Suspensions and polymer solutions

Solution of Exercise 7

1. We assume that the adsorbed polymer can be divided into blobs of g monomers and size ξ. The thickness of the adsorbed "cushion" is ξ, i.e., the rescaled chain of blobs lies flat on the surface. The blobs are defined such that the energy of adsorbtion per blob is equal to $k_\mathrm{B}T$. ξ and g are related by $\xi \sim a g^\nu$.

   (a) The monomer concentration within a blob is

   $$c \sim \frac{g}{\xi^3} \sim \frac{g}{a^3 g^{3\nu}} \sim \frac{1}{a^3} g^{1-3\nu}.$$

   Since the surface potential has a short range of a, only a thin layer of thickness a in the blob feels it. The volume of this layer is $\xi^2 a$. Hence, the number of monomers in a blob that are actually adsorbed on the surface is

   $$n_\mathrm{ads} \sim \xi^2 a c \sim a^2 g^{2\nu} a a^{-3} g^{1-3\nu} \sim g^{1-\nu}.$$

   The energy of adsorbtion per blob is, therefore,

   $$\varepsilon_\mathrm{ads} \sim n_\mathrm{ads} V_0 \sim g^{1-\nu} V_0,$$

   which, by the definition of the blob, is set equal to $k_\mathrm{B}T$. From this we find

   $$g \sim \left(\frac{k_\mathrm{B}T}{V_0}\right)^{\frac{1}{1-\nu}}, \quad \xi \sim a \left(\frac{k_\mathrm{B}T}{V_0}\right)^{\frac{\nu}{1-\nu}}. \tag{1}$$

   For a theta solvent (ideal chain, $\nu = 1/2$) we get a thickness of $\xi \sim a(k_\mathrm{B}T/V_0)$, whereas in a good solvent (real chain, $\nu \simeq 0.6$) $\xi \sim a(k_\mathrm{B}T/V_0)^{1.5}$.

   (b) The free energy of adsorbtion is

   $$F_\mathrm{ads} \sim \frac{N}{g}\varepsilon_\mathrm{ads} \sim \frac{N}{g} k_\mathrm{B}T \sim N k_\mathrm{B}T \left(\frac{V_0}{k_\mathrm{B}T}\right)^{\frac{1}{1-\nu}}. \tag{2}$$

   In a theta solvent it scales as T^{-1}, and in a good solvent as $T^{-1.5}$.

2. We assume again that the confined polymer can be divided into blobs of g monomers and size ξ. Inside a blob the chain is unperturbed by the confinement, while the rescaled chain of blobs has a straight configuration along the tube. Thus, $\xi \sim A$. The number of monomers in a blob is

   $$g \sim \left(\frac{\xi}{a}\right)^{1/\nu} \sim \left(\frac{A}{a}\right)^{1/\nu},$$

   so the number of blobs is

   $$n_\mathrm{blob} \sim \frac{N}{g} \sim N\left(\frac{a}{A}\right)^{1/\nu}.$$

Each blob represents a free energy of $k_{\rm B}T$. The free energy of confinement is, therefore,

$$F_{\rm conf} \sim n_{\rm blob} k_{\rm B} T \sim N k_{\rm B} T \left(\frac{a}{A}\right)^{1/\nu} . \tag{3}$$

The free energy increases as the tube gets thinner, as expected. It scales as A^{-2} for an ideal chain, and as $A^{-1.7}$ for a real chain. Since $a/A < 1$, the free energy is larger for a real chain — it is harder to squeeze a chain with internal repulsions into a tube. Another quantity of interest is the length $R_\parallel$ of the tube occupied by the polymer. It is

$$R_\parallel \sim n_{\rm blob} \xi \sim N A \left(\frac{a}{A}\right)^{1/\nu} . \tag{4}$$

Note that $R_\parallel \sim N$, i.e., the dimensionality of the chain became $D = 1$ because of the confinement. $R_\parallel$ has a nontrivial scaling with the tube diameter, $R_\parallel \sim A^{1-1/\nu}$, i.e., it scales as A^{-1} for an ideal chain and as $A^{-0.7}$ for a real one. In both cases, as expected, $R_\parallel$ increases as the tube gets thinner.