium and have the same temperature. Moreover, if body $C$ has not changed its properties during the contact with body $B$, then bodies $A$ and $B$ have the same temperature and their properties are not changing, which is confirmed experimentally. The above experimental result is the *zero law of thermodynamics*, which states that *if bodies A and B are each in thermal equilibrium with a third body C, then they are in thermal equilibrium with each other.*

We can use this law in order to build a *thermometer*, a device which will allow us to measure temperature. For instance we can use body $C$ as such a device. At first we had it in contact with body $A$, so observing its properties at that time we could measure the temperature of body $A$. Then we had it in contact with body $B$, so we could measure the temperature of $B$. The only thing we have to do is to calibrate $C$ for a certain scale, so we know which temperature refers to which state of body $C$. To do so we have to pick some reproducible thermal phenomenon (a standard fixed point) and set the temperature at this point to be equal to some given value. We shall use the *triple point of water* (at this point all three phases of water are in equilibrium) as a standard point. For this point the temperature in Kelvin scale is set to be exactly

$$T_3 = 273.16 K \quad (2.1.1)$$

So one degree of Kelvin scale is $1/273.16$ of the difference between the absolute zero and the triple point of water. This is the SI unit for temperature, known as Kelvin ($K$).

The standard thermometer (body $C$ in our example) is based on the properties of the gas's pressure at fixed volume. It is known as a *constant-volume gas thermometer*. In the reasonable temperature interval when this gas has low enough density, the relationship between its temperature and pressure is linear, so

$$T = Cp .$$
If the triple point is in this temperature interval, then we have
\[ T_3 = C p_3 \]
and we can measure any other temperature by measuring gas pressure as
\[ T = 273.16 K \frac{P}{p_3}. \]
Since the real gases are not ideal, this relation is not exactly linear unless we reduce the amount of gas to almost zero, so
\[ T = 273.16 K \left( \lim_{g \to 0} \frac{P}{p_3} \right), \]
shows the ideal gas temperature, which can be calculated by extrapolation from the real gas thermometer.

The Kelvin scale is the temperature scale usually used in physics. However, in everyday life nobody uses the Kelvin scale. Instead in most countries people use Celsius scale. One degree of the Celsius scale has the same magnitude as one Kelvin, but the origin of Celsius scale is shifted to make it more convenient for practical use. This shift is 273.15 degrees, so
\[ T_c = T - 273.15^\circ. \] (2.1.2)

In the United States the British system is in use. In this system the unit of temperature is degree of Fahrenheit. The relation between the Celsius and Fahrenheit scales is
\[ T_F = \frac{9}{5} T_c + 32^\circ. \] (2.1.3)

We have based our thermometer on the pressure changes for ideal gas. However, pressure is not the only property of a body, which changes with change of temperature. The size of the body changes too. In the case of ideal gas, we could fix its volume by fixing the volume of the container, because gas does not have any fixed shape and occupies the whole container. If however, we consider a solid body, we can see how its volume and linear dimensions are changing with temperature change. These changes are known as thermal expansion, which is the size of the body will increase as temperature increases and it will decrease with temperature decreasing. Some thermometers are based on that effect.

If temperature of a solid body (let us say a rod) increases by a small amount \( \Delta T \), then its linear size (length) will also increase by
\[ \Delta L = L_0 \alpha \Delta T, \]  
(2.1.4)

where \( L_0 \) is the original length of the body and \( \alpha \) is the coefficient of linear expansion. This coefficient only depends on properties of the material used but not on its size. You can find values of these coefficients for different substances in Table 18-2 in the book. As it can be seen from the equation 2.1.4, the SI unit for this \( \alpha \)-coefficient is \( 1/K \) or \( 1/\text{degree Celsius} \). To measure coefficient of linear expansion for several substances will be our task in the lab today.

Equation 2.1.4 can be applied to any linear dimension, not just to change of length. So, if one has a rectangular block, all of its sides will increase in length if the block is heated. This means that area of each of the surfaces and the volume of this block will increase as well. If you consider a liquid, which does not have a fixed shape, the change of volume is the only meaningful change in its size. In any case the volume change can be calculated as

\[ \Delta V = V_0 \beta \Delta T, \]  
(2.1.5)

where \( V_0 \) is the original volume of the body and \( \beta \) is the coefficient of volume expansion. It is approximately related to coefficient of the liner expansion by

\[ \beta = 3\alpha. \]  
(2.1.6)

The most well known exception from this rule, when volume increases with decrease of temperature, is water. It decreases in volume as temperature goes down but only till it reaches \( 4^\circ \text{C} \). After the temperature of water becomes less than this value, it starts increasing in volume again. The density of water decreases below \( 4^\circ \text{C} \) and the density of ice is even less than that of water, so that ice floats on the surface of water.

Example 2.1.1. An ordinary glass is filled to the brim with 350.0 mL of water at \( 100^\circ \text{C} \). If the temperature decreases to \( 20^\circ \text{C} \), how much water could be added to the glass?

When temperature decreases both the glass and water will reduce their volumes (at least in this temperature range). Since they have different expansion coefficients these changes are different. To find out how much water could be added we need to find the difference between the volume changes. So one has \( \Delta V_1 = \beta_1 V_0 \Delta T \) with \( \beta_1 = 210 \times 10^{-6} \text{C}^{-1} \) for water and \( \Delta V_2 = \beta_2 V_0 \Delta T \) with \( \beta_2 = 27 \times 10^{-6} \text{C}^{-1} \) for the glass. That means one can add the volume of

\[ |\Delta V| = |\Delta V_1 - \Delta V_2| = (\beta_1 - \beta_2)V_0|\Delta T| = (210 - 27) \times 10^{-6} \text{C}^{-1} \times 350 \text{mL} \times |20^\circ \text{C} - 100^\circ \text{C}| = 5.12 \text{mL}. \]
2. Temperature and Heat

We have already discussed that if one takes two bodies $A$ and $B$, with original temperatures $T_A$ and $T_B$, and brings them into contact the temperature of both bodies will eventually become the same. So the body, which had higher temperature, will be cooled and another body, which had lower temperature, will be heated. We can consider the system not just of two bodies, but the system consisting of one body and its environment. The process will be the same: the temperature of the body will become the same as the temperature of the environment. The environment will change its temperature just slightly while the change of the body’s temperature can be quite sufficient. This change of temperature occurs due to the energy transfer between the body and the environment. The internal (thermal) energy of the body, which is kinetic energy and potential energy associated with the motion of the molecules of the body, will change during this transfer. In this process the transferred energy is called heat. We shall use letter $Q$ to represent this energy. The heat is positive when it is absorbed by a body, and it is negative when it is lost by a body and transferred to the environment. This means that the heat is positive if the final temperature of the body is more than its original temperature. The heat is negative if the final temperature of the body is less than its original temperature. So, heat is the energy that is transferred between a system and its environment because of the temperature difference that exists between them. If the temperature difference is already zero, which means the body and the environment are already in equilibrium, then the transferred energy is going to be zero. Heat (as well as work) is not a function of the system's state, but rather depends on the process in which it was transferred.

The SI unit of heat is the same as the unit for energy and work, which is Joule. However, there is another unit, which is used very often, because it is associated with properties of a very common substance, water. This unit is calorie (cal), which is the amount of heat that would raise the temperature of 1 gram of water from 14.5 degrees Celsius to 15.5 degrees Celsius. In British system of units another unit British thermal unit (Btu), defined as the amount of heat needed to raise the temperature of 1 pound of water from 63 degrees Fahrenheit to 64 degrees Fahrenheit, is used. The relation between these units is the following

$$1 \text{ kcal} = 3.969 \times 10^{-3} \text{ Btu} = 4.1860 \text{ J}.$$ 

Heat absorbed by a body is proportional to the temperature change of this body. The coefficient of proportionality is called the heat capacity, $C$, of the body, which is
Heat capacity has the unit of energy per temperature $J/K$ or $J/°C$. Two objects made of the same material but with different masses will have heat capacity proportional to their masses with the same proportionality coefficient. It is convenient to define heat capacity per unit of mass, which is called specific heat, $c$, of the substance. It only depends on the object's material but not on its mass, so

$$Q = cm\Delta T = cm(T_f - T_i).$$

Table 18-3 in the book shows values for specific heats of some substances. Note that specific heat itself depends on temperature (Table 18-3 shows values at normal room temperature). Specific heat also depends on external conditions of the process, such as whether or not the process occurs at constant pressure or at constant volume. In most part of the cases we assume that the process takes place under condition of the constant pressure (usually atmospheric). On the other hand, sometimes we can assume that the sample is held under conditions of constant volume. In any case the difference between specific heat of solids/liquids under constant pressure and constant volume is almost negligible. The case of gasses is quite different. We shall address it in details later.

Let us consider a physical system, which consists of several parts exchanging heat. Since the total energy of the system has to be conserved during heat transfer process, the energy lost by some parts of the system should to be equal the energy gained by other parts of the system. This means that the total sum of all the heats transferred inside of the closed system is equal to zero

$$\sum Q = 0$$

Note that the system has to be closed, so no heat is lost to the environment. This means that the process has to be performed in a calorimeter, which insulates the system from the environment. Part of physics which studies processes taking place in such insulated systems is called Calorimetry.

When heat is adsorbed or lost by some substance, the temperature will change but not forever. At certain temperature, known as the temperature of the phase transition, the substance will change its phase. It can be melting from solid to liquid or evaporating from liquid to gas in the case of heating. Or it can be freezing from liquid to solid or condensation from gas to liquid in the case of cooling. During these phase transitions the temperature of the object is not changing. So the process of phase transition occurs at
constant temperature. These temperatures are also dependent on external conditions, such as pressure.

Let us see how the process of evaporation takes place. For a given value of pressure, usually atmospheric pressure, liquid and vapor phases are going to be in equilibrium at certain temperature. This equilibrium is actually a dynamic one. Certain "fast" molecules of liquid are leaving its surface and transferring into vapor, which always exists above the surface of liquid. At the same time the same amount of vapor molecules at given time interval are coming back to liquid, so the entire system is in equilibrium. If one changes the pressure or temperature, the equilibrium will be destroyed and one of the phases will become more stable than the other, so that the phase transition will take place.

One can achieve that by blowing wind above the open container with liquid. The pressure above the liquid will become smaller causing even more molecules to leave liquid’s surface. So the liquid will continuously evaporate until none is left. Since the fastest molecules are leaving liquid's surface during evaporation, the liquid loses its energy and then gains energy from the environment in order to maintain the same temperature. This is the reason why one can use evaporation in order to cool the surroundings.

If we still want to maintain equilibrium, we need to change both temperature and external pressure of the system along the vapor-pressure curve. It explains why water has different boiling temperatures at different conditions.

After the temperature reaches certain large value, known as the critical point, no one pressure will be able to keep the substance in liquid phase and it will eventually evaporate.

Similar equilibrium may exist between liquid and solid. It is called fusion curve, and between vapor and solid, it is called sublimation curve. The point, where these 3 curves cross each other is the point, where all 3 phases are in equilibrium and it is called the triple point. Now it is easy to see that this may only take place at certain temperature and pressure for any given substance. This is why we have chosen it as a reference point in constructing the temperature scale.

Even though temperature is not changing during phase transitions, the object still either absorbs or releases the energy. In the case of melting this energy goes to destroy crystalline lattice of the solid. In the case of evaporation the energy goes to free molecules from liquid clusters. Of course, this energy, which is either absorbed or
released during the phase transition, is proportional to the mass of the substance. So the heat needed to perform the phase transition is

\[ Q = Lm, \]  

(2.1.10)

where \( L \) is the energy per unit of mass that must be transferred as heat, when the sample undergoes a phase change which is also known as the \textit{heat of transformation} or \textit{latent heat}. Depending on the phase transition, it can either be the heat of vaporization of the heat of fusion. Table 18-4 in the book shows those values for some substances.

The energy balance in the system described by equation 2.1.9 is still maintained, even if there are phase transitions, but all the heats including the ones described by equation 2.1.10 must be included.