9.2: Thermal Equilibrium

For a statistical mixture at thermal equilibrium, individual molecules can occupy a distribution of energy states. An equilibrium system at temperature T has the canonical probability distribution

$$\rho_{eq} = \frac{e^{-\beta H}}{Z} \tag{9.2.1}$$

Z is the partition function and $\beta = (k_B T)^{-1}$. Classically, we can calculate the equilibrium ensemble average value of a variable A as

$$\langle A \rangle = \int d\mathbf{p} \int d\mathbf{q} A(\mathbf{p}, \mathbf{q}; t) \rho_{eq}(\mathbf{p}, \mathbf{q}) \tag{9.2.2}$$

In the quantum mechanical case, we can obtain an equilibrium expectation value of A by averaging $\langle A \rangle$ over the thermal occupation of quantum states:

$$\langle A \rangle = \operatorname{Tr}(\rho_{eq} A) \tag{9.2.3}$$

where ρ_{eq} is the density matrix at thermal equilibrium and is a diagonal matrix characterized by Boltzmann weighted populations in the quantum states:

$$\rho_{mn} = p_n = \frac{e^{-\beta E_s}}{Z} \tag{9.2.4}$$

In fact, the equilibrium density matrix is defined by Equation 9.2.1, as we can see by calculating its matrix elements using

$$(\rho_{eq})_{\mathrm{mm}} = \frac{1}{Z} \left\langle n \left| e^{-\beta \hat{H}} \right| m \right\rangle = \frac{e^{-\beta E_n}}{Z} \delta_{mm} = p_n \delta_{mm} \tag{9.2.5}$$

Note also that

$$Z = \operatorname{Tr}\left(e^{-\beta \hat{H}}\right) \tag{9.2.6}$$

Equation 9.2.3 can also be written as

$$\langle A \rangle = \sum_n p_n \langle n | A | n \rangle \tag{9.2.7}$$

It may not be obvious how this expression relates to our previous expression for mixed states

$$\langle A \rangle = \sum_{n,m} \langle c_n^* c_m \rangle A_{mn} = \operatorname{Tr}(\rho \hat{A}). \tag{9.2.8}$$

Remember that for an equilibrium system we are dealing with a statistical mixture in which no coherences (no phase relationships) are present in the sample. The lack of coherence is the important property that allows the equilibrium ensemble average of $\langle c_m c_n^* \rangle$ to be equated with the thermal population p_n. To evaluate this average we recognize that these are complex numbers, and that the equilibrium ensemble average of the expansion coefficients is equivalent to phase averaging over the expansion coefficients. Since at equilibrium all phases are equally probable

$$\langle c_n^* c_m \rangle = \frac{1}{2\pi} \int_0^{2\pi} c_n^* c_m d\phi = \frac{1}{2\pi} |c_n| |c_m| \int_0^{2\pi} e^{-i\phi_{mn}} d\phi_{nm} \tag{9.2.9}$$

where

$$c_n = |c_n| e^{i\phi_n} \tag{9.2.10}$$

and

$$\phi_{nm} = \phi_n - \phi_m. \tag{9.2.11}$$

The integral in Equation 9.2.9 is quite clearly zero unless $\phi_n = \phi_m$ giving

$$\langle c_n^* c_m \rangle = p_n = \frac{e^{-\beta E_s}}{Z} \tag{9.2.12}$$