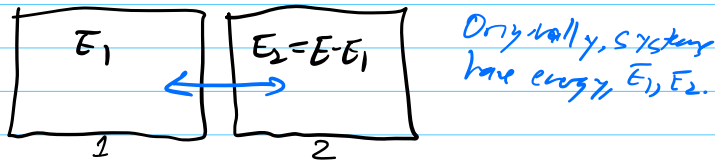


The Laws of Thermodynamics

0th Law: Bring together two previously isolated systems and allow them to exchange energy, but not work.

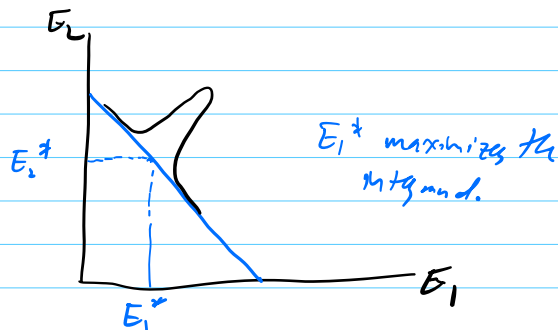


Joint system: Microstates $\mu = \mu_1 \otimes \mu_2$

Hamiltonian $\mathcal{H}(\mu) = \mathcal{H}(\mu_1) + \mathcal{H}(\mu_2)$
(assume only small interactions between the two systems)

$$\mathbb{P}_E(\mu_1 \otimes \mu_2) = \frac{1}{\Omega(E)} \begin{cases} 1 & \text{for } \mathcal{H}_1(\mu_1) + \mathcal{H}_2(\mu_2) = E \\ 0 & \text{otherwise} \end{cases}$$

$$\begin{aligned} \Omega(E) &= \int dE_1 \Omega_1(E_1) \Omega_2(E - E_1) \\ &= \int dE_1 \exp \left[\frac{S_1(E_1) + S_2(E - E_1)}{k_B} \right] \end{aligned}$$



$S_1(E_1)$ and $S_2(E_2)$ are $\mathcal{O}(N)$, so
as $N \rightarrow \infty$ we can use the saddle point
method to evaluate the integral.

→ Replace $S_1(E_1)$ by $S_1(E_1^*)$
 $S_2(E-E_1) \approx S_2(E_2^*) = S_2(E-E_1^*)$

$$S(E) = k_B \ln \Omega(E) \approx S_1(E_1^*) + S_2(E_2^*)$$

$$\text{At maximum } \frac{\partial S}{\partial E_1} = \left. \frac{\partial S_1}{\partial E_1} \right|_{x_1} - \left. \frac{\partial S_2}{\partial E_1} \right|_{x_2} = 0$$

$$\rightarrow \left. \frac{\partial S_1}{\partial E_1} \right|_{x_1} = \left. \frac{\partial S_2}{\partial E_1} \right|_{x_2}, \text{ or}$$

$$\frac{1}{T_1} = \frac{1}{T_2}$$

Hence, $\frac{\partial S}{\partial E} = \frac{1}{T}$ plays the role of

an empirical temperature.

1st Law: Suppose we allow the thermodynamic coordinates \vec{x} to change reversibly

$$\vec{x} \rightarrow \vec{x} + \delta\vec{x}$$

$$\text{Work done on system: } \delta W = \vec{J} \cdot \delta\vec{x}$$

$$E \rightarrow E + \vec{J} \cdot \delta\vec{x}$$

Change in entropy:

$$\delta S = S(E + \vec{J} \cdot \delta\vec{x}, \vec{x} + \delta\vec{x}) - S(E, \vec{x})$$

$$= \left(\frac{\partial S}{\partial E} \Big|_{\vec{x}} \vec{J} + \frac{\partial S}{\partial \vec{x}} \Big|_E \right) \cdot \delta\vec{x}$$

$$= \left(\frac{1}{T} \vec{J} + \frac{\partial S}{\partial \vec{x}} \Big|_E \right) \cdot \delta\vec{x}$$

$$\text{Reversible} \rightarrow \delta S = 0$$

$$\rightarrow \frac{\partial S}{\partial x_i} \Big|_{E, x_{j \neq i}} = - \frac{J_i}{T}$$

$$\Rightarrow dS(E, \vec{x}) = \frac{\partial S}{\partial E} \Big|_{\vec{x}} dE + \frac{\partial S}{\partial \vec{x}} \Big|_E \cdot d\vec{x}$$

$$= \frac{1}{T} dE - \frac{1}{T} \vec{J} \cdot d\vec{x}$$

$$\Rightarrow \boxed{dE = T dS + \vec{J} \cdot d\vec{x}} \rightarrow \begin{array}{l} \delta Q = T dS \\ \text{heat} \end{array}$$

2nd Law: Due to large N , it is

exponentially unlikely to find the combined system w/ energies different from E_1^* , E_2^* that maximize $S(E)$.

There are more states accessible in this combined system than any starting configuration:

$$\Omega_1(E_1^*, \vec{x}_1) \Omega_2(E_2^*, \vec{x}_2) \geq \Omega_1(E_1, \vec{x}_1) \Omega_2(E_2, \vec{x}_2)$$

$$\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geq 0$$

$$\delta S \geq 0$$

When two systems are brought together,

$$\delta S = \left(\left. \frac{\partial S_1}{\partial E_1} \right|_{\vec{x}_1} - \left. \frac{\partial S_2}{\partial E_2} \right|_{\vec{x}_2} \right) \delta E_1$$

$$\geq \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1 \geq 0$$

→ Heat energy flows from the hotter to the colder body. (c.f. Clausius)

(If $T_2 > T_1$, then $\delta E_1 > 0$, $\delta E_2 < 0$)

Two-Level Systems

Imagine that each particle can be in one of two states, with energies 0 and $E > 0$.

Microstates μ are specified by occupation numbers

$n_i = 0$ or 1 if the i th particle is in its ground state or first excited state.

$$\text{Energy: } H(\{n_i\}) = E \sum_{i=1}^N n_i = E N_1$$

Microcanonical ensemble?

$$P(\{n_i\}) = \frac{1}{\Omega(E, N)} \cdot \begin{cases} 1 & \text{if } E \sum n_i = E \\ 0 & \text{otherwise} \end{cases}$$

$$N_1 = \frac{E}{E} = \# \text{ excited impurities}$$

$\Omega = \#$ ways of choosing N_1 from N

$$\Omega(E, N) = \frac{N!}{N_1! (N - N_1)!}$$

$$S(E, N) = k_B \ln \Omega(E, N) = k_B \ln \frac{N!}{N_1! (N - N_1)!}$$

With $N_1, N \gg 1$, using Stirling's formula,
 $S(E, N) \approx -N k_B \left(\frac{N_1}{N} \ln \frac{N_1}{N} + \frac{(N-N_1)}{N} \ln \frac{(N-N_1)}{N} \right)$

$$S(E, N) = -N k_B \left(\frac{E}{N\epsilon} \ln \left(\frac{E}{N\epsilon} \right) + \left(1 - \frac{E}{N\epsilon} \right) \ln \left(1 - \frac{E}{N\epsilon} \right) \right)$$

Equilibrium temperature:

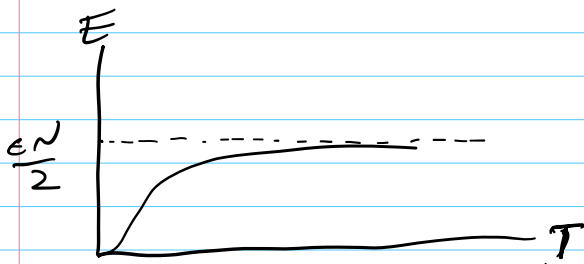
$$\frac{1}{T} = \frac{\partial S}{\partial E} \Big|_N = -\frac{k_B}{\epsilon} \ln \left(\frac{E}{N\epsilon - E} \right)$$

$$\Rightarrow \exp \left(\frac{E}{k_B T} \right) = \frac{N\epsilon}{E} - 1$$

$$E(T) = \frac{N\epsilon}{\exp \left(\frac{E}{k_B T} \right) + 1}$$

$$\text{Min } E = 0 \quad \text{for } T \rightarrow 0$$

$$\text{Max } E = \frac{N\epsilon}{2} \quad \text{for } T \rightarrow \infty$$



What if E starts at $E > \frac{EN}{2}$?

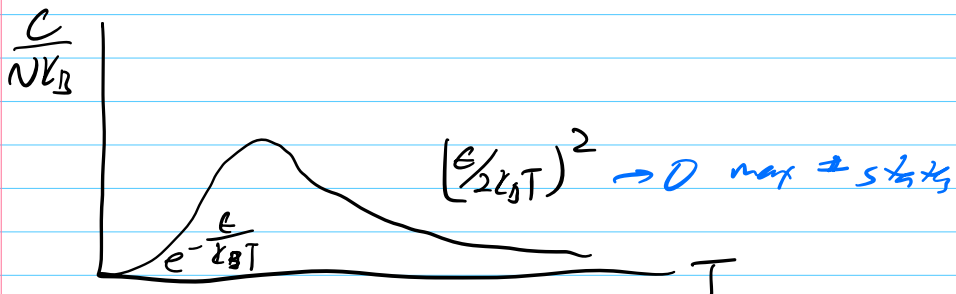
$$\text{Then } T = \frac{E}{k_B} \frac{1}{\ln\left(\frac{NE-E}{E}\right)} < 0$$

The reason is that at high energy, the number of available microstates decreases with increasing energy.

When brought into contact with a positive-temperature environment, the system comes to equilibrium at lower energy, w/ positive T .

Heat Capacity:

$$C = \frac{dE}{dT} = N k_B \left(\frac{E}{k_B T}\right)^2 \exp\left(\frac{E}{k_B T}\right) \left[\exp\left(\frac{E}{k_B T}\right) + 1\right]^{-2}$$



$\left(\frac{E}{2k_B T}\right)^2 \rightarrow 0$ max # states
 $e^{-\frac{E}{k_B T}}$
 energy gap bet. ground state and excited states.

Unconditional probability for finding a particular particle in its excited state:

$$P(n_1) = \sum_{\{n_2, \dots, n_N\}} P(\{n_i\}) = \frac{\Omega(E - n_1 \epsilon, N - 1)}{\Omega(E, N)}$$

$$\begin{aligned} P(n_1=0) &= \frac{\Omega(E, N-1)}{\Omega(E, N)} = \frac{(N-1)!}{N_1! (N-N_1-1)!} \cdot \frac{N_1! (N-N_1)!}{N!} \\ &= \frac{N-N_1}{N} = 1 - \frac{N_1}{N} \end{aligned}$$

Using $N_1 = E/\epsilon$,

$$P(n_1=0) = 1 - \frac{E}{N\epsilon}$$

Using $E(T) = \frac{N\epsilon}{e^{\epsilon/k_B T} + 1}$,

$$P(n_1=0, T) = \frac{1}{1 + \exp\left(-\frac{\epsilon}{k_B T}\right)}$$

$$P(n_1=1, T) = 1 - P(n_1=0, T)$$

$$P(n_1=1, T) = \frac{\exp\left(-\epsilon/k_B T\right)}{1 + \exp\left(-\epsilon/k_B T\right)}$$