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## ENERGY

Energy is important for two main reasons:

- Energy is a basic concept in physics, being one of the few conservative magnitudes (i.e. energy cannot change in the evolution of an isolated system, what is known as the First Law of thermodynamics).
- Energy is involved in most useful services to humankind: space heating, lighting, cooking, transport, material processing, refrigeration, communications... Engineering those energy services should be done efficiently.

### ENERGY CONCEPT

Energy, power, force, capability, potential, vitality... they are all related terms that may indicate the capability to change the motion, shape or relative position of objects. Physics has established very precise meanings for some of those concepts, and the key characteristic of energy is its conservation on the whole.

Energy is most of the times defined as the ability to do work, but it seems redundant from the above and it is inaccurate from what follows (e.g. what has more energy or ability to do work: a hot stone, a cold stone, two hot stones, one hot and the other cold?). As Thermodynamics show, it is [exergy](#) and not energy what measures the ability to do work; briefly, energy comes from Greek εν-εργεια ‘in work’, whereas exergy comes from εκ-εργια ‘out work’.

More properly, energy is a scalar property of a system of particles (usually with mass) depending on the position and velocities of those particles, and related to the homogeneity of the time origin in physical laws (Noether's theorem), such that energy remains constant with time in every isolated part, and, when passing through the system frontier, energy shows up as heat or work (for impermeable frontiers). The possibility of energy disappearing in one isolated system while appearing in another is prevented by relativity theory: simultaneity of events depends on the observer's motion. The unit for all kinds of energy is the joule (rhymes with 'cool').

Energy is a key concept in Thermodynamics, but it is also key to Mechanics, Electromagnetism, Chemistry, and so on. Macroscopic sciences base their study of Nature on some privileged functions that are conservative (to avoid its dependency on time origin) and additive (to avoid its dependency on size scale), and there are only a few such privileged functions: energy, momentum, electrical charge, spin... Thermodynamics focuses on the re-distribution of those functions after system evolution, what is governed by another function, [entropy](#), studied in the following chapter.

Energy is a basic human need, following respiration, water, food, shelter and other priorities. Beyond its key role in understanding how nature works, we need energy services to satisfy our basic needs of procuring water and food (and disposing wastes), shelter building (and its thermal conditioning in winter and summertime, and lighting), goods manufacturing, transportation, communication, and so on, although, as for food and water, it is difficult to draw a line between basic needs and surplus (see below on Energy price)

### Energy storage and energy flow

Thermodynamic analysis focuses on some part of the universe, called the system, and its interaction with the rest (the environment), the union of both (system+environment) is called thermodynamic universe (or global system). Hence, to analyse energy budget, we have to account for the energy stored within the system, and the energy exchanged through the frontier with the environment. It is essential to keep in mind the following mnemonic scheme, and associate the word energy primarily with energy storage, which is conservative for isolated systems, and associate the words heat and work exclusively with energy transit or energy flow through impermeable walls.

Energy in a closed system (control mass)	
Stored energy	Flow energy
Potential energy of the microscopic bonds and positions	Work at the frontier
Kinetic energy of the microscopic particles	Heat (by $\nabla T$ at the frontier)

Notice that if the user chooses the system with walls permeable to matter, another energy flow has to be attributed to the flow of matter.

For the computation of energy in a thermodynamic system, resort is made to the mechanical concept of work and the thermodynamic concept of adiabaticity, as shown below.

The concept of energy originated in the 17th c. when Galileo in 1610 first realised that when a given weight is lifted with a pulley system, the force applied,  $F$ , times the distance drawn,  $L$ , was a constant ( $FL=\text{constant}$ ) independent of the pulley system, and later Leibnitz in 1693 established that (under certain conditions) kinetic energy (*vis viva*) and potential energy (*vis mortua*) of a given mass could exchange so that  $mgh+\frac{1}{2}mv^2=\text{constant}$ . In the 19th c. energy became the common nexus of all the sciences and, besides the classical mechanical energies, elastic energy, thermal energy, electrical energy, chemical energy, radiant energy and later nuclear energy were introduced. The name energy was introduced by Young in 1807 as a synonym of *vis viva*, and later renamed 'kinetic energy' by Coriolis in 1829; in 1953 Rankine introduced the concept of 'potential energy'. Meanwhile, in the 1840s, Joule and others had verified that the amount of heating by work dissipation was conservative. The first general statement on the conservation of energy appears in 1847 in the works of Helmholtz on physiology, though he used the term 'force' instead of energy; he postulated that all kind of actions (mechanical, thermal, metabolic, electric, magnetic...) are different manifestations of a single force; i.e. energy can be converted from one form to another, but neither created nor destroyed. Table 1 presents some energy conversion examples.

Table 1. Energy conversion examples.

from to	Thermal	Mechanical (or Gravit.)	Electrical	Chemical	Radiant	Nuclear
Thermal	Heat transfer	Friction	Joule effect	Exothermic reaction	Solar heating	Isotopic source
Mechanical (or Gravit.)	Heat engine	Hydraulic wheel, Lever	Electrical motor	Explosions, Muscles	Solar sail	Nuclear weapon
Electrical	Thermoelectric pile	Electric generator	Transformer	Battery, Fuel cell	Photovoltaic cell	Nuclear power station
Chemical	Endothermic reaction	Reverse osmosis	Electrolysis	Rectification	Photography	
Radiant	Incandescence	Triboluminescence*	Luminescent lamps	Chemiluminescence	Stimulated emission	Nuclear weapon
Nuclear		Accelerators	Accelerators			Disintegration

\*Observable e.g. when a sugar-box is crumbed in darkness.

When energy is added to a system, certain changes take place. Take for instance some amount of water at ambient conditions; a small energy addition may cause internal or external motion, or just heat it up, expanding a little bit the liquid system, increasing the microscopic motion of its particles and consuming some 0.075 kJ/mol per 1 °C increase. To be able to fully separate the molecules of H<sub>2</sub>O one from the other, the hydrogen bonds amongst them must be broken, requiring some 40 kJ/mol to change from liquid to gas at 100 °C. If more energy is added to the vapour, the molecule of H<sub>2</sub>O may break up, and some 500 kJ/mol are required for the (chemical) transformation H<sub>2</sub>O→OH+H. Still further addition of energy not only breaks molecules but will pull out electrons from the atoms (the plasma state), with a need of 1310 kJ/mol for H=H<sup>+</sup>+e<sup>-</sup>. Even the nucleus of the atom may be torn apart if sufficient energy is added, 10<sup>9</sup> kJ/mol being needed to pull out neutrons from the deuterium isotope of hydrogen  ${}^2_1\text{H} \rightarrow {}^1_1\text{H} + n$  (normal hydrogen has only one nucleon). A simple candle flame illustrates the change from solid state (wax) to liquid state (melt), and then to gas state (vapours) and plasma state (flames are ionised).

As said before, all kind of energy changes can be computed based just on the mechanical concept of work and the thermodynamic concept of adiabaticity.

## Work

Since the book of Maxwell in 1871 on "The Mechanical Theory of Heat", the Thermodynamics formulation is usually based on the mechanical concept of work. Work is the transfer of energy (from the pushing to the pushed system) associated to the displacement of a force along a path; i.e. work is a scalar magnitude associated to a path integral; the force can be a point-force or a distributed-force (like pressure). In Thermodynamics, we define work by:

$$W \equiv - \int_{\text{frontier}} \vec{F}_{\text{int}} \cdot d\vec{r} = \int_{\text{non dissipative frontier}} \vec{F}_{\text{ext}} \cdot d\vec{r} \xrightarrow{E_{\text{mdf}}=0, \Delta E_m=0, \nabla p=0} W = - \int p dV \quad (1.1)$$

and the following peculiarities must be fully mastered: keep in mind the paradigm (i.e. reference model) of a compressible system in a piston/cylinder device as thermodynamic system (i.e. a gaseous mass within a tube with a piston):

- In Thermodynamics we choose a system for analysis, and work is associated to the system and its frontier (that's why 'frontier' appears in (1.1)). One says 'the work done on the system' (at the frontier). Only surface forces at the frontier are considered in (1.1); volumetric forces like the weight of the system are considered aside as potential energy (only valid for steady force fields) and not as work (on the contrary, in Fluid mechanics, both kind of forces, surface and volumetric, are equally treated).
- In Thermodynamics, work is assigned the positive sign if it forces energy to enter into the chosen system. Notice, however, that before 1948 it was the contrary, on reasons that Thermodynamics originated in the 19th c. from the desire to give out work in a heat engine to make or keep things moving (and there still few authors still adhering to the old convention, not following international recommendations). This is the reason for the minus sign in (1.1).
- Work is a scalar magnitude associated to a path integral; thus, it is not a vector, not a property; just a flow of energy at the frontier of the system, positive if it increases its energy, and negative if it decreases it. To pinpoint that, some authors write for instance the differential form of (1.1) as  $\delta W = -pdV$  instead of the  $dW = -pdV$  form to be used here.
- If the frontier has special characteristics, it is left out of the system; thus, the force applied to the interior side of the frontier is what matters, although in many cases there is a regular frontier and the force acting on the exterior side of the frontier can be used in (1.1), since in these circumstances  $d\vec{r}_{\text{ext}} = d\vec{r}_{\text{int}}$ , and always  $\vec{F}_{\text{ext}} = -\vec{F}_{\text{int}}$ . The typical case of non-regular frontier is the sliding frontier between two solid bodies with friction, where  $d\vec{r}_{\text{ext}} \neq d\vec{r}_{\text{int}}$ .
- The commonest form of thermodynamic work is the last form in (1.1), i.e. the integral of the internal pressure times the volume change of the system, changed of sign. But keep in mind that it only applies to a non-dissipative (without mechanical dissipation by friction,  $E_{\text{mdf}}=0$ ), simple compressible system (without kinetic energy, gravitational energy, elastic energy, or any other mechanical energy storage form,  $\Delta E_m=0$ ), suffering a quasi-static evolution where a single pressure value  $p$  can be defined for the whole system (fortunately, pressure waves travel at the speed of sound at least, what means that an imposed pressure on the piston-side of a cylinder-

piston system equalises nearly instantaneously in typical small systems). Mechanical springs may also appear in thermodynamic systems; they are modelled as point forces at their attachments, and energy storage devices that exchange a work  $W = \int k(x - x_n) dx$ , from (1.1), with  $x$  being the position of one end relative to a frame fixed to the other end,  $x_n$  the natural or unstressed position, and  $k$  the spring elastic constant..

- Only mechanical work was considered in (1.1), but electrical work is often involved in thermodynamic problems; although it is always computed by the product of voltage times charge-flow,  $dW \equiv V(t)I(t)dt$ , it might be viewed as the work of a microscopic piston pushing an electron gas inside the conductors, and electrical dissipation in a resistor viewed as mechanical dissipation of the flowing electrons against the fix-ion restriction to their motion. Notice that electrical voltage is just energy per unit amount of charge (1 V=1 J/C); the electron-volt (1 eV=1.6·10<sup>-19</sup> J) is often used as energy unit in nuclear reactions. Notice also that, if the observer chooses a thermodynamic system including an electrical resistance, electrical work enters through the wires, whereas, if the electrical resistance is excluded from the system, it is heat from Joule dissipation what enters the system. Non-thermal electromagnetic radiation (e.g. microwaves and lasers), i.e. radiation not coming from a hot object, can be thought of as work input to the system, too (once the radiation is absorbed, it heats up the system like in Joule effect or mechanical dissipation).
- The rate of work transfer is termed just 'power' (or mechanical or electrical power):  $\dot{W} \equiv dW / dt$ . However, many times the simple term 'work' is used to refer to work divided by time (power), work divided by mass (specific work), work divided by amount of substance (molar work), power divided by mass-flow rate (specific work), and so on, in a similar way as the term 'heat' being used for the energy transfer due to temperature gradient, or for its rate.

Although the Thermodynamics formalism may be applied to other kind of systems (e.g. electric and magnetic systems), we only consider compressible systems, most of the times in the presence of an infinite fluid environment (Earth atmosphere).

Remember that any kind of work may be ideally converted to any other kind of work, and particularly, all kind of work is equivalent to the lifting of a weight (i.e. the vertical displacement of a mass in a gravity field,  $W=mg\Delta z$ ).

Besides the general work exchanged by the system and given by (1.1), it is often important to consider the part of that work (called useful work,  $W_u$ ) that is not exchanged with the atmosphere but with some third system, and given by:

$$W_u \equiv W + \int p_{atm} dV \tag{1.2}$$

## ENERGY MEASUREMENT

Energy is ultimately measured as adiabatic work, i.e. it is not an absolute measure, but relative to a given reference state, as explained below.

## Adiabaticity

Similarly to the practical idealisation of the rigid system in Mechanics (one that opposes to a force without displacement, i.e. without work transfer), we can introduce in Thermodynamics the practical idealisation of the adiabatic system (one that opposes a thermal load on one side without any thermal effect on the other side, i.e. without heat transfer).

Heat transfer may be simply formulated as  $\dot{Q} = KA\Delta T$ , with  $K$  being the overall conductance,  $A$  the area of the frontier and  $\Delta T$  a representative temperature difference between in and out. Thence, for a given system area and  $\Delta T$ , a negligible heat transfer occurs when the thermal conductance is very low (thermal insulating materials or double-wall evacuated Dewar flask) or the time is very small.

Once that it has been shown feasible to guarantee adiabaticity (i.e. negligible heat-transfer processes,  $Q=0$ ), and based on the mechanical concept of work, energy can be measured (energy-changes, really) by performing an adiabatic experiment between the same initial and final states of a closed system, and measuring the work required:

$$\Delta E \equiv W|_{Q=0} \tag{1.3}$$

with the following peculiarities (recall that they apply to closed systems):

- If the process is without work-flow through the frontier, and adiabatic, energy is conserved. This conservation principle ( $\Delta E=0$  in isolated systems) can be called the First Law of Thermodynamics.
- The energy increase for the system equals the work input in an adiabatic process. Notice also that only energy changes,  $\Delta E$ , are defined, not absolute energy values, since there are always some energy contributions depending on the will of the observer choosing the reference frame (e.g. the kinetic energy of gravitational energy).
- Energy is considered a state function, i.e, a point value, not a path value function, inspite of work being a path function (adiabatic work is not). This is a basic assumption (related to the energy conservation principle), and was proposed by Carathéodory in 1909 as the First Law of Thermodynamics.

Subscripted conditions abound in thermodynamic notation; they are often just labelled with a symbol or initials (e.g.  $W_{ad}$  where ‘ad’ stands for adiabaticity, is written in many texts), but sometimes an algebraic condition is used (with the same meaning, but more direct, without the need of a glossary), like in (1.3).

Remember that any kind of energy variation in a system, between any two states (of equilibrium or not), can be measured by comparison with the required adiabatic work to pass from one state to the other. By the way, irrespective of the real initial and final states considered in (1.3) for the system, the adiabatic-work process is only one-way, i.e. given two states, A and B, the system can be forced to change adiabatically from A to B or from B to A (according to Nature and not to will), but not either way, in practice (but this is not related to Chapter 1: Energy but to [Chapter 2: Entropy](#)).

## HEAT CONCEPT AND MEASUREMENT

Once energy changes can be measured in terms of work, heat can be defined as the energy exchange of a closed system excluding the work actually exchanged. Heat is solely due to the temperature difference across the frontier, and can be measured as:

$$Q = W_{Q=0} - W \quad (1.4)$$

and the general relation, also known as the First Law of Thermodynamics, or the Principle of Energy Conservation, can be stated for a closed system as:

$$\boxed{\Delta E = W + Q} \quad (1.5)$$

which, in the case of an isolated system reduces to  $\Delta E = 0$ , meaning that energy cannot be generated or consumed in an isolated system (i.e., energy is conservative). Eq. (1.5) will be extended to systems with permeable walls in Chap. 5: [Control volume Thermodynamics](#). Notice that for a system undergoing a cyclic process, (1.5) implies that net work and net heat must balance out (another possible statement of the First Law of Thermodynamics).

The general Principle of Energy Conservation (First Law) was firmly established in the 1840s by key contributions of Mayer, Joule and Helmholtz, although more restricted energy conservation principles were stated as far back as Galileo around 1600 (conservation of the sum of potential and kinetic energy of a system). So rooted this conservation-of-energy principle was, that already in 1775 the French Academy decided not to consider any more 'inventions' to generate energy from nothing, the so-called perpetual motion machine (later qualified as of the first kind, when it was realised that it was impossible even balancing work-output with heat-input from a single source, i.e. that perpetual motion machines of the second kind, as the latter became known, are unfeasible too). The Principle of Mass Conservation was first made explicit by Lavoisier in 1785, and modified in 1905 by Einstein's relation  $E = mc^2$ , which shows that mass can be seen as concentrated energy, both being interchangeable, although mass changes due to energy changes are so small ( $1 \text{ J} \Leftrightarrow 1/(3 \cdot 10^8)^2 \text{ kg} = 10^{-17} \text{ kg}$ ), that energy effects can be neglected in mass conservation; mass effects could not be neglected in the energy balance, but they are not explicitly included (except for nuclear reactions) because equivalent energy terms are directly introduced (e.g. chemical energy).

When (1.5) is applied to infinitesimal changes it is often written as  $dE = dW + dQ$ , in spite of the fact that  $dE$  is an exact differential (a small change of a state function), and  $dW$  and  $dQ$  are not exact differentials but infinitesimal path values, as remarked above (in some texts, a more specific nomenclature is used, as  $dE = \delta W + \delta Q$ , with the finite form  $\Delta E = W + Q$  in any case).

### Heat rate by conduction, convection and radiation

The rate of heat transfer is termed 'heat rate':  $\dot{Q} \equiv dQ/dt$ , although a related variable is used most of the time, the heat rate per unit area or 'heat flux':  $\dot{q} \equiv \dot{Q}/A$ , a vector magnitude related to the temperature difference between the environment and the system. Note: although the recommended symbol for heat

flow rate in SI-units is  $\Phi$ , most thermodynamics and heat transfer books use  $\dot{Q}$  (the SI recommendation for the heat rate per unit area is  $q$  instead of  $\dot{q}$ , and, for thermal conductivity,  $\lambda$  instead of  $k$  here used).

Heat can be transmitted by short-distance ( $10^{-10}$  m) electromagnetic interaction between contacting molecules (diffusion of energy), or by long-distance electromagnetic interaction between non-contacting bodies (radiation of energy, as from Sun to Earth). In practice, when heat diffusion is enhanced by fluid motion the term 'heat convection' is used. Heat conduction in a non-flow material system is modelled by Fourier equation:  $\vec{q} = -k\nabla T$ , where  $k$  is the thermal conductivity of the material and  $\nabla T$  the temperature gradient ( $\dot{q} = -k \partial T / \partial x$ , for a one-dimensional planar geometry). Heat convection from a solid to a fluid is modelled by Newton equation,  $\dot{q} = -h(T - T_\infty)$ , where  $h$  is the convective coefficient (dependant on the fluid properties and flow characteristics) and  $T_\infty$  an appropriate bulk temperature of the fluid. Heat radiation between a system and some far radiating envelop (with a non-participating media in between), is modelled in the simplest case by the Stefan law,  $\dot{q} = -\sigma(T^4 - T_\infty^4)$ , with  $\sigma = 5.67 \cdot 10^{-8}$  W/(m<sup>2</sup>·K<sup>4</sup>) being Stefan-Boltzmann's constant, and  $T_\infty$  an appropriate temperature of the participating environment (for instance, solar radiation can be considered a heat input from a heat source at  $T_\infty = 5800$  K). In summary, any heat transfer process can be seen in Thermodynamics as  $dQ/dt = KA(T - T_\infty)$  with a global heat transfer coefficient  $K$  to be given by Heat Transfer theory, in a similar way as Heat Transfer theory synthesises Thermodynamics to just  $dE/dt = W + Q_{\text{net}}$ , with some given functions for energy and work, usually just  $mc dT/dt = Q_{\text{net}}$  (see Internal energy, below).

Remember that any kind of heat flow may be measured by the difference between the adiabatic work required associated, and the real work involved, (1.4), i.e. by an energy balance. Using heat-transfer rate equations as the Fourier law above, to measure heats is really an indirect way to apply the basic energy balance. In practice, added heat is measured by comparison with the consumption of an electric heater, whereas evacuated heat is best measured by means of the temperature increase of a calibrated cooling-water stream.

A final mention to some colloquial misunderstandings seems appropriate. The word energy usually conveys a positive attitude, nowadays associated to valuable electricity, whereas the word heat usually conveys a negative attitude (e.g. sweating), and in many textbooks is termed 'degraded energy'. And what about cold and cold transfer?

### [Exercise 1. Heat and work in a piston-cylinder system](#)

## MECHANICAL ENERGY

### Storage

It is important to split the total energy stored in a system,  $E$ , in two parts called mechanical energy,  $E_m$ , and internal energy,  $U$ , such that  $E = E_m + U$ . One such division may be to keep  $E_m$  as the part of the total energy that is dependent on the coordinate reference frame chosen by the observer, so that  $E_m = mgh + \frac{1}{2}mv^2$ , but we adopt here a wider definition for the mechanical energy stored in a system as:



$$\Delta E_m \equiv \left( W + \int p dV \right)_{E_{mdf}=0} \quad (1.6)$$

i.e., the part of the total work transfer that does not show up as a quasi-static work of compression in absence of friction, and that includes energy stored in internal subsystems like elastomers (natural and synthetic rubbers), elastic springs (and beams, and torsion springs), flywheels and weights, besides the overall potential and kinetic energies of the system, all of which can be easily computed aside.

### Dissipation

It follows from (1.6) that the mechanical energy-input degraded by friction,  $E_{mdf}$ , can be defined by:

$$E_{mdf} \equiv W + \int p dV - \Delta E_m \quad (1.7)$$

i.e., the mechanical input,  $W$ , not accounted neither in the quasi-static flow,  $\int p dV$ , nor in the mechanical accumulation,  $\Delta E_m$ , is dissipated (converted from ordered mechanical energy to disordered thermal energy). Note that pressure,  $p$ , in (1.7) implies a unique pressure representing the state of the system, and thus implies mechanical equilibrium inside, what is usually a very good hypothesis since pressure gradients travel at least at the speed of sound (hundreds of meters per second in gasses). Mechanical energy dissipation can take place both in the interior of the system under consideration, and at its frontier (in this later case, it is worth considering an auxiliary small system to encompass the dissipation in its interior).

### Friction modelling

Friction is resistance to relative motion (but there may be non-friction forces opposing motion too, as lift-induced drag in Fluid Mechanics). In a thermodynamic system, friction may take place at the frontier (when a solid acts upon a solid system, i.e. dry contact) or inside the system by internal dissipation in deformable systems (solid, liquid or gas). The first case is also named solid friction, a special case of interface science (solids and fluids), studied in tribology science (friction, lubrication and wear; Gr.  $\tau\rho\iota\beta\omega$ , to rub). The second case is studied in rheology science (viscous, elastic and viscoelastic; Gr.  $\rho\eta\varepsilon\nu$ , to flow).

In Engineering Thermodynamics, friction has a negative impact on process performance, being associated always to unwanted energy-dissipation. Notice, however, how difficult life could be in a hypothetical negligible-friction world: we could not walk without sliding, we could not start or stop our vehicles (railways were initially built with gears because they thought that metal-metal contact would slip instead of roll), our trousers may come down...

We only care here about mechanical energy dissipation by (solid) friction, but tribology (the science and technology of solid-contact motion, or rubbing) is not constrained to mechanical effects (e.g. tribo-electricity, tribo-luminescence, tribo-chemistry...). Friction occurs in linear motion, as our paradigmatic piston-and-cylinder mechanism, in circular motion, as wheel-axes and bearings, or in any other geometry, as wheel rolling, pulleys and gear transmissions.

Solid-friction modelling is really a difficult task, being an intrinsic non-linear effect (only viscous fluid flow can be appropriately modelled as a linear effect). In fact, a strict corollary of thermodynamic equilibrium (to be fully explained in the next chapter: Entropy), is that friction between undeformable solids cannot exist, since they must locally have no-relative velocity (as for the no-slip condition in a fluid at a wall). The key concept on solid friction is the friction force,  $F_f$ , defined as the component of the reaction of the reference solid against the imposed motion of the other solid in contact, located at the centre of the contact surface, and having the same direction of the motion opposite sense. The origin of this force lies in elastic and plastic deformations of the asperities in contact (if the contact surfaces were atom-size smooth, they would form a single solid (as can be done by rub-welding)).

The friction force depends on materials properties, compressive force, motion kinematics and interface topology (roughness). There is always air trapped in between the two contacting solids; friction under high vacuum is much larger, friction between moist surfaces is smaller, and friction between oiled surfaces is much smaller. In 1699 Amontons proposed that  $F_f \neq f(A)$ , i.e., a parallelepiped block sliding on a surface shows the same friction force whatever the side in contact.

In 1785 Coulomb proposed that  $F_f \neq f(\dot{x})$ , i.e. that the force is independent on the speed, and established the most-used model:  $F_f = \mu F_N$ , where  $F_N$  is the normal force that keeps both solids in contact (usually just the contribution of weight,  $F_N = mg \sin \theta$ , on a  $\theta$ -sloping plane), and  $\mu$  is a friction coefficient depending on the materials and surface state. Even this most-simple model has a profound non-linear character because it really means that  $F_f = -\text{sign}(\dot{x}) \mu F_N$  for  $\dot{x} \neq 0$  (sliding regime) and  $F_f = -\min(F_T, \mu F_N)$  for  $\dot{x} = 0$  (pre-sliding regime), where  $F_T$  is the applied tangential force. Moreover, it has been found that different values for  $\mu$  may give better results, a larger  $\mu_{\text{sta}}$  for the static or pre-sliding regime and a smaller  $\mu_{\text{dyn}}$  for the dynamic or sliding regime. Some common values are:  $\mu_{\text{sta}}=0.7$  and  $\mu_{\text{dyn}}=0.3$  for steel-on-steel sliding contact,  $\mu_{\text{sta}}=0.1$  and  $\mu_{\text{dyn}}=0.05$  for steel-on-ice,  $\mu_{\text{sta}}=0.05$  and  $\mu_{\text{dyn}}=0.05$  for teflon-on-teflon,  $\mu_{\text{sta}}=0.5$  and  $\mu_{\text{dyn}}=0.3$  for hardwood-on-hardwood,  $\mu_{\text{sta}}=1.0$  and  $\mu_{\text{dyn}}=0.8$  for rubber-on-asphalt-road,  $\mu_{\text{sta}}=0.7$  and  $\mu_{\text{dyn}}=0.7$  for rubber-on-concrete, etc.

Besides sliding friction, rolling friction and torsional friction are of interest. Rolling friction may be modelled with the same Coulomb law and smaller coefficients (e.g.  $\mu=0.01$  for rubber-tyre-on-asphalt-road and  $\mu=0.001$  for steel-wheel-on-steel-rail), or better modelled with a modified law,  $F_f = -\text{sign}(\dot{x}) \mu_R F_N^a$ , where  $\mu_R$  is a different friction coefficient for rolling and  $a$  is usually in the range 0.2..1.4, depending on softness of the contact. On top of that, solid friction shows hysteresis, i.e. a response depending on previous state and having some time lag (not recovering instantly).

Viscous fluid flow shows a linear resistive force,  $F_f = -\mu \dot{x}$ , so convenient for analysis, that even solid friction is sometimes modelled that way (it might be good for lubricated joints). Sometimes, for oscillating sliding solids, the law  $F_f = -\mu \dot{x} / \omega_0$  is used, where  $\omega_0$  is the applied oscillation frequency and  $x = A \sin(\omega_0 t)$ ; it is easy to deduce that this model yields an energy dissipation  $E_{\text{mdf}} = \pi \mu A^2 n$ ,  $n$  being the number of cycles executed, that is independent on the applied frequency, as the basic Coulomb law. High-Reynolds number flows show a quadratic resistance,  $F_f = -\text{sign}(\dot{x}) \mu \dot{x}^2$ . Figure 1.1 gives a summary view of what has been explained.

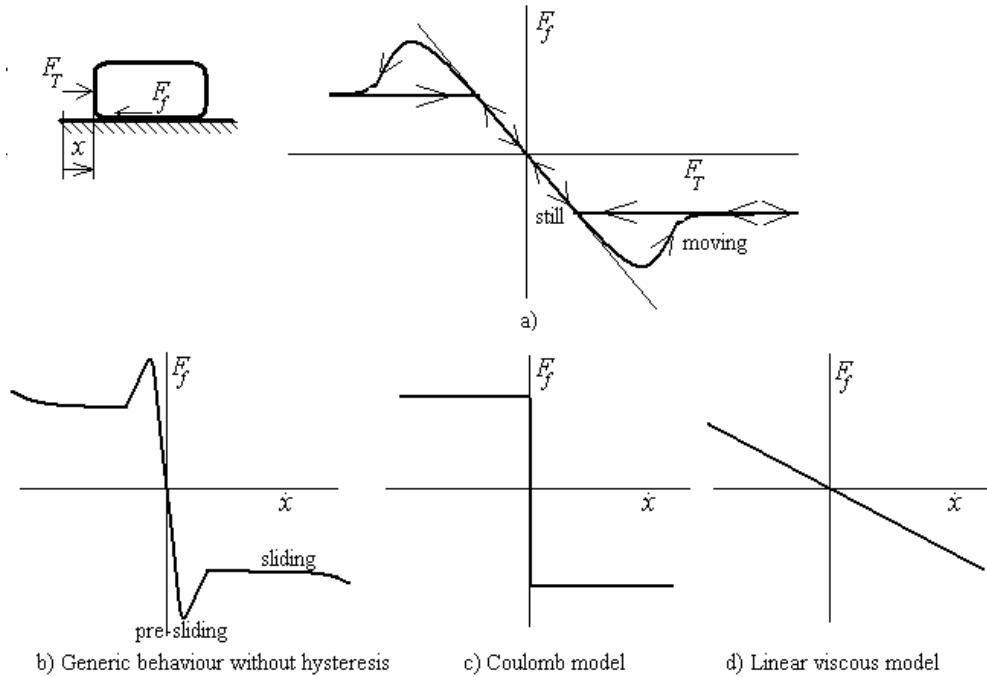


Fig. 1.1. Friction force  $F_f$  opposing an applied tangential force  $F_T$  on a sliding object, and some models for the dependence of friction force on relative speed.

## INTERNAL ENERGY

Since we split the total energy of a system  $E$  in two parts,  $E = E_m + U$ , internal energy,  $U$ , is defined by:

$$\Delta U \equiv \Delta E - \Delta E_m \quad (1.8)$$

and includes thermal energy, chemical energy, nuclear energy and any other not accounted for in (1.6). From (1.8), (1.5) and (1.7) one can deduce the so called internal energy equation (to be further analysed below under 'Refrigeration by sudden expansion'):

$$\Delta U = Q + E_{mdf} - \int p dV \quad (1.9)$$

### Perfect (calorific) substances

We here analyse (it will be presented in a broader context in Chap. 4: [Thermodynamic Potentials](#)) a simplified model of the macroscopic behaviour of a substance, the so called 'perfect calorific substance' (or simply perfect substance model, PSM), assumed to be known from former courses, and for which the thermal energy change is directly proportional to the temperature change, that is:

$$\Delta U = mc_v \Delta T \quad (1.10)$$

where  $c_v$  is a constant, later to be shown as the specific thermal capacity at constant volume, and temperature  $T$  is the measure of the thermal energy level of a system, characterised by the fact that its gradient forces the flow of heat, to be formally defined in Chap. 2: [Entropy](#).

When temperature appears in equations like (1.10) it is implied that the system may be characterised by a single temperature, a hypothesis that must be taken with care since temperature gradients decay much more slowly than pressure gradients. By the way, keep in mind that physical reality is much more complex than our models: the rigid solid, the incompressible liquid, the ideal gas, the perfect calorific

substance, the pure substance, the adiabatic wall, the temperature of a system, the pressure of a system... all are just approximations to the real facts. All real substances have thermal capacities varying with temperature (usually increasing) and in smaller terms with pressure, but the simple perfect model in (1.10) would give the same result if a suitable mean value is used for  $c_v$ .

Notice that no mention is made in (1.10) on the way the internal thermal energy is changed; equation (1.9) shows that it can be by heat transfer, or by work transfer (irreversible as with a stirrer, or reversible as in an ideal compression). In old times, when little care was paid to distinction between internal energy and heat (the former sometimes called stored heat),  $c_v$  in (1.10) was named specific heat, instead of thermal capacity.

Many practical thermal problems are of the 'calorimetric' type, where one looks for the temperature attained after mixing two systems at different temperature, usually assuming that heat losses to the environment are negligible. The solution with this perfect-calorific-substance model (PSM) is  $T_{\text{final}} = (m_1 c_{v1} T_1 + m_2 c_{v2} T_2) / (m_1 c_{v1} + m_2 c_{v2})$ . Obviously, the final temperature is in between the initial ones (but obvious things may be wrong sometimes: when mixing ice at 0 °C with salt at 20 °C you get temperatures well below 0 °C; do not forget that (1.10) only accounts for thermal energy, without any phase change or chemical reaction).

The mixing calorimeter can be used to find the thermal capacity of a sample relative to other substance, basically water. A rudimentary calorimeter can be just a couple of plastic cups for drinks, one inside the other, with some spacing in between (a 1 mm layer of air may be good enough for coarse trials); usually, a measured amount of water is inside at room temperature, and a weighed hot sample is introduced, measuring water temperature while stirring until a maximum is reached, assumed to be the equilibrium temperature, before the inevitable thermalisation with the ambient shows up. With the same setup, not only thermal capacities of solid or liquid substances can be found, but also heats of fusion (e.g. adding some ice cubes) and heats of condensation (e.g. bubbling some vapour within). Measuring heats of solution and heat of reactions usually demand more accurate and more enduring conditionings.

The small thermal contribution due to the unavoidable heating of the internal wall of the calorimeter during the trial (and other exposed items in the interior, as the stirrer), can be measured off-line by a control trial with some hot water as a sample of known thermal capacity, attributing the 'losses' to the calorimeter mass by means of a water equivalent, either in terms of mass of water equivalent,  $m_{we}$ , or in terms of heat capacity of water equivalent,  $C_{we} = m_{we} c_w$ , of the calorimeter, and using:.

$$\begin{aligned} \Delta E = Q + W \stackrel{Q=W=0}{=} 0 \stackrel{\Delta E_m=0}{=} \Delta U &= \Delta U_{\text{sample}} + \Delta U_{\text{water}} + \Delta U_{\text{calorim}} = \\ &= m_s c_s (T_F - T_I) + (m_w + m_{we}) c_w (T_F - T_0) \end{aligned} \quad (1.11)$$

## [Exercise 2. Measuring the thermal capacity of a solid](#)

### **Refrigeration by sudden expansion**

The internal energy equation (1.9) now may show how to get hot and cold temperatures; a system may be heated (really its temperature raised,  $\Delta T > 0$ ) by  $Q$  (contact with a higher temperature system), by  $E_{\text{mdf}}$

(friction) and by compression, whereas a system can only be cooled (really its temperature lowered,  $\Delta T < 0$ ) by  $Q$  (contact with a lower temperature system) and by expansion (we are here considering only closed systems without chemical reactions).

The refrigeration effect by sudden expansion is perhaps the easiest way (and most used in practice, see [Refrigeration](#)) to get low temperatures, a much more difficult task than producing high temperatures (see [Thermal Systems](#)).

### Adiabatic and non-dissipating evolution of a perfect gas

The ideal gas model is assumed to be known (it can be deduced from microscopic kinetic theory, and will be studied in its proper context in Chap. 4: [Thermodynamic Potentials](#)):

$$pV = mRT \quad (1.12)$$

i.e., in the evolution of an ideal gas, the product of pressure  $p$  times volume  $V$  is directly proportional to the absolute temperature  $T$ , the constant of proportionality being the gas mass  $m$  times a gas constant  $R$  (e.g.  $R_{\text{air}} = 287 \text{ J}/(\text{kg}\cdot\text{K})$ ). The ideal gas model in terms of amount of substance  $n$  instead of mass  $m$  is  $pV = nR_u T$ , with  $R_u$  being the universal gas constant  $R_u = 8.13 \text{ J}/(\text{mol}\cdot\text{K})$  and  $R = R_u/M$ , with  $M$  the molar mass of the gas (e.g.  $M_{\text{air}} = 0.029 \text{ kg}/\text{mol}$ ), so that also  $pV = mR_u T/M$ . The ideal gas model is adequate for many thermodynamic problems involving real gases at not-too-high pressures, and dates back to the isothermal model,  $pV = \text{constant}$ , due to R. Boyle (1662) and E. Mariotte (1676), and the isobaric model,  $V/T = \text{constant}$ , due to J.A. Charles (1787) and J.L. Gay Lussac (1802); the combined form,  $pV = mRT$ , is attributed to Émile Clapeyron, who in 1834 proposed  $pV = mR(T + T_0)$ , with  $T$  in degree Celsius and  $T_0 = 267 \text{ }^\circ\text{C}$  (now  $T_0 \equiv 273.15 \text{ }^\circ\text{C}$ ). Note: although the international standards recommend the symbol  $t$  for temperatures in the Celsius scale, we use  $T$  for both, thermodynamic temperature (in kelvin) and Celsius temperature (in  $^\circ\text{C}$ ), to avoid confusion with time  $t$ .

The ideal gas model is not a complete thermodynamic model of a substance (it lacks thermal capacity data). A perfect gas is an ideal gas,  $pV = mRT$ , with constant thermal capacity such as  $\Delta U = mc_v \Delta T$ . The perfect gas model (PGM) is a complete thermodynamic model of a simple compressible substance.

Several special cases for the evolution of a perfect gas can be considered. The trivial ones are: the isothermal evolution ( $T = \text{constant}$ ), the isobaric evolution ( $p = \text{constant}$ ), the isochoric evolution ( $V = \text{constant}$ ). But another most-important evolution in the modelling of compression/expansion gaseous system is the adiabatic non-dissipating evolution of a perfect gas, for which the following equations apply:

- Eq. (1.1), that in differential form reads  $dW = -pdV$ .
- Eq. (1.5) that in differential form reads  $dU = dW + dQ = -pdV$ .
- Eq. (1.10)  $dU = mc_v dT$ .
- Eq. (1.12),  $pV = mRT$ .

Combining them, one gets:

$$dU = -pdV = mc_v dT = -\frac{mRT}{V} dV \Rightarrow \frac{dT}{T} + \frac{R}{c_v} \frac{dV}{V} = 0 \Rightarrow TV^{\gamma-1} = \text{constant} \quad (1.13)$$

where the Mayer relation for ideal gases  $c_p - c_v = R$  was assumed known (it is analysed in detail in Chap. 4: [Thermodynamic Potentials](#)) and the quotient  $\gamma = c_p/c_v$ , known as thermal capacity ratio, or isentropic coefficient, is introduced (also studied in Chap. 4: [Thermodynamic Potentials](#)). If one of the two variables in (1.13) is eliminated from  $pV = mRT$ , one gets  $pV^\gamma = \text{constant}$  and  $T/p^{(\gamma-1)/\gamma} = \text{constant}$  as equivalent results to (1.13), termed isentropic relations for a perfect gas.

[Exercise 3. Push and release of a piston](#)

[Exercise 4. Sudden release of gas](#)

## ENERGY PRICE

The price (value or worth) of energy, as for food, water and other human necessities, is dictated by the availability of natural resources (at a convenient time and place), under acceptable circumstances: safety, liberty, economics, cleanliness, security, and in the desired form to satisfy individual needs (real or imaginary). As for other commodities in developed societies, commercial processes are established to make energy available to end-users in a convenient form, when and where needed, at a value added cost (market price, of the order of  $10^{-8}$  €/J for a western city-dweller). Similarly, as for other basic utilities (water supply, sewage, transportation...), there must be appropriate public regulations and provisions.

Energy (as well as mass) is a conservative physical magnitude, and, after use, goes back to the environment (i.e. out of the user-system, as waste heat and waste matter). Thus, it is not energy what has a price, but available energy (i.e. exergy). Even more, it must be emphasized here that end-user-concern focuses on energy services demanded (e.g. space heating to 20 °C in winter, space cooling at 20 °C in summer, refrigerated storage at some 0 °C or below freezing, cooking, illumination, stirring, transportation, communications...) and not on the energy carrier and energy amount they use to achieve the goals (except for side effects like cleanliness, readiness, safety...).

## World energy

Energy is abundant on Earth: globally, Earth gets from the Sun  $10^4$  times more energy than the whole present humankind usage, but solar energy is not available at night, not enough for home heating in winter, not directly usable for transportation or refrigeration, and too-much diluted for most applications.

Besides the tiny contributions from the gravitational pull of the Moon and Sun, and the residual nuclear energy in the Earth interior, practically all energy input into our ecosphere is solar electromagnetic radiation, that can be gathered thermally, photonically (biological photosynthesis and photovoltaic cells), or indirectly through the winds, hydrological cycle, ocean waves, etc. Energy input practically equals energy output at every instant on the whole Earth (the space-averaged temperature in the Earth surface is nearly 15 °C all the time; the worst fear of global warming is a few degrees by the year 2100); and both, input and output, correspond to electromagnetic radiation, but the input is half and half in the visible and the infrared region of the spectrum, whereas the output is mainly infrared.

One calls "primary energy" any kind of energy that has not undergone anthropogenic processing, encompassing not only solar radiation, but its spin-offs: hydraulic energy, wind energy, biomass, fossil fuels (long-term biomass residue), and non-solar-radiation related sources: nuclear energy, geothermal energy and tidal energy. One calls "secondary energy" or "final energy" any kind of energy carrier available to the end-user. At present, there are just two kinds of final energy forms:

- Electrical energy, flowing through solid conductor wires.
- Chemical energy, flowing through gas pipes, or batch delivered in solid, liquid, or gas form.

The most convenient final energy form (i.e. multipurpose, controllable and clean) happens to be electrical energy; but it has the drawbacks of inconvenient sources (environmentally) and inconvenient storage (electricity in the grid must be generated at the same rate it is consumed).

Chemical energy of fuels is most used presently, because energy storage is simply related to mass storage, and natural fuel-sources are more or less adequate: large fossil fuels deposits were found (although they are being commercially exhausted), and renewable fuel sources can be cropped.

Since the larger share of present world energy production is from fuels, and they are easily available (fossil or biomass), energy prices are comparatively low, of the order of  $10^{-8}$  €/J for a modern city dweller, corresponding to  $10^{-1}$  €/kg of coal, less expensive than basic food (1 €/kg of bread). Water may reach a city-home at  $10^{-3}$  €/kg and air is presently free, although many people in large cities would be willing to pay for good bottled-air or clean-air appliances, as they pay for good bottled-water, for good food and for good energy.

In spite of energy prices being low at present, we are approaching a [threatening energy future](#) because energy usage is the major Earth pollution activity (toxic fumes, oil spills, nuclear accidents, global climate change), and the end of some fossil-fuel sources appears close (crude oil and natural gas may reach a prohibitive price in a few decades). One might imagine a society scarcely dependent on energy, as in pre-industrial civilisations, but nowadays developed societies are based on energy even for their food production (agriculture mechanisation and artificial fertilisation allow a 5% of the population to feed the whole population; before mechanisation and artificial fertilisation, 95% of the population had to be engaged in agriculture). On the other hand, one may believe that renewable energy sources (of solar origin) may take over pollutant fossil sources, but the fact is that more than 80% of the energy consumption in whole world is presently transformed into useful services (heat, electricity or movement) by means of fossil-fuel combustion processes, generating a huge amount of greenhouse warming gases ( $21 \cdot 10^{12}$  kg/yr of  $\text{CO}_2$ , in 2005). The only way-out of this doom horizon lays is human creativity, guided by a sound education on Thermodynamics and other sciences.

## **TYPE OF PROBLEMS**

Besides housekeeping problems of how to deduce one equation from others, and some review exercises from background physics (e.g. hydrostatic pressure, friction), there are three basic types of problems in this chapter:

1. Find the final state of a system when some internal or external restrictions are released (e.g. Exercise 1). Finding the speed or duration of a process is a thermal problem usually addressed by 'extended Thermodynamics' sciences (Heat transfer, Fluid dynamics).
2. Compute energy changes for a given system between given states.
3. Find an unknown term in an energy balance.
4. Find a subset of initial and/or boundary conditions required for a given process.

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