Chapter 13

Thermodynamics (mostly Chapter 19)

13.1 Thermodynamics systems

Our main objective in this chapter is to understand the behavior of systems with a very large number of degrees of freedom \( N \gg 1 \) (e.g. \( N_A = 6.02214 \times 10^{23} \) molecules in a box). The task is (in some sense) much more ambitious than the problems we encountered so far where the number of degrees of freedom was usually small. For \( N \lesssim 10 \) analytical methods may be useful; for \( N \lesssim 10^{10} \) computer may work; for \( N \sim 1 \text{googol} = 10^{100} \) statistical physics may be the only tool. There are two standard ways to study the large \( N \) limit:

- phenomenological (e.g. thermodynamics) and
- fundamental (e.g. statistical mechanics).

We will only discuss a phenomenological approach, i.e. thermodynamics. The main idea is that only a small number of measurable (or thermodynamics) parameters:

- volume \( V \),
- pressure \( p \),
- temperature \( T \), etc.

should be sufficient for describing the so-called equilibrium states (i.e. state whose thermodynamic parameters do not change with time.) These thermodynamics parameters are related to each other by the so-called equation of
\[ f(p, V, T) = 0. \] (13.1)

The equation of state of the so-called ideal gas is given by

\[ pV = nRT \] (13.2)

and of the van de Waals gas

\[ \left( p + \frac{an^2}{V^2} \right)(V - nb) = nRT \] (13.3)

where \( n \) is the amount of substance described in moles,

\[ R = 8.31 \text{ J/mol-K} \] (13.4)

and \( a \) and \( b \) constant which (roughly speaking) represent the attractive intermolecular force and the size of molecules respectively. (Remember that one mole is an amount of substance with \( N_A = 6.02214 \times 10^{23} \) molecules.)

As the system evolves from one thermodynamic state to another the macroscopic parameters might only change is in such a way that the equation of state remains invariant. For example, if the system is an ideal gas, then

\[ \frac{dV}{dt} > 0 \text{ and } T = \text{const} \Rightarrow \frac{dp}{dt} < 0 \]
\[ \frac{dp}{dt} > 0 \text{ and } V = \text{const} \Rightarrow \frac{dT}{dt} > 0 \]
\[ \frac{dT}{dt} > 0 \text{ and } p = \text{const} \Rightarrow \frac{dV}{dt} > 0 \] (13.5)

and so on.

There are two different mechanisms that allow to change a thermodynamic state of the system from the outside. One can either transfer heat to the system

\[ Q > 0 \text{ when the system is heated} \]
\[ Q < 0 \text{ when the system is cooled} \] (13.6)

or the system can do work

\[ W > 0 \text{ when the system does work} \]
\[ W < 0 \text{ when work is done on the system.} \] (13.7)

(Note that the sign convention for work is different as compared to mechanics.)
13.2 Work Done During Volume Changes

The work done by a system can be calculated by considering transfer of energy by gas molecules when the piston is moving where the positive direction of $x$ axis corresponds to expansion

$$dW = Fdx = pAdx = pdV$$  \hfill (13.8)

By integrating both sides we obtain

$$W = \int_{V_1}^{V_2} p(V) dV.$$  \hfill (13.9)

On the so-called $pV$ diagram the work (up to a sign) equals to the area under function $p(V)$ between initial and final states.
When pressure does not change with volume an expression for work can be obtained by integrating Eq (13.9)

\[ W = p(V_2 - V_1). \]  

(13.10)

Expansion corresponds to positive \( dV \) and thus to positive work \( W \) done by the system, and contraction corresponds to negative \( dV \) and thus to negative work \( W \) done by the system.
Example 19.1. As an ideal gas undergoes an isothermal (constant temperature) expansion at temperature $T$, its volume changes from $V_1$ to $V_2$. How much work does the gas do?

Using the equation of state of ideal gas

$$pV = nRT \quad (13.11)$$

or

$$p(V) = \frac{nRT}{V} \quad (13.12)$$

we get

$$W = \int_{V_1}^{V_2} p(V) \, dV$$

$$= \int_{V_1}^{V_2} \frac{nRT}{V} \, dV$$

$$= nRT \left[ \log(V) \right]_{V_1}^{V_2}$$

$$= nRT \log \left( \frac{V_2}{V_1} \right). \quad (13.13)$$

Moreover, from the equation of state of ideal gas of isothermal process

$$P_1V_1 = P_2V_2 \quad (13.14)$$

or

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \quad (13.15)$$

and thus

$$W = nRT \log \left( \frac{P_1}{P_2} \right). \quad (13.16)$$

13.3 Paths Between Thermodynamic States

Work done by a thermodynamic system depends on the path it takes in $(p, V, T)$ space. Speaking mathematically $dW$ is not an exact differential and for this reason sometimes written as $\delta W$. For example, consider the following processes:
It is clear that areas under path on the \( pV \) diagram depend on the path and thus the work done by a system is not the same. Similarly the heat transferred to a system \( Q \) depends on the path it takes and thus \( dQ \) (or perhaps \( \delta Q \)) is not an exact differential. Processes corresponding to isothermal and free expansions are illustrated on the following figures:
13.4 Internal Energy and the First Law of Thermodynamics

There is, however, a thermodynamic quality whose change does not depend on the path it takes known as internal energy. In thermodynamics internal
energy is defined not an absolute sense, but as a differential

\[ dU = dQ - dW \]  \hspace{1cm} (13.17)

after integration

\[ \Delta U = U_2 - U_1 = Q - W \]  \hspace{1cm} (13.18)

Note that the potential energy corresponding to conservative forces (e.g. gravitational potential energy) is another physical quantity of the same type that we have already discussed in some details. Equation (13.18), which is strictly speaking a defining equation of (the change of) internal energy, is also known as the first law of thermodynamics.

We have already seen that \( W = pdV \) and \( dQ = SdT \), where \( S \) is another thermodynamic quantity known as entropy which measures the amount of disorder in the system. Then the first law of thermodynamics can be written as

\[ dU = SdT - pdV \]  \hspace{1cm} (13.19)

It is an important experimental fact that entropy almost always grows with time

\[ \frac{dS}{dt} \geq 0 \]  \hspace{1cm} (13.20)

which is also known as the second law of thermodynamics. There is also a third law of thermodynamics stating that there is an absolute zero temperature \( T = 0 \text{ K} \) at which entropy is zero

\[ S(0 \text{ K}) = 0. \]  \hspace{1cm} (13.21)

There are two special kinds of the thermodynamic processes we would like to highlight. The first one is a cyclic process where the system returns to its original state and thus

\[ U_2 = U_1 \quad \Rightarrow \quad Q = W \]  \hspace{1cm} (13.22)

and the second one is for a system in isolation

\[ W = Q = 0 \quad \Rightarrow \quad U_2 = U_1. \]  \hspace{1cm} (13.23)
Example 19.4. Consider the following pV-diagram.

In process $a \rightarrow b$, 150 J of heat is added to the system; in process $b \rightarrow d$, 600 J of heat is added to the system. Find
(a) the internal energy change in process $a \rightarrow b$
(b) the internal energy change in process $a \rightarrow b \rightarrow d$
(c) the total heat added in process $a \rightarrow c \rightarrow d$.

From the first law: (a) applied to process $a \rightarrow b$ we get

$$\Delta U_{a \rightarrow b} = Q_{a \rightarrow b} - W_{a \rightarrow b} = 150 \text{ J} - 0 \text{ J} = 150 \text{ J}.$$  \hspace{1cm} (13.24)

(b) applied to process $a \rightarrow b \rightarrow d$ we get

$$\Delta U_{a \rightarrow b \rightarrow d} = Q_{a \rightarrow b} + Q_{b \rightarrow d} - W_{a \rightarrow b} - W_{b \rightarrow d}$$
$$= 150 \text{ J} + 600 \text{ J} - 0 \text{ J} - (3.0 \times 10^{-3} \text{ m}^3) (8.0 \times 10^4 \text{ Pa})$$
$$= 510 \text{ J},$$  \hspace{1cm} (13.25)

where we used that

$$W_{b \rightarrow d} = p_{b \rightarrow d} (V_d - V_b)$$  \hspace{1cm} (13.26)

(c) and applied to process $a \rightarrow c \rightarrow d$ we get

$$Q_{a \rightarrow c \rightarrow d} = \Delta U_{a \rightarrow c \rightarrow d} + W_{a \rightarrow c \rightarrow d}.$$  \hspace{1cm} (13.27)

However since internal energy does not depend on path

$$\Delta U_{a \rightarrow c \rightarrow d} = \Delta U_{a \rightarrow b \rightarrow d} = 510 \text{ J},$$  \hspace{1cm} (13.28)

$$W_{a \rightarrow c \rightarrow d} = W_{a \rightarrow c} + W_{c \rightarrow d}$$
$$= 0 \text{ J} + (3.0 \times 10^{-3} \text{ m}^3) (3.0 \times 10^4 \text{ Pa})$$
$$= 90 \text{ J},$$  \hspace{1cm} (13.29)

and

$$Q_{a \rightarrow c \rightarrow d} = 510 \text{ J} + 90 \text{ J} = 600 \text{ J}.$$  \hspace{1cm} (13.30)

### 13.5 Kinds of Thermodynamic Processes

We now summarize the most common thermodynamics processes and the corresponding defining equations:

- adiabatic process
  $$Q = 0 \quad \Rightarrow \quad \Delta U = -W,$$  \hspace{1cm} (13.31)

- isochoric process
  $$dV = 0 \quad \Rightarrow \quad dW = pdV = 0 \quad \Rightarrow \quad \Delta U = Q,$$  \hspace{1cm} (13.32)
• isobaric process

\[ dp = 0 \quad \Rightarrow \quad dW = pdV \quad \Rightarrow \quad \Delta U = Q - p(V_2 - V_1), \quad (13.33) \]

• isothermal process

\[ dT = 0 \quad \Rightarrow \quad dU = 0 \quad \Rightarrow \quad Q = W. \quad (13.34) \]

13.6 Heat Capacities for an Ideal Gas

How much heat should be added to a system to change its temperature? This is described by

\[ \frac{dQ}{dT} = nC \quad (13.35) \]

where \( n \) is mass per unit mole of the material and \( C \) is a molar heat capacity (or simply heat capacity). The heat capacity depends on the material, but moreover it depends on the process by which the heat is added. If we consider isobaric and isochoric process, then the corresponding heat capacities are notated by \( C_p \) and \( C_V \) respectively.

These two constants can be related to each other by applying the first law to the following transformation

1. isochoric decrease in temperature and decrease in pressure
2. isobaric increase in volume and increase in temperature
Then

\[ \Delta U = Q - W \]

\[ 0 = nC_V (T_1 - T_2) + nC_V (T_2 - T_1) - p_1 (V_2 - V_1) \] (13.36)

and for ideal gas

\[ 0 = nC_V (T_1 - T_2) + nC_p (T_2 - T_1) - nR (T_2 - T_1) \] (13.37)

or

\[ C_p = C_V + R. \] (13.38)

Using the so-called kinetic theory of gases one can show that for the ideal monatomic gases

\[ C_V = \frac{3}{2} R \]

\[ C_p = \frac{5}{2} R \] (13.39)

and thus

\[ \gamma = \frac{C_p}{C_V} = \frac{5}{3} \approx 1.67 \] (13.40)

but from example for diatomic molecules

\[ \gamma = \frac{C_p}{C_V} = \frac{7}{5} = 1.4. \] (13.41)
Example 19.6. A typical dorm room or bedroom contains about 2500 moles of air. Find the change in the internal energy of this much air when it is cooled from 35.0°C to 20.0°C at constant pressure of 1.00 atm. Treat the air as an ideal gas with $\gamma = 1.400$.

For an ideal gas

$$C_p = C_V + R$$

and thus

$$C_V \gamma = C_V + R$$

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

$$C_V = \frac{8.314 \text{ J/mol}\cdot\text{K}}{1.400 - 1} = 20.79 \text{ J/mol}\cdot\text{K}.$$  \hspace{1cm} (13.43)

Since the volume did not change no work was done and from the first law of thermodynamics

$$\Delta U = Q$$

where

$$Q = nC_V (T_2 - T_1)$$

and thus

$$\Delta U = nC_V (T_2 - T_1)$$

$$\Delta U = (2500 \text{ mol}) (20.79 \text{ J/mol}\cdot\text{K}) (10.0^\circ\text{C} - 35.0^\circ\text{C}) = -4.68 \times 10^5 \text{ J}.$$  \hspace{1cm} (13.47)
13.7 Internal Energy of an Ideal Gas

The internal energy of an ideal gas depends only on its temperature, not on its pressure or volume. For example, when a partition is broken to start a free expansion of gas into the vacuum region, both the volume and pressure are changed in such a way that temperature remains constant.

Is is easy to see by considering isochoric process that

\[ dU = dQ - dW = dQ = nC_V dT \]  \hspace{1cm} (13.48)

13.8 Adiabatic Process for an ideal gas

During adiabatic process

\[ dQ = 0 \implies dU = -dW = -pdV. \]  \hspace{1cm} (13.49)
For an ideal gas the equation of state is

\[ pV = nRT \quad (13.50) \]

and

\[ dU = nC_VdT \quad (13.51) \]

which implies

\[
\begin{align*}
nC_VdT &= -\frac{nRT}{V}dV \\
d\left(\frac{T}{T}\right) + \frac{R}{C_V} \frac{dV}{V} &= 0 \\
\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} &= 0. \quad (13.52)
\end{align*}
\]

or

\[
TV^{\gamma-1} = \text{constant} \quad (13.55)
\]

By integrating both terms we get

\[
\log T + (\gamma - 1) \log V = \text{constant} \quad (13.54)
\]

or

\[
\frac{pV}{T} = pV^\gamma = \text{constant} \quad (13.56)
\]
It is also straightforward to calculate work on an ideal gas during adiabatic process

\[ W = -\Delta U = nC_V (T_1 - T_2) = nC_V \left( \frac{p_1V_1}{nR} - \frac{p_2V_2}{nR} \right) = \frac{1}{\gamma - 1} \left( p_1V_1 - p_2V_2 \right). \]  

(13.57)

**Example 19.7.** The compression ratio of a diesel engine is 15.0 to 1; that is, air in a cylinder is compressed to \( \frac{1}{15} \) of its initial volume.

- (a) If the initial pressure is \( 1.01 \times 10^5 \text{ Pa} \) and the initial temperature is \( 27^\circ \text{C} \) (300 K), find the final pressure and the temperature after adiabatic compression.
- (b) How much work does the gas do during the compression if the initial volume of the cylinder is \( 1.00 \text{ L} = 1.00 \times 10^{-3} \text{ m}^3 \)?

(Use the value \( C_V = 20.8 \text{ J/mol} \cdot \text{K} \) and \( \gamma = 1.400 \) for air.)

For adiabatic process

\[ T V^{\gamma-1} = \text{constant} \]

\[ T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = (300 \text{ K}) (15.0)^{0.400} = 886 \text{ K}, \]

\[ p V^\gamma = \text{constant} \]

\[ p_2 = p_1 \left( \frac{V_1}{V_2} \right)^\gamma = (1.01 \times 10^5 \text{ Pa}) (15.0)^{1.400} = 44.8 \times 10^5 \text{ Pa}. \]
\[ W = \frac{1}{\gamma - 1} (p_1 V_1 - p_2 V_2) \]
\[ = \frac{1}{1.400 - 1} \left( (1.01 \times 10^5 \text{ Pa}) \ (1.00 \times 10^{-3} \text{ m}^3) - (44.8 \times 10^5 \text{ Pa}) \left( \frac{1.00 \times 10^{-3} \text{ m}^3}{15.0} \right) \right) \]
\[ = -494 \text{ J} \]