note: bound only achieved (perfect efficiency) when $\dot{S}_i = 0 \iff$ all currents $J_{nm} = 0$
perfection means $\dot{Q}_1 = \dot{Q}_2 = 0$
$-\dot{W} = 0$
$\Rightarrow$ no power output!!

Carnot efficiency is practically useless, b/c it corresponds to an equilibrium system that does nothing (or equivalently a periodic driven system over an infinite period, driven so slowly it remains always nearly at equilibrium).

For our ratchet-pawl system if
\[ mg \Delta x = \sum E = E_2 - E_1 = E_3 - E_2 \]
and $T_2 \gg T_1 \Rightarrow$ stat. state with $J^s = 0$
mass gets lifted up and $-\dot{W} = P_{out} \gg 0$
at the cost of $\dot{Q}_1 < 0$
heat dissipated into

---

Case 2: $\dot{Q}_2 < 0$ (hot bath absorbs heat)
$\dot{Q}_1 > 0$ (cold bath gets colder)
$\Rightarrow$ a refrigerator!

Define $\dot{Q}_2 = -\frac{T_2}{T_1} (\dot{Q}_1 + T_1 \dot{S}_i) < 0$ (hot bath must get hotter)
plug into $0 = \dot{Q}_1 + \dot{Q}_2 + \dot{W}$ (note $\dot{W} > 0$ since $|\dot{Q}_2| > |\dot{Q}_1|$)
and calculate $\eta_{R} = \frac{\dot{Q}_1}{\dot{W}} = \frac{T_1}{T_2 - T_1} \frac{1}{\dot{W}} \left( -\frac{T_2 \dot{S}_i}{\dot{W}} \right) \leq \frac{T_1}{T_2 - T_1}$
refrigerator coeff. of performance
Since \( T_2 - T_1 \) can be small vs. \( T_1 \),
\[ \eta_R > 1 \Rightarrow \text{you can extract more heat than the work you put in} \]
(transferring disorder b/t reservoirs is easier than changing disorder into "work"
by running the system as an engine).

Of course a refrigerator is equivalent of a heat pump moving heat into \( T_2 \) reservoir:
\[ \eta_H = \frac{-\dot{Q}_2}{\dot{W}} = 1 + \eta_R > \eta_R \]
(heat pumping is more efficient than refrigeration)

Can we get universal relationships for systems actually outputting power,
for example: efficiency of an engine at maximum power?

Answer: Yes, but confined near equilibrium.

Linear (near-equilibrium) thermodynamics

For simplicity, consider time-independent \( W_{nm} \)
(and hence stationary state).

Potential change \( V_{nm} = f \times nm \)
\[ mg \]
power \[ \dot{W} = - \sum_{n,m} J_{n,m}(t) V_{nm} \]

\[ = \dot{f} \sum_{n,m} J_{n,m}(t) \cdot x_{nm} \]

\[ = \dot{f} \cdot x \]

\[ \rightarrow \text{avg. velocity of mass} \]

\( (\dot{x} > 0 \Rightarrow \dot{W} < 0 \text{ sys doer work on environment}) \)

Assume \( \text{In stationary state:} \)

\[ \dot{S} = 0 = \dot{Q}_1 \frac{1}{T_1} + \dot{Q}_2 \frac{1}{T_2} + \dot{S}^i \]

\[ 0 = \dot{E} = \dot{Q}_1 + \dot{Q}_2 + \dot{W} \]

\[ \Rightarrow \dot{S}^i = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \dot{Q}_2 + \frac{\dot{W}}{T_1} \]

Assume small \( f \) and \( T_2 = T + \Delta T \)

\[ T_1 = T \]

\[ \text{where } \Delta T \ll T \]

\[ \Rightarrow \frac{1}{T_1} - \frac{1}{T_2} \approx \frac{\Delta T}{T^2} \]

\[ \Rightarrow \dot{S}^i = \dot{Q}_2 \frac{\Delta T}{T^2} + \left( -\dot{x} \right) \frac{f}{T} \]

If both \( \frac{\Delta T}{T^2} = 0 \) and \( \frac{f}{T} = 0 \) \( \Rightarrow \) no currents

\[ \dot{S}^i = 0 \text{ and } \dot{Q}_2 = 0, \dot{x} = 0 \]

If either or both are nonzero \( \Rightarrow \) currents and \( \dot{S}^i > 0 \)

\[ \dot{Q}_2 \neq 0, \dot{x} \neq 0 \]

In the small \( \frac{\Delta T}{T^2} \), small \( \frac{f}{T} \)

regime, we can define;
\[ \dot{S}^i = \dot{I}_H \phi_H + \dot{I}_M \phi_M \equiv \dot{S}^i (\phi_H, \phi_M) \]

\[ \phi_H = \frac{\Delta T}{T^2} \quad \dot{I}_H = \dot{Q}_2 \text{ "heat flux" from hot reservoir} \]

\[ \phi_M = \frac{f}{T} \quad \dot{I}_M = -\dot{x} \]

\[ \dot{I}_M = \dot{I}_M (\phi_H, \phi_M) \text{ "mass flux" due to moving mass} \]

\[ \text{"thermodynamic forces" in the literature} \]

\[ \text{called "thermo fluxes"} \]

In the small \( \phi_H, \phi_M \) limit, Taylor expansion implies:

\[ \dot{I}_H \approx \frac{\partial \dot{S}^i (\phi_H, \phi_M)}{\partial \phi_H} |_{\phi_H=\phi_M=0} \]

\[ \dot{I}_M \approx \frac{\partial \dot{S}^i (\phi_H, \phi_M)}{\partial \phi_M} |_{\phi_H=\phi_M=0} \]

\[ \text{note: } \dot{S}^i (0,0) = 0 \]

We know that \( \dot{I}_H \) and \( \dot{I}_M \) are zero when \( \phi_H = \phi_M = 0 \), hence Taylor expanding we can define \textbf{Onsager coefficient}:

\[ \dot{I}_H \approx L_{HH} \phi_H + L_{HM} \phi_M \]

\[ \dot{I}_M \approx L_{MH} \phi_H + L_{MM} \phi_M \]

\[ \text{there are transport coefficients relating fluxes to forces:} \]

\[ \text{i.e., } L_{HH} \Rightarrow \dot{Q}_2 = L_{HH} \left( \frac{\Delta T}{T^2} \right) \text{ when } f = 0 \]

\[ \text{Fourier's law } \quad L_{HH} \sim k T^2 \text{ where } k = \text{thermal conductivity} \]
\[
\dot{\mathbf{x}} = L_{MM} \frac{f}{T} \quad \text{when } \Delta T = 0
\]

\[
\begin{align*}
L_{MM} \sim \mu T & \quad \text{where } \mu = \text{mobility} = \frac{1}{\text{drag friction}} \\
\sim \frac{D}{K_0} & \quad \text{where } D = \text{diffusivity}
\end{align*}
\]

Plug into \( \dot{S}^i \) equation \( \Rightarrow \)

\[
\dot{S}^i = L_{HH} \phi_H^2 + L_{HM} \phi_H \phi_M + L_{MH} \phi_M \phi_H + L_{MM} \phi_M^2
\]

\[
\begin{align*}
\frac{1}{2} \frac{\partial^2 S^i}{\partial \phi_H^2} & + \frac{1}{2} \frac{\partial^2 S^i}{\partial \phi_M \partial \phi_H} & + \frac{1}{2} \frac{\partial^2 S^i}{\partial \phi_H \partial \phi_M} & + \frac{1}{2} \frac{\partial^2 S^i}{\partial \phi_M^2}
\end{align*}
\]

By symmetry of second derivatives (assuming \( \dot{S}^i \) is well behaved):

\[
L_{HM} = L_{MH}
\]

Onsager reciprocal relations \( (1931) \) [Nobel prize in chemistry in 1968]

Example: set \( \Delta T = 0 \), apply small \( f \):

\[
\dot{Q}_2 \approx L_{HM} \left( \frac{f}{T} \right)
\]

\( \uparrow \)

heat dumped into reservoir 2

Small \( \Delta T \), limit of vanishing \( f \):

\[
\dot{\mathbf{x}} \approx L_{MH} \left( \frac{\Delta T}{T^2} \right)
\]

\[
\begin{align*}
\{ \text{Constants of proportionality are same in both cases:} \\
\text{non-trivial!} \}
\end{align*}
\]

Let us do a more careful derivation of reciprocity to see the physical principles underlying the \( L_{ij} \).
\[
\dot{S}_i = \frac{\Delta T}{T^2} \dot{Q}_2 + \frac{f}{T} (-\dot{x})
\]

\[
\dot{Q}_2 = \sum_{(n,m)} J^{(2)}_{nm} (E_n - E_m - f x_{nm})
\]

\[
-\dot{x} = - \sum_{(n,m)} J^{(1)}_{nm} x_{nm} - \sum_{(n,m)} J^{(2)}_{nm} x_{nm}
\]

Compare to:

\[
\dot{S}_i = k_B \sum_{(n,m)} J^{(1)}_{nm} \ln \frac{W(C)_{nm}^{(1)} P_m^s}{W(C)_{nm} P_m^s} + k_B \sum_{(n,m)} J^{(2)}_{nm} \ln \frac{W(C)_{nm}^{(2)} P_m^s}{W(C)_{nm} P_m^s}
\]

Expand \( W_{nm} P_m^s = W_{nm}^{eq} P_m^{eq} \)

\[
W_{nm}^{eq} P_m^{eq} = W_{nm}^{eq} P_m^{eq} \left( 1 + C_n^{(j)} \frac{\Delta T}{T^2} + d_n^{(j)} \frac{f}{T} \right)
\]

Then:

\[
J^{(j)}_{nm} = W_{nm}^{eq} P_m^{eq} \left( C_{nm}^{(j)} \frac{\Delta T}{T^2} + d_{nm}^{(j)} \frac{f}{T} \right)
\]

where \( C_{nm}^{(j)} \equiv C_n^{(j)} - C_m^{(j)} \)

and we have used \( W_{nm}^{eq} P_m^{eq} = W_{mn}^{eq} P_n^{eq} \)

Similarly:

\[
\ln \frac{W(C)_{nm}^{(j)} P_m^s}{W(C)_{nm} P_m^s} \approx C_{nm}^{(j)} \frac{\Delta T}{T^2} + d_{nm}^{(j)} \frac{f}{T}
\]

Using the comparison + matching coefficients, then 2nd order, we find:

\[
C_{nm}^{(2)} = \frac{E_n - E_m}{k_B}
\]

\[
C_{nm}^{(1)} = 0
\]

\[
d_{nm}^{(2)} = -\frac{x_{nm}^{(2)}}{k_B}
\]

\[
d_{nm}^{(1)} = -\frac{x_{nm}^{(1)}}{k_B}
\]
Now plug into $Q_2$ and $-\bar{\xi}$ expressions to read off $Li_j$:

$$L_{HH} = \left. \frac{\partial Q_2}{\partial \phi_H} \right|_{\phi_H=0, \phi_m=0} = \sum_{(n,m)} \frac{C^{(2)}_{nm}(E_n-E_m)}{\Delta E} W_{nm}^e p_m^e$$

$$= k_b^{-1} \sum_{(n,m)} (E_n-E_m)^2 W_{nm}^e p_m^e$$

↑

note: this depends on fluctuations in equilibrium state: a manifestation of the fluctuation-dissipation relationship relating $\dot{S}i$ to equilibrium fluctuations thru $Li_j$

$$L_{HM} = \left. \frac{\partial Q_2}{\partial \phi_M} \right|_0 = \sum_{(n,m)} d^{(2)}_{nm}(E_n-E_m) W_{nm}^e p_m^e$$

$$= -k_b^{-1} \sum_{(n,m)} X_{nm}(E_n-E_m) W_{nm}^e p_m^e$$

$$L_{MH} = \left. \frac{\partial (-\bar{\xi})}{\partial \phi_H} \right|_0 = -k_b^{-1} \sum_{(n,m)} C^{(2)}_{nm} W_{nm}^e p_m^e$$

$$= -k_b^{-1} \sum_{(n,m)} (E_n-E_m) W_{nm}^e p_m^e$$

$$L_{MM} = \left. \frac{\partial (-\bar{\xi})}{\partial \phi_M} \right|_0 = k_b^{-1} \sum_{(n,m)} [X_{nm}^{(1)}]^2 W_{nm}^e p_m^e$$

$$+ k_b^{-1} \sum_{(n,m)} [X_{nm}^{(2)}]^2 W_{nm}^e p_m^e$$