Solution 13

Scaling Theory of Polyelectrolytes

1. Assuming the blob size to be the larger length scale at which entropy dominates the scaling behavior, D_e and the number of monomers in a blob g_e will be related by the classic ideal chain statistics:
$$D_e \sim b g_e^{\frac{1}{2}} \,. \tag{1}$$
On the other hand, the blob is by definition the length scale at which the electrostatic interaction U and thermal fluctuations have roughly the same magnitude. Since there are f elementary charges per monomer and g_e monomers per blob, the total charge inside a blob is efg_e, so that we can conclude that
$$U \sim \frac{(efg_e)^2}{\epsilon_0\epsilon_r D_e} \sim \frac{1}{b}\frac{e^2}{k_BT\epsilon_0\epsilon_r} k_BTf^2 g_e^{\frac{3}{2}} \sim \frac{l_B}{b} f^2 k_BT g_e^{\frac{3}{2}} \sim k_BT \Rightarrow g_e \sim \left(uf^2\right)^{-\frac{2}{3}} \,,$$
where we have substituted the formula (1) in the second step. By making use of (1) again, we then find
$$D_e \sim b\left(uf^2\right)^{-\frac{1}{3}} \,.$$

2. From the electrostatic point of view, the best situation would be for the blobs to be scattered at infinite distance with respect to each other. Of course, this is not possible if we do not break the polymer. Thus, the best thing they can do is to maximize their distance, i.e. by arranging themselves on a straight line. Naturally, this will go on as long as the screening is not that strong, i.e. up to the Debye length l_D. The number of monomers g_D inside a Debye length is easily computable. Indeed:
$$l_D \sim \frac{g_D}{g_e} D_e \Rightarrow g_D \sim \frac{l_D}{D_e} g_e \sim \frac{l_D}{b}\left(uf^2\right)^{-\frac{1}{3}} \,.$$

3. In order for the various “rods” inside each Debye blob not to interact with each other (as we expect at larger length scales), they always have to stay at distances at least of the order of l_D, i.e. the Debye blobs will form a coarse-grained self-avoiding polymer. The number of Debye blobs is simply given by N/g_D, so that the size of the chain R will be given by
$$R \sim l_D\left(\frac{N}{g_D}\right)^{\frac{3}{5}} \sim N^{\frac{3}{5}} l_D \left[\frac{l_D}{b}\left(uf^2\right)^{-\frac{1}{3}}\right]^{-\frac{3}{5}} \propto l_D^{\frac{2}{5}} \propto c^{-\frac{1}{5}} \,.$$