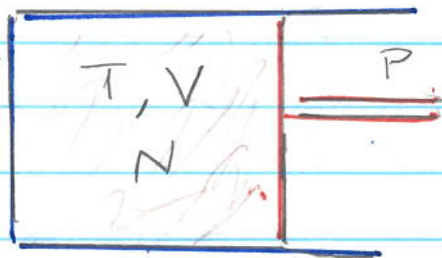


Equation of State (EoS)

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



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

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

We usually don't write N since it is fixed

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

EoS $pV = Nk_B T$ is only
one example

- Since N is held fixed the dependence on V describes 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:

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

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

$$p(T, V) = nk_B T (1 + B(T)n + C(T)n^2 + \dots)$$

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

↑ this is called a "virial" coefficient. It is the first correction to ideal gas:

$$\Delta p \propto B(T)n^2$$

Now

$$P(T, V) = \frac{N}{V} k_B T (1 + B(T) \frac{N}{V} + C(T) \left(\frac{N}{V}\right)^2 + \dots)$$

- More generally this 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 interferometry (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 contract as pressure is increased

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

$$P = P(T, V(T, P)) \quad \text{so at fixed } T$$

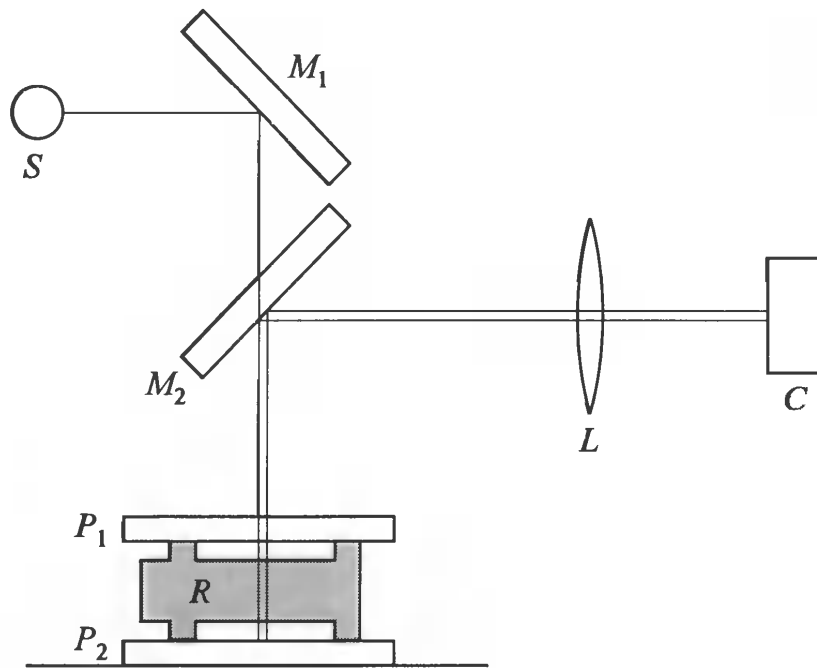
$$1 \cancel{dP} = \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T \cancel{dP} \quad \text{so} \quad \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\left(\frac{\partial P}{\partial V} \right)_T}$$

Simplest way to measure the volume expansion (gasses, liquids etc)



Simply measure the change in volume of the liquid (dilatometry)

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

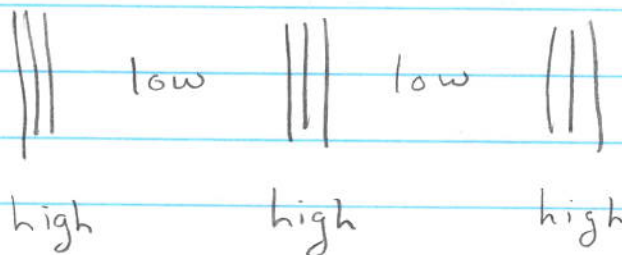
$$K_T^{-1} = -V \left(\frac{\partial P}{\partial V} \right)_T = B_T = \text{"the bulk modulus at fixed temperature"}$$

- So for a small change in volume ΔV we have

$$\Delta P = -B \frac{\Delta V}{V}$$

$$\frac{\text{Force}}{A} \propto A \Delta x$$

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

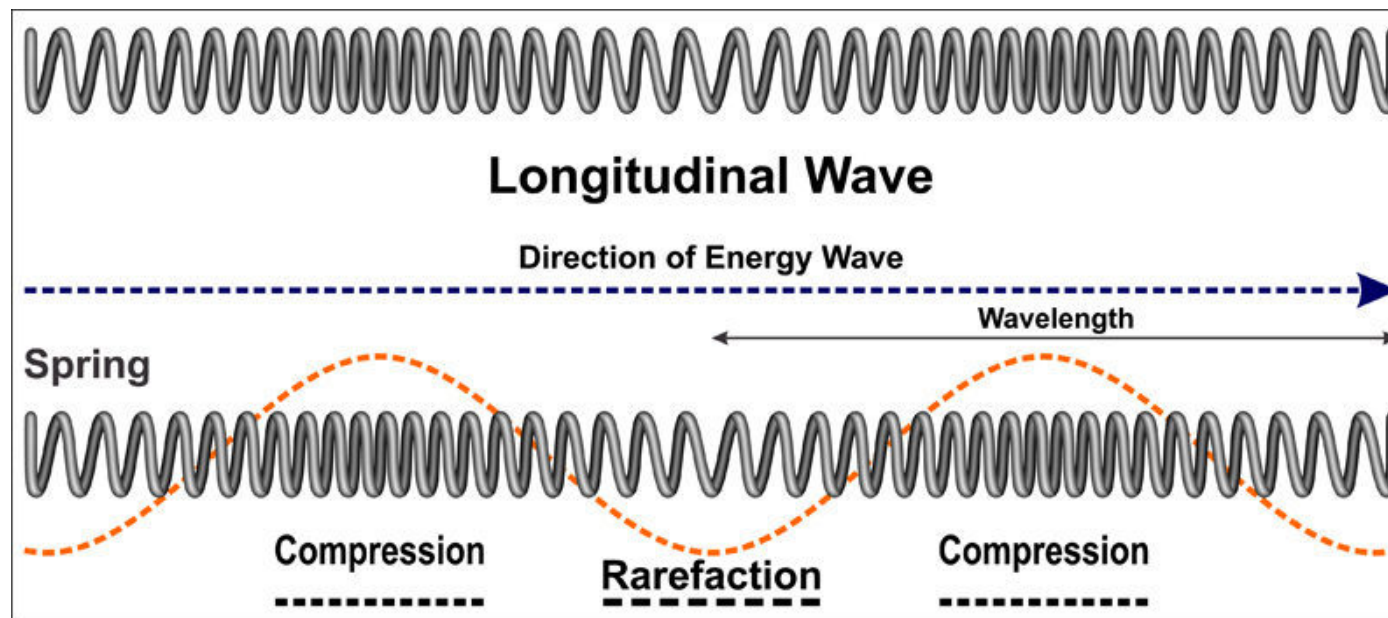


B acts like the spring constant.

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

Summary: 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

The speed of waves in fluid or solid determine the Bulk Modulus:



full disclosure: It is the adiabatic compressibility that actually determines the speed. But the adiabatic compressibility can be related to the isothermal one as we will see. The formula for the speed of sound is

$c_s = \sqrt{B_s / \rho}$ where ρ is the mass per volume., and B_s is the adiabatic compressibility. We have been talking about the isothermal compressibility which can be determined from B_T and the specific heats.

$B = -V \left(\frac{\partial P}{\partial V} \right)$ serves as spring constant, determining the wave speed.

Isothermal Compressibility of Water

