Two energy level system: Schottky-type heat capacity

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Here we discuss the Schottky-type heat capacity for the two energy level systems using both the microcanonical ensemble and canonical ensemble.

1. Schottky-type specific heat: two level system: microcanonical ensemble

Suppose that there are two energy levels at $\varepsilon = 0$ and ε_0. The total number of atoms is *f*.

$$l_+ + l_- = f$$

where l_- atoms are at the energy level ($\varepsilon = 0$) and l_+ atoms are at the energy level ($\varepsilon = \varepsilon_0$). The total energy *E* is given by

$$E = \varepsilon_0 l_+$$

The number of ways to pick up l_+ atoms out of *f* atoms is

$$W(f, E) = \frac{f!}{l_+! l_-!}.$$

The entropy *S* is given by

$$S = k_B \ln W(f, E)$$

Using the Stirling relation, we get

$$\begin{aligned}
S &= k_B \ln \frac{f!}{l_+! l_-!} \\
&= k_B (\ln f! - \ln l_+! - \ln l_-!) \\
&= k_B [f \ln f - f - l_+ \ln l_+ + l_+ - l_- \ln l_- + l_-) \\
&= k_B [f \ln f - l_+ \ln l_+ - (f - l_+) \ln(f - l_+)] \\
&= k_B [f \ln\left(\frac{f}{f - l_+}\right) + l_+ \ln\left(\frac{f - l_+}{l_+}\right)]
\end{aligned}$$

Since $E = \varepsilon_0 l_+$, we have

$$S(E,f) = k_B f[\ln\left(\frac{f}{f-l_+}\right) + \frac{l_+}{f}\ln\left(\frac{f-l_+}{l_+}\right)]$$

$$= k_B f[\ln\left(\frac{f\varepsilon_0}{f\varepsilon_0 - E}\right) + \frac{E}{f\varepsilon_0}\ln\left(\frac{f\varepsilon_0 - E}{E}\right)]$$

$$= k_B f[-(1-\frac{E}{f\varepsilon_0})\ln(1-\frac{E}{f\varepsilon_0}) - \frac{E}{f\varepsilon_0}\ln\frac{E}{f\varepsilon_0}]$$

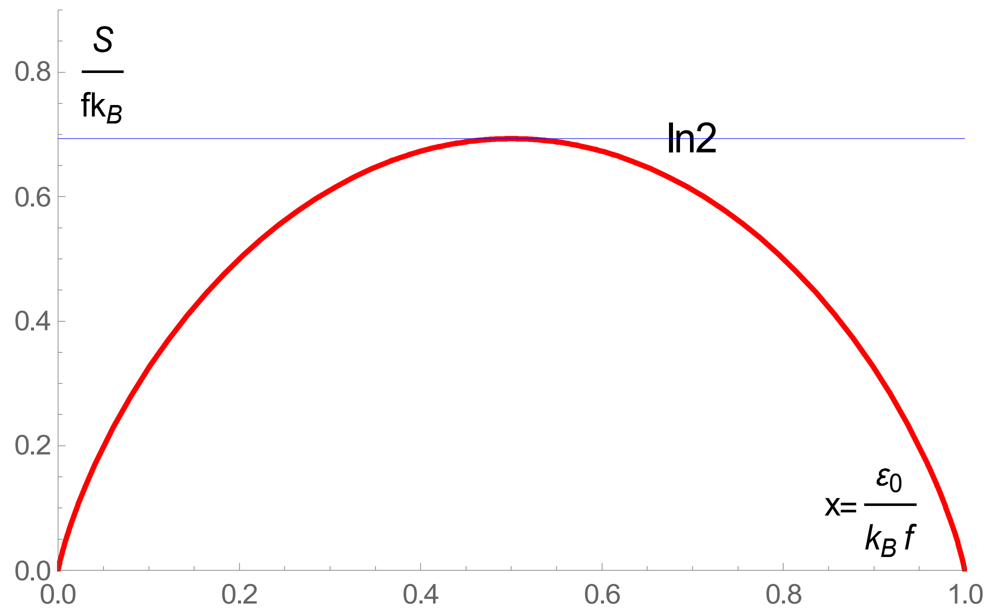


Fig. $S/(fk_B)$ vs $x = \frac{\varepsilon_0}{k_B f}$. $S/(fk_B)$ has a peak (ln2=0.693147 at $x = 0.5$.

From the definition of temperature T, we have

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\varepsilon_0}\ln\left(\frac{f\varepsilon_0 - E}{E}\right)$$

The total energy:

$$E = \frac{f\varepsilon_0}{1+e^{\beta\varepsilon_0}}$$

The heat capacity

$$C = \frac{\partial E}{\partial T} = f k_B \left(\frac{\varepsilon_0}{k_B T} \right)^2 \frac{e^{\beta\varepsilon_0}}{\left(1 + e^{\beta\varepsilon_0}\right)^2}$$ (Schottky type)

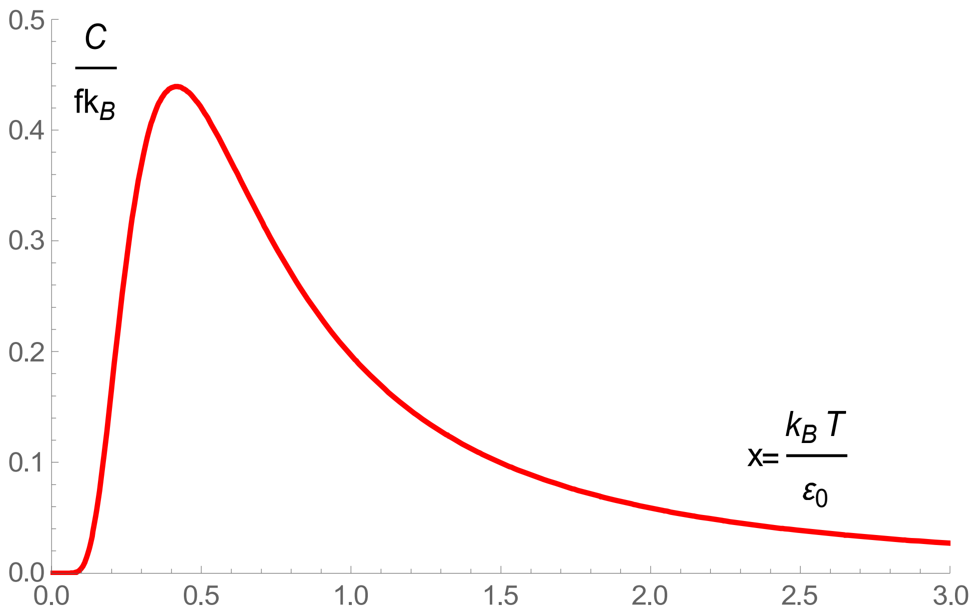


Fig. Schottky-type heat capacity. $C/(fk_B)$ has a peak (0.439229) at x = 0.416778.

2. Canonical ensemble for the *f* particle

The partition function

$$\begin{aligned} Z_{Cf} &= \sum_{l_+=0}^{f} \frac{f!}{l_+! l_-!} \exp(-\beta\varepsilon_0 l_+) \\ &= \sum_{l_+=0}^{f} \frac{f!}{l_+!(f-l_+)!} (e^{-\beta\varepsilon_0})^{l_+} \\ &= (1 + e^{-\beta\varepsilon_0})^f \end{aligned}$$

$$\ln Z_{Cf} = f \ln(1 + e^{-\beta\varepsilon_0})$$

$$F = -k_B T \ln Z_{Cf} = -f k_B T \ln(1 + e^{-\beta\varepsilon_0})$$

The average energy:

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z_{Cf} = \frac{f\varepsilon_0 e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}} = \frac{f\varepsilon_0}{e^{\beta\varepsilon_0}+1}$$

3. Canonical ensemble for the one particle

We consider the system with one particle. The partition function is given by

$$Z_1 = 1 + e^{-\beta\varepsilon_0}$$

The probability of finding the particle at $\varepsilon = 0$ is

$$P(\varepsilon = 0) = \frac{1}{Z_1} = \frac{1}{1+e^{-\beta\varepsilon_0}}.$$

The probability of finding the particle at $\varepsilon = 0$ is

$$P(\varepsilon = \varepsilon_0) = \frac{1}{Z_1} = \frac{e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}}.$$

The average energy for the particle is

$$\langle \varepsilon\rangle = 0\,P(\varepsilon = 0) + \varepsilon_0\,P(\varepsilon = \varepsilon_0 0) = \frac{\varepsilon_0 e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}} = \frac{\varepsilon_0}{1+e^{\beta\varepsilon_0}}.$$

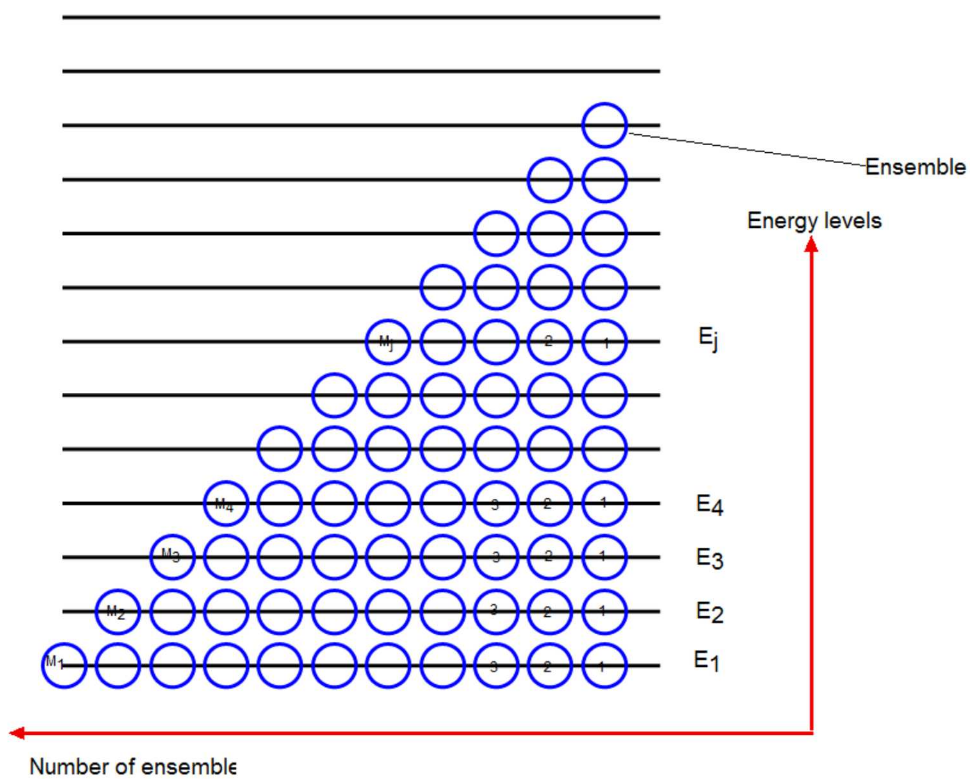
Note that

$$\langle \varepsilon\rangle = -\frac{\partial}{\partial\beta}\ln Z_{C1} = \frac{\varepsilon_0 e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}} = \frac{\varepsilon_0}{e^{\beta\varepsilon_0}+1}$$

For the *f* particle systems, we have the average energy *E* as

$$\langle E\rangle = f\varepsilon = \frac{\varepsilon_0}{1+e^{\beta\varepsilon_0}}$$

4. Canonical ensemble for many particles



Suppose that there are many energy levels (ε_1 , ε_2 , ε_3 , ε_4 ,…) with number occupancy ($n_1, n_2, n_3, ...$) . The energy of the system is given by

$$E_i = n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots$$

where

$$n_1 + n_2 + \cdots = N \qquad \text{(constant)}$$

The partition function is obtained as

$$\begin{aligned} Z_{CN} &= \sum_{n_1, n_2, \cdots} \frac{N!}{n_1! n_2! n_3! \cdots} \exp[-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots)] \\ &= (e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \cdots)^N \\ &= Z_{C1}{}^N \end{aligned}$$

where

$$Z_{C1} = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \cdots$$