Osmotic Pressure for
Excluded Volume Coils and Concentration Blobs.

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

$$\Pi = (kT/V_c) [\varphi/N + (1/2 - \chi) \varphi^2 + \varphi^3/3 + \varphi^4/4 + \ldots]$$

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 form 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,

$$\Pi = (kT \varphi) f(\varphi b^3, N)$$

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

$$\Pi = (kT \varphi/\lambda) f(\varphi \lambda^{3\nu-1} b^3, N/\lambda)$$

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

$$\Pi = (kT \varphi/N) f(\varphi/N (N^{\nu}b)^3)$$

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

$$\Pi = (kT \varphi/N) f(\varphi/\varphi)$$

For $\varphi > \varphi^*$, Π is independent of N. Then $f(\varphi/\varphi)$ must have a linear molecular weight dependence and since $\varphi/\varphi = (N^{\nu}b)^3/N \varphi$ or $N^{3\nu-1} b^3 \varphi$, we have,

$$\Pi = (kT\ \varphi/N)\ (\varphi/\varphi)^{1/(3\nu-1)}$$

For theta solvent scaling and concentrations above the overlap concentration this results in $\Pi_\theta = K\ c^2$, as predicted from the viral 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.