

## Thermodynamics of ideal gases

An ideal gas is a nice *laboratory* for understanding the thermodynamics of a fluid with a non-trivial equation of state. In this section we shall recapitulate the conventional thermodynamics of an ideal gas with constant heat capacity.

### 1. Internal energy

Using the ideal gas law the total molecular kinetic energy contained in an amount  $M = \rho V$  of the gas becomes,

$$\frac{1}{2}Mv^2 = \frac{3}{2}PV = \frac{3}{2}NkT. \quad (1)$$

The factor 3 stems from the three independent translational degrees of freedom available to point-like particles. The above formula thus expresses that there is an internal kinetic energy  $\frac{1}{2}kT$  associated with each translational degree of freedom. Whereas monatomic gases like Argon have spherical molecules and thus only the three translational degrees of freedom, diatomic gases like nitrogen and oxygen have stick-like molecules with two extra rotational degrees of freedom orthogonally to the bridge connecting the atoms, and multi-atomic gases like carbon dioxide and methane have the three extra rotational degrees of freedom. According to the equipartition theorem of statistical mechanics these degrees of freedom will also carry a kinetic energy  $\frac{1}{2}kT$  per particle. Molecules also possess vibrational degrees of freedom that may become excited, but we shall disregard them here. The internal energy of  $N$  particles of an ideal gas is defined to be,

$$U = \frac{\beta}{2}NkT, \quad (2)$$

where  $\beta$  is the number of degrees of freedom. Physically a gas may dissociate or even ionize when heated, and thereby change its value of  $\beta$ , but we shall for simplicity assume that  $\beta$  is in fact constant with  $\beta = 3$  for monatomic,  $\beta = 5$  for diatomic, and  $\beta = 6$  for multiatomic gases. For mixtures of gases the number of degrees of freedom is the molar average of the degrees of freedom of the pure components.

#### 1.1. Heat Capacity

Suppose that we raise the temperature of the gas by  $\delta T$  without changing its volume. Since no work is performed, and since energy is conserved, the necessary amount of heat is  $\delta Q = \delta U = C_V \delta T$  where the constant,

$$C_V = \frac{\beta}{2}Nk, \quad (3)$$

is naturally called the heat capacity at constant volume.

If instead the pressure of the gas is kept constant while the temperature is raised by  $\delta T$ , we must also take into account that the volume expands by a certain amount  $\delta V$  and thereby performs work on the surroundings. The necessary amount of heat is now larger by this work,  $\delta Q = \delta U + P\delta V$ . Using the ideal gas law we have for constant pressure  $P\delta V = \delta(PV) = Nk\delta T$ . Consequently, the amount of heat which must be added per unit of increase in temperature at constant pressure is

$$C_P = C_V + Nk, \tag{4}$$

called the heat capacity at constant pressure. It is always larger than  $C_V$  because it includes the work of expansion.

### 1.2. The adiabatic index

The dimensionless ratio of the heat capacities,

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{2}{\beta} \tag{5}$$

is for reasons that will become clear in the following called the adiabatic index. It is customary to express the heat capacities in terms of  $\gamma$  rather than  $\beta$ ,

$$C_V = \frac{1}{\gamma - 1}Nk, \quad C_P = \frac{\gamma}{\gamma - 1}Nk. \tag{6}$$

### 1.3. Entropy

When neither the volume nor the pressure are kept constant, the heat that must be added to the system in an infinitesimal process is,

$$\delta Q = \delta U + P\delta V = C_V\delta T + NkT\frac{\delta V}{V}. \tag{7}$$

It is a mathematical fact that there exists no function,  $Q(T, V)$ , which has this expression as differential. It may on the other hand be directly verified (by insertion) that

$$\delta S = \frac{\delta Q}{T} + C_V\frac{\delta T}{T} + Nk\frac{\delta V}{V} \tag{8}$$

can be integrated to yield a function,

$$S = C_V \log T + Nk \log V + \text{const}, \tag{9}$$

called the entropy of the amount of ideal gas. Being an integral the entropy is only defined up to an arbitrary constant. The entropy of the gas is, like its energy, an abstract quantity which cannot be directly measured. But since both quantities depend on the measurable thermodynamic quantities that characterize the state of the gas, we can calculate the value of energy and entropy in any state. But why bother to do so at all?

#### 1.4. The two fundamental laws of thermodynamics

The reason is that the two fundamental laws of thermodynamics are formulated in terms of the energy and the entropy. Both laws concern processes that may take place in an isolated system which is not allowed to exchange heat with or perform work on the environment. The First Law states that the energy is unchanged under any process in an isolated system. This implies that the energy of an open system can only change by exchange of heat or work with the environment. We actually used this law implicitly in deriving the heat capacities and the entropy. The Second Law states that the entropy cannot decrease. In the real world, the entropy of an isolated system must in fact grow. Only if all the processes taking place in the system are completely reversible at all times, will the entropy stay constant. Reversibility is an ideal which can only be approached by very slow quasistatic processes, consisting of infinitely many infinitesimal reversible steps. Essentially all real-world processes are irreversible to some degree.

#### 1.5. Isentropic processes

Any process in an open system which does not exchange heat with the environment is said to be adiabatic. If the process is furthermore reversible, it follows that  $\partial Q = 0$  in each infinitesimal step, so that the  $\partial S = \partial Q/T = 0$ . The entropy must in other words stay constant in any reversible, adiabatic process. Such a process is for this reason called isentropic. By means of the adiabatic index we may write the entropy as,

$$S = C_V \log(TV^{\gamma-1}) + \text{const}, \quad (10)$$

From this it follows that

$$TV^{\gamma-1} = \text{const}, \quad (11)$$

for any isentropic process in an ideal gas. Using the ideal gas law to eliminate  $V \sim T/P$ , this may be written equivalently as,

$$T^\gamma P^{1-\gamma} = \text{const}. \quad (12)$$

Eliminating instead  $T \sim PV$ , the isentropic condition takes its most common form,

$$PV^\gamma = \text{const}. \quad (13)$$

Notice that the constants are different in these three equations.

#### 1.6. Isothermal versus isentropic bulk modulus

The bulk modulus of a strictly isothermal ideal gas with  $P = nkT$  is equal to the pressure,

$$K_T = \rho \left( \frac{\partial P}{\partial \rho} \right)_T = P \quad (14)$$

Here the index T (in the usual thermodynamic way of writing derivatives) signals that the temperature must be held constant while we differentiate. In terms of the mass density  $\rho$  the isentropic condition may be written in any of three different ways (with three different constants),

$$P\rho^{-\gamma} = \text{const}, \quad T\rho^{1-\gamma} = \text{const}, \quad T^\gamma P^{1-\gamma} = \text{const}. \quad (15)$$

Using the first we find the isentropic bulk modulus of an ideal gas,

$$K_S = \rho \left( \frac{\partial P}{\partial \rho} \right)_S = \gamma P \quad (16)$$

where the index S now signals that the entropy must be held constant. The distinction between the isothermal and isentropic bulk modulus is necessary in all materials, but for nearly incompressible liquids there is not a great difference between  $K_S$  and  $K_T$ .

Among Isaac Newton's great achievements was the first calculation of the speed of sound in air, using essentially the ideal gas law with constant temperature. His result did not agree with experiment, because normal sound waves oscillate so rapidly that compression and expansion are essentially isentropic processes.

The speed of sound is

$$c = \sqrt{K/\rho}, \quad (17)$$

such that the ratio between the isentropic and isothermal sound velocities is  $c_S/c_T = \sqrt{\gamma}$ . For air with  $\gamma = 1.4$  this amounts to an 18% error in the sound velocity. Much later in 1799, Laplace derived the correct value for the speed of sound.

## 1.7. Specific quantities

In classical thermodynamics we always think of a macroscopic volume of matter with the same thermodynamic properties throughout the volume. Volume, mass, energy, entropy, and the specific heats are all extensive quantities, meaning that the amount of any such quantity in a composite system is the sum of the amounts in the parts. Pressure, temperature, and density are in contrast intensive quantities, that may not be added when a system is put together from its parts. In continuum physics, an intensive quantity becomes a field that may vary from place to place, whereas an extensive quantity becomes an integral over the density of the quantity. Since a material particle with a fixed number of molecules has a fixed mass, the natural field to introduce for an extensive quantity like the energy is the specific internal energy  $u = dU/dM$ , which is the amount of energy per unit of mass in the neighborhood of a given point. The actual energy density becomes  $dU/dV = \rho u$ , and the total energy in a volume

$$U = \int_V \rho u dV. \quad (18)$$

The specific energy is an intensive quantity like temperature, pressure or density. Similarly, we define the specific heat as the local heat capacity per unit of mass, one can write

$$u = c_V T = \frac{P}{\gamma - 1} \quad (19)$$

The specific energy of an ideal gas is the specific heat times the absolute temperature.

## 2. Sound Speeds in Different Environments

We wish to derive the sound speed in a variety of physical environments, including the ideal gas, radiation pressure dominated plasmas, and degenerate matter. In order to explore the implications these environments, let us first derive the wave equation for a pressure/density perturbation.

### 2.1. Sound Wave Derivation

Consider a fluid in equilibrium (background pressure and density uniform in time and space) obeying the continuity and momentum equations

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (20)$$

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{\nabla P}{\rho}, \quad (21)$$

where  $\rho$  is the fluid density,  $P$  the pressure, and  $\mathbf{u}$  the fluid velocity in an Eulerian coordinate system. We can then introduce the perturbations to our initial equilibrium state

$$p = p_0 + \Delta P \quad (22)$$

$$\rho = \rho_0 + \Delta \rho \quad (23)$$

$$\mathbf{u} = \Delta \mathbf{u} \quad (24)$$

Plugging these in to equations 1 and 2, we have

$$\frac{\partial(\rho_0 + \Delta \rho)}{\partial t} + \nabla \cdot ((\rho_0 + \Delta \rho)\Delta \mathbf{u}) = 0$$

$$\frac{\partial \Delta \mathbf{u}}{\partial t} + \Delta \mathbf{u} \cdot \nabla \Delta \mathbf{u} = -\frac{\nabla(P_0 + \Delta P)}{\rho_0 + \Delta \rho}$$

Multiplying these out and keeping only terms to first order in  $\Delta$  yields

$$\frac{\partial \Delta \rho}{\partial t} + \rho_0 \nabla \cdot (\Delta \mathbf{u}) = 0 \quad (25)$$

$$\frac{\partial \Delta \mathbf{u}}{\partial t} = -\frac{\nabla \Delta P}{\rho_0} = -\frac{dP}{d\rho} \frac{\nabla \Delta \rho}{\rho_0}. \quad (26)$$

The last equality in equation 7 is the *crucial* step in this derivation. It is here that we assume the fluid to be “barotropic,” that is, that the pressure can be expressed in terms of the density alone, making this total derivative expansion possible. We will see later that this ostensible leap of faith is valid in all of our cases of interest.

Finally, we can  $\partial/\partial t(6)$  and  $-\rho \nabla \cdot (7)$  to obtain an equation for  $\Delta \rho$ , yielding

$$\frac{\partial^2 \Delta \rho}{\partial t^2} = \frac{dP}{d\rho} \nabla^2 \Delta \rho. \quad (27)$$

This is of course, the wave equation with solution

$$\Delta \rho = \Delta \rho_0 e^{\mathbf{k} \cdot \mathbf{x} - \omega t}, \quad (28)$$

and sound speed

$$c_s^2 = \left(\frac{\omega}{k}\right)^2 = \frac{dP}{d\rho}. \quad (29)$$

Calculating  $dP/d\rho$  depends on the equation of state, and is not always immediately straightforward. For now, let’s start with the simplest case.

## 2.2. The Ideal Gas

For the first case, let us consider an ideal gas which responds adiabatically to our perturbations. Then, from the first law of thermodynamics, we have

$$dE = \frac{\beta}{2} N k dT = -P dV \quad (30)$$

where  $\beta$  is the number of degrees of freedom for our particles. From the ideal gas law,  $P = NkT/V$ , so we can write

$$\begin{aligned} \frac{\beta}{2} N k dT &= -\frac{NkT}{V} dV \\ \implies \frac{\beta}{2} d \ln T &= \frac{\beta}{2} (d \ln P + d \ln V) = -d \ln V \\ \implies \frac{d \ln P}{d \ln V} &= -\left(1 + \frac{2}{\beta}\right) \\ \implies P &\propto V^{-\left(1 + \frac{2}{\beta}\right)} \propto \rho^{\left(1 + \frac{2}{\beta}\right)}, \end{aligned} \quad (31)$$

or  $P = K\rho^\gamma$ , where  $\gamma = 1 + 2/\beta$ . For a monatomic ideal gas,  $\beta = 3$  and we recover the well known  $\gamma = 5/3$  polytrope. This leads to an adiabatic sound speed given by

$$c_s^2 = \left. \frac{dP}{d\rho} \right|_{\text{adi}} = \gamma K \rho^{\gamma-1} = \frac{\gamma P}{\rho}. \quad (32)$$

For the isothermal ideal gas, the derivation is even simpler since we can use the ideal gas law to say

$$c_s^2 = \left. \frac{dP}{d\rho} \right|_{\text{iso}} = \frac{kT}{\mu m_p} = \frac{P}{\rho}, \quad (33)$$

where  $\mu$  is the mean molecular weight and  $m_p$  is the proton mass. Thus, demanding an isothermal gas is the same as setting  $\gamma$  equal to 1. Next, we will do the same analysis for a radiation pressure dominated gas.

### 2.3. Radiation Pressure Dominated Gas

Our next step is to derive a sound speed for a radiation pressure dominated gas, where

$$P = \frac{1}{3}aT^4 = \frac{E}{3V}. \quad (34)$$

At first glance, one may be hesitant to define a sound speed given that it is not immediately clear how  $T$  depends on  $\rho$ . Let us again examine the case of the adiabatic gas. Again, we have

$$dE = 4VaT^3dT + aT^4dV = -PdV = -\frac{1}{3}aT^4dV. \quad (35)$$

Simplifying a bit, we obtain

$$-\frac{1}{3}d\ln V = d\ln T = \frac{1}{4}d\ln P \implies P \propto V^{-\frac{4}{3}} \propto \rho^{\frac{4}{3}}. \quad (36)$$

Through the same analysis as with the ideal adiabatic gas, we can now see that

$$c_s^2 = \left. \frac{dP}{d\rho} \right|_{\text{rad,adi}} = \frac{4P}{3\rho}, \quad (37)$$

which is equivalent to setting  $\gamma = 4/3$ . By adding the constraint that the gas responds adiabatically, we were able to eliminate  $T$  in order to solve for a sound speed.

One might wonder how to go through the derivation for an isothermal radiative gas. However, in order for radiation pressure to dominate, we must have an optically thick medium. This means that the cooling timescale is not sufficiently small to keep its temperature constant, so such a setup is not physical. In the last section, we will explore the sound speed of a degenerate gas.

### 2.4. The Degenerate Gas

In this case, we have a gas where the pressure is supplied from neither an ideal gas nor radiation, but from degeneracy pressure. Here

$$P \propto \rho E_F, \quad (38)$$

where  $E_F$  is the Fermi energy. In the non-relativistic regime,

$$E_F = \frac{p^2}{2m} = \frac{1}{2m} \left( \frac{h}{\lambda} \right)^2, \quad (39)$$

where  $h$  is Planck's constant. When fully degenerate, the wavelength of the particle is equal to the mean spacing between particles, so that

$$\lambda = n^{-\frac{1}{3}} \propto \rho^{\frac{1}{3}}. \quad (40)$$

Putting this all together we find that

$$P \propto \rho E_F \propto \rho \rho^{\frac{2}{3}} = \rho^{\frac{5}{3}}. \quad (41)$$

Thus we find that in the non-relativistic case,

$$c_s^2 = \left. \frac{dP}{d\rho} \right|_{\text{deg,nr}} = \frac{5P}{3\rho}, \quad (42)$$

which is equivalent to the monatomic, adiabatic ideal gas.

For the relativistic case, we have

$$E_F \sim pc = c \left( \frac{h}{\lambda} \right), \quad (43)$$

which through the exact same analysis leads to

$$c_s^2 = \left. \frac{dP}{d\rho} \right|_{\text{deg,rel}} = \frac{4P}{3\rho}. \quad (44)$$

Thus we see that a fully degenerate, relativistic gas also obeys a  $\gamma = 4/3$  polytrope.