

Conservation of mass and of momentum give two equations relating the density  $\rho(\mathbf{x}, t)$  and the velocity  $\mathbf{u}(\mathbf{x}, \mathbf{t})$ . The latter equation introduces another variable, the pressure  $p(\mathbf{x}, t)$ . In a compressible fluid (gas or liquid), an equation of state gives a relation between the pressure and density, which unfortunately introduces a further variable, temperature  $T(\mathbf{x}, t)$ . Hence we need a diversion into thermodynamics. The only result that we need from this diversion is the relationship between pressure and density when entropy is constant

$$\frac{p}{p_0} = \left( \frac{\rho}{\rho_0} \right)^\gamma,$$

### 1.3 \*A little thermodynamics\*

The *equation of state* is in general a relation  $F(p, \rho, T) = 0$ . For a *perfect gas* (dilute, spacing between molecules is many molecules, air is 10) it is

$$p = \rho RT,$$

with gas constant  $R = 8314 \text{ m}^2 \text{ s}^{-2} \text{ K}^{-1} (\text{mole wt})^{-1}$ , mole wt for dry air is 29.

**0th law** – there exists temperature  $T$

After several collisions with other molecules, the velocity of a molecule becomes randomised and the gas attains *thermal equilibrium* characterised by a *temperature*  $T$ . The time for air is  $10^{-9}$  s and for water  $10^{-12}$  s. *Reversible* change means slow compared with above times, so that remain near thermal equilibrium.

**1st law** – energy is conserved if count all forms

We consider a unit mass of gas. Then *specific volume* (volume per unit mass) is  $V = 1/\rho$ , and it has (specific) *internal energy*  $E(\rho, T)$  from kinetic energy of thermal motion of molecules and possibly potential energy of excited vibrational modes; NB depends strongly on temperature and on density **now** and not past values.

Mechanical work done on simple gas against pressure is  $-p dV$  (positive work if compress,  $dV < 0$ ). Heat energy input (by molecular conduction)  $\delta Q$ . Then 1st law:

$$dE = \delta Q - p dV.$$

### Specific heats

Heat input to increase temperature of unit mass by 1 K. Two varieties – inputting heat while keeping volume constant, or while keeping pressure constant

$$c_V = \left( \frac{\delta Q}{\delta T} \right)_V = \left( \frac{\partial E}{\partial T} \right)_{V \text{ or } \rho},$$

$$c_p = \left( \frac{\delta Q}{\delta T} \right)_p = \left( \frac{\partial E}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p.$$

Warning: thermodynamics is full of partial derivatives with different things being held constant. Be careful!

## 2nd law – chaos increases

Experimentally it is found that the total heat  $Q$  is not a well defined function of  $\rho$  and  $T$ , but depends on path taken to move between two  $\rho$  and  $T$  values. Instead there is another quantity **entropy**  $S(\rho, T)$  which is well-defined independent of path

$$\delta Q = T dS.$$

For an isolated system, entropy must increase  $\dot{S} \geq 0$ . Roughly  $S$  is proportional to the number of arrangements of the molecules at a given volume  $V$  and temperature  $T$ /internal energy  $E$ . Thence increasing entropy means increasing chaos, e.g. heat flows from hot to cold.

In our sound, there is not sufficient time to conduct heat from peak to trough of a wave, and so  $\delta Q = 0$ , equivalent  $dS = 0$  which is called *isentropic/adiabatic*. Actually not quite true, because there is important heat transport across the very thin shock-waves, i.e.  $dS > 0$  across a shock.

## Maxwell relations – mad maths of partial differentiation

Very important to display what is a function of what, and so what is being held constant during the partial differentiation. One is permitted to take any two as independent variables, e.g.  $\rho$  &  $T$  or  $\rho$  &  $p$  or  $S$  &  $\rho$ .

For  $dE = T dS - p dV$ , viewing all variables ( $E, T, \rho$ ) as functions of  $S$  &  $V$  ( $= 1/\rho$ ), so

$$T = \left( \frac{\partial E}{\partial S} \right)_V \quad \text{and} \quad p = - \left( \frac{\partial E}{\partial V} \right)_S.$$

But by cross differentiation

$$\left( \frac{\partial T}{\partial V} \right)_S = \frac{\partial^2 E}{\partial S \partial V} = - \left( \frac{\partial p}{\partial S} \right)_V.$$

Another Maxwell relation is obtained by the following trick  $d(E + pV) = T dS + V dp$ , so

$$\left( \frac{\partial T}{\partial p} \right)_S = \left( \frac{\partial V}{\partial S} \right)_p.$$

The combination  $H = E + pV$  is important in fluid mechanics, called *enthalpy*.

## 3rd law – exists $T = 0$

There is a universal absolute zero where all thermal motion stops. Not useful in acoustics at room temperature.

### 1.4 \*Perfect gas\*

For dilute gases, fine for air as  $\rho_{\text{air}} = 10^{-3} \rho_{\text{liquid air}}$ . This course will only use perfect gas laws, although generalisations to dense gases are not too difficult.

## Pressure

Pressure force on a surface is momentum exchanged from collisions in unit time  $p = Nm\langle v_x^2 \rangle$ , where  $N$  is the number of molecules per volume and  $m\langle v_x^2 \rangle = kT$  with Boltzmann's constant  $k = 1.38 \cdot 10^{-23} \text{ J K}^{-1}$ . Hence

$$p = \rho RT$$

with gas constant  $R = N_A k$ , with Avogadro's number  $N_A = 6.02 \cdot 10^{23}$  per mole (1 mole of  $\text{C}_{12}$  weights 12 gm).

## Internal energy

In a perfect gas, the internal energy  $E$  varies with temperature  $T$  but **not** with density  $\rho$  because dilute means the size of the molecules is irrelevant. If we further assume that the specific heats do not vary with temperature (OK for 100-2000 K when do not excite vibrational modes), then

$$c_V = \left( \frac{\partial E}{\partial T} \right)_V = \text{constant} \quad \text{and} \quad \left( \frac{\partial E}{\partial V} \right)_T = 0$$

so

$$E = c_V T$$

setting constant of integration to zero.

From *Kinetic Theory*,  $E = \frac{1}{2}kT$  per degree of freedom of the internal motion possessing energy, i.e.  $\frac{3}{2}NkT = \frac{3}{2}RT$  for monatomic gases He and Ar, and  $\frac{5}{2}NkT$  for diatomic gases  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , CO – rigid with rotational KE but no vibrational modes.

The other specific heat is

$$c_p = \left( \frac{\partial E}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p = c_V + R$$

using  $E = c_V T$  and  $V = 1/\rho = RT/p$ . Thence the *ratio of specific heats*

$$\gamma = \frac{c_p}{c_V} = \frac{c_V + R}{c_V}$$

$\frac{5}{3}$  for monatomic and  $\frac{7}{5}$  for diatomic gases. A useful alternative expression for the internal energy is then

$$E = c_V \left( T = \frac{pV}{R} \right) = \frac{c_V}{c_V + R} \frac{p}{\rho} = \frac{1}{\gamma - 1} \frac{p}{\rho},$$

and for enthalpy

$$H = E + \frac{p}{\rho} = \frac{\gamma}{\gamma - 1} \frac{p}{\rho}.$$

### Entropy of a perfect gas

Now  $T dS = dE + p dV$  and  $E = c_V T$  and  $p = RT/\rho$ , so

$$dS = c_V \frac{dT}{T} + \frac{R}{V} dV$$

Integrating

$$\begin{aligned} S - S_0 &= c_V \ln \frac{T}{T_0} + R \ln \frac{V}{V_0} \\ &= c_V \ln \left[ \left( \frac{T}{T_0} = \frac{pV}{p_0 V_0} \right) \left( \frac{V}{V_0} \right)^{R/c_V} = \frac{p}{p_0} \left( \frac{V}{V_0} \right)^{1+R/c_V=\gamma} \right]. \end{aligned}$$

So

$$S = S_0 + c_V \ln \left[ \frac{p}{p_0} \left( \frac{\rho_0}{\rho} \right)^\gamma \right].$$

### Adiabatic/isentropic changes

In sound, where there is insufficient time to conduct heat across one wavelength,  $\delta Q = 0$ , so  $dS = 0$ , so  $S$  is constant, so

$$\frac{p}{p_0} = \left( \frac{\rho}{\rho_0} \right)^\gamma,$$

and also  $T/T_0 = (\rho/\rho_0)^{\gamma-1}$  from  $p = \rho kT$ .

For small changes, we need the differential

$$\left( \frac{\partial p}{\partial \rho} \right)_S = \gamma \frac{p}{\rho} = \gamma RT,$$

which will find is  $c^2$  the square of the speed of sound, which is  $340 \text{ m s}^{-1}$  for dry air. Newton made a mistake of assuming an isothermal change  $(\partial p/\partial \rho)_T = RT$  missing the factor of  $\gamma$  which is 1.4 for dry air. It can be shown for non-perfect gases (exercise in partial differentiation for student) that  $(\partial p/\partial \rho)_S = \gamma(\partial p/\partial \rho)_T$ .