Osmotic Pressure for Excluded Volume Coils and Concentration Blobs.

Using the Flory-Huggins equation an expression for the osmotic pressure can be obtained.

\[ \Pi = \frac{(kT)}{V_c} \left[ \phi/N + (1/2 - \chi) \phi^2 + \phi^3/3 + \phi^4/4 + \ldots \right] \]

The Flory-Huggins equation assumes in its derivation that the spatial distribution of monomers is random. This means that the Flory-Huggins equation is restricted to Gaussian Coils and is not strictly appropriate for the normal condition of polymers in a good solvent, i.e. F-H is not appropriate for self-avoiding walks. The F-H expression for osmotic pressure is also not appropriate for concentrations above the overlap concentration in good-solvent systems. F-H is only appropriate for theta-temperature solutions.

Resolution of good-solvent behavior for osmotic pressure resulted from the work of des Cloizeaux and is one of the major contributions of modern polymer physics.

The approach is based on renormalization of a good-solvent coil using the blob concept. First, a generic expression of osmotic pressure can be written, based on the F-H result,

\[ \Pi = (kT) \phi f(\phi b^3, N) \]

Assuming that the low concentration limit depends linearly on concentration, \( \phi \), and that the viral expansion will be dependent on molecular weight, \( N \), and the volume physically occupied by the polymer chains, \( \phi b^3 = b^3 \frac{n_p}{N} N/(n_p N + n_s) \). This expression can be renormalized to account for concentration blobs by defining \( \lambda \) as the number of units of persistence length \( b \) in a blob, so that the number of blob units in a chain is \( N/\lambda \) (replacing \( N \)), the step length is the size of a blob, \( b_{\text{blob}} = b \lambda^v \), where \( v \) is 1/d_p, and the concentration of blobs (rather than statistical segments, \( \phi \)) is \( \phi_{\text{blob}} = \phi/\lambda \). Then,

\[ \Pi = (kT \phi/\lambda) f(\phi \lambda^{3v-1} b^3, N/\lambda) \]

and the osmotic pressure is unchanged by renormalization so the two expressions for \( \Pi \) are equivalent. \( \lambda \) can vary from 1 to \( N \). For the limit of \( \lambda = N \) the osmotic pressure is proportional to \( \phi/N \), so the generic expression must be proportional to \( \phi/N \). The \( N/\lambda \) dependence already exists in the \( \phi \) term so the two components are redundant. At the limit of \( \lambda=N \) the \( \phi \) expression becomes \((N^v b)^3\), and the generic expression becomes

\[ \Pi = (kT \phi/N) f(\phi/N) (N^v b)^3 \]

We can recognize \( 1/c^* = (N^v b)^3/N \) and rewrite the expression in terms of \( c^* \),

\[ \Pi = (kT \phi/N) f(\phi/c^*) \]

For \( \phi > \phi^* \), \( \Pi \) is independent of \( N \). Then \( f(\phi/c^*) \) must have a linear molecular weight dependence and since \( \phi/c^* = (N^v b)^3/N \phi \) or \( N^{3v-1} b^3 \phi \), we have,
\[ \Pi = (kT \, \phi/N) \left( \phi/\phi^* \right)^{1/(3\nu-1)} \]

For theta solvent scaling and concentrations above the overlap concentration this results in \( \Pi_\theta = K c^2 \), as predicted from the virial expansion of the F-H equation. For good solvents \( \Pi_{\text{good}} = K c^{9/4} \). This result has been experimentally verified. The F-H result is retained at low concentrations even for good solvent coils, while above the overlap concentration a stronger dependence on concentration of the osmotic pressure is predicted by scaling arguments and renormalization.