

Figure 3.4 Energy and heat capacity of a two state system as functions of the temperature τ . The energy is plotted in units of ε .

The average energy refers to those states of a system that can exchange energy with a reservoir. The notation $\langle \cdot \cdot \cdot \rangle$ denotes such an average value and is called the **thermal average** or **ensemble average**. In (12) the symbol U is used for $\langle \varepsilon \rangle$ in conformity with common practice; U will now refer to the system and not, as earlier, to the system + reservoir.

Example: Energy and heat capacity of a two state system. We treat a system of one particle with two states, one of energy 0 and one of energy ε . The particle is in thermal contact with a reservoir at temperature τ . We want to find the energy and the heat capacity of the system as a function of the temperature τ . The partition function for the two states of the particle is

$$Z = \exp(-0/\tau) + \exp(-\varepsilon/\tau) = 1 + \exp(-\varepsilon/\tau). \tag{13}$$

The average energy is

$$U \equiv \langle \varepsilon \rangle = \frac{\varepsilon \exp(-\varepsilon/\tau)}{Z} = \varepsilon \frac{\exp(-\varepsilon/\tau)}{1 + \exp(-\varepsilon/\tau)}.$$
 (14)

This function is plotted in Figure 3.4.

If we shift the zero of energy and take the energies of the two states as $-\frac{1}{2}\varepsilon$ and $+\frac{1}{2}\varepsilon$, instead of as 0 and ε , the results appear differently. We have

$$Z = \exp(\varepsilon/2\tau) + \exp(-\varepsilon/2\tau) = 2\cosh(\varepsilon/2\tau) , \qquad (15)$$