and

$$\langle\varepsilon\rangle = \frac{(-\tfrac{1}{2}\varepsilon)\exp(\varepsilon/2\tau) + (\tfrac{1}{2}\varepsilon)\exp(-\varepsilon/2\tau)}{Z} = -\varepsilon\frac{\sinh(\varepsilon/2\tau)}{2\cosh(\varepsilon/2\tau)}$$

$$= -\tfrac{1}{2}\varepsilon\tanh(\varepsilon/2\tau). \tag{16}$$

The **heat capacity** C_V of a system at constant volume is defined as

$$C_V \equiv \tau(\partial\sigma/\partial\tau)_V \ , \tag{17a}$$

which by the thermodynamic identity (34a) derived below is equivalent to the alternate definition

$$C_V \equiv (\partial U/\partial\tau)_V. \tag{17b}$$

We hold V constant because the values of the energy are calculated for a system at a specified volume. From (14) and (17b),

$$C_V = \varepsilon\frac{\partial}{\partial\tau}\frac{1}{\exp(\varepsilon/\tau) + 1} = \left(\frac{\varepsilon}{\tau}\right)^2\frac{\exp(\varepsilon/\tau)}{[\exp(\varepsilon/\tau) + 1]^2}. \tag{18a}$$

The same result follows from (16).

In conventional units C_V is defined as $T(\partial S/\partial T)_V$ or $(\partial U/\partial T)_V$, whence

$$\text{(conventional)} \qquad C_V = k_B\left(\frac{\varepsilon}{k_BT}\right)^2\frac{\exp(\varepsilon/k_BT)}{[\exp(\varepsilon/k_BT) + 1]^2}. \tag{18b}$$

In fundamental units the heat capacity is dimensionless; in conventional units it has the dimensions of energy per kelvin. The **specific heat** is defined as the heat capacity per unit mass.

The hump in the plot of heat capacity versus temperature in Figure 3.4 is called a Schottky anomaly. For $\tau \gg \varepsilon$ the heat capacity (18a) becomes

$$C_V \simeq (\varepsilon/2\tau)^2. \tag{19}$$

Notice that $C_V \propto \tau^{-2}$ in this high temperature limit. In the low temperature limit the temperature is small in comparison with the energy level spacing ε. For $\tau \ll \varepsilon$ we have

$$C_V \simeq (\varepsilon/\tau)^2\exp(-\varepsilon/\tau). \tag{20}$$

The exponential factor $\exp(-\varepsilon/\tau)$ reduces C_V rapidly as τ decreases, because $\exp(-1/x) \to 0$ as $x \to 0$.