We consider a single particle in a two-state system whose energy levels are separated by ε. We compute the basic thermodynamic properties of this system.

(Source: Undergraduate stat mech course)

We first compute $\langle E \rangle$.

Without loss of generality, suppose the first energy level has $E=0$. Then, the partition function for this system is given by

$$Z = 1 + e^{-\beta\varepsilon} \implies \langle E \rangle = -\frac{\partial}{\partial\beta} \log Z$$

$$= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \boxed{\frac{\varepsilon}{1+e^{\beta\varepsilon}}}$$

In the limit $T \to \infty$ $(\beta \to 0)$, we expect

$$\langle E \rangle \to \varepsilon/2,$$

so the particle will not favor one state over the other.

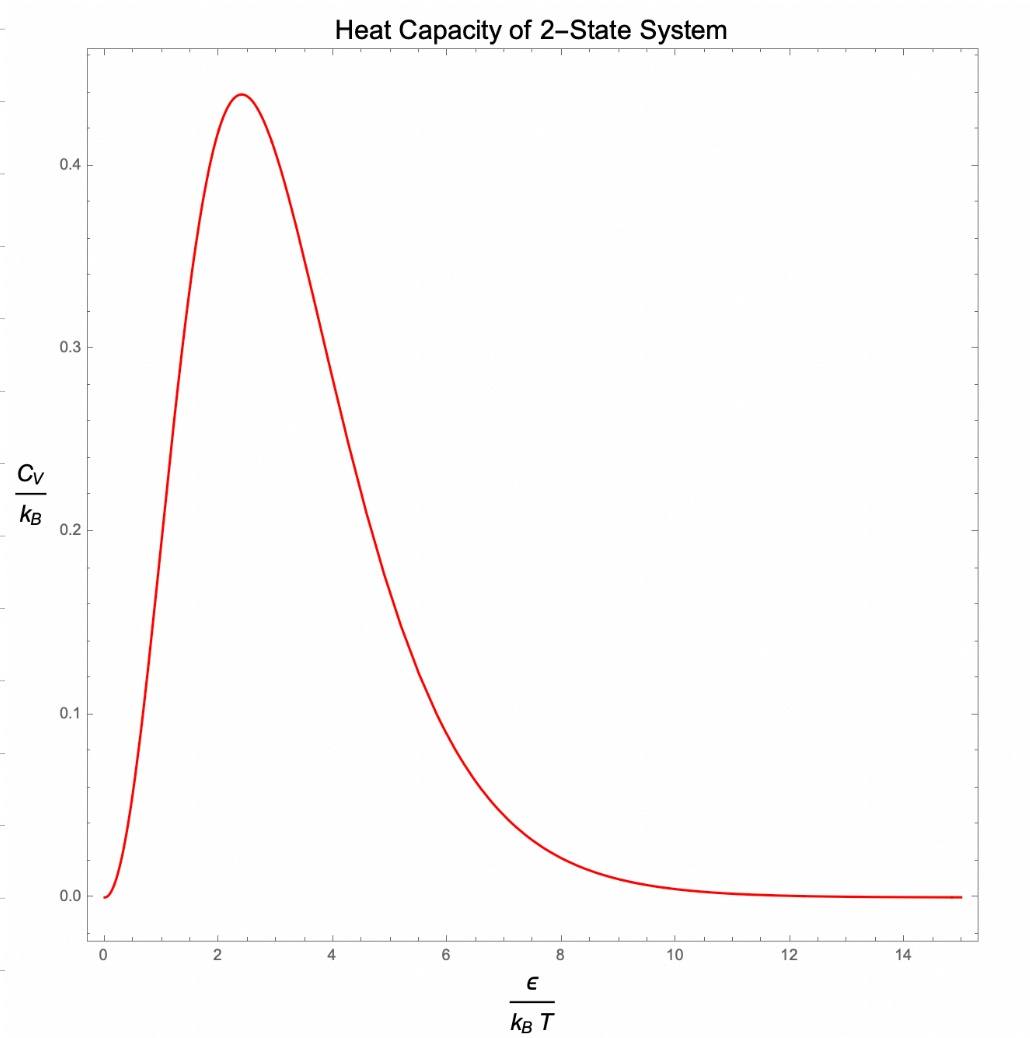
From the internal energy, we can compute the heat capacity:

$$C = \frac{\partial \langle E \rangle}{\partial T}$$

$$= -\varepsilon\left(1+e^{\varepsilon/k_BT}\right)^{-2}\cdot e^{\varepsilon/k_BT}\cdot\frac{\varepsilon}{k_B}\cdot\frac{-1}{T^2}$$

$$= \frac{\varepsilon^2}{k_B^2T^2}\cdot k_B\,\frac{e^{\varepsilon/k_BT}}{\left(1+e^{\varepsilon/k_BT}\right)^2}\cdot\frac{e^{-\varepsilon/k_BT}}{e^{-\varepsilon/k_BT}} =$$

$$\boxed{k_B\left(\frac{\varepsilon}{k_BT}\right)^2\cdot\frac{1}{4\cosh^2 \varepsilon/2k_BT}}$$



The peak in this plot, originally labeled the Schottky Anomaly, arises from the fact that the energy will only change significantly near state transition point, and not elsewhere.

The entropy of the system can subsequently be computed using

$$T = \frac{\partial\langle E\rangle}{\partial S} \Longrightarrow S(T) = \int \frac{d\langle E\rangle}{T} = \int_0^{T} \frac{C_V(\tilde{T})}{\tilde{T}}\, d\tilde{T}$$

$$S(T) = \int_0^T \frac{k_B}{T}\left(\frac{\varepsilon}{k_B T}\right)^2 \cdot \frac{1}{4\cosh^2 \varepsilon/2k_B T}\, dT =$$

$$\int \left(\frac{\varepsilon}{k_B T}\right)^3 \cdot \frac{k_B^2}{\varepsilon} \cdot \frac{1}{4\cosh^2 \varepsilon/2k_B T} \cdot \underbrace{\frac{dT}{d(\varepsilon/k_B T)}}\, d(\varepsilon/k_B T) =$$

$$\left(= \left(\frac{d(\varepsilon/k_B T)}{dT}\right)^{-1} = \left(-\frac{\varepsilon}{k_B T^2}\right)^{-1}\right)$$

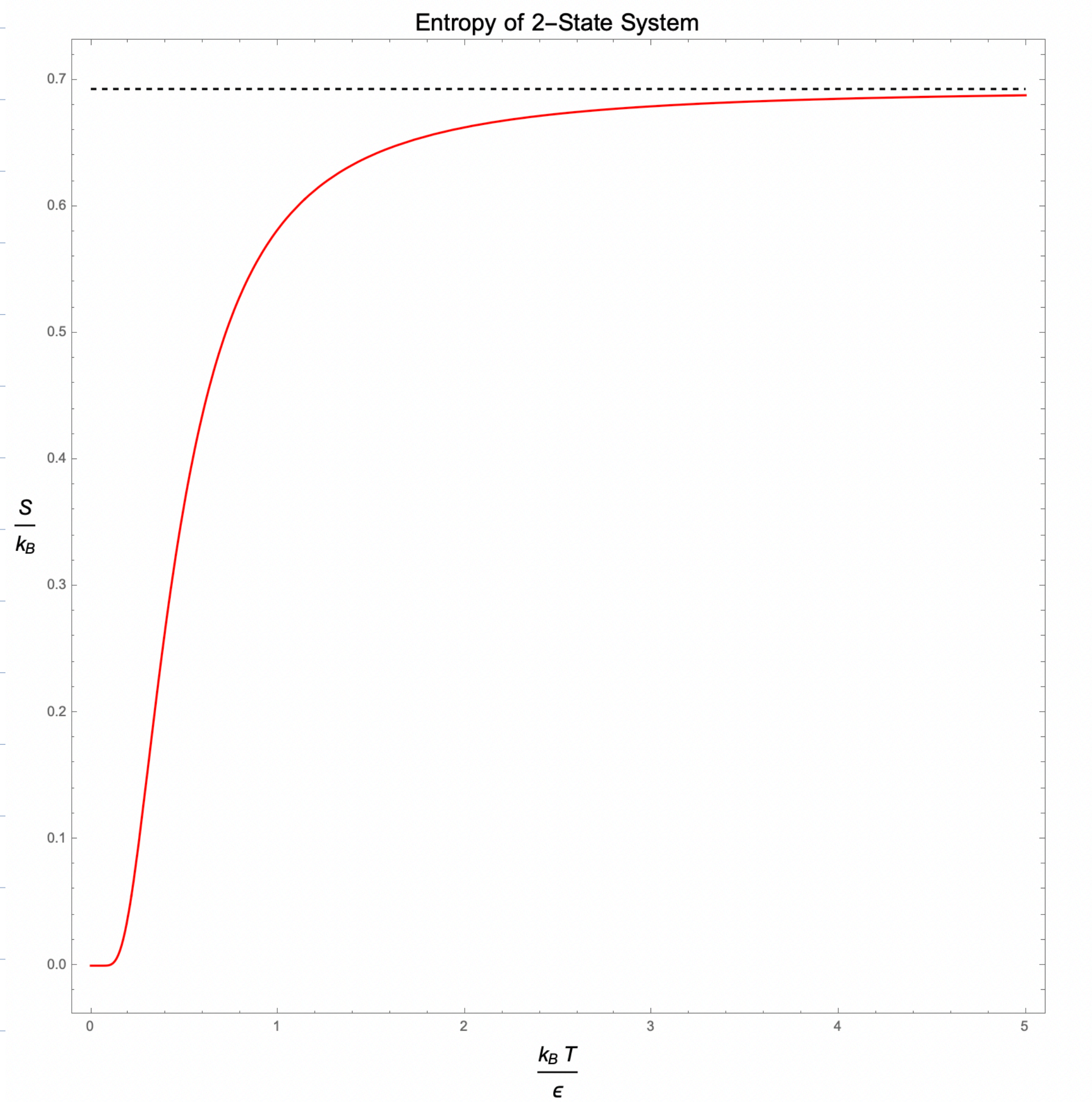
$$-\int \left(\frac{\varepsilon}{k_B T}\right)^3 \frac{k_B^2}{\varepsilon} \cdot \frac{k_B T^2}{\varepsilon} \frac{1}{4\cosh^2(\varepsilon/2k_B T)}\, d(\varepsilon/k_B T) =$$

$$= -\int \left(\frac{\varepsilon}{k_B T}\right)^3 \left(\frac{k_B T}{\varepsilon}\right)^2 k_B \frac{1}{4\cosh^2(\varepsilon/2k_B T)}\, d(\varepsilon/k_B T)$$

$$= k_B \int_{\varepsilon/k_B T}^{\infty} \frac{x}{4\cosh^2 x/2}\, dx =$$

$$\boxed{k_B\left[\log\left(2\cosh \varepsilon/2k_BT\right) - \frac{1}{2}\frac{\varepsilon}{k_BT}\tanh\left(\varepsilon/2k_BT\right)\right]}$$

Plotting so as to see the temperature dependence, we have



As $T \to \infty$, the entropy approaches $\ln 2$. We can see why this is a sensible value if we consider another formula for computing the entropy: the Shannon entropy formula

$$S = -\sum_i p_i \ln p_i$$

where p_i is the probability that state i is occupied. Plugging in $p_0 = p_\varepsilon = 1/2$, this formula gives

$$\frac{S}{k_B} = -\frac{1}{2}\ln\frac{1}{2} - \frac{1}{2}\ln 1/2 = -\ln 1/2 = \ln 2.$$

Thus, the asymptotic value of the entropy of this system at high temperatures reflects the fact that, again, neither state is favored over any other in this limit.