The Gibbs sum is written as

$$\mathcal{Z} = \sum_N \sum_s \lambda^N \exp(-\varepsilon_s/\tau) = \sum_{\text{ASN}} \lambda^N \exp(-\varepsilon_s/\tau) , \tag{61}$$

and the ensemble average number of particles (57) is

$$\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log \mathcal{Z} . \tag{62}$$

This relation is useful, because in many actual problems we determine λ by finding the value that will make $\langle N \rangle$ come out equal to the given number of particles.

Energy. The thermal average energy of the system is

$$U = \langle \varepsilon \rangle = \frac{\sum_{\text{ASN}} \varepsilon_s \exp[\beta(N\mu - \varepsilon_s)]}{\mathcal{Z}} , \tag{63}$$

where we have temporarily introduced the notation $\beta \equiv 1/\tau$. We shall usually write U for $\langle \varepsilon \rangle$. Observe that

$$\langle N\mu - \varepsilon \rangle = \langle N \rangle \mu - U = \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} = \frac{\partial}{\partial \beta} \log \mathcal{Z} , \tag{64}$$

so that (59) and (63) may be combined to give

$$U = \left(\frac{\mu}{\beta} \frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta} \right) \log \mathcal{Z} = \left(\tau\mu \frac{\partial}{\partial \mu} - \frac{\partial}{\partial (1/\tau)} \right) \log \mathcal{Z} . \tag{65}$$

A simpler expression that is more widely used in calculations was obtained in Chapter 3 in terms of the partition function Z.

!! *Example: Occupancy zero or one.* A red-blooded example of a system that may be occupied by zero molecules or by one molecule is the heme group, which may be vacant or may be occupied by one O_2 molecule—and never by more than one O_2 molecule (Figure 5.10). A single heme group occurs in the protein myoglobin, which is responsible for the red color of meat. If ε is the energy of an adsorbed molecule of O_2 relative to O_2 at rest at