Osmotic pressure of catenanes in solution

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Summary

We propose a nonuniversal scaling for the osmotic pressure in the case of concatenating ring polymers. The size exponent depends on the molecular weight of the catenans. The effect is more significant the shorter and the stiffer the molecules are.

There is considerable interest in topologically entangled macromolecules, such as catenanes, knots, interpenetrating polymer networks, etc [1-5]. Unfortunately no exact analytical results are available for these species. In this note we point out that a particular simple case is aforded by a catenane formed from two interlocking rigid planar rings of equal radius σ (and effectively negligible thickeness). We will obtain the expected scaling of the osmotic pressure of a semi-diluted solution of catenanes with molecular weight or length. A straightforward application of the Mayer-Mc Millan solution theory [6] allows us to write for the first two terms of the virial expansion of the osmotic presssure Π, of a dilute solution of N, rigid ring catenanes in a box of volume V.

$$\Pi_c/kT = N/V + h\sigma^3(N/V)^2 + \cdots \tag{1}$$

where h is a pure numerical factor. The first term is the ideal van't Hoff contibution, which is indeed smaller by a factor of two in the catenane compared to the corresponding solution of N free planar rings of the same diameter (as the individual, equal rings of the catenane) since the molecular weight is twice as large. The second term arises from the second

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osmotic virial coefficient and is scaled by σ^3. The number h reflects all orientations (intra and intermolecular) of two colliding catenanes which interact only on contact, and are otherwise free to assume all internal orientations. The constant h is of course larger than the corresponding factor in an equation similar to (1) for the interaction of two, free, unentangled rings since the collision cross section of the catenanes must be larger than that of free rings. For our purpose the magnidude of h is immaterial as long as it is bounded. From the geometry of rigid equal ring catenanes $3h/4\pi$ is bounded from below by 8 and from above by 64.

These consideration suggest immediately an approximate expression for the osmotic pressure of athermal catenanes fromed from two self-avoiding random walks of n statistical Kuhn segments of length ℓ. The volume occupied by such rings is determined by the radius of gyration equal to $\ell^2 n^{\nu_c}$, where ν_c is the Flory exponent of an individual ring in the catenane. For sufficiently large rings $(n>10^3)$ one expects that ν_c is very close to the free ring exponent ν_r, i.e. $\nu_r \approx 3/5$ in three dimensions. This suggests that ν_c is a non-universal exponent, i.e. $\nu_c \approx \nu_r + O(n^{-1/2})$. This estimate follows from the fact that a simple catenane requires one segment of a ring to thread the second ring of the catenane, and the effective number of such segments of a ring of the catenan is roughly proportional to $n/n^{3/2} \sim n^{-1/2}$. To a first approximation we can equate σ in eq(1) with the radius of gyration and eq(1) becomes for a sufficiently diluted solution of polymeric catenanes

$$\Pi_p/kT = N/V + h_p \ell^3 n^{\nu_c}(N/V)^2 + \cdots \qquad (3)$$

where h_p is a trivial constant of proportionality (which we have not calculated). Introducing volume fractions ϕ, of the catenanes, eq(2) can be expressed as

$$\Pi_p \ell^3/kT = \phi/n + g n^{3\nu_c - 2}\phi^2 + \cdots \qquad (3)$$

where g is a numerical factor. In the ideal limit the $\phi \to 0$ the second term is negligible, and van't Hoff's law is recovered. Applying the standard scaling

argument for the osmotic pressure of semi-dilute solutions [7] we find $\Pi \sim \phi^{\upsilon_c d/(\upsilon_c d-1)}$. For very large rings we expect this to be the same scaling law as for free rings, but there are corrections for smaller rings coming from the difference $\upsilon_c - \upsilon_r \sim O(n^{-1/2})$. A suitable experiment would be to measure the osmotic pressure for a dilute free ring solution and an equivalent dilute catenane solution to see whether there is a difference in the osmotic pressure, i.e. $\log(\Pi_{cat} - \Pi_{ring}) \sim \Delta\upsilon\log\phi$. This suggests an additional contribution from the entanglement in the dilute limit which might be observable if n is not too large. These estimates are at least consistent with those given by Binder and Frisch [5].

References
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