2.3 Internal energy U and First Law

There are several equivalent formulations of the first law of thermodynamics, some of which we will state before starting a discussion:

- The inner energy U is a state function of a thermodynamic system, i.e.

$$\int_1^2 dU = U_2 - U_1 = \Delta U \quad . \tag{2.7}$$

  Thus $\Delta U = 0$ for cyclic processes, or

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{2.8}$$

  Here the second term is zero for a perfect gas: Changing the (average) distance between molecules will not affect the inner energy since no repulsive or attractive forces exist.

- There exists no perpetual motion machine of the first kind.
- U of an isolated system is constant, i.e. the principle of energy conservation holds.
- U can be changed by heat and work being transferred from the surrounding, i.e.

$$\text{system} \quad \rightarrow \quad \Delta U = q + w \quad \leftarrow \quad \text{surrounding.} \tag{2.9}$$

  Here U is a property of the system and q and w are measured in the surrounding. By (modern) convention $w, q < 0$ if done/released by the system, i.e. a decrease of U (system) gives the ability to transfer w, q to the surrounding. Heat and (all kinds of) work are equivalent for changing the internal energy U:

$$dU = \delta q + \delta w \quad . \tag{2.10}$$

  q denotes the amount of heat energy absorbed by a system during some given thermodynamic process, δq denotes a differential amount of heat energy. δ indicates an "inexact differential", i.e. heat is not a state function: there is no "heat function" $Q(T, p, V)$ (in contrast to U).

The inner energy is an extensive quantity, it's unit of measurement is 1 J = 1 kg $\times$ m^2/s^2.
While once heat was thought to be a type of fluid, nowadays heat is understood in terms of the kinetic theory of gases, liquids, and solids as a form of energy stored in the disordered motion of constituent particles. The unit of heat is energy as well; thus, it is appropriate to speak about heat energy which we shall simply abbreviate as heat:

- 1 J is approximately the energy consumed for one heart beat.
- 1 J is the energy needed to raise the temperature T of 0.238 g water from 14.5 to 15.5 °C (at standard atmospheric pressure).

The difference in any state function is identical for every process that takes the system from the same given initial state to the same given final state. Work and heat are not associated with one given state of the system, but are defined only in a transformation of the system. The energy of a system is its capacity to do work. When the energy of a system changes as a result of temperature differences between the system and its surroundings, the energy has been transferred as heat. As with heat, δw is an inexact differential, and work w is not a state variable, since it is path-dependent. There is no general "work function" $w(T, p, V)$. Some famous results leading to the first law:

- Count Runford (1798), first suggestion: while boring of cannons more heat was transferred after deeper boring (more work performed), thus a correlation between heat and work exists.
- Experiments of Joule (during honeymoon): temperature of water is higher at the bottom of a waterfall
- James Joule (from 1840), firm quantitative basis as a result of many experiments: "Whenever any process occurs, the sum of all changes in energy, taken over all the systems participating in the process, is zero".

So the first law is a statement of energy conservation. It says, quite simply, that during a thermodynamic process, the change in a closed system's internal energy U is given by the heat energy q added to the system, minus the work w done by the system. This sign convention has been introduced by Clausius and is optimal for the study of heat engines, which provide useful work that is regarded as positive. In modern style of teaching science, however, it is conventional to use the IUPAC convention by which the first law is formulated in terms of the work done on the system. With this alternate sign convention for work, the first law for a closed system may be written with a plus. This convention follows physicists such as Max Planck, and considers all net energy transfers to the system as positive and all net energy transfers from the system as negative, irrespective of any use for the system as an engine or other device.