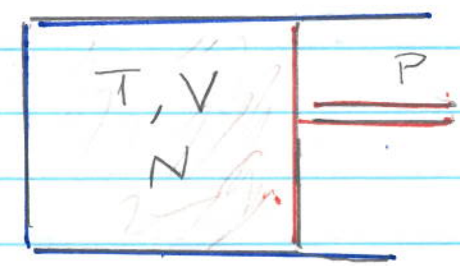
Equation of State (EOS)

- Consider a cylinder with a real substance, liquid or gas with a fixed number of particle



- The equation of state is a relation between, number volume, temperature, and pressure

$$P = P(T, V; N)$$

We usally dont write N since it is fixed

$$\boxed{P = P(T, V)}$$

EOS $pV = Nk_BT$ is only one exapple

- Since N is held fixed the dependence on V discribes how the pressure changes with density $n = N/V$

$$P = p(T, n)$$

- If we double N and V, keeping T fixed, the pressure remains the same. At low densities we can make a Taylor expansion in the density. We expand P/kT for convenience:

$$\frac{p}{kT} = A(T)\, n + B(T)\, n^2 + C(T)\, n^3 \ldots$$

So the first term in the expansion is the ideal gas. We know $p = n k_B T$ for ideal gas, so $A(T) = 1$

$$p(T,V) = n k_B T \left(1 + B(T)\, n + C(T)\, n^2 + \ldots\right)$$

$n \equiv \frac{N}{V}$

← this is called a "virial" coefficient. It is the first correction to ideal gas: $\Delta p \propto B(T)\, n^2$

Parametrizing the EoS

- More generally the expansion breaks down and we have simply a function

$$P(T, V)$$

- Alternatively we have the volume vs. T, P

$$V = V(T, P)$$

To characterize the Equation of State we consider the mechanical response to T, P:

how volume responds to changes in T and P

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dp$$

The terms in this differential are physically significant

$$\beta_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \equiv \text{volume expansion coefficient}$$

- For gasses and some liquids the change can be measured directly (like a thermometer) (see slide)
- For solids, the changes are smaller but can be measured with a variety of techniques, such as iterferometry (see slide)

The second term is the isothermal compressibility

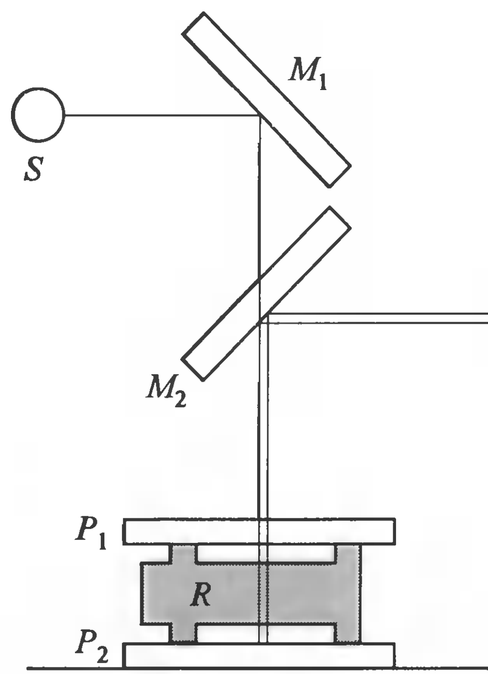
$$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

the negative is inserted since things contact as pressure is increased

The compessibility can be measured from speed of sound waves. First note:

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial p}\right)_T}$$

Measuring the change in volume with temperature, β_p (solids)



$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

As the system expands can measure how the interference pattern changes

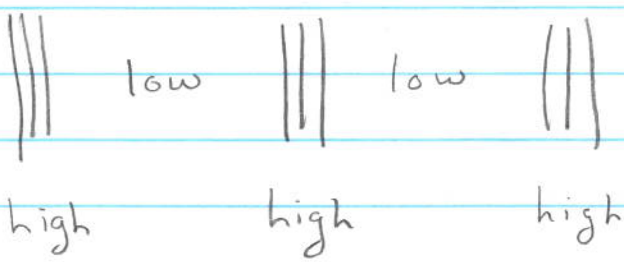
So

$$\frac{1}{K_T} = -V\left(\frac{\partial P}{\partial V}\right)_T \equiv B_T = \text{"the bulk modulus at fixed temperature"}$$

- So for a small change in volume ΔV we have

$$\Delta P = -B\,\frac{\Delta V}{V} \quad \text{or} \quad \frac{Force}{A} \propto A\,\Delta x$$

- Sound is a pressure wave, and is a sequence of high and density regions (see slide)



B acts like the spring constant.

The speed of the wave is $c_s^2 = \frac{B}{\rho}$ where ρ is the density. The speed of the waves can be measured in a number of ways

<u>Summary</u>: The properties of the EOS, can be measured with K_T and β_P. They record changes in the mechanical properties with temperature and pressure. With the specific heats, C_p and C_v, the system is completely characterized

A Look Ahead: The speed of Sound, C_p and C_V

- The speed of sound is actually determined by the adiabatic compressibility, and adiabatic bulk modulus

$$K_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{adiab} \qquad B_S = \frac{1}{K_S}$$

$$\boxed{B_S \equiv \frac{1}{K_S} = -V\left(\frac{\partial p}{\partial V}\right)_{adiab}}$$

- The "adiab" means no heat flow, $đQ = 0$, and so $pV^\gamma = \text{const}$ for an ideal gas. It is adiabatic because the period of sound oscillations is short compared to the timescale of conduction. Fortunately B_S is related to B_T. We will show later

$$\boxed{B_S = \gamma B_T} \qquad \gamma \equiv C_p / C_V$$

The speed of sound is

$$\boxed{C_s = \sqrt{\frac{B_s}{\rho}}} \qquad \rho \equiv \text{mass density } kg/m^3$$

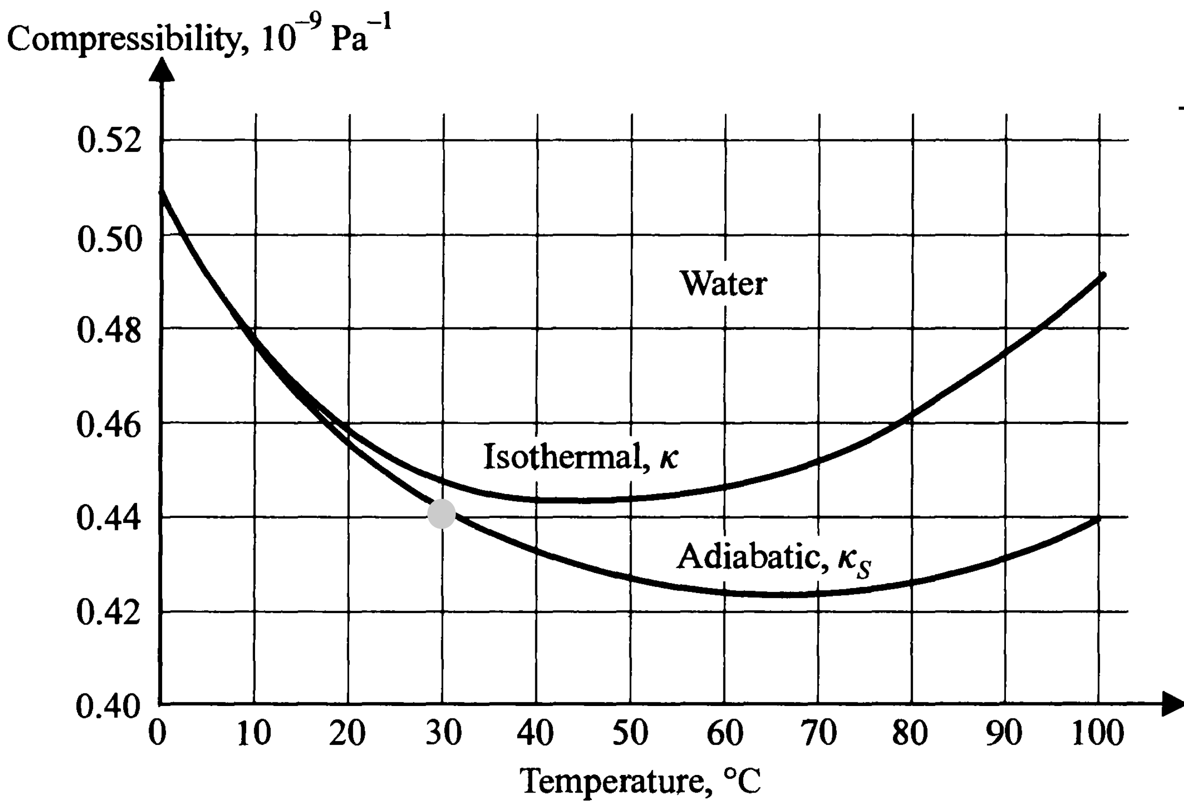
- The specific heats C_p and C_V are also related. We will show later

$$C_p = C_V + \frac{V T \beta_p^2}{\kappa_T}$$

For an ideal gas this formula reduces to $C_p = C_V + N k_B$

This gives an experimental way to determine C_V given C_p in solids. Recall that C_p is bigger than C_V because some of the input heat is used by the system to do work as it expands. The factor $V T \beta_p^2 / \kappa_T$ records how much the system expanded and how much work was done in the process

Isothermal Compressibility of Water and Sound Speed



The speed of sound is related to these curves

$$c_s = \sqrt{\frac{B_s}{\rho}} = \sqrt{\frac{1}{\rho \kappa_S}}$$

For water $\rho = 1\ \mathrm{g/cm^3}$ and

$$c_s \simeq 1500\,\mathrm{m/s}$$

at 30 degrees celsius