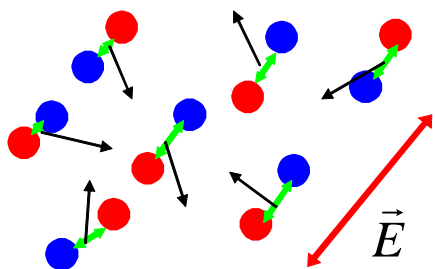


The First Law: Conservation of Energy

The energy of a system and its exchange with the surroundings plays an important role in nearly all physical processes. For example, a mechanical system will always tend to minimize the potential energy. Two atoms will bind and form a molecule, if their combined potential energy can be lowered this way. Why this is so seems to be a philosophically interesting question. R.J. Mayer (1842) discovered that **the total energy U is conserved in all processes, it merely changes its form All forms are equivalent.**

For example, energy associated with **mechanical work w** can be converted back and forth into other types such as electromagnetic, chemical, mass, or yet other types of energy. Energy flow associated with a change in temperature, the **heat energy q** , is also just one type of energy. Heat energy was associated by Claudius (1857) with a **random distribution of energy** among

*Vibrating Diatomic Molecules in
Random Translational Motion*



the constituents (or degrees of freedom) of a system. This has to be contrasted with the orderly motion of parts of the system along some **collective or coherent degrees of freedom**. During times, a system may contain different types of energy. As an example, one can consider a gas of diatomic molecules, aligned in an oscillating electric field \vec{E} . The molecules vibrate collectively, in an orderly fashion, while simultaneously

undergoing random collisions with other gas molecules. Eventually, the collisions randomize also the collective motion. This transfer from collective, orderly motion to chaotic motion is called **dissipation**. For long times, and after the external field has been switched off, an equilibrium state is attained. In this thermodynamic state, all motion is completely random. Also the vibrating molecules in the above example are no longer aligned with a particular direction.

Every system has certain characteristic energy states U_i . The **internal energy U is a state function.**

The **First Law of Thermodynamics** states:

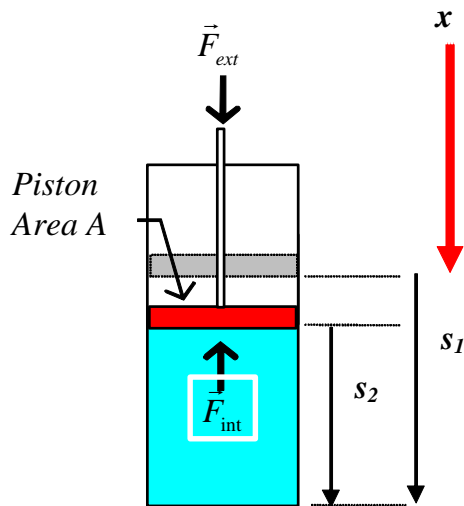
An isolated system remains always at the same energy.

The energy state of a system can only be changed if the system is either closed or open, and when there is exchange of energy forms with its surroundings, such that

$$dU = dw_{mech} + dw_{electr} + dw_{surf} + dw_{N\dots} + dq \quad (1)$$

The different energy exchanges with the surroundings typically to be considered are mechanical (dw_{mech}), electric (dw_{electr}), surface tension (dw_{surf}), energy changes due to particle transfer (dw_N), heat exchange (dq), etc. Of course, $dw_N \neq 0$ makes sense only for an open system. Equation (1) states the First Law in differential form.

Volume-Pressure Work



Mechanical work on (or by) a gas is the easiest to visualize. Compressional work has already been mentioned in the context of the equation of state of the ideal gas. Consider, for example, a cylinder filled with an ideal gas at pressure p , which is closed by a movable piston

of area A exposed to the gas. The gas can be compressed or decompressed by the movement of the piston. If an **external force \vec{F}_{ext}** acts on the piston from the outside, the gas will be compressed and the height s_1 of the column will decrease by an amount of $-\delta s = s_1 - s_2$. The gas will continue to be compressed, until the external force \vec{F}_{ext} is compensated by the rising internal pressure p_{int} of the gas, which tends to push the cylinder the opposite way with a force

$$\vec{F}_{int} = -p_{int} \cdot A < 0 \quad (2)$$

which points in the negative x direction, outwards of the gas volume. The **work done on the gas** is equal to

$$\delta W_{\text{ext}} = \vec{F}_{\text{ext}} \cdot \overrightarrow{\delta X} = -F_{\text{ext}} \cdot (s_2 - s_1) > 0 \quad (3)$$

This is the amount of **potential energy expended in the compression process ($s_2 - s_1 < 0$) and represents an energy gain by the gas, $dU > 0$** . It can also be expressed in terms of the **work done by the surroundings against the internal pressure**,

$$\delta W_{\text{int}} = -\vec{F}_{\text{int}} \cdot \overrightarrow{\delta X} = -F_{\text{int}} \cdot (s_2 - s_1) > 0 \quad (4)$$

In an actual compressional process, the work done by the external force has to be at least this large. However, this external work can be larger than the minimum required for a given compression. For example, if $\vec{F}_{\text{ext}} \gg -\vec{F}_{\text{int}}$, the external force can accelerate the gas particles, leading to **a pressure shock wave starting from the piston, i.e., a time dependent pressure differential**. This non-uniformity of the pressure corresponds to a **non-equilibrium situation**, not a thermodynamically well defined state of the system. At late times, this pressure gradient will have been dissipated, and a **new equilibrium situation (system state) will have been established** containing the extra work as additional internal energy or emitting it as waste heat back into the surroundings.

For mechanical compression, the externally applied force \vec{F}_{ext} **has to be stronger or equal to the force $\vec{F}_{\text{ext}} = -\vec{F}_{\text{int}}$ that just compensates for the gas pressure**. Otherwise the piston will be pushed outwards, until the pressure has decreased enough to be balanced by the external force. In practice, it is often unfeasible to calculate the energy gain by the gas, if such non-equilibrium processes are present.

Therefore, rather than dealing with these more complex non-equilibrium situations, one considers a process of **infinitesimally small changes δs** effected by an **external force in equilibrium with the internal gas pressure p , i.e., an equilibrium of forces where**

$$\vec{F}_{\text{ext}} = -\vec{F}_{\text{int}} \quad (5)$$

Then, one can write down immediately the **energy gain** by the gas:

$$\delta w = -\delta w_{\text{int}} = \delta w_{\text{ext}} = p \cdot A \cdot |\delta s| > 0 \quad (6)$$

Obviously, the sign of this work has been chosen such that **$\delta w_{\text{int}} > 0$ when the energy of the system increases**. If dV is the change in volume associated with the compression $\delta s < 0$, then the **pressure-volume work done the gas is counted positive ($\delta w > 0$)**, an energy **loss by the on the gas** can be expressed as

$$\delta w = -p \cdot dV > 0 \quad (7)$$

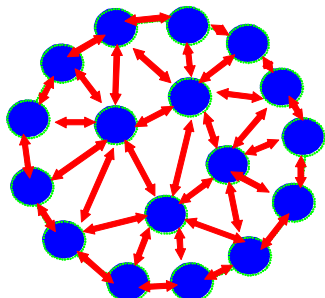
Again, work **δw is counted positive when it leads to an energy gain by the gas ($\delta w > 0$, if $dU > 0$)**. Similarly, work is counted negative when an energy loss by the gas ensues. Although it is the **internal pressure $p = p_{\text{int}}$** of the gas that appears in Equ. (7), it is understood that it is the **external force which does the work ($\delta w > 0$) or against which the gas does the work ($\delta w < 0$)**. **Otherwise the term 'work' has no simple meaning.** For example, gas that escapes through a hole pierced into a balloon does not do any work. Its unknown energy is wasted.

It is straightforward to calculate the internal energy gain ΔU in the compression $V_1 > V_2$ of an ideal gas of N particles held at constant temperature T by an external heat bath:

$$\Delta U = -\int_{V_1}^{V_2} p(V) dV = -\int_{V_1}^{V_2} \frac{Nk_B T}{V} dV = Nk_B \ln\left(\frac{V_1}{V_2}\right) > 0 \quad (8)$$

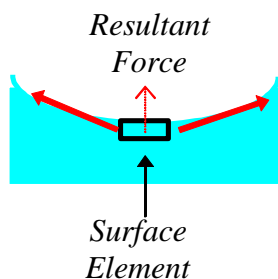
Here, the ideal-gas equation of state, $pV = Nk_B T$, has been used. For one mole of the gas, the corresponding calculation yields

$$\Delta U = -\int_{V_1}^{V_2} p(V) dV = RT \ln\left(\frac{V_1}{V_2}\right) > 0 \quad (9)$$

The Origin of Surface Tension

Another type of mechanical energy that is important for liquid and gaseous systems is that of **surface energy** or **surface tension**. As illustrated in the figure, the particles in the interior of a **droplet of matter** are attracted to all sides from their nearest neighbors, such that the resultant force is approximately zero. The resultant force acting on particles in the surface is directed inside (radially inwards). The **pressure on the concave side of the surface of the droplet is obviously larger than on its convex side**.

For a **curved surface (e.g., that of a liquid)**, the **effective pressure is also higher on the concave side of the surface**, even if there is no liquid on that side. This is illustrated in the sketch on the left.

Forces at the Surface of a Liquid

Here, the forces working on a particular surface element are shown. Because of the curvature, there is an **effective force component in the direction of the center of the radius of curvature**. It looks as if the surface element is pulled more from the outside than on the inside. The effect is equivalent to that of a **decompression of the liquid** underneath the curved surface, i.e., the internal pressure decreases. This radial force component vanishes, as the radius r of curvature becomes very large, $r \rightarrow \infty$, i.e., for a flat surface.

The above effects are more readily observed with a (relatively dense) liquid than with a (relatively dilute) gas. However, these **surface effects are present for all materials**. They are of great technical importance.

To **increase a (curved) surface by an area $\delta\sigma > 0$, the work**

$$\delta W = \gamma \cdot \delta\sigma \quad (10)$$

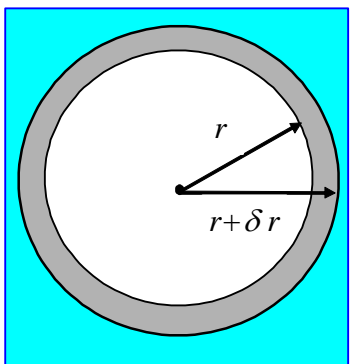
has to be done **on the droplet against its surface tension** γ . The sign of δw is positive in Equ. (10), because the **droplet gains energy when its surface is increased**. This is opposite to pressure-volume work done on a gas (cf. Equ. (7)).

Surface tension has a great influence on the **formation of vapor bubbles in liquids**. For a spherical bubble of radius r , the surface energy is equal to $E_{surf} = 4\pi r^2\gamma$. Increasing the radius r by δr , the energy increases by

$$\delta E_{surf} = 8\pi r\gamma \delta r \quad (11)$$

As discussed previously, the surface tension tends to decrease the surface and, hence, the radius of the bubble, and increases the effective pressure inside the bubble. This effect of the surface tension is counteracted by the gas pressure inside the bubble, preventing the bubble from collapsing. **Equilibrium** is achieved, when the **work done by the pressure** for an infinitesimally small change in radius, δr , **cancels the change in surface energy**:

Vapor Bubble in a Liquid



$$8\pi r \delta r \gamma = \delta E_{surf}$$

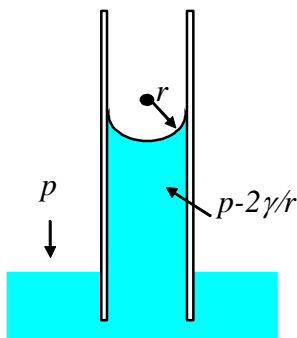
$$(12)$$

$$\delta w = 4\pi r^2 \delta r \cdot p =$$

This condition determines the **equilibrium radius of the vapor bubble** for a given pressure p ,

$$r = 2\gamma/p \quad (13)$$

It is consistent with the discussion of the effects of the forces acting on an element in a curved surface that the pressure inside (on the concave side of the surface) increases with decreasing radius of curvature and *vice versa*. If the **bubble is inside a liquid with an internal pressure p_{liqu}** , this latter pressure works in the same direction as the surface tension, i.e., it tends to decrease the radius of the bubble. Then the pressure p in Equ. (13) is actually the **pressure differential $p = p_{vapor} - p_{liqu}$** .

Capillarity Effect

The result of Equ. (12) appears somewhat counter-intuitive. For example, for a balloon in air, one would expect an increase in radius with increasing inside pressure. The difference between the behavior of a balloon and a bubble in a pure liquid is due to the fact that, **unlike for rubber and other elastic materials**, the **surface tension for a pure substance does not depend on the amount of surface area stretched**. This leads to the condition of constant product of pressure and bubble radius,

$$p \cdot r = 2\gamma = \text{const.} \quad (14)$$

The effect above is responsible for the rising of a liquid in a small capillary (see figure above).

Yet another type of energy is associated with the **changes in the energetics of a system due to the addition of particles to a system**. It is clear, for example, that adding a second electron to a hydrogen atom makes the whole atom unstable, i.e., changes its total energy from a negative to a positive value. **Even for particles that do not interact**, changes in the particle number of a system at equilibrium will change the energetics. The energy required per added particle is the **chemical potential** μ . That is, changing the number N of particles by an amount dN **increases the energy of the system by**

$$\delta w = \mu \cdot dN \quad (15)$$

The chemical potential is an **intensive variable**.

Heat q is a special type of energy which is associated with **chaotic (random) motion**, as discussed before. Other types of energy, such as mechanical or electrical energy, can easily be **transformed into heat**. The **reverse is possible only to a certain extent** and much more difficult to accomplish, even at this incomplete level.

Absorption of an amount δq by a system leads to a change dT in its temperature T . One knows from experiment that **there are ranges in temperature for some, but not other, materials, where the temperature increase is proportional to the transferred amount of heat energy,**

$$\delta q = C \cdot dT \quad (16)$$

The quantity C is the **heat capacity** measured in units of J/K (Joule per Kelvin). For **monatomic ideal gases**, $C = N(3/2)k_B$ is in fact a constant. The same is true for **metals** ($C \approx C_p \approx 25.94 \text{ JK}^{-1} \text{ mol}^{-1}$). This behavior can be related to the degrees of freedom the gas particles have for their motion. Monatomic gas particles have only translational degrees of freedom.

However, there are different heat capacities at constant pressure (C_p) and constant volume (C_V). Relative to one mole of substance, the heat capacities are called **specific heat**. In general,

$$C_p > C_V \quad (17)$$

This is intuitively clear, because of the expansion that is possible for a heated system that is not confined to a certain fixed volume. The transfer of heat to the system will then **cause the system to expand, in addition to raising its temperature.**

For an **isolated system**, where no energy of any kind is exchanged between system and surroundings, **the total internal energy of the system remains constant**. In other words, the first law states that an increase dE in internal energy has to be the result of **mechanical work δw performed on the system or the gain δq in heat or of other types of energy** taken up by the system from the surroundings, i.e.,

$$dU = \delta w + \delta q + \dots \quad (18)$$

or transferred to its surroundings. **The internal energy U can only be changed by an energy flow into or out of the system (1st Law).**