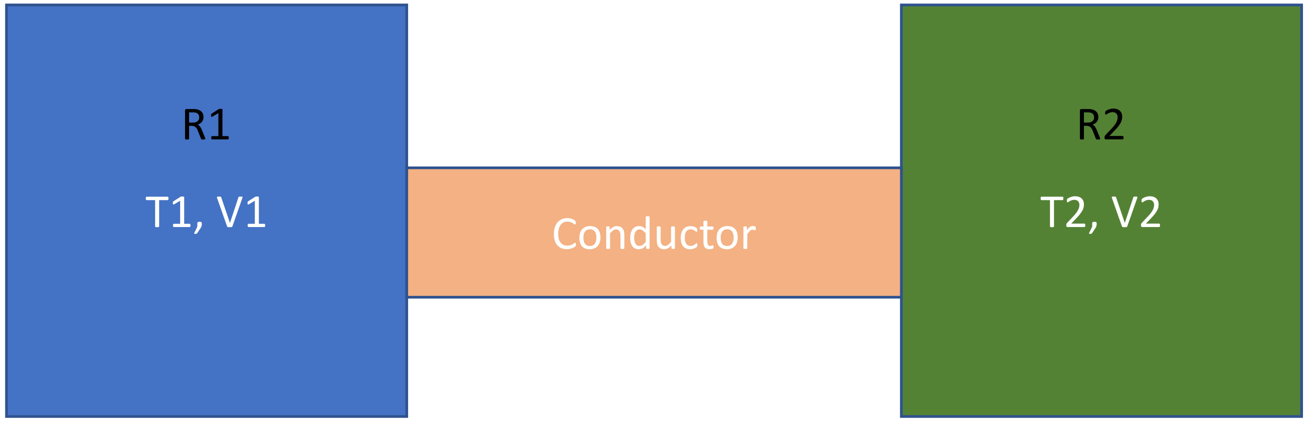
Tutorial #6 :

Irreversible thermodynamics

Exercise #1 : Onsager reciprocity relations



Because of the gradient in temperature and voltage, we can express the flux between the two reservoirs :

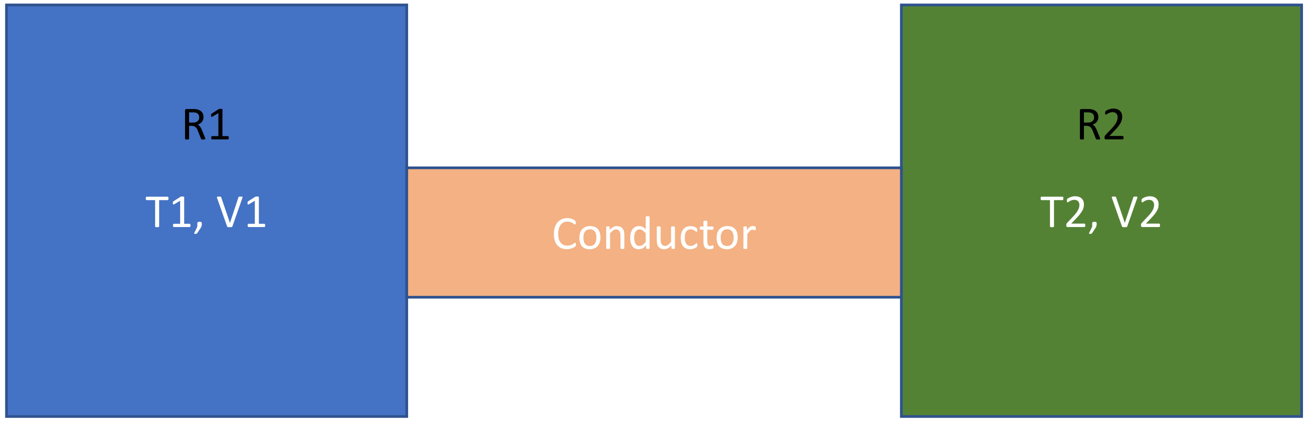
$$\begin{aligned} I_q &= l_{11}\Delta V + l_{12}\Delta T \\ I_U &= l_{21}\Delta V + l_{22}\Delta T \end{aligned}$$

But with this formulation, there is no reciprocity of the coefficients : l21 = L12 is NOT satisfied

In this exercise, we will define adequate quantities and derive coefficients satisfying recirpocity relations.

Generalized force + exchange of an extensive physical quantity.

Exercise #1 : Onsager reciprocity relations



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1) Write an energy and charge budget between the two réservoirs:

2) Derive the variation of entropy in R1 and R2. You can use the thermodynamic identity :

$$dU = TdS + \mu dN + Vdq$$

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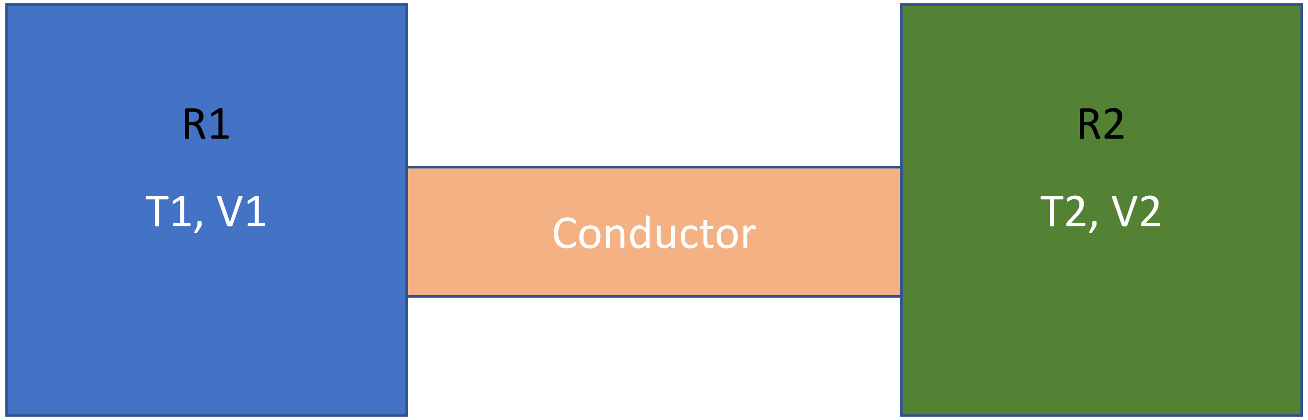

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$$I_q = l_{11}\Delta V + l_{12}\Delta T$$
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1) Write an energy and charge budget between the two réservoirs:

$$q\delta N_1 = -q\delta N_2$$

$$\delta U_1 = -\delta U_2$$

2) Derive the variation of entropy in R1 and R2. You can use the thermodynamic identity :

$$\delta S_1 = \frac{\delta U_1}{T_1} - \frac{\mu(T_1) - qV_1}{T_1}\delta N_1$$
$$= -\frac{\delta U_2}{T_1} + \frac{\mu(T_1) - qV_1}{T_1}\delta N_2$$

$$\delta S_2 = \frac{\delta U_2}{T_2} - \frac{\mu(T_2) + qV_2}{T_2}\delta N_2$$

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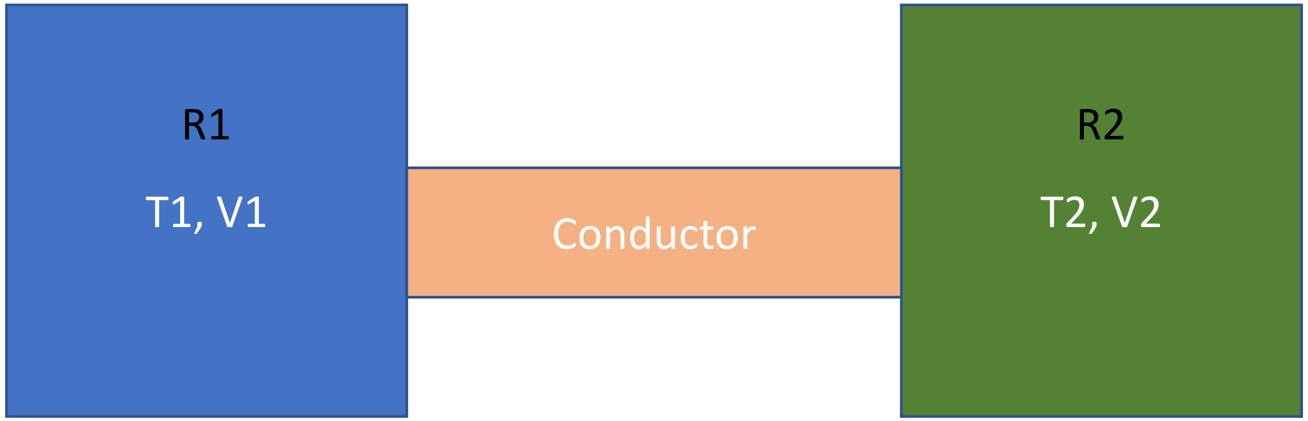

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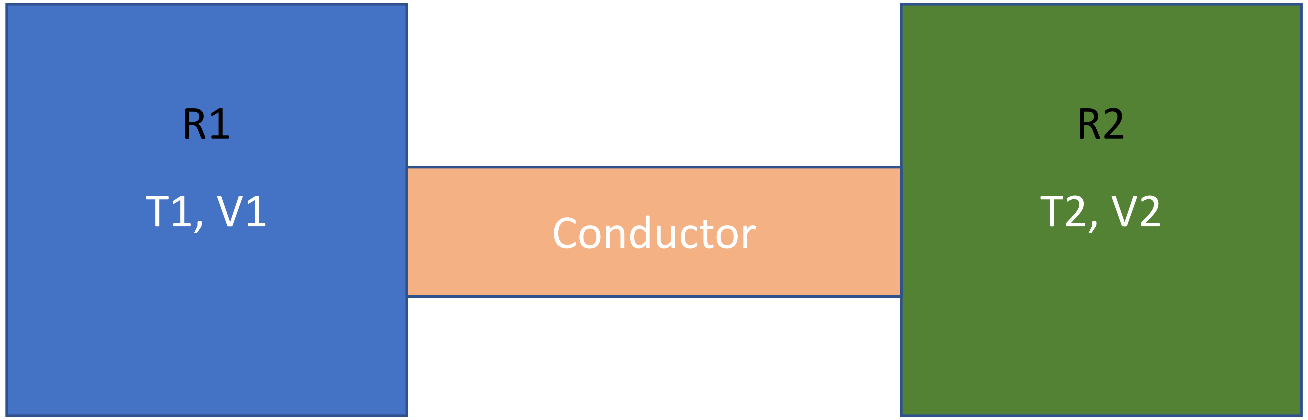

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3) Derive the total variation of entropy (i.e. variation in both réservoirs)

$$\begin{aligned} \delta S &= \delta S_1 + \delta S_2 \\ &= (\frac{1}{T_2} - \frac{1}{T_1})\delta U_2 + (\frac{\mu(T_1) + qV_1}{T_1} - \frac{\mu(T_2) + qV_2}{T_2})\delta N_2 \end{aligned}$$

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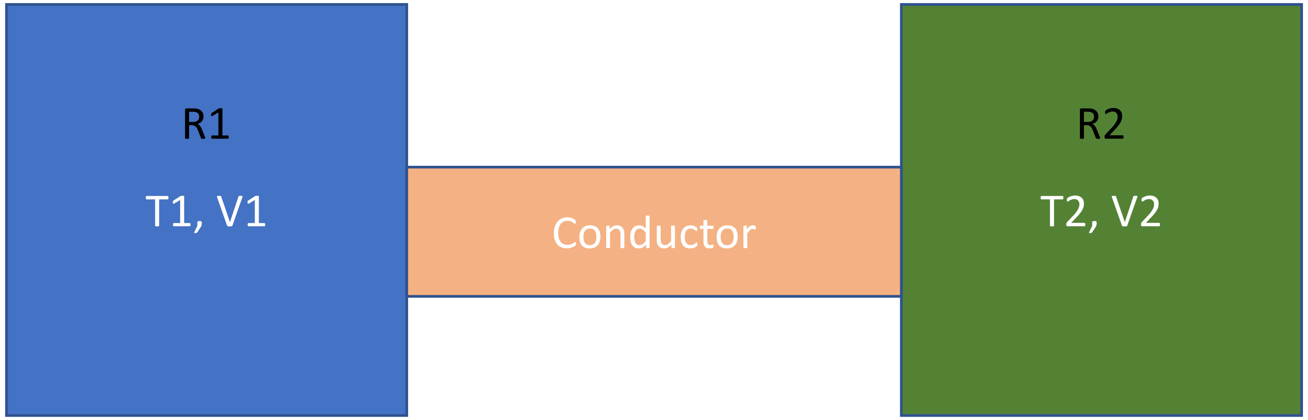

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$$\begin{aligned} I_q &= l_{11}\Delta V + l_{12}\Delta T \\ I_U &= l_{21}\Delta V + l_{22}\Delta T \end{aligned}$$

4) Derive the generalized forces Xu and Xq associated to the exchange of energy and charge, knowing that the rate of creation of entropy can be expressed using :

$$\frac{\Delta S}{\Delta t} = \sum_i J_i X_i,$$

With rate of extensive variables given by :

$$J_U = \frac{\Delta U}{\Delta t} \quad J_q = q\frac{\Delta N}{\Delta t}.$$

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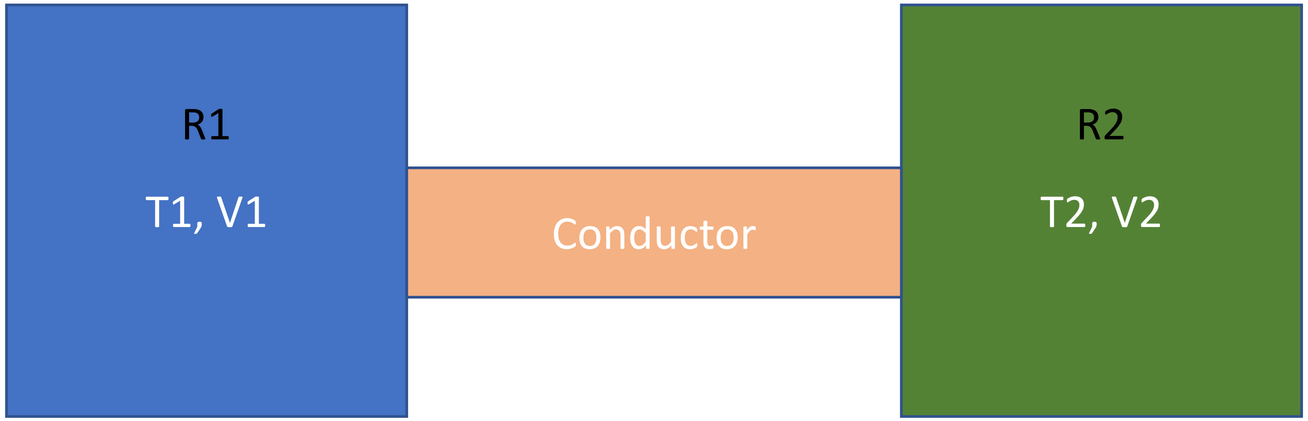

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$$\frac{\delta S}{\delta t} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\underbrace{\frac{\delta U_2}{\delta t}}_{J_U} + \left(\frac{\mu(T_1)/q + V_1}{T_1} - \frac{\mu(T_2)/q + V_2}{T_2}\right) q\underbrace{\frac{\delta N_2}{\delta t}}_{J_q}$$

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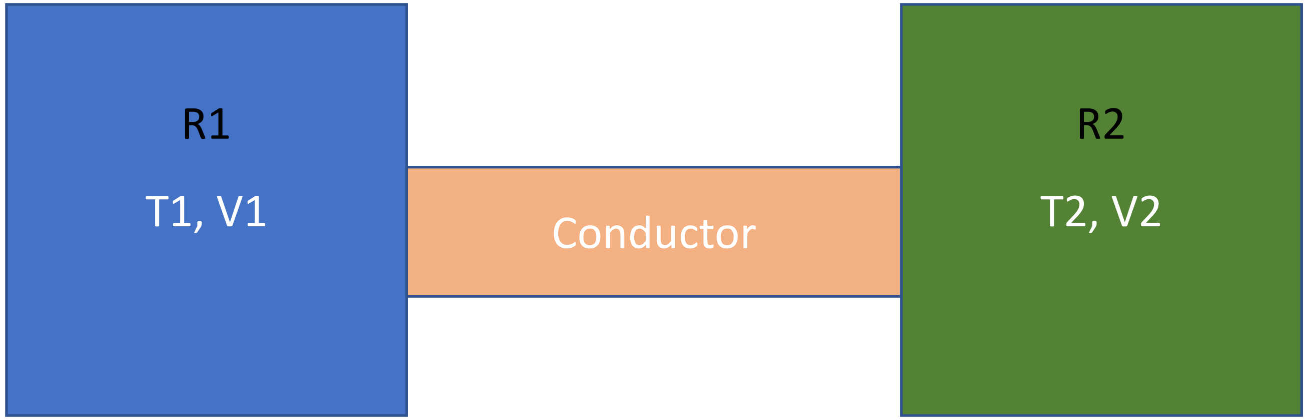

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$$= \Delta\left(\frac{1}{T}\right)J_U - \frac{1}{q}\Delta\left(\frac{\mu + qV}{T}\right)J_q$$

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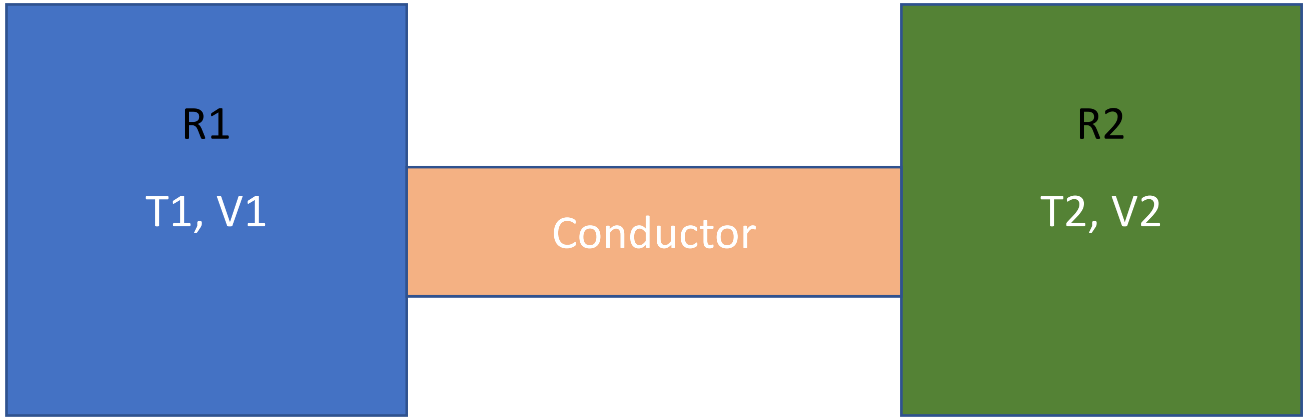

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$$\frac{\delta S}{\delta t} = \Delta(\frac{1}{T})J_U - \frac{1}{q}\Delta(\frac{\mu + qV}{T})J_q$$

$$X_U = \Delta(\frac{1}{T}) = -\frac{\Delta T}{T^2} \qquad X_q = -\frac{1}{q}\Delta(\frac{\mu_{ec}}{T})$$

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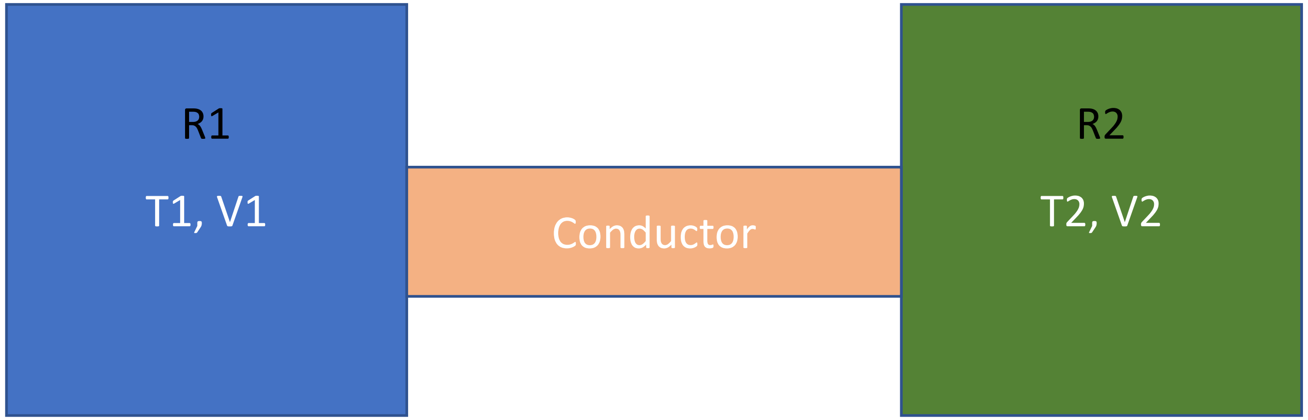

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$$\begin{aligned} I_q &= l_{11}\Delta V + l_{12}\Delta T \\ I_U &= l_{21}\Delta V + l_{22}\Delta T \end{aligned}$$

$$\begin{aligned} J_q &= L_{11}X_q + L_{12}X_U \\ J_U &= L_{21}X_q + L_{22}X_U \end{aligned}$$

We know now how to define coefficients that satisfy Onsager reciprocity

5) Derive the thermal conductance given by $J_U = -\Gamma\Delta T$

<u>Which is given in absence of charge flux (instead of zero voltage) !</u>

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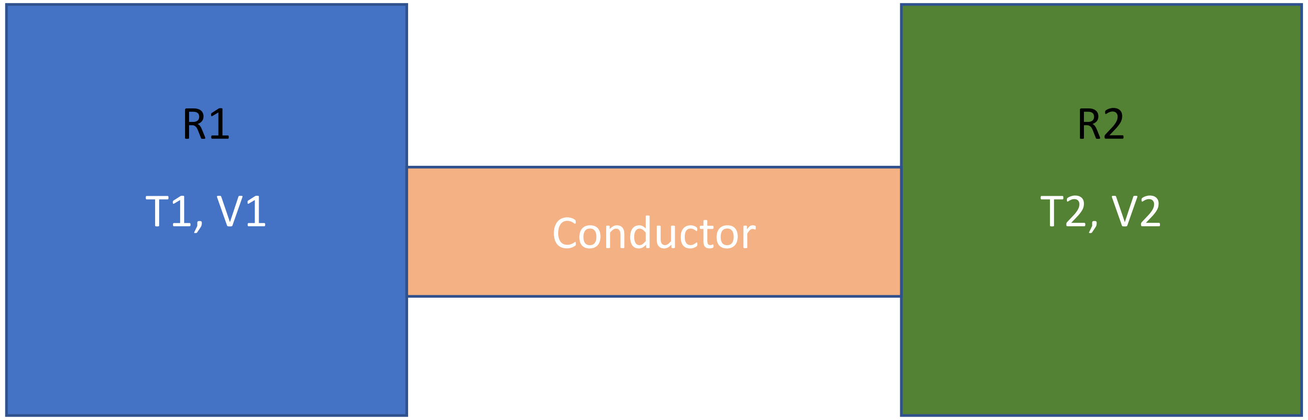

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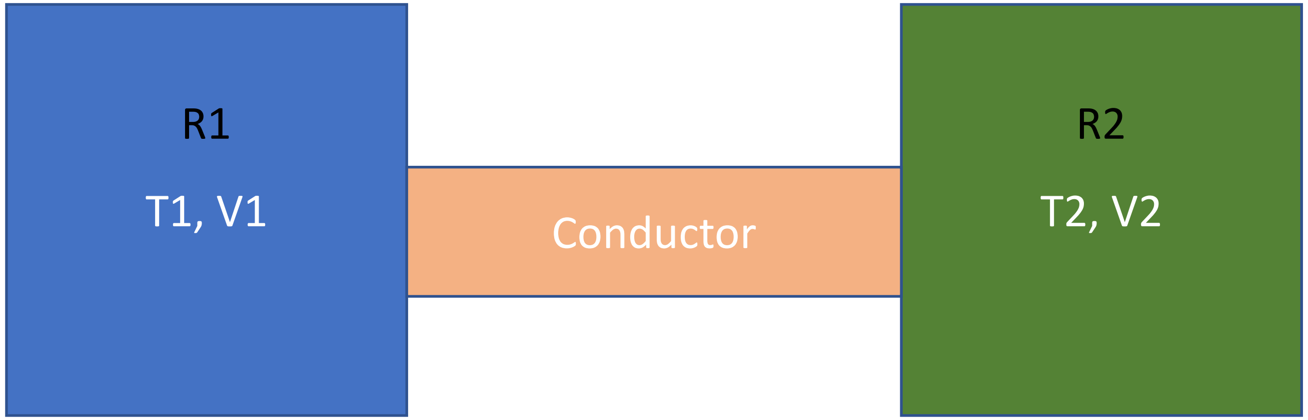

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$$\begin{aligned} J_U &= -\Gamma\Delta T \\ &= L_{21}X_q + L_{22}X_U \end{aligned}$$

$$J_q = 0$$

$$X_q = -\frac{L_{12}}{L_{11}}X_U$$ with $X_U = \Delta(\frac{1}{T}) = -\frac{\Delta T}{T^2}$

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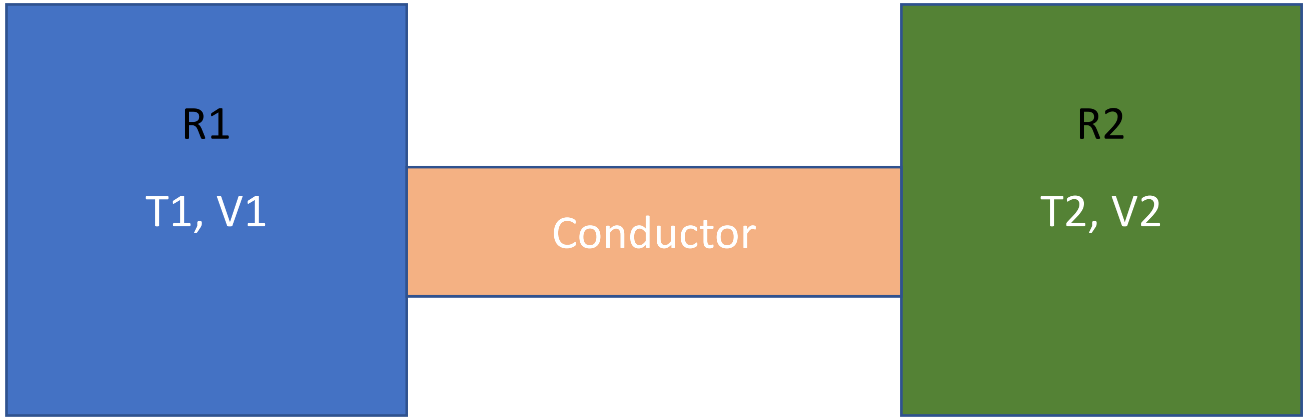

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$$\begin{aligned} J_U &= -\Gamma\Delta T \\ &= L_{21}X_q + L_{22}X_U \end{aligned}$$

$$J_q = 0$$

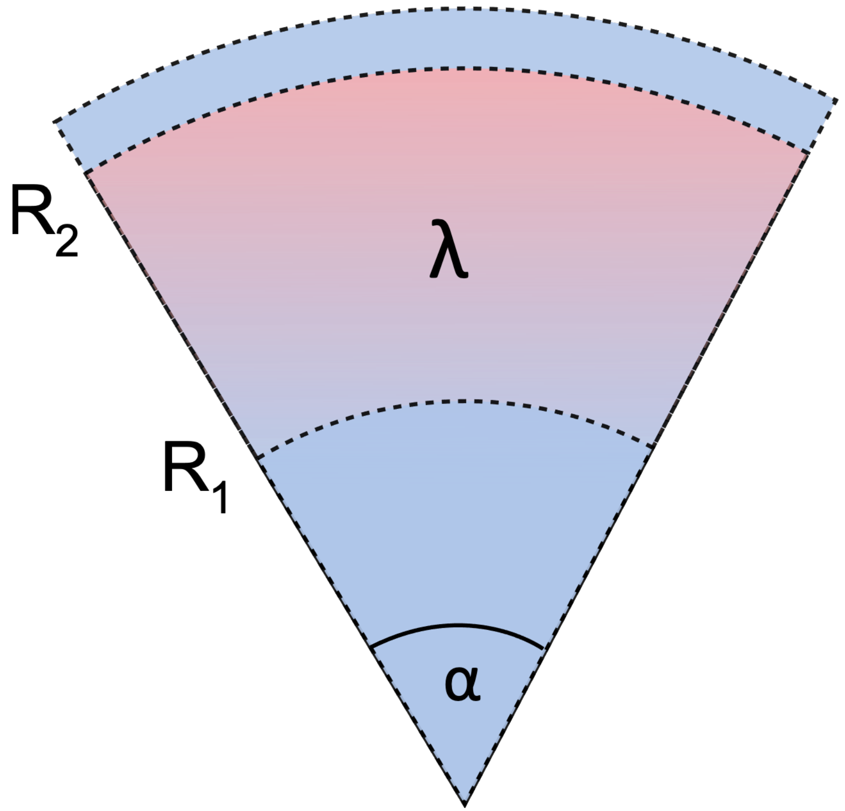
$X_q = -\frac{L_{12}}{L_{11}}X_U$ with $X_U = \Delta(\frac{1}{T}) = -\frac{\Delta T}{T^2}$

$$-\Gamma\Delta T = -\frac{L_{21}L_{12}}{L_{11}}X_U + L_{22}X_U$$

$$\Gamma = \frac{L_{21}L_{12} - L_{22}L_{11}}{L11}\frac{-1}{T^2}$$

$$= \frac{L_{22}L_{11} - L12^2}{L_{11}T^2}$$

Exercise #2 : Heat exchange in a constriction



$$\mathbf{J_U} = -\lambda \vec{\nabla} T = -\lambda \frac{\partial T}{\partial r} \mathbf{u_r}$$

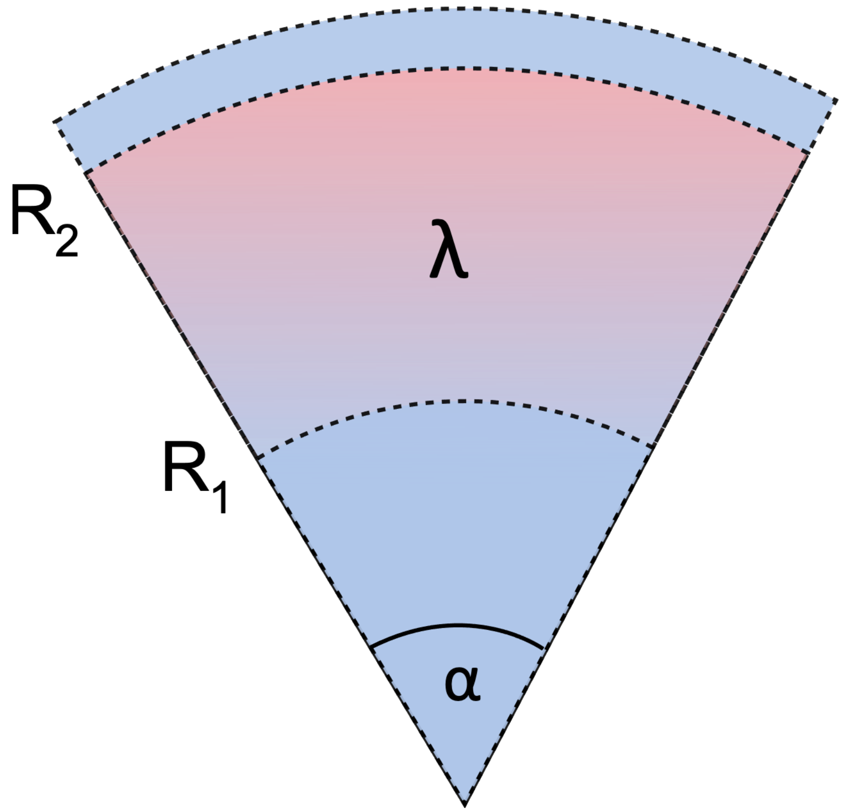
$$\Omega = 2\pi(1 - \cos\alpha)$$

$$\Sigma(r) = \Omega r^2 = 2\pi(1 - \cos\alpha) r^2$$

Radial flux of heat across
« shell portions » defined by Sigma(r)

1) Rate of local volumic entropy creation ? (remember it is affinity x flux)
2) Show that it is proportionnal to $1/r^4$ (use the fact that the flux is constant across Sigma(r))
3) Where do irreversible phenomena occur most in the system ?

Exercise #2 : Heat exchange in a constriction



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1) Rate of local volumic entropy creation ? (remember it is affinity x flux)

$$\frac{\partial s}{\partial t} = \vec{\nabla}\left(\frac{1}{T}\right) \cdot \mathbf{J_U}$$

$$= \frac{\lambda}{T^2} \vec{\nabla} T \cdot \vec{\nabla} T$$

$$= \frac{\lambda}{T^2} \left(\frac{\partial T}{\partial r}\right)^2$$

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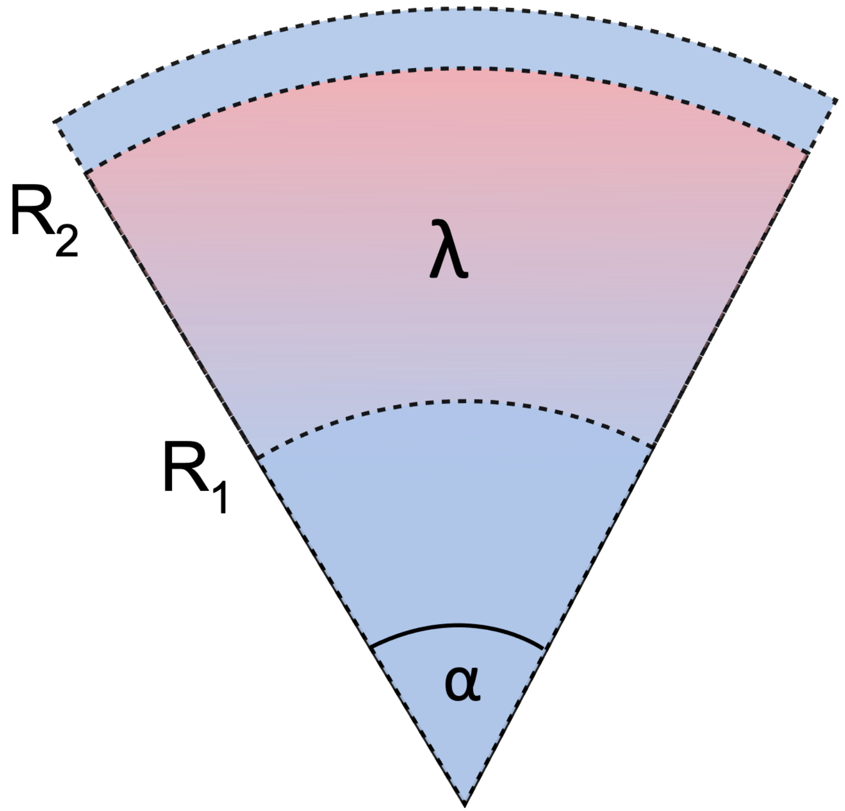

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2) Show that it is proportionnal to $1/r^4$ (use the fact that the flux is constant across Sigma(r))

$$\mathbf{J_u}(r) \cdot \mathbf{\Sigma}(r) = \text{cste}$$

$$-\lambda \frac{\partial T}{\partial r} 2\pi(1 - \cos\alpha) r^2 = \text{cste}$$

$$\frac{\partial T}{\partial r} = \frac{A}{r^2}$$

$$\frac{\partial s}{\partial t} = \frac{\lambda}{T^2} \left(\frac{A}{r^2}\right)^2 \approx \frac{1}{r^4}$$