Simple proof of the second law of thermodynamics that uses the Kullback-Leibler divergence.

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Consider an isolated thermodynamic system with a random discrete energy variable E. The first law of thermodynamics states that the internal energy $U = \langle E \rangle = \sum_i p_i E_i$ is constant in an isolated system. The system may start in a nonequilibrium state, but it approaches an equilibrium state $p_i = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$. We consider the set of discrete energy levels $\mathcal{E} \ni E_i$ not to change in time, and the temperature of the system to be a constant $\beta = k_B T$.

p_{now} is our model of the system's energy now, and p_{eq} is the unique marginal of $\mathcal{E}$'s equilibrium; p_{eq} is "the heat death of the universe." $\beta = 1/k_B T$ is inverse temperature, or coldness. p_{now} is compared against p_{eq} with the Kullback-Leibler divergence (KLD). p_{now} can be any marginal over $\mathcal{E}$, 1. Define KLD:

$$D[p_{\text{now}} \| p_{\text{eq}}] = \sum_{i=1}^{N} p_{\text{now}}(E_i) \ln \left(\frac{p_{\text{now}}(E_i)}{p_{\text{eq}}(E_i)} \right) = \sum_{i=1}^{N} p_{\text{now}}(E_i) \ln p_{\text{now}}(E_i) - \sum_{i=1}^{N} p_{\text{now}}(E_i) \ln p_{\text{eq}}(E_i)$$

2. Expand and add a special zero

$$\begin{aligned} D[p_{\text{now}} \| p_{\text{eq}}] = &\sum_{i=1}^{N} p_{\text{now}}(E_i) \ln p_{\text{now}}(E_i) - \sum_{i=1}^{N} p_{\text{now}}(E_i) \ln p_{\text{eq}}(E_i) \\ &+ \left(\sum_{i=1}^{N} p_{\text{eq}}(E_i) \ln p_{\text{eq}}(E_i) - \sum_{i=1}^{N} p_{\text{eq}}(E_i) \ln p_{\text{eq}}(E_i) \right) \end{aligned}$$

3. Convert to macroscopic variables with $\frac{1}{k_B} S = -\sum_{i=1}^{N} p_i \ln p_i$

$$\begin{aligned} D[p_{\text{now}} \| p_{\text{eq}}] &= \frac{1}{k_B} \Delta S - \sum_{i=1}^{N} p_{\text{now}}(E_i) \ln p_{\text{eq}}(E_i) \\ &+ \sum_{i=1}^{N} p_{\text{eq}}(E_i) \ln p_{\text{eq}}(E_i) \\ &= \frac{1}{k_B} \Delta S + \sum_{i=1}^{N} [p_{\text{eq}}(E_i) - p_{\text{now}}(E_i)] \ln p_{\text{eq}}(E_i) \end{aligned}$$

4. Plug in the "heat death" partition function: $p_{\text{eq}}(E_i) = \frac{e^{-\beta E_i}}{\sum_{j=1}^{N} e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Z}$,

$$
\begin{aligned}
D[p_{\text{now}} \| p_{\text{eq}}] &= \frac{1}{k_B}\Delta S + \sum_{i=1}^{N}[p_{\text{eq}}(E_i) - p_{\text{now}}(E_i)] \ln\left(\frac{e^{-\beta E_i}}{\sum_{j=1}^{N} e^{-\beta E_j}}\right) \\
&= \frac{1}{k_B}\Delta S + \sum_{i=1}^{N}[p_{\text{now}}(E_i) - p_{\text{eq}}(E_i)] \cdot [\beta E_i] + \sum_{i=1}^{N}[p_{\text{now}}(E_i) - p_{\text{eq}}(E_i)] \ln Z
\end{aligned}
$$

5. Notice that

   $$\sum_{i=1}^{N}[p_{\text{now}}(E_i) - p_{\text{eq}}(E_i)] \ln Z = \ln Z[\sum_{i=1}^{N} p_{\text{now}}(E_i) - \sum_{i=1}^{N} p_{\text{eq}}(E_i)] = \ln Z - \ln Z = 0$$

   So,

   $$D[p_{\text{now}} \| p_{\text{eq}}] = \frac{1}{k_B}\Delta S + \sum_{i=1}^{N}[p_{\text{now}}(E_i) - p_{\text{eq}}(E_i)] \cdot [\beta E_i]$$

6. The following step gives a difference in the expectation values of energy if and only if every E_i is the same in p_{eq} and p_{now}; the energy levels did not change, but only their probabilities changed.

   $$
   \begin{aligned}
   D[p_{\text{now}} \| p_{\text{eq}}] &= \frac{1}{k_B}\Delta S + \sum_{i=1}^{N} p_{\text{now}}(E_i)\beta E_i - \sum_{i=1}^{N} p_{\text{eq}}(E_i)\beta E_i \\
   &= \frac{1}{k_B}\Delta S - \beta\Delta\langle E\rangle
   \end{aligned}
   $$

7. Internal energy $U = \langle E\rangle$ is a constant,

   $$k_B D[p_{\text{now}} \| p_{\text{eq}}] = \Delta S,$$

8. KLD is non-negative, so

   $$\Delta S \geq 0$$

QED, that is the second law of thermodynamics. **The entropy of an isolated thermodynamic system can only increase or stay the same, but never decrease!**