Proving the second law of thermodynamics

How do we show $P_n(t) \to P_n^{eq}$ as $t \to \infty$ for arbitrary system?

Let us start by defining a joint probability for a time interval $t$ to $t+\delta t$:

$P_{mn}(t) = \text{prob. of being in state } n \text{ at time } t$ and then of being in state $m$ at time $t+\delta t$

Note, by definition:

$\sum_n P_n(t) = P_n(t)$

$\sum_m P_{mn}(t) = P_m(t+\delta t)$

$\sum_{m,n} P_{mn}(t) = 1$
Given transition matrix $\Omega$

$$p_{mn}(t) = \begin{cases} 
\Omega_{mn} \delta t \cdot p_n(t) & \text{if } m \neq n \\
(1 + \Omega_{nn} \delta t) p_n(t) & \text{if } m = n 
\end{cases}$$

$$= 1 - \sum_{n' \neq n} \Omega_{n'n} \delta t$$

= prob. of being in $n$ at time $t$

Define an "irreversibility" measure for the transition $n \rightarrow m$ between time $t$ and $t + \delta t$:

$$I_{mn}(t) \equiv \ln \frac{p_{mn}(t)}{p_{nm}(t+\delta t)}$$

denominator is the prob. that transition will be reversed in the next time step $t + \delta t \rightarrow t + 2\delta t$

$\Rightarrow$ could be positive or negative

If $p_{mn}(t) \gg p_{nm}(t+\delta t)$

immediate reversal very unlikely $\Rightarrow I_{mn}(t) \gg 0$

$I_{mn}(t) = \infty$ would be truly irreversible (physically not possible)
What can we say about $I_{mn}(t)$ in general?
(not necessarily in equilibrium)

Define average over all transition pairs $m, n$:

$$
\langle I \rangle_t \equiv \langle I(t) \rangle = \sum_{m,n} P_{mn}(t) I_{mn}(t)
$$

= average irreversibility of system at time $t$
Mathematical identity:
\[
< e^{-I} >_t = \sum_{m,n} p_{m,n}(t) e^{-I_{m,n}(t)}
\]

Called "non-equilibrium partition identity"

Can actually be measured and verified in single molecule pulling experiment

But we can also write:
\[
< e^{-I} >_t = e^{-<I>_t} \sum_{m,n} p_{m,n}(t) \frac{<I>_t - I_{m,n}(t)}{1 + ( <I>_t - I_{m,n}(t) )}
\]

\[
\Rightarrow < e^{-I} >_t \geq e^{-<I>_t} \sum_{m,n} p_{m,n}(t) \left[ 1 + <I>_t - <I>_t \right]
\]

\[
= e^{-<I>_t} \left( 1 + <I>_t - <I>_t \right)
\]

\[
= e^{-<I>_t}
\]

\[
1 = < e^{-I} >_t \geq e^{-<I>_t}
\]

Hence \[
< e^{-I} >_t \geq e^{-<I>_t}
\]

Jensen's inequality

Take ln of both sides:

\[
0 \geq -<I>_t
\]

\[
\Rightarrow <I>_t \geq 0
\]

Mean irreversibility always greater or equal to zero at all times.

On average, system likes to make transitions with irrev \geq 0
When $I_{mn}(t) = 0$ for all $m, n$ and $\langle I(t) \rangle = 0$ we see the system is undergoing reversible transitions (i.e. any transition has equal prob. of being reversed).

When $\langle I(t) \rangle > 0$ we say the transitions are on average irreversible (bad terminology, since the microscopic processes are not actually irreversible, just have smaller prob. of being reversed, on average).

So far we have not used the information in the DB condition. Let us now decompose $\langle I(t) \rangle$:

$$\langle I(t) \rangle = \sum_{n,m} P_{mn}(t) I_{mn}(t)$$

$$= \sum_{n,m} P_{mn}(t) \ln \left\{ \begin{array}{ll} \frac{\Omega_{mn} \delta t}{\Omega_{nm} \delta t} \frac{p_n(t)}{p_m(t+\delta t)} & \text{if } m \neq n \\ \frac{(1+\Omega_{nn} \delta t)}{(1+\Omega_{nn} \delta t)} \frac{p_n(t)}{P_m(t+\delta t)} & \text{if } m = n \end{array} \right\}$$

$$= \sum_{m,n} P_{mn}(t) \ln \frac{p_n(t)}{p_m(t+\delta t)} + \sum_{m,n} P_{mn}(t) \ln \frac{\Omega_{mn}}{\Omega_{nm}}$$

term 1

term 2 (needs DB to simplify!)