5.9 The equipartition law of classical thermodynamics

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

$$E(\vec{\xi}) = \sum_{i,j=1}^{s} a_{ij}\xi_i\xi_j \qquad \text{(bilinear form)} \qquad . \tag{5.73}$$

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

$$\sum_{j=1}^{s} \xi_j \frac{\partial E}{\partial \xi_j} = 2E \qquad . \tag{5.74}$$

Nearly all types of kinetic energy and many types of potential energy like that of a harmonic oscillator are written as a bilinear form of Eq. (5.73), i.e. are homogeneous of second order.
For classical particles the Boltzmann approximation holds:

$$f(E,T) = \frac{\exp\left(-\frac{E}{kT}\right)}{Z} \qquad . \tag{5.75}$$

Thus we find for the inner energy

$$U = \langle E\rangle = \iiint E(\vec{\xi})\frac{\exp\left(-\frac{E(\vec{\xi})}{kT}\right)}{Z} d\xi_1...d\xi_s = \frac{1}{2}\sum_{j=1}^{s}\iiint \xi_j \frac{\partial E(\vec{\xi})}{\partial \xi_j}\frac{\exp\left(-\frac{E(\vec{\xi})}{kT}\right)}{Z} d\xi_1...d\xi_s \qquad . \tag{5.76}$$

For the norm we find:

$$1 = \iiint \frac{\exp\left(-\frac{E(\vec{\xi})}{kT}\right)}{Z} d\xi_1...d\xi_s \qquad . \tag{5.77}$$

Therefore we get finally

$$U = \frac{-kT}{2Z}\sum_{j=1}^{s}\iiint \xi_j \frac{\partial}{\partial \xi_j}\left[\exp\left(-\frac{E}{kT}\right)\right] d\xi_1\cdots d\xi_s \qquad , \tag{5.78}$$

and after partial integration:

$$U = \frac{-kT}{2Z}\sum_{j=1}^{s}\left[\xi_j \exp\left(-\frac{E(\vec{\xi})}{kT}\right)_{boundaries} - \iiint \exp\left(-\frac{E(\vec{\xi})}{kT}\right) d\xi_1\cdots d\xi_s\right] \qquad . \tag{5.79}$$

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

$$U = \frac{kT}{2}s \qquad . \tag{5.80}$$

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

$$C = \frac{k}{2}s \qquad , \tag{5.81}$$

independent of the temperature. This is the famous equipartition law of classical thermodynamics.