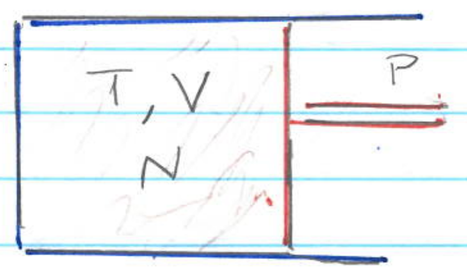
# Equation of State (EOS)

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




- The equation of state is a relation between 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 example

- 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 $A(T) = 1$

$$\boxed{p(T,V) = n k_B T \, (1 + B(T)\, n + C(T)\, n^2 + \ldots)}$$

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

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

Now

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

- 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

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

- 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

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

the negative is inserted since things contact as pressure is increased

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

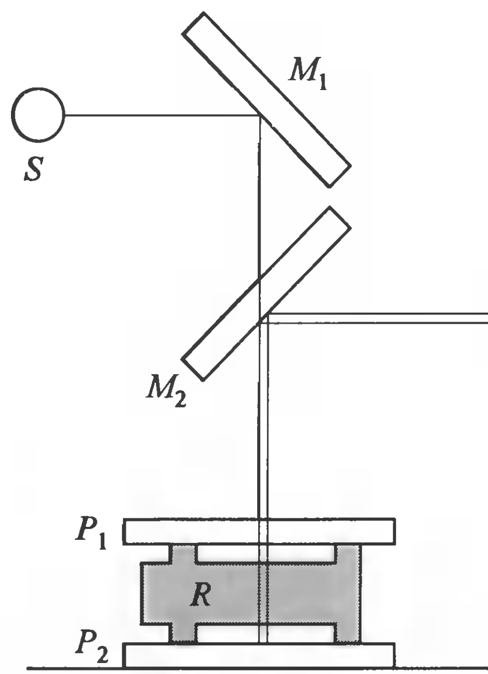
$P = P(T, V(T,P))$ so at fixed T

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

# 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, $\beta_p$ (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

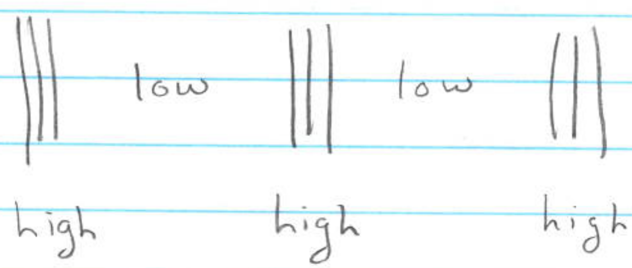
So

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

- So for a small change in volume $\Delta V$ we have

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

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

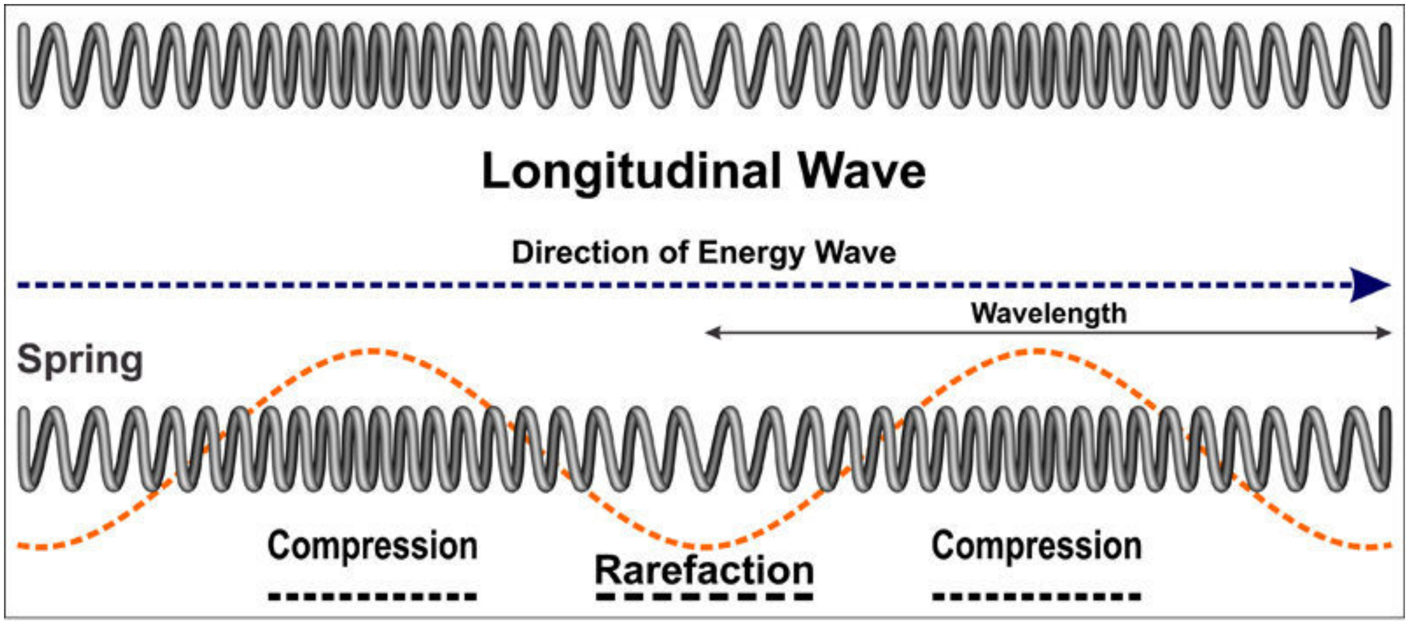



B acts like the spring constant.

The speed of the wave is $c_s^2 = \frac{B}{\rho}$ where $\rho$ 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 $\kappa_T$ and $\beta_P$. 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 $\rho$ is the mass per volumes., 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.

# A Look Ahead

We will prove the relations in this section later. It is still worth recording them here.

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

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

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

- The "adiab" means that no heat is exchanged -- so $pV^{\gamma} = \text{const}$ for an ideal gas. Fortunately the adiabatic and isothermal compressibilities are related to each other (proved later!)

$$\boxed{K_S = \frac{K_T}{\gamma} \qquad B_S = \gamma B_T} \qquad \gamma \equiv \frac{C_p}{C_V}$$

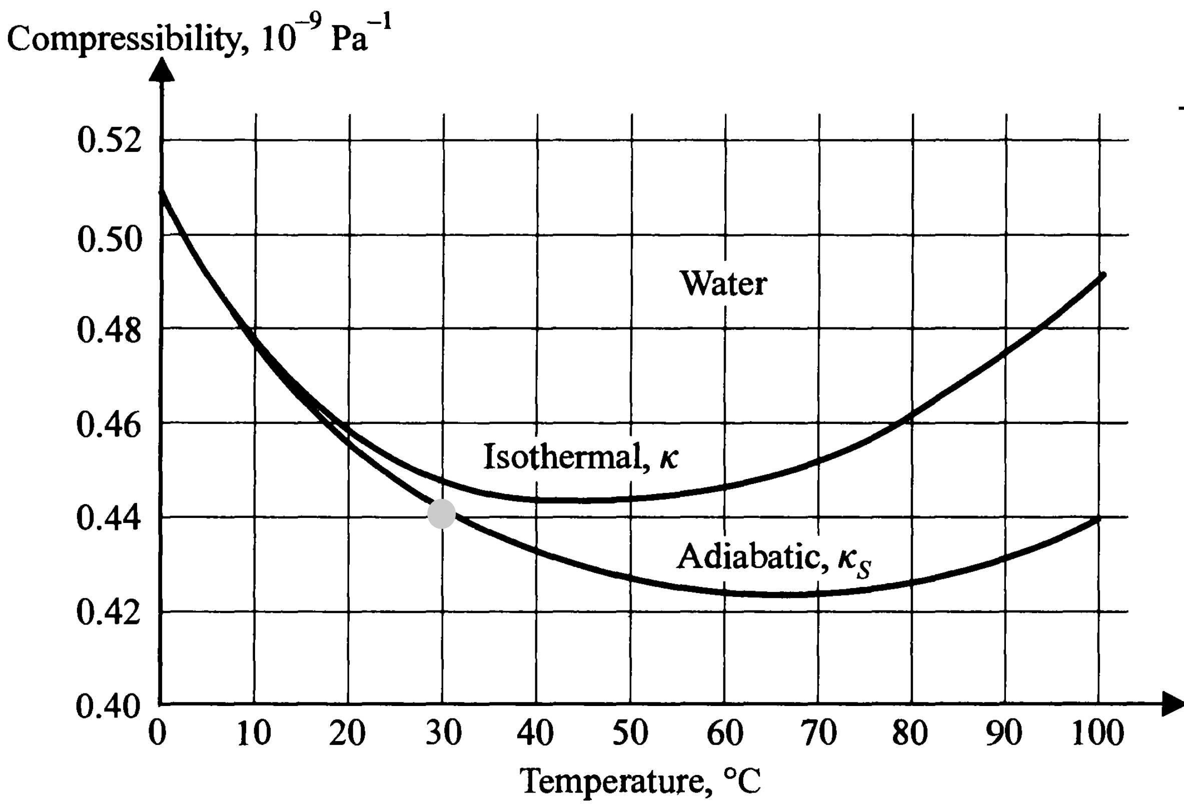
The speed of sound is

$$\boxed{c_s = \sqrt{\frac{B_s}{\rho}} = \frac{1}{\sqrt{K_s \rho}}}$$

See the next slide for application of this formula to water

- The specific heats $C_p$ and $C_V$ are also related. We will prove that (later)

# 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

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

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