3.3 The equipartition law of classical thermodynamics

We now will investigate systems for which the one particle energy is written as

$$E(\vec{\xi}) = \sum_{i,j=1}^{s} a_{ij}\xi_i\xi_j \text{(bilinear form)} \qquad (3.10)$$

This function is homogeneous of second order, i.e.:

$$\sum_{j=1}^{s} \xi_j \frac{\partial E}{\partial \xi_j} = 2E \qquad . \tag{3.11}$$

For classical particles the Boltzmann approximation holds:

$$f(E,T) = \frac{\exp\left(-\frac{E}{kT}\right)}{Z} \qquad (3.12)$$

For the inner energy we find:

$$U = \langle E \rangle = \iiint E(\vec{\xi}) \frac{\exp\left(-\frac{E(\vec{\xi})}{kT}\right)}{Z} d\xi_1 \dots d\xi_s = \frac{1}{2} \sum_{j=1}^s \iiint \xi_j \frac{\partial E(\vec{\xi})}{\partial \xi_j} \frac{\exp\left(-\frac{E(\vec{\xi})}{kT}\right)}{Z} d\xi_1 \dots d\xi_s \qquad (3.13)$$

For the norm we find:

$$1 = \iiint \frac{\exp\left(-\frac{E(\vec{\xi})}{kT}\right)}{Z} d\xi_1 \dots d\xi_s \qquad (3.14)$$

Finally we get

$$U = \frac{-kT}{2Z} \sum_{j=1}^{s} \iiint \xi_j \frac{\partial}{\partial \xi_j} \left[\exp\left(-\frac{E}{kT}\right) \right] d\xi_1 \dots d\xi_s \qquad , \tag{3.15}$$

and after partial integration:

$$U = \frac{-kT}{2Z} \sum_{j=1}^{s} \left[\xi_j \exp\left(-\frac{E(\vec{\xi})}{kT}\right)_{boundaries} - \iiint \exp\left(-\frac{E(\vec{\xi})}{kT}\right) d\xi_1 \dots d\xi_s \right] \qquad (3.16)$$

The first term vanishes at the boundaries, the second one is the partition function; thus we find

$$U = \frac{kT}{2}s \qquad . \tag{3.17}$$

Independent of the special form of the energy function each degree of freedom adds 0.5kT to the inner energy of the system.

The specific heat capacity is

$$C = \frac{k}{2}s \qquad , \tag{3.18}$$

independent of the temperature.