

Lecture_03

September 15, 2023

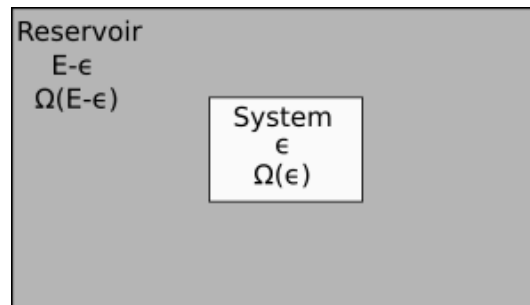
1 Introduction to Thermodynamics and Statistical Physics

In this lecture, we are going to continue introducing some topics which are needed to fully explore thermal physics. In particular, we'll cover:

- The Boltzmann Distribution
- Partition Function and Energy
- The First Law of Thermodynamics
- Reversibility, Isothermal Expansions, and Adiabatic expansions

1.1 The Boltzmann Distribution

Ok, now let's consider the above example again. However, we're going to change one of the systems such that it acts as a reservoir (or heat bath). We then place the other system into thermal contact with the reservoir. The reservoir has such an enormous amount of energy compared to the system that any change in its temperature as it heats the smaller system is completely negligible. This is the canonical ensemble discussed previously.



Now, we're going to assume that for each energy of the system, there is only a single allowed microstate. As such, $\Omega(\epsilon) = 1$.

So, the probability that the system has energy ϵ is proportional to the number of microstates of the reservoir times the number of microstates of the system:

$$P(\epsilon) \propto \Omega(E - \epsilon)\Omega(\epsilon) = \Omega(E - \epsilon)$$

Now using

$$\frac{1}{k_B T} = \frac{d \ln \Omega}{d E}$$

and given that $\epsilon \ll E$, we can Taylor expand $\ln\Omega$ around 0 to give

$$\ln\Omega(E - \epsilon) = \ln\Omega(E) - \frac{d\ln\Omega(E)}{dE}\epsilon + \dots$$

which gives

$$\ln\Omega(E - \epsilon) = \ln\Omega(E) - \frac{\epsilon}{k_B T} + \dots$$

This then gives

$$\Omega(E - \epsilon) = \Omega(E)e^{-\frac{\epsilon}{k_B T}}$$

Finally, this gives

$$P(\epsilon) \propto e^{-\frac{\epsilon}{k_B T}}$$

This probability tells us how the system reacts to being placed in the bath. There is a high probability that the system will achieve an energy ϵ which is less than $k_B T$, but it quickly decays above this energy, meaning we are unlikely to observe the system to have an energy much higher than the reservoir. Now, to normalise the probability, we must divide by all possible microstates:

$$P(E_r) = \frac{e^{-E_r/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

This is known as the **Boltzmann distribution**. It is also written as

$$P(E_r) = \frac{1}{Z}e^{-\beta E_r}$$

where

$$Z = \sum_i e^{-\beta E_i}$$

is called the **partition function**. In deriving this, we have assumed that every energy has a single microstate which describes it. This is not necessarily true, and so we can modify the equations above to be

$$P(E_r) = \frac{1}{Z}g(E_r)e^{-\beta E_r}$$

$$Z = \sum_{E_i} g(E_i)e^{-\beta E_i}$$

where we are now summing over energies instead of microstates. $g(E_i)$ is then the number of microstates possessing energy E_i . It is called the degeneracy of the energy eigenvalue E_i , and will come up in quantum mechanics.

Finally, it's useful to note that $1/k_B T$ comes up a lot in statistical mechanics. As such, it's often simply written as

$$\beta \equiv \frac{1}{k_B T}$$

to save time.

1.2 The partition function and Energy

So now assume we have some system with internal energy U . What is the average energy of the system? To calculate this, we need to take the energy of each state and multiply it by the probability that each state will occur. This gives

$$\bar{U} = \sum_i P(E_i) E_i = \frac{1}{Z} \sum_i E_i e^{(-\beta E_i)}.$$

However,

$$\sum_i E_i e^{(-\beta E_i)} = -\frac{dZ}{d\beta}$$

so we get

$$\bar{U} = -\frac{1}{Z} \frac{dZ}{d\beta} = -\frac{d \ln Z}{d\beta}$$

1.3 Some final definitions

Right, we need a few final terms before we can move on.

Thermal equilibrium : A system is in thermal equilibrium when its macroscopic properties have ceased to change with time.

Functions of state : Any physical quantity that has a well defined value for each equilibrium state of a system. For example: Pressure, temperature, volume. In mathematical terms, these are exact differentials.

Work put into a system and total heat put into or out of a system are thus **not** functions of state. They are inexact differentials.

As a nice example, consider warming up your hands. If you change the temperature of your hands, they achieve an equilibrium state with a given temperature, independent of how you managed to get them to this temperature. That is, you could rub them together (performing work on them) or sinking them into a tub of hot water (adding heat to them).

In this course, we will endeavour to write exact differentials as dT , and inexact differentials as dQ . However, some times latex doesn't work with this symbol, so always check one of the course books to be sure whether an equation involves an exact or an inexact differential.

Equation of state: An equation of state links together functions of state. For example, $PV = Nk_B T$ is the equation of state of an Ideal Gas.

1.4 The First Law of Thermodynamics

So, now we are in a position to state the first law of thermodynamics, which says:

The first law of thermodynamics Energy is conserved, and heat and work are both forms of energy.

This was shown experimentally by Joule, who changed the temperature of a mass of water in two ways: rotating a paddle through it, and by placing a heating element in it, and for a fixed temperature change, found that the energy from both methods was the same.

Mathematically, we can write the first law as

$$\Delta U = \Delta Q + \Delta W.$$

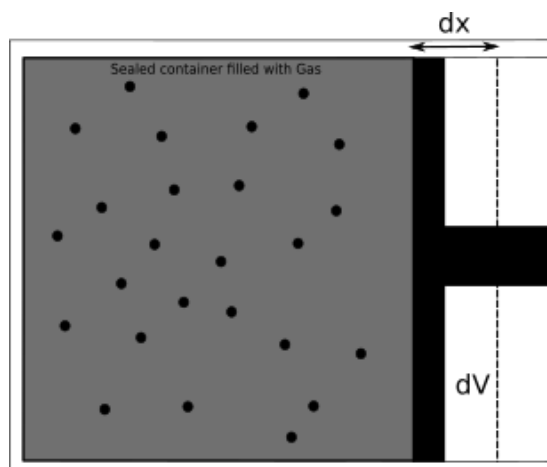
That is, the change in internal energy of a system, ΔU , is equal to the sum of the heat supplied to the system ΔQ and the work done on the system ΔW . Writing it for differential changes gives

$$dU = dQ + dW.$$

At the end of the last lecture, we stated the first law. In mathematical form, this is:

$$dU = dQ + dW.$$

Our first task is to see if there's an easy form for expressing how the dW term behaves. To do this, consider the below setup.



The force used on the piston to compress the gas is $F = PA$, where A is the area of the piston. By compressing the gas such that its change in volume is $-dV$, we also get that $A dx = -dV$. Thus, the work done in compressing the gas is given by

$$dW = F dx = -P dV$$

This assumes that the process is reversible, but we'll come back to that later on. So, the first law can also be written as

$$dU = dQ - P dV$$

for reversible processes.

1.5 Revisiting Heat Capacity

Ok, let's return to our definition of heat capacity from lecture 1, which stated that

$$dQ = C dT \Rightarrow C = \frac{dQ}{dT}$$

We now want to use this expression in combination with the first law to see how adding heat changes the internal energy of a gas.

To do this, let's start with the internal energy of gas, and say that this is only a function of temperature and volume such that $U = U(T, V)$. A small change in the internal energy can thus be written as

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

which is a mathematical operation we can do as U is a function of state (i.e. dU is an exact differential). Rearranging the first law such that it's in relation to dQ gives

$$dQ = dU + PdV = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV.$$

Now, taking the derivative of this with respect to dT gives

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T} \right)_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \frac{dV}{dT}$$

So the heat capacity at constant volume then becomes

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

The heat capacity at constant pressure is then

$$C_P = \left(\frac{dQ}{dT} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{dV}{dT} \right)_P$$

which then gives

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{dV}{dT} \right)_P.$$

Finally, the ratio of these two heat capacities is called the Adiabatic Index, and is given by

$$\gamma = \frac{C_P}{C_V}$$

1.6 The Heat Capacity of an Ideal Gas

Given that the internal energy of one mole of ideal gas is given by $U = \frac{3}{2}RT$, let's derive expressions for C_P and C_V . First, note that the internal energy is independent of volume. As such

$$\frac{\partial U}{\partial V} = 0.$$

For one mole of ideal gas, we know that $PV = RT$, so

$$V = \frac{RT}{P}$$

which gives

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

So then the heat capacities are

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2}R \tag{1}$$

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{dV}{dT} \right)_P = R \tag{2}$$

$$C_P = \frac{5}{2}R \tag{3}$$

1.7 Reversibility, Isothermal Expansions, and Adiabatic expansions

In most scenarios, a physical process involves heat being dissipated away into the surrounding environment. This means that such a process is very difficult to naturally reverse as it is very unlikely that the lost energy will flow back into the system. A nice example of this is to consider an egg falling off a table. It will hit the floor and shatter, losing some energy into the ground in the process.

A more formal way of thinking about this is that, for large numbers, the statistical behaviour of them make more outcomes more likely than order (remember how graph of the statistical weight looked). As such, this suggests that when dealing with large numbers, physical changes appear to be driven in an irreversible direction.

Our challenge now is to come up with a way of carrying out a process reversibly (and was the challenge faced by physicists when attempting to construct the most efficient engine possible).

So, how do we do things reversibly? Consider expanding or compressing a gas. If we do it very, very slowly, then the gas will remain in equilibrium throughout the process. Such a process is referred to as **quasistatic**.

There are two such processes which we consider below.

1.8 Isothermal expansion of an Ideal Gas

Consider a reversible, isothermal expansion of an ideal gas. Isothermal here means “at constant temperature”, such that $T = 0$. We want to know what the heat change of such a gas is. As a starting point, let’s consider the internal energy of the gas:

$$dU = CdT = 0.$$

This means that, from the first law,

$$dQ = -dW$$

So, the work done by the gas as it expands is equal to the heat it absorbs from its surroundings. Recalling from earlier that $dW = -PdV$ for a reversible process, we can then obtain the total heat absorbed by the gas:

$$Q = \int dQ \tag{4}$$

$$= - \int dW \tag{5}$$

$$= \int_{V_1}^{V_2} PdV \tag{6}$$

$$= \int_{V_1}^{V_2} \frac{Nk_B T}{V} dV \tag{7}$$

$$= Nk_B T \ln \frac{V_2}{V_1} \tag{8}$$

$$= RT \ln \frac{V_2}{V_1} \tag{9}$$

where that last expression is for one mole of ideal gas.

So, for an expansion $V_2 > V_1$, so $Q > 0$

1.9 Adiabatic expansion of an Ideal Gas

Consider a reversible, adiathermal expansion of an ideal gas. Adiathermal here means “without flow of heat”. A process which is both adiathermal and reversible is **adiabatic**. For this process

$$dQ = 0.$$

This means that, from the first law,

$$dU = dW$$

For an ideal gas, we have that $dU = C_V dT$, and because the process is reversible we again have that $dW = -PdV$. As such, we have that

$$C_V dT = -PdV = -\frac{Nk_B}{V}dV \quad (10)$$

$$(11)$$

Let's work with one mole of ideal gas for the moment ($N_A k_B = R$). As such, we get

$$\ln \frac{T_2}{T_1} = -\frac{R}{C_V} \ln \frac{V_2}{V_1}. \quad (12)$$

Recalling that $C_P = C_V + R$ we find that

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{R}{C_V}$$

which gives

$$-\frac{R}{C_V} = 1 - \gamma.$$

This let's us simplify the above expression to get

$$\ln \frac{T_2}{T_1} = (1 - \gamma) \ln \frac{V_2}{V_1} = \ln \left(\frac{V_2}{V_1} \right)^{1-\gamma}$$

Finally, we get that

$$TV^{\gamma-1} = \text{const}$$

Using the ideal gas law ($PV \propto T$) let's us rewrites this as both

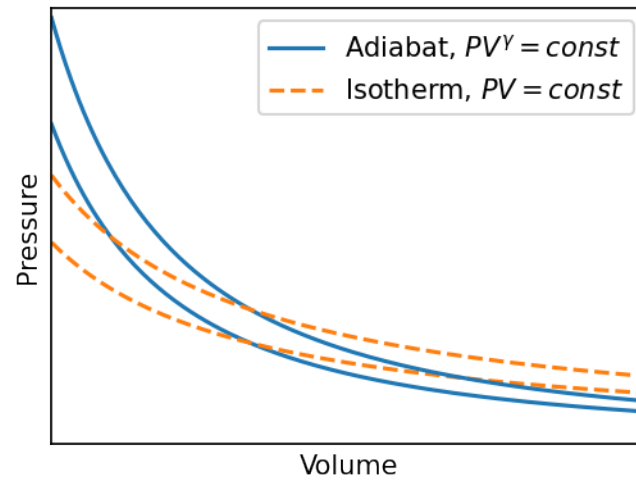
$$P^{1-\gamma} T^\gamma = \text{const} \quad (13)$$

$$PV^\gamma = \text{const} \quad (14)$$

1.10 Isotherms & Adiabats

So now we have two scenarios for working an ideal gas. It can undergo an adiabatic process, in which case $PV^\gamma = \text{const}$, or it can undergo an isothermal expansion, in which case $PV = \text{const}$. We'll cover what these processes can be used for later, but the below can be treated as a prelude, as it plots pressure versus volume for both processes for two different initial conditions.

Adiabats and Isotherms for different initial conditions.



2 The second law of thermodynamics

There are two ways of stating this:

1. No process is possible whose sole result is the transfer of heat from a colder to a hotter body.
2. No process is possible whose sole result is the complete conversion of heat into work.