

Chapter 1

Scope of Thermodynamics

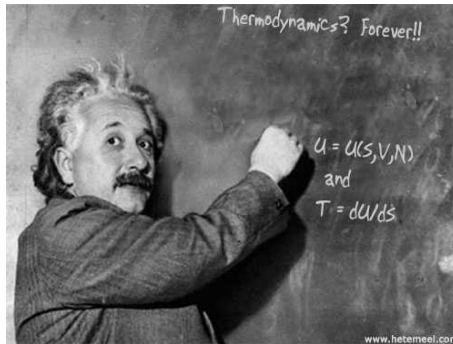
The aim of physics is to explain the static and dynamic properties of matter and energy in space and time. Matter is made up of atoms which in turn are composed of electrons and nuclei, the latter being conglomerates of elementary particles, mostly protons and neutrons. From X-ray scattering we know that in crystalline solids, as an example, atoms are spaced a few angstroms ($1 \text{ \AA} = 10^{-10} \text{ m}$) apart. In conjunction with the fact that solids are fairly incompressible, one concludes that the size of atoms is a few \AA . This implies that a macroscopic piece of matter consists of a large number of atoms, typically 10^{23} per cm^3 in solids and, as another example of a macroscopic object, about 10^{19} per cm^3 in a gas at atmospheric pressure and room temperature. The question then arises: must we know everything about the motion of this tremendous number of building blocks to understand properties of macroscopic objects? The answer is no, as thermodynamics provides a theoretical framework to deal with the properties of **macroscopic** systems. Its structure is so general that it can deal not only with physical systems but also with biology, environmental issues, and even financial systems. What is new in thermodynamics, as compared to mechanics or electromagnetism, is the fact that thermal effects are accounted for by including temperature and entropy among its variables and laws. One might say that thermodynamics is the science of heat transfer.

From its beginnings, thermodynamics was developed and used in the physical sciences, chemistry, and physics. Early investigations of thermodynamic principles were also undertaken in physiology and the medical sciences. And with the rise of engineering in the Industrial Age of the nineteenth century, thermodynamics became a cornerstone in practical issues of building machines and running factories. In recent decades new applications for thermodynamic principles have been explored in such di-

verse fields as economics, manufacturing, financial markets, and ecological sciences. And the list goes on!

To put the importance and uniqueness of thermodynamics into perspective we quote two outstanding scientists.

1.1 The verdict on thermodynamics

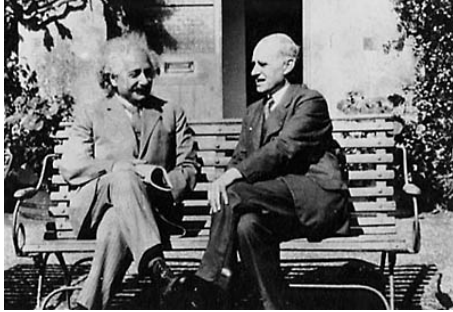


Albert Einstein

“A theory is the more impressive the greater the simplicity of its premises, the more varied the kinds of things that it relates and the more extended the area of its applicability. Therefore classical thermodynamics has made a deep impression on me. It is the only physical theory of universal content which I am convinced, within the areas of the applicability of its basic concepts, will never be overthrown.”

Sir Arthur Stanley Eddington

“The law that entropy always increases – the second law of thermodynamics – holds I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations - then so much worse for Maxwell equations. If it is found to be contradicted by observation - well these experimentalists do bungle things sometimes.



But if your theory is found to be against the second law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.”

1.2 The need for a macroscopic description

To understand that a macroscopic description of matter is actually meaningful and needed, let us look at two simple examples.

A solid: The atoms or ions making up a solid are confined to regular lattice sites by the sum total of the interactions with all their neighbors. They are however not at rest at the bottom of their respective potential wells, but vibrate around these minima incessantly. To estimate these vibrational frequencies, note that the potential wells must have widths of the order of the interatomic spacing, a , in a solid, i.e. of the order of a few Å. On the other hand, the depth of these potentials is the energy needed to remove an atom from the solid, i.e. the cohesive energy, V_c , of the solid which is typically a few electron volt ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$), e.g. 6.2 eV for tungsten. If we approximate the site potential by a harmonic oscillator

$$V(r) = \frac{1}{2}kr^2 \quad (1.1)$$

we get

$$k = 2V_c/a^2 \quad (1.2)$$

and the frequency of vibration

$$\nu = \sqrt{k/m}/2\pi \quad (1.3)$$

where m is the mass of one solid atom, say tungsten. Putting in numbers we get $\nu \approx 10^{13} \text{ s}^{-1}$ as a typical vibrational frequency in the solid.

Now, the energy stored in these vibrations is proportional to the square of their amplitudes. Although every 10^{-13} s the energy is redistributed among those 10^{23} atoms in the solid, the total energy is constant, as long as the solid is isolated. If we heat up the solid, the vibrations increase in amplitude and the total energy goes up. Not only that, the volume of the solid increases; this is called thermal expansion. Although on a microscopic scale, the state of the system, i.e. the position and velocities of the constituent atoms, changes every 10^{-13} s, we can still meaningfully describe the thermodynamic state of the system by specifying, so far, three quantities, namely its **mass**, **volume**, and **energy**. Not only that, it would be quite impossible and utterly useless to follow the motion of all 10^{23} atoms anyway.

The ideal gas: Let us look, as another example, at a gas at room temperature and atmospheric pressure enclosed in a volume. Its density is about 10^{25} molecules per m^3 . A typical velocity of a gas molecule is the speed of sound in the gas, i.e. about 10^3 m/s. It will collide every 10^{-10} s with another molecule in the gas resulting in a redistribution of momentum and energy. Yet, the total energy is conserved again and is a measure of the macroscopic state of the gas.

1.2.1 *Ideal gas: A macroscopic description*

A gas of mass M is confined in a container of volume V . It exerts a pressure P - force per area - on the walls of the container. If the density of the gas, i.e. mass per volume, is “low” enough it was found by Boyle that

$$P \sim \frac{M}{V} \quad (1.4)$$

provided the temperature is held constant. Boyle’s experiment is simple: he took a flask with a movable piston and filled it with a gas which he then immersed into a large bucket of water of constant temperature. By putting various weights on the piston, Boyle was able to change the pressure and measure the corresponding change in volume. He found that volume changes inversely to the pressure. Doing a similar experiment, Charles and Gay-Lussac found that at constant pressure the volume of the flask grew as its temperature increased. Combining these two findings and expressing the mass of the gas in terms of the number of moles N , i.e. $M \sim N$, results in the “ideal gas law”

$$PV = NRT \quad (1.5)$$

It was found that the constant of proportionality, R , in this equation is the same for all gases at low density. This is a remarkable finding: no matter what the gas is made of, be it oxygen, gasoline vapor, or a high temperature vapor of several metals all mixed together, the relation between pressure, density and temperature is the same.

Remark 1.1. “Ideal Gas” is actually a misnomer as the ideal gas law applies to real gases such as the air in a lecture hall. What made the term “ideal” stick is the fact that it applies to all gases at low densities irrespective of their composition. To understand this remarkable fact, recall that a gas consists of many particles that move around at high speeds summing up to a considerable kinetic energy of all the particles. In addition to the kinetic energy we must also consider the potential energy of the interactions between the particles because only the sum of kinetic and potential energy is conserved according to Newton. However, the collisions are rare and thus the interactions are small and the potential energy can be neglected. Thus in an ideal gas the interaction energy is negligible compared to the kinetic energy. And because the atom- or molecule-specific characteristics of a gas are expressed in their interactions (two helium atoms interact differently from two oxygen molecules), the fact that at low density the potential energy of interactions is negligible makes it “ideal”.

Remark 1.2. The ideal gas law, although so simple, already demonstrates an inherent usefulness of thermodynamic relations. It allows us to calculate further properties of a gas, e.g.

- (a) its isothermal compressibility, the relative change in volume when changing pressure at fixed temperature,

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T = \frac{1}{P} \quad (1.6)$$

- (b) or its thermal expansion coefficient, the relative volume change when changing temperature at constant pressure,

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P = \frac{1}{T} \quad (1.7)$$

Both quantities are relevant when designing devices involving expanding gases.

The variables pressure P , volume V , and mole number N (or mass) are known from mechanics and can be measured by mechanical means. We have introduced temperature without proper definition and thus without a

prescription on how to measure it. Temperature is understood to provide a measure for our sense of hot and cold. As well, two objects in contact with each other for a long time are said to have the same temperature and to be in equilibrium with each other.

1.2.2 *Measurement of temperature*

To design a measuring device for temperature we need to identify material properties that depend on it. Examples are: (i) the expansion of gases, liquids and solids with temperature, (ii) changes in conduction of metals and semiconductors with temperature, (iii) changes in color with temperature, and many more as listed in the table:

Thermometer	Thermometric property
Gas (constant volume)	Pressure
Electric resistor (constant tension)	electric resistance
Thermocouple (constant tension)	Thermal EMF
Paramagnetic salt	magnetic susceptibility
Blackbody radiation	radiant emittance

1.2.2.1 *Constant volume gas thermometer*

The simplest thermometric property is no doubt the change in pressure in a gas at constant volume with temperature; it is also the most fundamental because it applies to all gases at low density. This is the basis of the Constant Volume Gas thermometer depicted below.

It consists of a bulb (originally glass, but these days usually platinum or a platinum alloy) connected to a U-tube which itself is connected to a flexible tube leading to a reservoir with a liquid such as mercury or alcohol¹. The reservoir is open to ensure that the reference pressure is the atmosphere, or an artificial atmosphere of an inert gas to avoid contamination of the liquid. The volume of the gas is kept constant by adjusting the height of the mercury column M to touch a mark on the tube called the indicial point. The difference h between the levels in the two columns of the U-tube determines the pressure in the bulb: $P = P_{atm} + \rho gh$ where P_{atm} is the atmospheric pressure, ρ is the mass density of the mercury, and g is gravity. To calibrate the thermometer we must find a reference

¹The kind of liquid used depends on the temperature range of interest. For example, water would not do below freezing or above boiling.

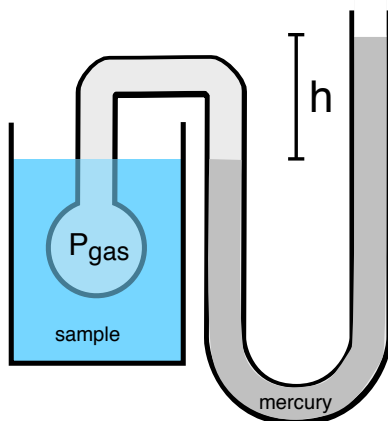


Fig. 1.1 Constant volume gas thermometer. Pressure relative to the atmosphere is measured based on the height of the liquid column. This pressure is related to the gas temperature by the ideal gas law.

or standard system to which we assign a numerical value for its temperature. Any reference system would do as long as it is easily reproducible and universally accessible. In 1954 it was decided worldwide that the standard reference point is the triple point of water, i.e. the state of ultra pure water with a well-defined isotope composition in which ice, liquid, and vapor co-exist. At the triple point ice cubes float in liquid water with saturated water vapor above it; this state will remain the same as long as it is undisturbed: no melting, no freezing, no evaporation. This happens at a partial water pressure of $P_t = 611.73$ Pa and also at a unique temperature to which the value $T_t = 273.16$ K is arbitrarily assigned. The symbol K has been adopted to honor Lord Kelvin, a great thermodynamician who perfected the gas thermometer.

Bringing the gas bulb of the thermometer in contact with water at its triple point we measure the pressure in the bulb, and call this pressure P_t . Next we bring the thermometer into contact with the system whose temperature we want to determine, measure again the pressure in the gas bulb, call it P , and calculate its temperature according to the ideal gas law

$$T = \frac{T_t}{P_t} P \quad (1.8)$$

A series of such measurements is performed at smaller and smaller gas densities in the bulb to extrapolate to the limit of vanishing density. Marks on the U-tube will indicate the temperature scale.

To achieve maximum accuracy a number of corrections must be made such as:

- (1) The gas in the U-tube and connecting capillary is not necessarily at the same temperature as the bulb itself;
- (2) The capillary and the bulb itself change volume due to thermal expansion (that is why platinum alloys are used which can be designed to undergo minimal thermal expansion);
- (3) Some gas is adsorbed to the walls of the bulb and the capillary in different amounts as temperature changes;
- (4) The mercury itself undergoes thermal expansion.

Sophisticated Constant Volume Gas thermometers are maintained at national bureaus of standards such as NIST in Washington DC, NRC in Ottawa and are used to calibrate household and industrial thermometers. Practical temperature readings are made in degrees Celsius ($0^\circ \text{C} = 273.15 \text{K}$). 100°C is the temperature at which pure water boils and evaporates at standard atmospheric pressure.

Having properly defined temperature we can now also assign a (measured) value to the universal gas constant per mole

$$R = 8.31441 \text{ JK}^{-1}/\text{mol} \quad (1.9)$$

Remark 1.3. At the triple point of any gas-liquid-solid system an arbitrarily small decrease in temperature or increase in pressure will cause all the material to freeze. Look at the phase diagram in Figure 1.2 to follow this argument. A triple point cell is made by adding the right amount of material so that at the triple point temperature it leads to the triple point pressure. This is tricky, but can be done for many liquids to fit various temperature regimes.

Substance	Acetylene	Argon	graphite	CO ₂	CO	Ethanol
T_t[K]	192.4	83.81	4766	216.55	68.10	150
P_t[Pa]	120	68.9	10132	517	15.37	4.3×10^{-7}
Substance	hydrogen	mercury	nitrogen	platinum	water	
T_t[K]	13.84	234.2	63.18	2045	273.16	
P_t[Pa]	7.04	1.65×10^{-7}	12.6	2.0×10^{-4}	0.6117	

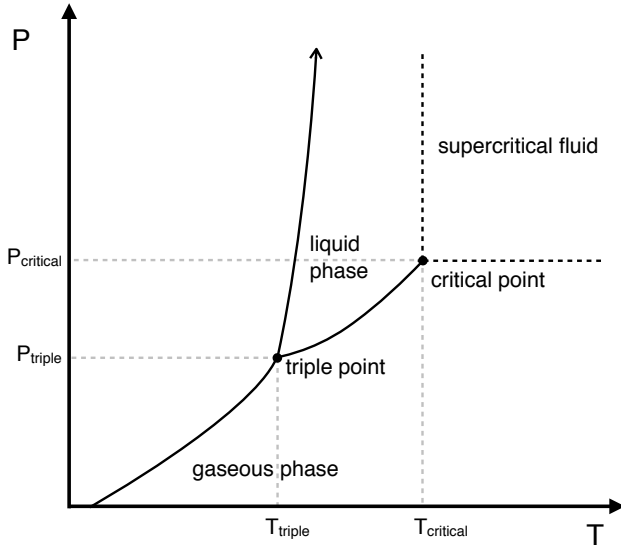


Fig. 1.2 A typical single component equilibrium phase diagram. For points away from the transition line, the system is homogenous. For those on the transition line, co-existence of two phases such as gas-liquid and liquid-solid is possible. At the conditions corresponding to the triple point, all three phases (gas, liquid, and solid) can exist simultaneously.

1.2.2.2 Blackbody radiation

Any object (in equilibrium at some temperature) will emit electromagnetic radiation with a characteristic power spectrum called blackbody radiation. A small hole in a cardboard box of any color appears black at room temperature, a clay pot in a kiln glows red, and steel being forged may be red to white. The explanation of this spectrum led Max Planck in 1900 to the discovery of quantum physics. He derived his celebrated equation for the spectral radiance, the energy per unit time and unit surface area in a wavelength interval between λ and $\lambda + d\lambda$,

$$I(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{\exp[hc/(\lambda k_B T)] + 1} \quad (1.10)$$

where h is Planck's constant and c is the speed of light. Note that this spectrum only depends on temperature!

Thus measuring an emission spectrum and fitting it to Planck's formula determines the temperature of the body. No contact with the object is needed; the measurement is remote and does not disturb the object. This

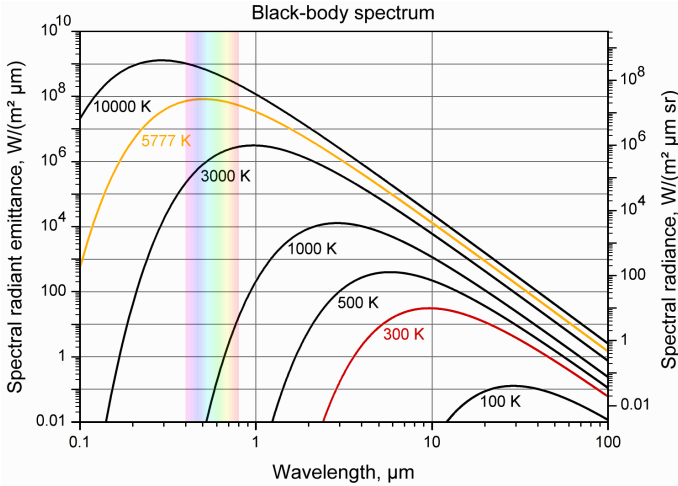


Fig. 1.3 The spectral radiance (or emittance) of a blackbody as a function of wavelength according to Planck's law. For a given temperature, a blackbody radiator will emit radiation across a continuum of wavelengths. Changes in temperature result in both an increase in the total output as well as a shift in the relative contribution from different wavelengths. Image adapted from [WikimediaCommons (2006)].

is the way the extreme temperatures in a coke oven, a nuclear blast, or on the surface of the Sun can be measured. Furthermore, it was the way that Penzias and Wilson detected the cosmic background radiation of the universe that had been predicted as a remnant of the Big Bang - the latest measurements yield a temperature of 2.725 K, rather cold but largely isotropic in the universe.

The spectrum from the sun is distorted due to absorption of some of the light on its way to earth; but overall a fit with Planck's law yields a good estimate of the temperature of the Sun's surface of 5323 K.

Remark 1.4. Why is the hole in a box at room temperature black? First of all, the color of the box itself is determined by those frequencies from the light that fall onto it that are not absorbed. Any light that hits the hole will be reflected off or absorbed by the interior side of the walls. Thus it thermalizes with the walls before it can escape from the hole. What is the characteristic wavelength or frequency of light at the maximum of the Planck distribution? Differentiation leads to $\lambda_{\max} = 2.89776829 \frac{1}{T} \times 10^6$ nm. Thus at room temperature we have $\lambda_{\max} \approx 10^4$ nm = 0.01 mm; this is a wavelength which our eyes do not register. On the other hand for sunlight

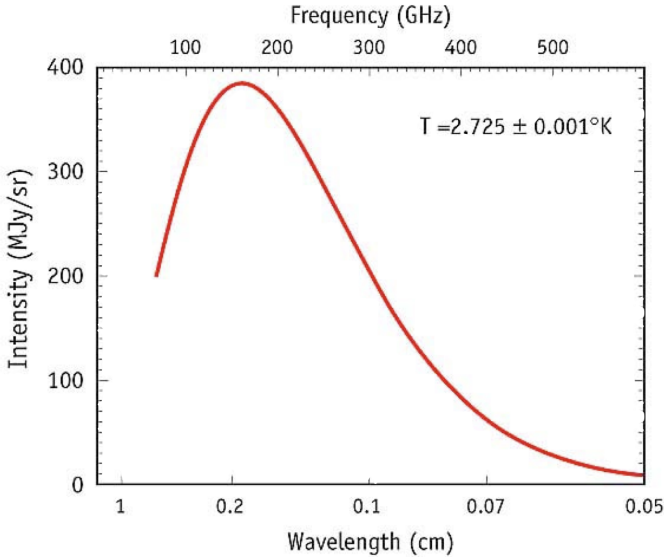


Fig. 1.4 Telescopes detect low levels of radiation from regions of space that are seemingly empty. The wavelength dependence of this radiation is consistent with a cosmic background temperature of roughly 3 K. Note that this curve is experimental data, not simply a curve fit.

at $T_{sun} = 5323 \text{ K}$ we get at the maximum of the emission spectrum $\lambda_{max} \approx 500 \text{ nm}$ which we register as green light. As our eyes have adapted to sunlight over eons of evolution green light is the easiest and thus most pleasant light whereas for red light the eyes are less adapted. Therefore red signals danger in traffic and green is a go-ahead.

1.2.3 *Ideal gas: A microscopic description*

Thermodynamics is a macroscopic theory and thus does not require input from the microscopic dynamics of the molecular or atomic building blocks making up the macroscopic system. Still, it is useful at this stage to have a microscopic view of an ideal gas to contrast it with the macroscopic view just presented. We can do this in the framework of some simple kinetic gas theory or statistical mechanics of a dilute gas. These ideas go back to Daniel Bernoulli (1738), rejected at the time but resurrected in the early 1800's in the form presented here.

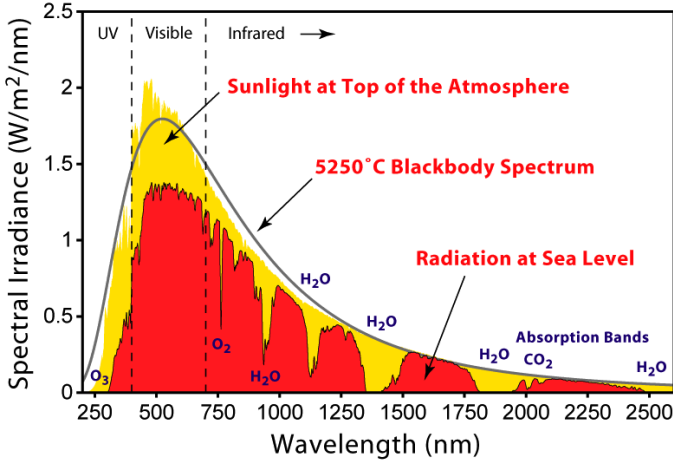


Fig. 1.5 The temperature of the surface of the Sun can be inferred from the radiation it emits (a fit of 5323 K is shown). At the surface of the Earth, this spectrum is modified from what is measured in space due to the presence of the atmosphere. Different molecular species selectively absorb energy, resulting in gaps in the spectrum. The Sun emits the most power at wavelengths corresponding to what humans refer to as visible light. This is an evolutionary artifact - human eyes have evolved to be sensitive to the light emitted by our Sun. Image adapted from [WikimediaCommons (2007a)].

Let us consider a dilute gas of \tilde{N} atoms, each of mass m , contained in a cubic volume $V = L^3$. The i^{th} atom, treated as a mass point for simplicity, has, at a given time, a velocity $\mathbf{v}^{(i)}$ with a component $v_z^{(i)}$ in the z -direction perpendicular to one of the walls of the cube.

When it collides with the wall, it is reflected and moves away from it with the z -component of its velocity reversed, so that its total momentum is changed by $-2m|v_z^{(i)}|$ imparting an impulse $2m|v_z^{(i)}|$ to the wall (Newton's second law). The force on the wall is given by the product of the momentum change per atom times the number of impacts this atom makes with the wall per unit time. The latter is given by $|v_z^{(i)}|/2L$. Thus the pressure on the wall (force per unit area) is

$$P = \sum_{i=1}^{\tilde{N}} 2m|v_z^{(i)}| \frac{|v_z^{(i)}|}{2L} \frac{1}{L^2} = \sum_{i=1}^{\tilde{N}} \frac{m(v_z^{(i)})^2}{L^3} \quad (1.11)$$

or

$$PV = \sum_{i=1}^{\tilde{N}} m(v_z^{(i)})^2 \quad (1.12)$$

To evaluate the sum exactly we would need the velocities of all \tilde{N} atoms, typically 10^{19} per cm^3 . This is impossible, in particular if you consider that in a gas the atoms collide with each other on average every nanosecond, changing their velocities each time. It is not only impossible to know this in practice but also unnecessary. All we need is the most probable distribution of such velocities; this function can be measured in a molecular beam experiment. For our purposes here, even that much information is not needed. We can introduce a mean squared velocity of the \tilde{N} atoms

$$\overline{\mathbf{v}^2} = \frac{1}{\tilde{N}} \sum_{i=1}^{\tilde{N}} \left[(v_x^{(i)})^2 + (v_y^{(i)})^2 + (v_z^{(i)})^2 \right] \quad (1.13)$$

If the velocity distribution of the atoms is isotropic in space (which it is if there is no external potential such as gravity around, or is negligible) then the mean square averages of the three velocity components are equal and we get

$$\begin{aligned} PV &= \frac{2}{3} \left(\frac{1}{2} M \overline{\mathbf{v}^2} \right) \\ &= \frac{2}{3} U \end{aligned} \quad (1.14)$$

U is the total kinetic energy of the atoms flying around in the gas; it is called in thermodynamics the **internal energy** because it accounts for the motion of the constituent particles of our macroscopic system (the gas in V). Also note that with m , the mass of one of the \tilde{N} gas particles, the total mass of the gas is $M = \tilde{N}m$.

Remark 1.5. If the interaction between gas particles is no longer negligible as their density increases, the internal energy would also have a contribution from the potential energy of that interaction. But in any case the internal energy, say of an ice cube, has nothing to do with its kinetic energy as a whole as it is somehow hurled through space.

Comparing this to the ideal gas law we see that the internal energy is related to temperature

$$\begin{aligned} U &= \frac{3}{2} NRT \\ &= \frac{3}{2} \tilde{N} k_B T \end{aligned} \quad (1.15)$$

Here

$$\begin{aligned} k_B &= \frac{R}{N_{\text{Avogadro}}} = 1.38066 \times 10^{-23} \text{ J/K} \\ N_{\text{Avogadro}} &= 6.02205 \times 10^{23} / \text{mol} \end{aligned} \quad (1.16)$$

k_B is called Boltzmann's constant; it is the universal gas constant per atom or molecule. Remember that the mole number is the total number of particles in the system divided by Avogadro's number (which is the number of particles in one mole).

This derivation makes clear that to describe a macroscopic system we do need additional variables, such as temperature, which account for the effect of the myriads of degrees of freedom of the atoms or molecules which we choose to ignore in a macroscopic or thermodynamic approach.

Example 1.1. What is the thermal speed of a helium atom at room temperature?

Combining (1.14) and (1.15) we get for the root mean square (rms) speed in one direction at $T = 300$ K with $m = 4 \times 1.67 \times 10^{-27}$ kg the mass of a helium atom

$$\sqrt{v^2} = \sqrt{3k_B T/m} = 1,367 \text{ m/s} \quad (1.17)$$

This compares well with the speed of sound for helium $v_{sound} = \sqrt{\gamma k_B T/m} = 927$ m/s. Here γ is called the adiabatic constant and has a value of $5/3$ for an atomic gas.

Does helium escape into outer space from the Earth's atmosphere?

The escape velocity from a gravitational body is obtained by equating the initial upward kinetic energy to the gravitational energy at a distance R from the center of the Earth: $(m/2)v_{esc}^2 = GmM/R$ or $v_{esc} = \sqrt{2GM/R}$. The Earth's mass is $M = 5.97 \times 10^{24}$ kg, so an object can escape if its speed at the Earth's surface ($R = 6400$ km) is $v_{esc} = 11.2$ km/s, much larger than the average speed of helium. Yet, helium escapes anyway. There are several contributing factors of which we just list two: (1) the speed of any gas particle varies from zero to many times the average speed. Thus energetic atoms can have speeds larger than the escape velocity. (2) In the ionosphere and exosphere at heights above 300 km the temperature is in excess of 1200 K so the escape is possible. In addition, the solar wind sweeps away light atoms such as helium.

Example 1.2. How often do helium atoms collide with each other at room temperature and atmospheric pressure and how far do they travel between collisions?

The flux of particles in a gas in any direction is given by the particle density and the average velocity: $j_{th} = (\tilde{N}/V)\sqrt{v^2} \approx 2.7 \times 10^{25} \times 10^3$ particles per square meter and second. Approximating a gas particle by a sphere of radius r those particles that are within a disc of area πr^2 will

collide. With $r \approx 1 \text{ \AA}$ we thus get for the number of collisions per second $\tau_{\text{coll}}^{-1} \approx 2 \times 10^9 \text{ s}^{-1}$ or $\tau_{\text{coll}} \approx 5 \times 10^{-10} \text{ s}$. The distance traveled between any two collisions is called the mean free path; it is $\lambda_{\text{mfp}} = \tau_{\text{coll}} \sqrt{\mathbf{v}^2} \approx 1 \text{ \mu m}$.

1.3 What will thermodynamics do for you?

Given a macroscopic system you can do a lot of experiments on it: you can measure the length of a steel beam as you heat it up, keeping the pressure constant thus obtaining the expansion coefficient; this is important information when an engineer designs a bridge because its steel structure will expand in summer and it must still fit into its foundation. Similarly you could measure the length as pressure is varied, keeping the temperature constant; this is important knowledge for constructing high pressure or vacuum vessels. You could also do either experiment not keeping pressure or, respectively, temperature constant. The question arises how many such experiments do you have to perform to know everything about the macroscopic or thermodynamic properties of a system. Infinitely many? Thermodynamics will tell you that there are very few such independent experiments, e.g. for a simple system just three. All other data you can generate from these very few experiments by using thermodynamic formulae. Thus thermodynamics facilitates an enormous reduction in work. Not only that, by providing formulae to calculate the results of related experimental set ups, it has predictive power, e.g. in the construction of engines. Lastly, if you were to perform redundant experiments, you could find out whether you are making systematic errors, as the thermodynamic formulae provide consistency checks. Many new physical phenomena have been found in this way, e.g. Planck's law of blackbody radiation and thus the discovery of quantum physics. As Einstein said, all other physical theories must conform to thermodynamics.

1.4 What does thermodynamics not do for you?

As we said, thermodynamics ignores all those myriads of degrees of freedom associated with the constituent atoms and molecules of a large system, and deals with just a few macroscopic variables. In thermodynamics we take the fact that lead is more pliable than steel or that you can liquify carbon dioxide as a given and use it to make predictions for other properties of

lead, steel, and carbon dioxide. To understand why this is so we need to incorporate the electronic properties of lead, steel, carbon dioxide etc. into a theory. This is done in statistical mechanics where one actually starts from Newton's or Schrödinger equations for all degrees of freedom, and then performs a statistical average over them to arrive at thermodynamics. In the course of doing this, one also gets, in favorable model cases such as a dilute gas or a harmonic solid, expressions for the characteristic properties such as expansion coefficients, compressibilities, etc. Thus statistical mechanics provides the link between the microscopic and the macroscopic world. The reason why you do not learn about statistical mechanics right away, is that (i) you must first know what to derive, and more importantly (ii) in statistical mechanics you solve simplified models of systems, whereas thermodynamics provides a theoretical framework to which all systems must adhere.

1.5 Problems

Problem 1.1. *A gas is confined to a cylinder of volume $V = 100$ l at a pressure $P = 2$ MPa.*

- (a) *Calculate the rms velocity of the gas particles.*
- (b) *Assume the gas is molecular nitrogen. How many moles are in the gas cylinder? At what temperature is the gas cylinder?*

Problem 1.2. *In nuclear fusion as it occurs in stars, fusion bombs and hopefully soon in fusion reactors, temperatures must be of the order of 10^9 K before deuterons (the nuclei of deuterium consisting of a proton and a neutron) smashing into each other have a chance to fuse into helium. What is the rms speed of deuterons at that temperature. How does that compare to the speed of light?*

Problem 1.3. *It is estimated that the universe contains a total mass of 10^{80} proton masses ($m_p = 1.67 \times 10^{-27}$ kg). Its present volume is estimated to be about 10^{80} m³. Its temperature is that of the cosmic background radiation, $T = 2.7$ K.*

- (a) *Assume that the mass is distributed uniformly ignoring aggregation into stars and galaxies. What is the matter density of the universe and what is the average distance between any two protons?*

(b) Because of the low density we can treat the protons as an ideal gas. What is the pressure?

Problem 1.4. A hot air balloon carries a payload of mass M_{load} (including the skin of the balloon and the gondola). The hot air inside the balloon is at a temperature T_b and the temperature of the surrounding atmosphere is T_a . The balloon will expand until the pressures inside and out are equal. The balloon will remain stationary once the buoyant force on the balloon, given by the weight of the replaced cool air, is compensated by the weight of the hot air and of the payload.

(a) Treating the air as an ideal gas and the balloon as a sphere, derive a formula for the diameter D of the stationary balloon.

(b) Take $T_a = 20^\circ \text{C}$, $T_b = 40^\circ \text{C}$ and the molar mass of air as $M_{\text{air}} = 1.2 \text{ kg/mol}$. What is D for a payload of $M_{\text{load}} = 3000 \text{ kg}$?

Problem 1.5. A gas cylinder is divided into two volumes V_1 and V_2 , separated by a thin membrane. The first chamber contains helium at a temperature T_1 and pressure P_1 ; the second chamber is initially evacuated. The membrane is punctured to allow the gas to also fill the second chamber. Because nothing is done to the system (aside from puncturing the membrane) the internal energy before and after the puncture remains the same; this is called a free expansion.

Treating the gas as ideal with an internal energy $U = (3/2)NRT = (3/2)PV$, determine the final temperature T_f , volume V_f and pressure P_f .

Problem 1.6. In the gas cylinder of Problem 1.5 the volume V_1 contains helium at pressure P_1 and temperature T_1 . Also, volume V_2 contains argon at pressure P_2 and temperature T_2 . Puncturing the membrane will now allow the two gases to mix.

Determine the final temperature T_f , volume V_f and pressure P_f .

Problem 1.7. On a hot summer day ($T = 30^\circ \text{C}$) car tires are inflated to their normal pressure of 32 psi. As the temperature drops so does the tire pressure.

(a) At what temperature has the pressure dropped to 30 psi?

(b) What will it be at $T = -10^\circ \text{C}$?

Problem 1.8. The vibrational frequency of an atom around its equilibrium lattice position in a crystalline solid is $\nu = \sqrt{k/m}/2\pi$. Here $k = 2V_c/a^2$

is the force constant of the (approximately) harmonic restoring force. Aluminum has a mole number 27. What is the mass of one aluminum atom?

- (a) For a typical vibrational frequency $\nu = 5 \times 10^{12} \text{ s}^{-1}$ what is k ?
- (b) Solid aluminum has a density of 2.7 g/cm^3 . What is the average distance between atoms?
- (c) What is your estimate for the cohesive energy V_c of aluminum in Joules and in electron volts?

Problem 1.9. The resistance of a doped germanium crystal is found to be well represented by the equation $\ln R = 10.8031 - 9.0291 \ln T$ where, for this calibration, T was measured by a gas thermometer.

- (a) In a bath of liquid helium the resistance is measured to be $R = 218 \Omega$. What was the temperature?
- (b) Make a log-log plot (not \ln - \ln) for the range 200Ω to $30,000 \Omega$.

Chapter Summary

- (1) The Verdict on Thermodynamics by Einstein and Eddington!
- (2) Looking at the ideal gas from a macroscopic and microscopic point of view.
- (3) Measurement of temperature by the ideal gas thermometer and black-body radiation.
- (4) What can thermodynamics do for you?