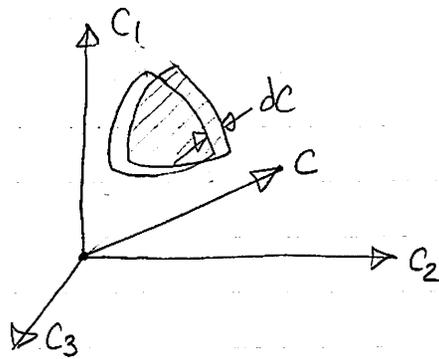


$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{m(c_1^2 + c_2^2 + c_3^2)}{2k_B T}} dc_1 dc_2 dc_3 = 1$$

we know that $c^2 = c_1^2 + c_2^2 + c_3^2$

$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{mc^2}{2k_B T}} dc_1 dc_2 dc_3$$



For a sphere: $4\pi c^2$ (surface area)
 $dV_c = 4\pi c^2 dc = dc_1 dc_2 dc_3$
 Thin shell approx.

Our integral becomes much simpler.

$$4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^{\infty} e^{-\frac{mc^2}{2k_B T}} c^2 dc = 1$$

So we previously defined $\hat{c} = c \left(\frac{m}{2k_B T}\right)^{1/2} \Rightarrow c = \frac{\hat{c}}{\left(\frac{m}{2k_B T}\right)^{1/2}}$

$$d\hat{c} = \left(\frac{m}{2k_B T}\right)^{1/2} dc$$

Back substituting:

$$= \frac{4\pi}{\pi^{3/2}} \left(\frac{m}{2k_B T}\right)^{3/2} \int_0^{\infty} e^{-\hat{c}^2} \hat{c}^2 \left(\frac{1}{\left(\frac{m}{2k_B T}\right)}\right) \frac{d\hat{c}}{\left(\frac{m}{2k_B T}\right)^{1/2}}$$

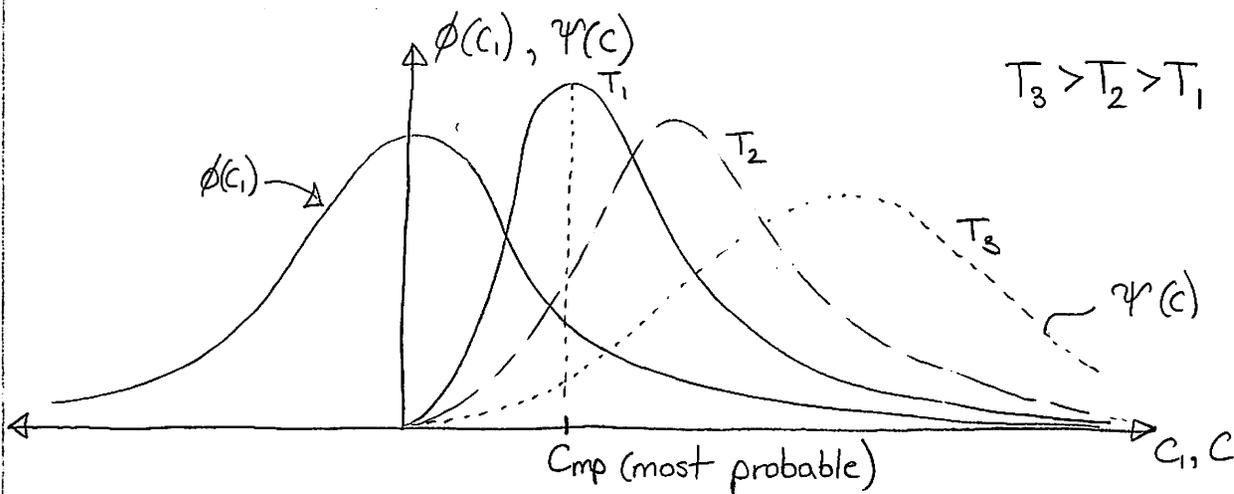
$$= \frac{4}{\sqrt{\pi}} \int_0^{\infty} \hat{c}^2 e^{-\hat{c}^2} d\hat{c} = 1 \Rightarrow \text{Works out}$$

$$I_2 = \frac{\sqrt{\pi}}{4}$$

From this, we see that the general speed distribution is:

$$\psi(c) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{3/2} c^2 e^{-\frac{mc^2}{2k_B T}}$$

So what do our distributions look like?



So if we want to calculate the mean molecule speed (\bar{c})

$$\bar{c} = \int_0^{\infty} c \psi(c) dc$$

$$\bar{c} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \int_0^{\infty} c^3 e^{-\frac{mc^2}{2k_B T}} dc$$

Doing our usual tricks $\hat{c} = c \left(\frac{m}{2k_B T} \right)^{1/2}$

$$\bar{c} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^2 \int_0^{\infty} \hat{c}^3 e^{-\hat{c}^2} d\hat{c}$$

Aside:

$$\int_0^{\infty} \hat{c}^3 e^{-\hat{c}^2} d\hat{c} = I_3$$

$$I_3 = \frac{n-1}{2} I_{n-2} = \frac{3-1}{2} I_1 = \frac{2}{2} \left(\frac{1}{2} \right)$$

We know this from our previous calculations as $I_3 = \frac{1}{2}$

$$\bar{c} = \frac{1}{2} \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^2 \frac{1}{2}$$

$$\boxed{\bar{c} = \sqrt{\frac{8k_B T}{\pi m}}}$$

\Rightarrow Average speed $\Rightarrow \bar{c} \sim \sqrt{T}$, as $T \uparrow, \bar{c} \uparrow$

So how about $\overline{c^2}$?

$$\overline{c^2} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \int_0^{\infty} c^4 e^{-\frac{mc^2}{2k_B T}} dc \Rightarrow \hat{c} = c \left(\frac{m}{2k_B T} \right)^{1/2}$$

$$\overline{c^2} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^{5/2} \int \hat{c}^4 e^{-\hat{c}^2} d\hat{c}$$

$$\begin{aligned} \overline{c^2} &= \frac{4}{\sqrt{\pi}} \cdot \frac{3\sqrt{\pi}}{8} \left(\frac{m}{2k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^{5/2} I_4 = \frac{n-1}{2} I_{n-2} = \frac{4-1}{2} I_{4-2} \\ &= \frac{3}{2} I_2 = \frac{3}{2} \frac{\sqrt{\pi}}{4} \\ &= \frac{3\sqrt{\pi}}{8} \end{aligned}$$

$$\boxed{\overline{c^2} = \frac{3k_B T}{m}}$$

or

$$\boxed{C_{rms} = \sqrt{\frac{3k_B T}{m}}}$$

\Rightarrow Root mean square speed.

Looks familiar right?

We've proven that our average molecule kinetic energy assumption is indeed correct:

$$\frac{1}{2} m \overline{c^2} \approx \frac{3}{2} k_B T$$

How about the most probable velocity?

For this, we need to differentiate: $\frac{d}{dc} (\psi(c)) = 0$

$$\frac{d}{dc} \left(\frac{4}{\sqrt{\pi}} \cdot \left(\frac{m}{2k_B T} \right)^{3/2} c^2 e^{-\frac{mc^2}{2k_B T}} \right) = 0$$

$$\frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \frac{d}{dc} (c^2 e^{-\frac{mc^2}{2k_B T}}) = 0$$

$$\frac{d}{dc} (c^2) \cdot e^{-\frac{mc^2}{2k_B T}} + c^2 \frac{d}{dc} (e^{-\frac{mc^2}{2k_B T}}) = 0$$

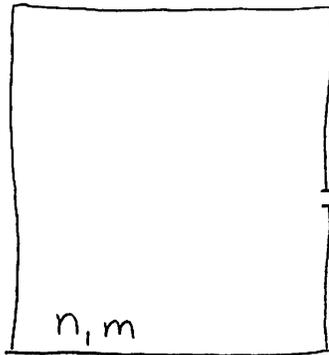
$$2c e^{-\frac{mc^2}{2k_B T}} + c^2 \left(-\frac{2mc}{2k_B T} \right) e^{-\frac{mc^2}{2k_B T}} = 0$$

$$1 - \frac{mc^2}{2k_B T} = 0 \Rightarrow$$

$$\boxed{C_{mp} = \sqrt{\frac{2k_B T}{m}}} \Rightarrow \text{most probable speed.}$$

To give you some insight, the speed of sound is $C_{sound} \approx 0.84 C_{mp}$ and $C_{sound} \approx 0.74 C_{mp} \Rightarrow$ Since sound waves propagate via molecular motion, makes sense that they are slightly slower than C_{mp} . (20)

Example #2 Reservoir full of air. What is the mass flux out of the orifice?



$d < D < \lambda$ where $n = \#$ of molecules/volume
 $d =$ size of molecule
 $D =$ orifice opening
 $\lambda =$ mean free path
 $m =$ mass per molecule
 $A =$ orifice area

$$\dot{m} = nmA \int_0^{\infty} c_1 \phi(c_1) \underbrace{\int_{-\infty}^{\infty} \phi(c_2) dc_2}_1 \underbrace{\int_{-\infty}^{\infty} \phi(c_3) dc_3}_1$$

\Rightarrow We don't care about the molecules y or z velocity
 Note, 0 is lower bound since we only want molecules that travel in the +x direction out of the reservoir.

$$\dot{m} = nmA \frac{1}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{1/2} \int_0^{\infty} c_1 e^{-\frac{m c_1^2}{2k_B T}} dc_1$$

Using our old trick, and knowing that $n = \frac{p}{m}$

$$\dot{m} = pA \frac{1}{\sqrt{\pi}} \left(\frac{2k_B T}{m} \right)^{1/2} \underbrace{\int_0^{\infty} \hat{c}_1 e^{-\hat{c}_1^2} d\hat{c}_1}_{I_1 = \frac{1}{2}}$$

$$= \frac{pA}{2\sqrt{\pi}} \left(\frac{2k_B T}{m} \right)^{1/2}$$

\Rightarrow multiply by $\left(\frac{2}{2} \right)$

$$= \frac{pA}{4} \underbrace{\left(\frac{8k_B T}{\pi m} \right)^{1/2}}_{\bar{c}} = \boxed{\frac{pA\bar{c}}{4} = \dot{m}}$$

Another way to write it is:

$$\dot{m} = \frac{pA}{4} \left(\frac{8k_B T}{\pi m} \right)^{1/2} = \frac{\sqrt{8} pA}{4\sqrt{\pi}} \sqrt{\frac{k_B T}{m}} = \frac{2^{3/2} pA}{2^2 \pi^{1/2}} \sqrt{\frac{k_B T}{m}}$$

We also know that: $R_{\text{gas}} = \frac{k_B}{m}$ ^{Aside} \Rightarrow

$$\dot{m} = \frac{pA}{\sqrt{2\pi}} \sqrt{R_{\text{gas}} T} \approx 0.4 pA \sqrt{RT}$$

$$R_{\text{gas}} = \frac{R}{M}$$

$$k_B = \frac{R}{A} = \frac{M R_{\text{gas}}}{A}$$

but $M = A \cdot m$

$$k_B = \frac{A m R_{\text{gas}}}{A} = R_{\text{gas}} m$$

Avogadro
NOT!
Area.

For comparison, what if $D > \lambda$, so we can use continuum mechanics to solve for \dot{m} . Now we have a choked flow condition. From compressible fluid mechanics:

$$\dot{m} = pA \sqrt{R_{\text{gas}} T} \cdot \underbrace{\left[\gamma \left(\frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{\gamma-1}} \right]^{1/2}}_{0.684}$$

$$\dot{m} = 0.684 pA \sqrt{RT} \Rightarrow \text{Using continuum mechanics}$$

We overestimate the result by 50% using continuum mechanics when compared to rarified gas theory.

So what is the energy of the escaping gas molecules? Solve for $\overline{c^2}$ and c_{esc} . You will see that

$$\overline{c_{\text{esc}}^2} = 4 \frac{R_{\text{gas}} T}{m} = \frac{4k_B T}{m}$$

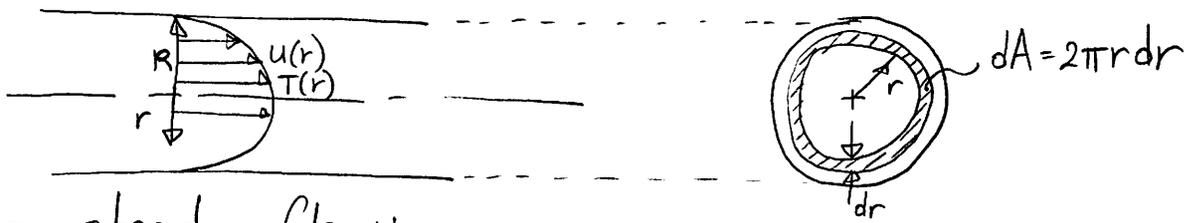
$$\frac{4k_B T}{m} > \frac{3k_B T}{m} = \langle E \rangle_{\text{reservoir}}$$

\hookrightarrow Escaping molecules have on average a larger energy than the rest of the molecules in the reservoir. Makes sense, they travel faster and scatter off the walls more frequently. (22)

Extra Derivation (Pinhole problem)

Solution to energy of escaping gas molecules from a pinhole:

The way to solve this problem is analogous to calculating bulk flow temperature of a fluid in a pipe.



For a steady flow:

$$\bar{u} = \frac{1}{\rho \pi R^2} \int_0^R \rho u(r) 2\pi r dr$$

$$\bar{T} = \frac{1}{\rho c_p \bar{u} \pi R^2} \int_0^R \rho c_p T(r) u(r) 2\pi r dr$$

So we now have: Total convected energy in the flow.

$$\bar{u} = \frac{1}{\pi R^2} \int_0^R u 2\pi r dr$$

$$\bar{T} = \frac{1}{\pi R^2 \bar{u}} \int_0^R (uT) 2\pi r dr$$

⇒ We will need to use an analogous approach.

In our case, we need $\overline{C_{esc}^2}$. We can write:

$$\overline{C_{esc}^2} = \frac{1}{\overline{C_{esc}}} \left(\frac{m}{2k_B T} \right)^{3/2} \frac{1}{\pi^{3/2}} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty C_1 (c^2) e^{-\frac{mc^2}{2k_B T}} dC_1 dC_2 dC_3$$

Need to divide by $\overline{C_{esc}}$ due to the C_1 in the integral.

↳ energy advected in the 1th component

This term is like the \bar{T} calculation. We are computing the average energy, $\overline{C^2}$, advected in the C_1 direction

We can also express $\overline{C_{esc}}$ as: $\overline{C_{esc}} = \frac{\dot{m}}{\rho A}$

Expanding our integral and back substituting $\overline{C_{esc}}$:

$$\overline{C_{esc}^2} = \frac{\rho A}{\dot{m}} \left(\frac{m}{2k_B T} \right)^{3/2} \frac{1}{\pi^{3/2}} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_1 (C_1^2 + C_2^2 + C_3^2) e^{-\frac{mC_1^2}{2k_B T}} e^{-\frac{mC_2^2}{2k_B T}} e^{-\frac{mC_3^2}{2k_B T}} \cdot dC_1 dC_2 dC_3$$

Now we can expand the integral

$$\overline{C_{esc}^2} = \underbrace{\frac{\rho A}{\dot{m}} \left(\frac{m}{2k_B T} \right)^{3/2} \frac{1}{\pi^{3/2}} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_1^3 e^{-\frac{mC_1^2}{2k_B T}} e^{-\frac{mC_2^2}{2k_B T}} e^{-\frac{mC_3^2}{2k_B T}} dC_1 dC_2 dC_3}_{X}$$

$$+ \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_1 C_2^2 e^{-\frac{mC_1^2}{2k_B T}} e^{-\frac{mC_2^2}{2k_B T}} e^{-\frac{mC_3^2}{2k_B T}} dC_1 dC_2 dC_3$$

$$+ \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_1 C_3^2 e^{-\frac{mC_1^2}{2k_B T}} e^{-\frac{mC_2^2}{2k_B T}} e^{-\frac{mC_3^2}{2k_B T}} dC_1 dC_2 dC_3 \Bigg]$$

$$\begin{aligned} \overline{C_{esc}^2} = X & \left[\int_0^{\infty} C_1^3 e^{-\frac{mC_1^2}{2k_B T}} dC_1 \int_{-\infty}^{\infty} e^{-\frac{mC_2^2}{2k_B T}} dC_2 \int_{-\infty}^{\infty} e^{-\frac{mC_3^2}{2k_B T}} dC_3 \right. \\ & + \int_0^{\infty} C_1 e^{-\frac{mC_1^2}{2k_B T}} dC_1 \int_{-\infty}^{\infty} C_2^2 e^{-\frac{mC_2^2}{2k_B T}} dC_2 \int_{-\infty}^{\infty} e^{-\frac{mC_3^2}{2k_B T}} dC_3 \\ & \left. + \int_0^{\infty} C_1 e^{-\frac{mC_1^2}{2k_B T}} dC_1 \int_{-\infty}^{\infty} e^{-\frac{mC_2^2}{2k_B T}} dC_2 \int_{-\infty}^{\infty} C_3^2 e^{-\frac{mC_3^2}{2k_B T}} dC_3 \right] \end{aligned}$$

Now we can normalize to make our integral simpler

$$\text{Let: } c_1 = \frac{\hat{c}_1}{\left(\frac{m}{2k_B T}\right)^{1/2}}, \quad c_2 = \frac{\hat{c}_2}{\left(\frac{m}{2k_B T}\right)^{1/2}}, \quad c_3 = \frac{\hat{c}_3}{\left(\frac{m}{2k_B T}\right)^{1/2}}$$

$$dc_1 = \frac{d\hat{c}_1}{\left(\frac{m}{2k_B T}\right)^{1/2}}, \quad dc_2 = \frac{d\hat{c}_2}{\left(\frac{m}{2k_B T}\right)^{1/2}}, \quad dc_3 = \frac{d\hat{c}_3}{\left(\frac{m}{2k_B T}\right)^{1/2}}$$

Back substituting

$$\overline{c_{esc}^2} = \underbrace{\prod \left(\frac{2k_B T}{m}\right)^{3/2}}_{\text{from } \hat{c}} \underbrace{\left(\frac{2k_B T}{m}\right)^{3/2}}_{\text{from } d\hat{c}} \cdot \underbrace{\int_0^\infty \hat{c}_1 e^{-\hat{c}_1^2} d\hat{c}_1}_{I_3} \underbrace{\int_{-\infty}^\infty e^{-\hat{c}_2^2} d\hat{c}_2}_{2I_0} \underbrace{\int_{-\infty}^\infty e^{-\hat{c}_3^2} d\hat{c}_3}_{2I_0}$$

$$+ \underbrace{\int_0^\infty \hat{c}_1 e^{\hat{c}_1^2} d\hat{c}_1}_{I_1} \underbrace{\int_{-\infty}^\infty \hat{c}_2 e^{-\hat{c}_2^2} d\hat{c}_2}_{2I_2} \underbrace{\int_{-\infty}^\infty e^{-\hat{c}_3^2} d\hat{c}_3}_{2I_0}$$

$$+ \underbrace{\int_0^\infty \hat{c}_1 e^{-\hat{c}_1^2} d\hat{c}_1}_{I_1} \underbrace{\int_{-\infty}^\infty e^{-\hat{c}_2^2} d\hat{c}_2}_{2I_0} \underbrace{\int_{-\infty}^\infty \hat{c}_3^2 e^{-\hat{c}_3^2} d\hat{c}_3}_{2I_2}$$

Putting everything together,

$$\overline{c_{esc}^2} = \frac{\rho A}{m} \left(\frac{m}{2k_B T}\right)^{3/2} \frac{1}{\pi^{3/2}} \left(\frac{2k_B T}{m}\right)^{3/2} \left[I_3 (2I_0)^2 + I_1 (2I_2)(2I_0) + 4I_0 I_1 I_2 \right]$$

$$= \frac{\rho A}{m} \frac{1}{\pi^{3/2}} \left(\frac{2k_B T}{m}\right)^{3/2} \left[\frac{1}{2} \left(2 \frac{\sqrt{\pi}}{2}\right)^2 + \frac{1}{2} \left(2 \frac{\sqrt{\pi}}{4}\right) \left(2 \frac{\sqrt{\pi}}{2}\right) + \frac{1}{2} \left(2 \frac{\sqrt{\pi}}{2}\right) \left(2 \frac{\sqrt{\pi}}{4}\right) \right]$$

$$= \frac{\rho A}{m} \frac{1}{\pi^{3/2}} \left(\frac{2k_B T}{m}\right)^{3/2} \left[\frac{\pi}{2} + \frac{\pi}{2} \right] = \frac{\rho A}{m} \left(\frac{2k_B T}{m}\right)^{3/2} \frac{1}{\sqrt{\pi}}$$

But we already solved that

$$\dot{m} = \frac{pA}{4} \left(\frac{8k_B T}{\pi m} \right)^{1/2}$$

Back substituting:

$$\begin{aligned} \overline{z}_{\text{Cesc}}^2 &= \frac{pA}{\frac{pA}{4} \left(\frac{8k_B T}{\pi m} \right)^{1/2}} \cdot \left(\frac{2k_B T}{m} \right)^{3/2} \frac{1}{\sqrt{\pi}} \\ &= 4 \left(\frac{\pi m}{8k_B T} \right)^{1/2} \left(\frac{2k_B T}{m} \right)^{3/2} \frac{1}{\sqrt{\pi}} \\ &= 4 \frac{k_B T}{m} \end{aligned}$$

$$\therefore \boxed{\overline{z}_{\text{Cesc}}^2 = \frac{4k_B T}{m}} > \frac{3k_B T}{m} = \langle E \rangle_{\text{Reservoir}}$$

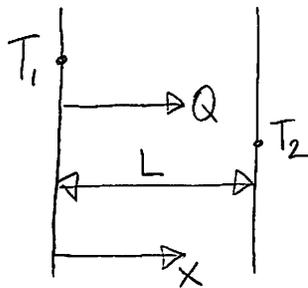
Result seems counter intuitive, but actually makes sense. Molecules with a larger energy move at a higher speed, and scatter off the reservoir walls more frequently. This makes them more probable to hit the pinhole and escape, hence the larger average energy.

Conduction

$\vec{v} = 0$, $1-D$, Steady State, $\dot{Q}''' = 0$, $k = \text{constant}$

We know that $\nabla^2 T = 0$ (heat equation)

① Slab



$Q = \text{heat transfer rate [W]}$

Using our heat equation

$$\int \frac{\partial^2 T}{\partial x^2} = \int 0$$

$$\int \frac{\partial T}{\partial x} = \int C_1$$

$$T(x) = C_1 x + C_2 \Rightarrow \text{B.C.'s} \Rightarrow \begin{aligned} T(x=0) &= T_1 \\ T(x=L) &= T_2 \end{aligned}$$

$$T(x=0) = T_1 = C_1(0) + C_2 \Rightarrow C_2 = T_1$$

$$T(x=L) = T_2 = C_1 L + T_1 \Rightarrow C_1 = \frac{T_2 - T_1}{L}$$

$$\boxed{T(x) = \frac{T_2 - T_1}{L} x + T_1} \Rightarrow \text{Temperature profile in the solid. Linear and decreasing from hot to cold}$$

So if we define a heat transfer resistance; R , $A = \text{area}$

Aside:
Flow of Current:
 $I = \frac{\Delta V}{R}$

$$Q = \frac{\Delta T}{R} \Rightarrow Q = -kA \frac{\partial T}{\partial x} \Rightarrow \text{from above } \frac{\partial T}{\partial x} = \frac{T_2 - T_1}{L}$$

$$\frac{\partial T}{\partial x} = -\frac{(T_1 - T_2)}{L} = -\frac{\Delta T}{L} \Rightarrow \text{Back substituting}$$

$$Q = \frac{kA}{L} \Delta T$$

$$= \frac{kA}{L} \Delta T$$

$$\frac{1}{R} \Rightarrow$$

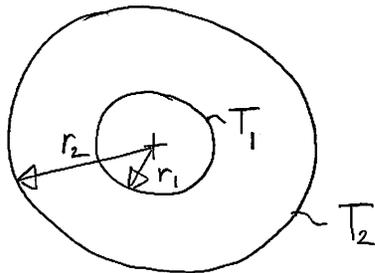
$$R_{\text{SLAB}} = \frac{L}{kA}$$

\Rightarrow Thermal Resistance of a solid slab.

*(Read the interesting paper about Fourier)

L = slab thickness
 A = heat transfer area
 k = thermal conductivity

② Circular cylinder



We know our heat equation in radial coordinates is:

$$\frac{1}{r} \cdot \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = 0$$

$$\int \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = \int 0$$

$$r \frac{\partial T}{\partial r} = C_1$$

$$\int \frac{\partial T}{\partial r} = \int \frac{C_1}{r}$$

$$T(r) = C_1 \ln r + C_2$$

Applying our boundary conditions:

$$T_1 = C_1 \ln r_1 + C_2 \quad \text{①}$$

$$T_2 = C_1 \ln r_2 + C_2 \quad \text{②}$$

Subtract ① & ② to get

$$C_1 = \frac{T_1 - T_2}{\ln r_1 - \ln r_2} = \frac{T_1 - T_2}{\ln(r_1/r_2)}$$

Back substitute into ①

$$C_2 = T_1 - \frac{(T_1 - T_2)}{\ln(r_1/r_2)} \ln(r_1)$$

Back substituting into our initial equation $T(r)$

$$T = \frac{T_1 - T_2}{\ln(r_1/r_2)} \ln r + T_1 - \frac{(T_1 - T_2) \ln r_1}{\ln(r_1/r_2)}$$

Finally:

$$\frac{T - T_1}{T_1 - T_2} = \frac{\ln(r/r_1)}{\ln(r_1/r_2)}$$

or

$$\boxed{\frac{T - T_1}{T_2 - T_1} = \frac{\ln(r/r_1)}{\ln(r_2/r_1)}}$$

↳ Radial temperature profile.

Calculating the thermal resistance:

$$Q = \frac{\Delta T}{R} = -k A \left. \frac{\partial T}{\partial r} \right|_r = -k (2\pi r L) \frac{\overbrace{T_2 - T_1}^{\Delta T}}{\ln(r_2/r_1)} \cdot \frac{1}{r}$$

$$\boxed{R_{cyl} = \left| \frac{\ln(r_2/r_1)}{2\pi k L} \right|}$$

⇒ Cylindrical thermal resistance
Note the absolute value on the resistance. Doesn't matter if $r_2 > r_1$, or $r_1 > r_2$ ⇒ resistance is the same.

