

Introduction: basic ideas, equation of state and the first law of thermodynamics

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1. Macroscopic Physics: introduction

Physical systems are composed of particles that interact with each other. In everyday life (namely, not in the relativistic or the quantum limits) the motion of the particles and the interactions between them are well described by **Newton's laws**. In principle, this approach should be sufficient to describe the evolution of *any* system. However, in many systems which we encounter in everyday life, we simply cannot use this straight-forward approach. The reason is that some systems are simply composed of too many molecules for this approach to have any use. An example of such system is 1 liter of air in atmospheric pressure and room temperature: the number of molecules is of the order of Avogadro's number, $\approx 6 \times 10^{23}$. No one - and no computer - can solve the equations of motion of 10^{23} particles, or any number even remotely close to that, in a finite amount of time.

Systems that are composed of such huge number of particles (atoms or molecules) are called **macroscopic systems**. Although it is practically impossible to solve the equations of motion for any individual particle, we know from everyday life (as well as from detailed experiments) that such systems do obey certain physical laws, and can be quantified by meaningful quantities, such as pressure or temperature. These quantities in fact represent some average over microscopic properties, such as the energy or momentum of the atoms composing the system. The branch of physics developed to study these systems is called **statistical physics**.

Of course, when we average over quantities we lose information: there are always *fluctuations* around the mean value. However, due to the enormous number of particles involved, the fluctuations, which are an essential part of any statistical theory, will turn out to be negligible. This is known as the **thermodynamic limit**. In practice, the statistical laws will lead to statements of complete certainty.

As an example, consider the pressure exerted by a gas on the walls of a containing vessel (see Figure 1). We measure the pressure by means of a gauge attached to the vessel. This

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gauge is a freely moving piston, to which a variable force, \vec{F} is applied. When at rest, the force balances the pressure p , as $p = |\vec{F}|/A$, where A is the cross-sectional area of the piston.

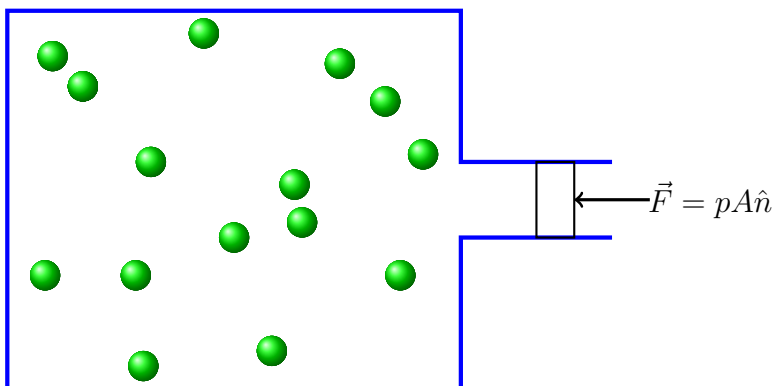


Fig. 1.— A container filled with gas is closed by a freely moving piston of cross sectional area A .

If we now turn to a *microscopic* view, we find that according to the kinetic theory of gases, the pressure results from elastic collisions between the gas molecules and the walls, in which the molecules transfer their momentum to the walls. Thus, the pressure cannot be exactly time-independent: on the contrary, the instantaneous force acting on the walls is a rapidly fluctuating quantity. By **pressure** we really mean the average force (per unit area) exerted by the molecules on the walls, *averaged over a very long time*. By “long time” we mean long compared to the time between collisions, so that many collisions ($N \gg 1$) occur during the period in which we make our measurement. Thus, if we apply an external force on the piston (to match the momentum exerted by the molecules), the piston is at rest - *on the average*. However, a very close look reveals that the piston performs small, irregular vibrations about its equilibrium position, resulting from the individual molecular collisions. These small movements are known as **Brownian motion**. Often these are too small to be observed, apart when using designated techniques. However, **these represent one of the ultimate limitations on the theoretical accuracy of measurements that can be achieved**.

There are two approaches to the study of macroscopic systems. The first, developed by the first half of the 19th century is **classical thermodynamics**. This is based on a finite set of basic principles (the laws of thermodynamics), which are deduced from experiments, and are thus *phenomenological laws*. These were developed independently of the microscopic description of molecular interactions, and contain macroscopic variables such as *pressure*, *temperature* and *volume*. As these were derived independent of the atomic concepts, this

approach is very limited. Nonetheless, it is very useful in describing many systems, and often it is very handy and much simpler to see than the full microscopic description.

The second approach is that of **statistical mechanics**. The idea is to start from the atomic properties (e.g., equations of motion of single atoms) and show how the macroscopic properties of the system are obtained. Into this line of reasoning falls the **kinetic theory of gases**, first derived by Maxwell, and followed by Boltzmann and Gibbs. Essentially, the macroscopic properties of the system are obtained by averaging over (unobservables) microscopic quantities. Clearly, both approaches complement each other; during the semester, we will therefore follow both paths simultaneously.

2. Equilibrium

Every macroscopic system can be described by several macroscopic variables, such as pressure, volume and temperature. As we know from everyday experience, if we take two bodies at different temperatures (one hot and one cold) and let them be in contact, heat flows from the hot body to the colder one. If we wait long enough, both bodies will have the same, final temperature. A similar thing happens if we have a system composed of a gas filling a divided container in such a way that the pressure in one side is higher than the pressure in the other side. If the barrier that separates the two sides is removed, after long enough time the pressure in both sides is the same. In both cases we say that the system reached an **equilibrium state** (or, equilibrium for short).

When a system is in equilibrium, there are no detectable changes in the macroscopic variables (pressure, temperature or volume) with time. This does *not* mean that the system is completely **static**: Very refined experiments will detect thermal motion of the molecules (on a microscopic scale), such as the Brownian motion. These fluctuations, however, average to zero.

The time it takes the system to reach equilibrium depends on its initial conditions, as well as the processes involved. Naturally, every process has its own time scale, which gives the **relaxation time**, often denoted by τ_i of the process. (We used here the notation τ_i to discriminate between different processes). The relaxation time of the system is thus the maximum of all relaxation times of the relevant processes, $\tau = \max(\tau_i)$. **A system will thus be in equilibrium if observed at times**

$$t \gg \tau = \max(\tau_i). \tag{1}$$

There is another frequently encountered situation which is of interest. If the relaxation time of a certain process τ_i is much longer than the time in which we observe the system,

Δt , one can simply ignore this process, as it occurs too slowly to have any observational consequences.

3. Function of state and equation of state

In equilibrium state, the description of a system is particularly simple: for example, if a fluid is not in equilibrium, then one needs to specify the pressure, density and temperature at every point in space as a function of time, while at equilibrium, the pressure, temperature and density are steady.

It turns out that the equilibrium state is fully determined by a few macroscopic variables. Other properties of the system are then fully determined. A **function of a state** is a macroscopic property that depends only on the current state of the system (and not, e.g. on how it got into this state). Examples are the pressure, temperature and volume.

In some systems, some parameters depend not only on its current state, but also on the history of the system - how it got into its current state. Such a dependence is called **hysteresis**, and it arises because the system can be in more than one internal state. One example is the magnetization of a certain type of materials known as *Ferromagnets* when exposed to external magnetic field. We will postpone further discussion on that to later stages.

Let us return to discuss functions of state. The **equation of state** relates the values of these functions in a given state of the system. While generally it can be complicated, it is found experimentally that for real gases at sufficiently low pressure and constant temperature,

$$pV = \text{Const.} \tag{2}$$

In fact an **ideal gas** is defined as a fluid for which Equation 2 holds exactly (which can only happen in the limit $p \rightarrow 0$). We can use this to define a temperature scale T by the relation

$$T \propto \lim_{p \rightarrow 0} pV \tag{3}$$

In order to determine the scale, we need to fix one point; it is chosen to be the triple point of water, which is the temperature in which water, ice and water vapor coexist in equilibrium. The temperature of the triple point is $T = 273.16^\circ \text{ K}$.

Accurate measurements give the constant of proportionality in Equation 3,

$$pV = nRT, \tag{4}$$

where n is the number of moles, and $R \equiv 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ is the **gas constant**.

Using Avogadro's number, $N_0 = 6.02 \times 10^{23}$ which gives the number of molecules in one mole, we can write the equation of state (Equation 4) in an equivalent form,

$$pV = Nk_B T, \tag{5}$$

where N is the number of molecules (or atoms) in the gas, and $k_B \equiv R/N_0 = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is known as **Boltzmann's constant**.

4. The first law of thermodynamics

The first law of thermodynamics is nothing but conservation of energy. When external heat is added to a system, it contributes to increasing both to the **energy** of the system, ΔE (sometimes denoted also by ΔU) and to do **mechanical work** as the body expands against an external force or pressure, $\Delta W = p\Delta V$. Thus, denoting by ΔQ the amount of heat added to a thermal system, one can write

$$\Delta Q = \Delta E + \Delta W = \Delta E + p\Delta V. \tag{6}$$

Equation 6 represent energy conservation, where energy can appear both as mechanical energy and thermal energy. It is known as **the first law of thermodynamics**.

The energy of a system, E , is a *function of state*. It can be viewed as the sum of two contributions:

1. The energy of the **macroscopic** motion of the system (e.g.: the bulk velocity associated with the motion of the center of mass, potential energy associated with external gravitational field, etc.)
2. The **internal energy** associated with the **microscopic** random motion of the particles in the system. This is the energy associated with the kinetic motion of the molecules, potential energy of interaction between the molecules, translational and rotational motion (inner motion) of the molecules, vibration of atoms in a crystal, etc. This energy is measured by the **temperature**.

Often, we consider systems at rest, and thus the **macroscopic** part can be neglected, and we do not distinguish between energy and **internal energy**.

The internal energy is a function of state: $E = E(p, T)$ or $E = E(p, V)$ (we omit the dependence on the mass, which is trivial). Thus, ΔE is the change in energy of a system when it is shifted from state A to state B .

The quantity Q is the amount of *external heat* supplied to the system: for example, if you want to boil water, you put a pot full of water on the gas, and lit fire. Thus, you supply external heat (gas fire) to the water. Being external to the system, Q is *not* a function of state. Similarly, the work W is *not* a function of state. In some textbooks, the first law of thermodynamics is written in a differential form as $dQ = dE + dW$, where dQ and dW (as opposed to dQ, dW) emphasize that Q and W are *not* functions of state. Their exact values therefore depends on the *path* the system takes from state A to state B .

We use the following convention: the work done *by the gas* is *positive* if the gas expands, and negative if it is compressed. Conversely, the work done *on the gas* by external force (e.g., a moving piston) is *positive* for compression, and negative when the gas expands.

4.1. Reversible processes

As their name implies, **reversible processes** are processes that can reverse their direction by making an infinitesimal change in the applied conditions. For a process to be reversible, it must fulfill two conditions:

1. It must be **quasi-static**. This means that the system must pass through a series of states which are arbitrary close to equilibrium at any instant. This is of course an idealized situation. In practice, it means that processes must be very slow - slower compared to all relevant relaxation times. Such a process is called *quasi-static*.
2. There should be no hysteresis effects. The system should be able to return to its initial state along the same path it took.

The importance of reversible processes is that for these processes, the work performed on a system is well defined by the properties of the system.

Example. Consider an *isothermal compression* of a gas in a cylinder. Compression means that we increase the force on a piston enclosing the system, such that it compresses. Isothermal implies that the gas is in contact with some external *heat bath*, thus its temperature is kept constant during the process. For this to happen, the process must be very slow.

The work done on the gas when it compresses from volume V_1 to volume V_2 ($V_1 > V_2$) is

$$W = - \int_{V_1}^{V_2} p dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \log \frac{V_1}{V_2} \quad (7)$$

This is correct in the limit of no friction. If there is a friction between the piston and the cylinder, then the force we have to apply, hence the external pressure on the piston when compressing the gas, p_0 must be greater than the gas pressure, p . Thus, the net work done when the gas goes a full cycle: first compressed and then expands to its original volume, must be greater than 0. This work is converted into thermal energy due to friction: namely, the gas temperature rises. In this case, the cycle is *irreversible*: on reversing the initial conditions, the system will not follow the initial path in the reverse direction. Thus, we can summarize that the external work done when a gas is compressed is

$$dW \geq -pdV \quad (8)$$

where equality sign holds for reversible processes, while the greater than sign is for non-reversible. Note that p and V are parameters of the state of a system, while dW is the external work. The minus sign is needed in order for the external work to be positive when the system is compressed.

4.2. Work and energy in reversible, cyclic processes

Consider a reversible process (not necessarily an isotherm), that changes the state of a system from state A to state B ; e.g., the system is compressed from V_1 to V_2 along some path, call it *path 1* (see Figure 2). The work done is

$$W_{path\ 1} = - \int_{V_1}^{V_2} pdV \quad (9)$$

If the system then returns to its original state along a different path, *path 2*, then a similar equation holds for the second path. The total work done on the system is equal to the shaded area in Figure 2, and is

$$W_{cycle} = \oint pdV = - \int_{V_1}^{V_2} pdV_{(path\ 1)} + \int_{V_1}^{V_2} pdV_{(path\ 2)} \neq 0 \quad (10)$$

Thus, work in a complete cycle does not vanish. In contrast, the energy is a function of state and have a well defined value at any point along the path; thus,

$$\oint dE = 0 \quad (11)$$

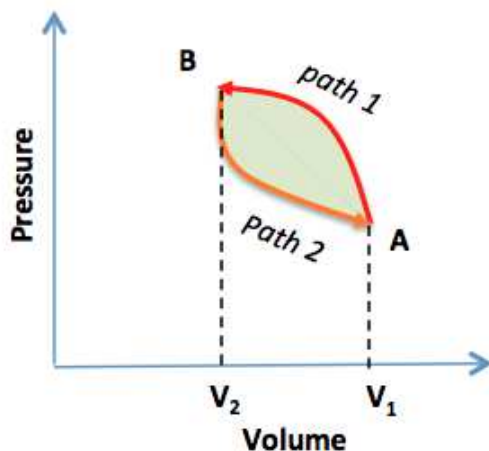


Fig. 2.— The state of a system is described by a point in pressure-volume (pV) diagram. The system can change its state, in which case it travels from point *A* to point *B* in the diagram along *path 1*, and back to state *A* along *path 2*. The total work done on the system in this cycle is equal to the shaded (green) area.

5. Heat capacities

Heat capacity is defined as *the amount of heat needed to raise the temperature of an object by a given amount*. For example, the heat may be measured in Joule, while the temperature in Kelvin (“how many Joules needed to raise the temperature by 1 °K”). Thus,

$$C \equiv \frac{dQ}{dT} = \frac{dE}{dT} + p \frac{dV}{dT} \quad (12)$$

Thus, the heat capacity depends on (1) the rate of change of internal energy on the temperature; and (2) on whether work is being done on the system.

We can consider 2 limiting cases: (1) If the volume is kept fixed: the **heat capacity at constant volume** is defined by

$$C_V \equiv \left(\frac{dQ}{dT} \right)_{V=const} = \left(\frac{\partial E}{\partial T} \right)_{V=const} \quad (13)$$

In the last equality we used the quantity ∂E to denote **partial derivative** of the internal energy E with respect to T : E is a function of *both* T and V , and partial derivative means that we keep V constant when measuring the change of E when T changes. (For more on partial derivatives, see my lecture notes on PY1052).

(2) The second case is **heat capacity at constant pressure**, which is similarly defined by

$$C_p \equiv \left(\frac{dQ}{dT} \right)_{p=const} = \left(\frac{\partial E}{\partial T} \right)_{P=const} + p \left(\frac{\partial V}{\partial T} \right)_{p=const}. \quad (14)$$

We now think of both E and V as functions of p and T .

In **ideal gas**, *the internal energy depends on the temperature only* (and NOT on V or p). (The physical explanation is that in ideal gas the volume occupied by the molecules is negligible, and thus does not affect the internal energy). Thus,

$$\left(\frac{\partial E}{\partial T} \right)_{p=const} = \frac{\partial E}{\partial T} = \left(\frac{\partial E}{\partial T} \right)_{V=const} = C_V, \quad (15)$$

and one gets

$$C_p = C_V + p \left(\frac{\partial V}{\partial T} \right)_{p=const} = C_V + nR, \quad (16)$$

where in the last step we have used the equation of state (Equation 4). We thus obtain

$$C_p - C_V = \frac{pV}{T} \quad \rightarrow \quad pV = (C_p - C_V)T. \quad (17)$$

We thus find that $C_p > C_V$. As the gas expands, it does work displacing the atmosphere \rightarrow we need to supply heat to compensate for this work.

6. Adiabatic process

A process that occurs without any energy exchange with the surroundings is called **adiabatic process**. Such processes can occur in closed (thermally isolated) systems, or if the processes are so rapid that there is no time for the external system to exchange energy with the environment. **In such processes, thus $\Delta Q = 0$** . Using the first law (Equation 6) and the definition of C_V (Equation 15), we find that in adiabatic process

$$\Delta Q = 0 = \Delta E + p\Delta V = C_V\Delta T + p\Delta V \rightarrow \Delta T = -\frac{p}{C_V}\Delta V. \quad (18)$$

Differentiating the Equation of state of an ideal gas (Equation 17) using Equation 18,

one finds

$$\begin{aligned}
 \Delta(pV) &= (C_p - C_V)\Delta T = -\frac{C_p - C_V}{C_V}p(\Delta V) \\
 p(\Delta V) + V(\Delta p) &= -\frac{C_p}{C_V}p(\Delta V) + p(\Delta V) \\
 V\Delta p + \frac{C_p}{C_V}p(\Delta V) &= 0 \\
 \frac{\Delta p}{p} + \frac{C_p}{C_V}\frac{\Delta V}{V} &= 0 \\
 \int \frac{dp}{p} + \frac{C_p}{C_V}\int \frac{dV}{V} &= 0 \\
 \log p + \frac{C_p}{C_V}\log V &= \text{Const.}
 \end{aligned} \tag{19}$$

It is convenient to define

$$\gamma \equiv \frac{C_p}{C_V}, \tag{20}$$

and write Equation 19 in the form

$$pV^\gamma = \text{Const.} \tag{21}$$

which is satisfied for any adiabatic process. The factor γ is known as [adiabatic index](#), and is in general different for different gases. For example, for non-relativistic, mono-atomic ideal gas, $\gamma = 5/3$ while for relativistic ideal gas, $\gamma = 4/3$; for non-relativistic, diatomic gas, $\gamma = 7/5$.

Since in ideal gas $pV/T = \text{Const.}$, Equation 21 can also be written as $TV^{\gamma-1} = \text{Const.}$ Since $\gamma > 1$, **in adiabatic expansion a system ends up at a lower temperature**; heat was converted to mechanical energy of expansion.

The mechanical work done in adiabatic expansion of an ideal gas from volume V_1 to V_2 is

$$W_{1 \rightarrow 2} = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{\text{const}}{V^\gamma} dV = \text{const} \left(\frac{V_2^{1-\gamma}}{1-\gamma} - \frac{V_1^{1-\gamma}}{1-\gamma} \right) = \frac{1}{1-\gamma} (p_2 V_2 - p_1 V_1) \tag{22}$$

6.1. Free expansion (also: adiabatic free expansion)

Consider an isolated container divided into two. In one side, of volume V_1 there is a gas, held there by a partition that can be removed. At a certain time the partition is removed. The gas expands freely into the vacuum until it ultimately sets into new equilibrium filling the entire container.

During the expansion, a state of thermal equilibrium does not exist: for example, the pressure may not be identical at all points. Therefore, there is no path in the pV diagram which the gas takes. This process is **irreversible**.

As the gas expands into vacuum, there is no external pressure acting upon it, and thus there is no mechanical work done by the gas and $\Delta W = 0$. Since the system is insulated, $\Delta Q = 0$, and thus, using the first law of thermodynamics $\Delta E = 0$. It was checked experimentally (first by Joule) that the gas temperature remains constant. Since the pressure and volume change in this process, this means that **in ideal gas, the internal energy depends only on the temperature**, $E = E(T)$.

Note the following. While in *adiabatic* expansion, the temperature drops as $T_{final} = T_{initial} \times (V_{final}/V_{initial})^{1-\gamma}$ and $\gamma > 1$, in *free expansion*, the temperature is fixed, although there is no heat exchange ($\Delta Q = 0$). The reason is that adiabatic process is **reversible**: the expansion is done by “pushing the walls”, namely converting the internal energy (temperature) to mechanical work. In a free expansion, on the other hand, no work is done, and the process is **irreversible**.