Putting the dynamics back in thermodynamics

Let us consider a system with states \( n \) in an environment at temp. \( T \). How do the quantities defined so far, \( S(t) \) and \( E(t) \), vary with time?

\[
\bar{E} = \sum_n p_n(t) E_n
\]

\[
\dot{\bar{E}}(t) = \sum_n \dot{p}_n(t) E_n
\]

Master equation

\[
\dot{p}_n(t) = \sum_m \left[ W_{nm} p_m(t) - W_{mn} p_n(t) \right]
\]

\[
\Rightarrow \dot{\bar{E}}(t) = \sum_{n,m} J_{nm}(t) E_n
\]

\[
= \sum_n \sum_{m \neq n} J_{nm}(t) E_n \quad \text{since } J_{nn}(t) = 0 \text{ by definition}
\]

\[
= \sum_{(n,m)} J_{nm}(t) \left[ E_n - E_m \right]
\]

where \( \sum_{(n,m)} \equiv \sum_n \sum_{m \neq n} \) = sum over all distinct pairs \( (n,m) \) irrespective of ordering, i.e. \( (1,2) \) is the same pair as \( (2,1) \).

Note nice physical interpretation:

\[
\dot{\bar{E}}(t) = \sum_{(n,m)} J_{nm}(t) \left[ E_n - E_m \right] = \text{"energy flow" from env. to sys.}
\]

\[
\text{change in energy of system from } m \text{ to } n \text{ going from } m \text{ to } n
\]
Since \( E_{tot} = E_m + E_q = \text{constant} \)
\[ \downarrow \]
\[ \text{system} \]
\[ \text{+ environ.} \]
\[ \downarrow \]
\[ \text{energy} \]
\[ \text{energy} \]

\[ m \rightarrow n \]
\[ \text{transition} \]
\[ \text{in system} \]

\[ E_{tot} = E_n + E_q' \]
\[ E_q' = E_{tot} - E_n \]

Hence \( E_n - E_m = -(E_q' - E_q) \) \{ energy flow into system \}
\[ \text{flow out of environment} \]

So \( \dot{E}(t) = -\dot{E}_{env}(t) \)

simple example: three-state system

\[ J_{21} \quad 2 \quad J_{32} \quad 3 \]
\[ J_{31} \quad 1 \quad J_{13} \]

Since all \( E_n \) are different here, every transition involves some exchange of energy w/ environment, i.e. \( 1 \rightarrow 2 \) has rate \( W_{21} \)
+ requires absorbing \( \Delta E = E_2 - E_1 \)
energy from environment
\[ 2 \rightarrow 1 \] dumps that \( \Delta E \) back into environment

Stationary state: constantly transitioning, absorbing + releasing energy, but average gain = average loss + hence
\[ \dot{E}(t) = 0 \]
We can also see this in the current picture:

\[
\dot{E}(t) = J_{21} (E_2 - E_1) + J_{32} (E_3 - E_2) + J_{13} (E_1 - E_3)
\]

\[
= (-J_{21} + J_{13}) E_1 + (J_{21} + J_{32}) E_2 + (J_{32} - J_{13}) E_3
\]

\[
= (J_{12} + J_{13}) E_1 + (J_{21} + J_{23}) E_2 + (J_{31} + J_{32}) E_3
\]

In stat. state, current is conserved at each node:

\[
\frac{dp_n}{dt} = \sum_{m \neq n} J_{nm}(t) \Rightarrow 0 = \sum_{m \neq n} J_{nm}^s
\]

(Kirchoff's law)

\[\Rightarrow\] hence \(\dot{E}(t) = 0\)

Note: nothing here has ruled out the possibility that \(J_{nm}^s\) is nonzero (so far).

For example \(J_{12}^s = J_{32}^s = J_{13}^s > 0\) satisfies \(\dot{E} = 0\).

---

Important question: can a system in an weakly coupled to an environment at temp. \(T\) (w/ only exchange of energy) have a nonzero current in its canonical stationary state?

\{ important case: 2-state system \}

\[
\begin{array}{c}
1 \\
W_{12} \\
\downarrow \\
J_{21} \\
\end{array} \quad \begin{array}{c}
2 \\
W_{12} \\
\downarrow \\
J_{21} \\
\end{array}
\]

here only one current \(\Rightarrow\) at \(t \to \infty\)

\[
J_{21}^s = W_{21}^s P_1^s - W_{12}^s P_2^s = 0
\]

hence in a 2-state system any \(p^s\) is always an equilibrium state.
so system must satisfy detailed balance, i.e.

\[ W_{21} \frac{e^{-\beta E_1}}{Z} = W_{12} \frac{e^{-\beta E_2}}{Z} \]

\[ \Rightarrow \frac{W_{21}}{W_{12}} = e^{-\beta (E_2 - E_1)} \]

this ratio depends on energy difference & temperature

\[ \text{ratio applies to } \frac{W_{21}}{W_{12}} \text{ at all times} \]

(since W matrix time-indep.), even when \( p_n(t) \neq p_n^s \) at \( +\infty \), and \( J_{21}(t) \neq 0 \).

But what about a system with > 2 states (i.e. our 3-state cycle)?

note: for systems with no cycles the solution is easy:

\[ J_{21} = J_{32} + J_{42} \]

\[ J_{32} = J_{42} = 0 \]

any "leaf" node in the tree must have zero current b/c only one current enters node

Any linear or tree-like network only has equilibrium stationary states, (assuming it is strongly connected).

The case w/ cycles is more interesting.