

## Introduction

The central themes of this course are the nature of heat, the meaning of temperature, and the behavior of matter as temperature is varied. Each section of this course is centered on particular features, but all the ideas that are used are interrelated, to a large extent by the central ideas of mechanics, momentum, force, and energy. A new central idea is that matter of a given composition in thermal equilibrium has an equation of state, so that properties such as density and energy are characteristics of the material determined by the pressure and temperature. An important new concept is entropy, which gives limits on the availability of thermal energy.

## Pressure and density: hydrostatics

The **density** of any material is the ratio of mass to volume. Density is a characteristic of the material, so you can look up tables of density. For gases there is a strong dependence of the density on pressure and temperature, but for liquids and solids there are relatively small changes of density when pressure and temperature are varied.

The **pressure** in a fluid (liquid or gas) is the outward normal force per unit area exerted by the fluid on any real or imaginary surface. Pressure in a liquid increases linearly with depth  $d$ ,  $p = p_0 + \rho g d$ , because the liquid has to support the weight of the fluid immediately above it. For the pressure in the atmosphere one has to take account of the variation of density with height, and it would fall exponentially with height if the temperature were constant.

If a solid object is placed in the fluid the pressure of the fluid is unchanged (except in a small container of liquid, where the level of the surface may be changed), and the total force exerted by the fluid pressure on the solid is exactly the same force that was supporting the weight of the displaced fluid. This is true both for floating and for totally immersed bodies, and saved Archimedes from having to do unpleasant volume integrals.

## Temperature and equations of state

At this stage **temperature** is defined as something which can be measured by a thermometer, because, when bodies are brought into contact, heat flows from the higher temperature body to the lower temperature body until they are in **thermal equilibrium** at the same temperature.

**Thermometers** exploit the fact that materials have properties such as density, electrical resistivity, and so on, that depend uniquely on temperature. The equation of state of a material gives its density as a function of temperature and pressure.

There are special values of temperature and pressure where matter can exist in more than one phase, and so the density is not unique. At the melting temperature ice and water can coexist, occupying a volume which is intermediate between the volume occupied by pure water and pure ice. Similarly, at the temperature-dependent **vapor pressure** of a liquid (or solid), any ratio of the liquid and vapor can coexist at the same pressure and temperature. There is a unique pressure and temperature at which all three phases can coexist, and this is the **triple point**. Triple points give useful standard temperatures for calibration and definition of thermometers.

The gas law  $pV = nR(T + T_0)$ , which holds for all sufficiently dilute gases, enables a temperature scale to be defined which does not depend on the use of a particular type of thermometer. In the kelvin scale  $T_0$  is taken to be zero, and the triple point of ice is defined as 273.16 K.

### Heat, work and energy. Transfer of heat

Specific heat is a characteristic of materials, so heat capacity can be found by multiplying the mass of a body by the heat capacity per unit mass of the material of which it is composed. **Calorimeters** work by allowing a body at one temperature to come into equilibrium with a body of known heat capacity.

**Heat** is not conserved, but is a manifestation of **energy**, so it is measured in joules. Heat capacities are measured in J/K, specific heats in J/kg K or J/mole K.

The increase of **internal energy** of a body is equal to the sum of the work done on it and the heat supplied to it. This is the **First Law of Thermodynamics**.

**Latent heat** of melting or vaporization is the heat that must be supplied to melt a solid at the melting temperature or vaporize a liquid at its vapor pressure. When these processes occur at constant temperature and pressure some of the energy supplied as latent heat goes into the work against the external pressure needed to expand the materials, rather than into their internal energy.

Ideal gases have an internal energy that depends on temperature but not on pressure. A monatomic gas has constant volume heat capacity  $C_v = 3nR/2$ , diatomic gases often have  $C_v \approx 5nR/2$  around room temperature, rising at higher temperatures. The difference  $C_p - C_v$  is due to the work done in expansion at constant pressure, and is  $nR$  for an ideal gas.

In an adiabatic expansion of an ideal gas, pressure and volume are related by  $pV^\gamma$  constant, where  $\gamma = C_p/C_v$

Many solids have a room temperature heat capacity close to  $3n_A R$ , where  $n_A$  is the number of atoms divided by the Avogadro number.

Heat can be transferred by thermal conduction, convection, or radiation.

Conduction is a slow diffusion of the heat through a material, and the rate of heat transfer is proportional to the temperature gradient.

Convection involves the transfer of heat by the movement of the fluid holding the heat. The latent heat of evaporation can enhance convection.

Radiation involves the unimpeded flow of electromagnetic radiation through a vacuum or transparent medium. Emission of radiation is proportional to  $T^4$ , and the characteristic frequency of radiation is proportional to  $T$ .

### Kinetic theory. Pressure, temperature, energy in terms of molecular motion

In this section the things studied up to this point are explained in terms of the motion of atoms and molecules. We describe things in terms of the number  $N$  of molecules rather than the number  $n$  of moles, and in terms of the Boltzmann constant  $k_B$  rather than the gas constant  $R$ . Density is envisaged as the average mass of atoms in a given volume, but the actual number of atoms in a given volume fluctuates.

The **pressure** of an ideal gas is the average force exerted by molecules bouncing off the walls, and is readily shown to be equal to  $p = (Nm/V)\overline{v_x^2}$ , where  $m$  is the molecular mass. Comparison of this with the gas law shows that  $k_B T = m\overline{v_x^2}$ . Typical speeds of molecules are proportional to  $(k_B T/m)^{1/2}$ . Different types of molecules contribute independently to the pressure and to the internal energy.

Detailed arguments show that, in classical mechanics, randomly colliding particles tend to share their kinetic energy equally, which gives the principle of **equipartition of energy**. This

gives a new interpretation of the Kelvin **temperature** in the form that  $k_B T/2$  is the average kinetic energy associated with each degree of freedom in any material, solid, liquid, or gas.

The **mean free path** is the distance a molecule goes before its momentum changes direction. For molecules surrounded by similar or more massive molecules this is roughly the distance gone between collisions, but for massive molecules surrounded by less massive molecules it will be much more than this.

Equipartition only applies to vibrational modes of motion if the frequency  $\nu$  is less than  $k_B T/h$ , where  $h$  is Planck's constant. When equipartition does hold, the potential energy contributes equally with the kinetic energy, since the average potential energy of a harmonic oscillator is equal to the average kinetic energy.

The heat capacity  $5Nk_B/2$  for diatomic gases results from  $k_B T/2$  energy in the translational motion and each of the two rotational modes, but very little excitation of the energy of the vibrational mode. More complex molecules show a third rotational mode, and gradual excitation of the vibrational modes as the temperature is increased. The heat capacity  $3N_A k_B$  of typical solids suggests full vibrational motion of each atom at room temperature.

Molecular speeds are comparable with the speed of sound in gases, but the sound waves are adiabatic, and their speeds depend on the ratio of specific heats through a factor  $\sqrt{\gamma}$ .

**Brownian movement** of particles large enough to be seen but small enough that their random thermal motion is detectable show molecular motions directly. Direct observation of the thermal motion is not easy, but random diffusive motion must be interpreted by more detailed theory. Distribution of heights in thermal equilibrium shows thermal distribution of gravitational potential energy.

**Boltzmann distribution**, with probabilities of states with energy  $E_n$  that are proportional to  $\exp(-E_n/k_B T)$ , leads to equipartition, the isothermal atmosphere, etc. For the ideal gas, this gives the distribution of velocity components as

$$n(v_x) \propto \exp(-mv_x^2/2k_B T) .$$

Similarly, when the potential energy of a particle as a function of height is  $U(z) = mgz$ , the distribution of heights of the molecules is given by

$$n(z) \propto \exp(-mgz/k_B T) .$$

**Radiation** is in equilibrium in a cavity surrounded by walls of uniform temperature, but quantum theory is needed to explain why the energy density is finite, and the energy spectrum is peaked near  $\nu = k_B T/h$ . The peak enables temperatures of very hot bodies, such as the surfaces of stars or interiors of furnaces, to be measured by spectroscopy. Infra-red detectors can be used to measure temperatures quite close to the ambient temperature.

### Entropy and the second law

The **second law of thermodynamics** says that thermal energy can only be used for a price. **Work** must be done to pump heat from a low temperature to a higher temperature, no work can be obtained without having heat flow from a higher temperature to a lower temperature.

Analysis of an ideal reversible engine, with ideal gas as its working material, shows that the efficiency, the ratio of heat taken in at the higher temperature to work done, is  $e = 1 - T_l/T_h$ .

For a refrigerator or air conditioner we are interested in the ratio of heat removed to the work done by the pump, and for a reversible engine this gives a coefficient of performance  $CP = T_l/(T_h - T_l) = 1/e - 1$ . This must be true for **all reversible devices**, or else they could be coupled with a Carnot engine to pump heat to higher temperatures for no net work, or to run a heat engine with net work done and no net heat input.

In reversible processes **entropy** is conserved and the change in entropy in each part of the system is  $Q/T$ . In irreversible processes, such as thermal conduction, friction, mixing of different gases by diffusion, entropy increases.

This can be combined with the first law of thermodynamics to give the relation  $dU = -p dV + T dS$ , where the two parts of the change in internal energy are the work done on the system, and the heat that flows in. This gives  $C_v = T(\partial S/\partial T)_V$ , or  $C_p = T(\partial S/\partial T)_p$ , which integrate to  $S(T) = \int^T (C_V/T') dT'$ . The entropy  $S$  becomes an extensive variable that goes with  $T$ , just as  $p, V$  go together.

The internal energy  $U$  can be expressed as the average of the energy values  $E_n$  with probabilities proportional to  $\exp(-E_n/k_B T)$ , and the relation  $\partial U/\partial T = T\partial S/\partial T$  integrated to give the entropy as

$$S = -k_B \sum_n P_n \ln P_n .$$

This is very like the expression used for information, and shows that entropy is degree of disorder.

Entropy goes to zero in the zero temperature limit, where  $P_n$  is unity for the lowest energy state and zero for all the rest. This is the **Third Law of Thermodynamics**.

For fixed energy and volume, entropy is maximized in equilibrium, and all nonequilibrium systems at constant energy tend to this maximum.

If we want to use pressure and temperature as variables, a very useful quantity is the **Gibbs free energy**  $G = U + pV - TS$ , for which

$$dG = V dp - S dT .$$

When a liquid at its vapor pressure is evaporated at constant temperature and pressure,  $G$  does not change, so the Gibbs free energy per molecule must be the same in the two phases in equilibrium.