

Average values over the systems in diffusive and thermal contact with a reservoir are easily found. If $X(N,s)$ is the value of X when the system has N particles and is in the quantum state s , then the thermal average of X over all N and all s is

$$\langle X \rangle = \sum_{ASN} X(N,s) P(N,s) = \frac{\sum_{ASN} X(N,s) \exp[(N\mu - \epsilon_s)/\tau]}{\mathcal{Z}} \quad (56)$$

We shall use this result to calculate thermal averages.

Number of particles. The number of particles in the system can vary because the system is in diffusive contact with a reservoir. The thermal average of the number of particles in the system is

$$\langle N \rangle = \frac{\sum_{ASN} N \exp[(N\mu - \epsilon_s)/\tau]}{\mathcal{Z}}, \quad (57)$$

according to (56). To obtain the numerator, each term in the Gibbs sum has been multiplied by the appropriate value of N . More convenient forms of $\langle N \rangle$ can be obtained from the definition of \mathcal{Z} :

$$\frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\tau} \sum_{ASN} N \exp[(N\mu - \epsilon_s)/\tau], \quad (58)$$

whence

$$\langle N \rangle = \frac{\tau}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \tau \frac{\partial \log \mathcal{Z}}{\partial \mu}. \quad (59)$$

The thermal average number of particles is easily found from the Gibbs sum \mathcal{Z} by direct use of (59). When no confusion arises, we shall write N for the thermal average $\langle N \rangle$. When we speak later of the occupancy of an orbital, f or $\langle f \rangle$ will be written interchangeably for N or $\langle N \rangle$.

We often employ the handy notation

$$\lambda \equiv \exp(\mu/\tau), \quad (60)$$

where λ is called the **absolute activity**. Here λ is the Greek letter lambda. We see from (12) that for an ideal gas λ is directly proportional to the concentration.

$$\mu = (k_B T) \ln \frac{n}{n_Q} = -(k_B T) \ln \frac{V}{N \lambda_T^3}$$

$$\left(n \equiv \frac{N}{V}, n_Q \equiv \frac{1}{\lambda_T^3} \right)$$