

Diffusion of a Single Polymer Chain in Colloidal Suspensions in Narrow Channels

Amir Amini¹ and Marc. A. Robert^{1,2,3}

¹Department of Chemical and Biomolecular Engineering, ²Rice Quantum Institute, ³Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX, USA

Introduction

It is known that the addition of soluble polymer to colloidal dispersions, even in small amounts, has a significant effect on transport properties of colloids¹. However the effect of colloids on the dynamics of polymer has not been investigated. Transport properties of macromolecules in confined geometries, especially in narrow channels, offer many technological applications in processes such as membrane filtration and gel electrophoresis. A good starting point to obtain quantitative results for the translational diffusion rate of the center of mass of a polymer in solution is the Kirkwood formula. We extend the treatment of Harden and Doi² where no colloid is in the solution to the case where polymer is immersed in a colloidal solution, focusing on the diffusion of a linear flexible chain in a narrow cylindrical channel.

Polymer dynamics in theta and good solvents

Consider a single polymer in a colloidal solution confined in a cylindrical narrow channel. We assume the physical picture of a diffusing polymer in which the dominant mode of transport is cage diffusion³: the polymer tries to escape from the dynamic cage created by its two neighboring colloids. The size of colloids, which are modeled as hard spheres of radius a , is such that they cannot pass each other and the radius of the channel is smaller than the radius of gyration of the polymer. Thus, the polymer essentially adopts a cigar-shaped conformation in the confining channel (de Gennes regime)⁴.

The Kirkwood formula corresponds to the diffusion coefficient obtained from the initial decay rate in intensity of the scattered light in scattering experiments⁵. It therefore gives the short-time diffusion coefficient. For short times, the polymer is still trapped inside the cage and just rattles between the colloids. During this time, the colloids, which are much larger than the monomers, have hardly moved. Thus we will neglect their influence on the hydrodynamic motion of monomers. However, the two neighboring colloids act as barriers against the motion of the chain. As a first approximation, the associated barrier potential for the two colloids, located a distance L apart, may be described by a combination of delta functions

$$U(z) = S[\delta(z - L/2) + \delta(z + L/2)],$$

where we assume the channel is in the z -direction and the S is the strength of the barrier which depends on the size of colloids and the diameter of the cylinder. Furthermore, the polymer can be regarded as a Gaussian chain in which the excluded volume effects are taken into account depending on the quality of the solvent.

In the narrow capillary limit, where the ground-state dominance approximation is valid, the diffusion coefficient is given by²

$$D = \frac{2\alpha_{01}^2 k_B T}{\pi^2 N \eta R^8} \left[\int_0^R \left(\frac{J_0(\alpha_{01} \rho / R)}{J_1(\alpha_{01})} \right)^3 \rho d\rho \right]^2 \int_{-\infty}^{+\infty} \frac{g_{theta}(k) dk}{(k^2 + (\alpha_{01} / R)^2)^2}$$

for ideal chains in Θ solvents, and is given by

$$D = \frac{\alpha_{01}^2 k_B T}{2\pi^2 N \eta R^4} \left[\int_0^R \frac{J_0(\alpha_{01} \rho / R)}{J_1(\alpha_{01})} \left(A \tanh\left(\frac{R-\rho}{\xi}\right) \right)^2 \rho d\rho \right]^2 \int_{-\infty}^{+\infty} \frac{g_{good}(k) dk}{(k^2 + (\alpha_{01}/R)^2)^2}$$

for swollen chains in good solvents.

In the above expressions, N is the number of monomers; η is the viscosity of the solvent; R is the radius of the channel; J_0 and J_1 are Bessel functions of the first kind of zero and first order, respectively, and α_{01} is the first zero of J_0 . g_{θ} and g_{good} are the one-dimensional structure factors of the chain in theta and good solvent conditions, respectively.

Moreover, $\xi \cong 0.227b \left(\frac{R}{b}\right)^{3/4}$ (for athermal solvents), with b the size of the monomer,

$$\text{and } A = \left[\int_0^R \left(\tanh\left(\frac{R-\rho}{\xi}\right) \right)^2 \rho d\rho \right]^{-1/2}.$$

To proceed further, knowledge of the structure factors is called for. When the chain is subject to an external potential $U(z)$, an approximate expression for the pair correlation function is⁶

$$g(z) - g^0(z) = - \int g^0(z-z') \frac{cU(z')}{k_B T} dz', \text{ provided that } S / ak_B T \ll 1 \text{ (} NS / ak_B T = O(1) \text{),}$$

where c is the average linear monomer concentration and $g^0(z)$ is the pair correlation function in the absence of the external potential. Taking the Fourier transform of this equation using the given barrier potential leads to the following relation for the structure factor

$$g(k) = g^0(k)[1 - \alpha \cos(kL/2)], \text{ with } \alpha = cS / k_B T \text{ (} 0 \leq \alpha \leq 1 \text{).}$$

This relation gives the diffusion coefficient for a particular configuration of the two neighboring colloids separated by a distance L which then has to be averaged over all possible distances using the nearest-neighbor distribution function of colloids, $H(L)$. Fortunately, $H(L)$ for pure colloids modeled as hard spheres (hard rods) in one dimension, is exactly known⁷, and the presence of a single polymer in the solution will not significantly change this distribution

$$H(L) = \kappa \exp[-\kappa(L/\sigma - 1)],$$

where $\kappa = 2\eta_c / (1 - \eta_c)$, with η_c the colloids packing fraction and $\sigma = 2a$ the diameter of the colloids.

Results and discussion

Figs.1 and 2 show the dramatic reduction of the normalized diffusion coefficient upon increasing the colloids concentration for different values of the barrier strength. The decay rate is much larger for dilute colloidal solutions compared to highly concentrated solutions.

Next, the variation of D with polymerization index N is explored and compared with previous results² when there is no colloid in the system ($\alpha = 0$). D exhibits a power-law behavior for large N and scales as $D \sim N^{-\nu}$. The growth of the scaling exponent ν with increasing α (or S) is illustrated in Fig.3. It suggests that the diffusion coefficient becomes more sensitive to the number of monomers as the height of the barrier is increased. The details of the growth depend on the model potential. Nevertheless, setting α equal to 1 yields an upper bound for ν , that is, $\nu \leq 1$ for theta conditions and $\nu \leq 2$ for good solvents.

The major advantage of this simple model is that it has only one free parameter which controls the strength of the confinement created by the colloids. However, it also has some limitations. For instance, the scaling of D with R cannot be examined due to the lack of information about how S changes with respect to R .

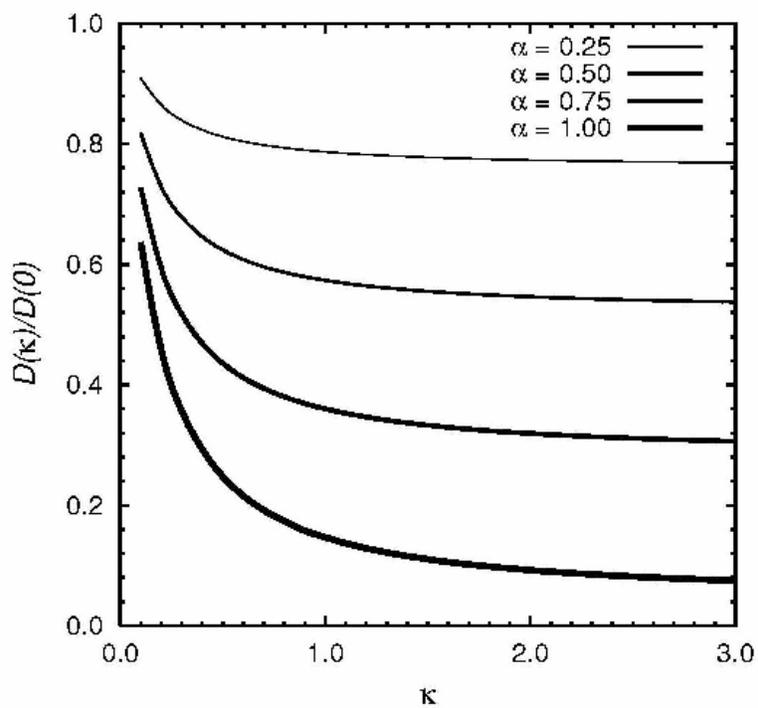


Fig.1: Normalized diffusion coefficient at theta conditions for different barrier strengths.

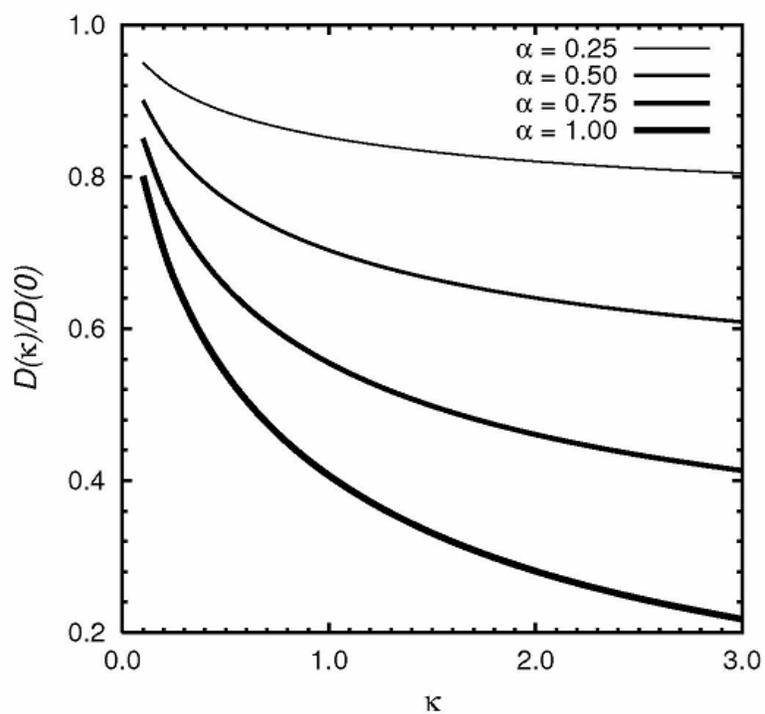


Fig.2: Normalized diffusion coefficient in a good solvent for different barrier strengths.

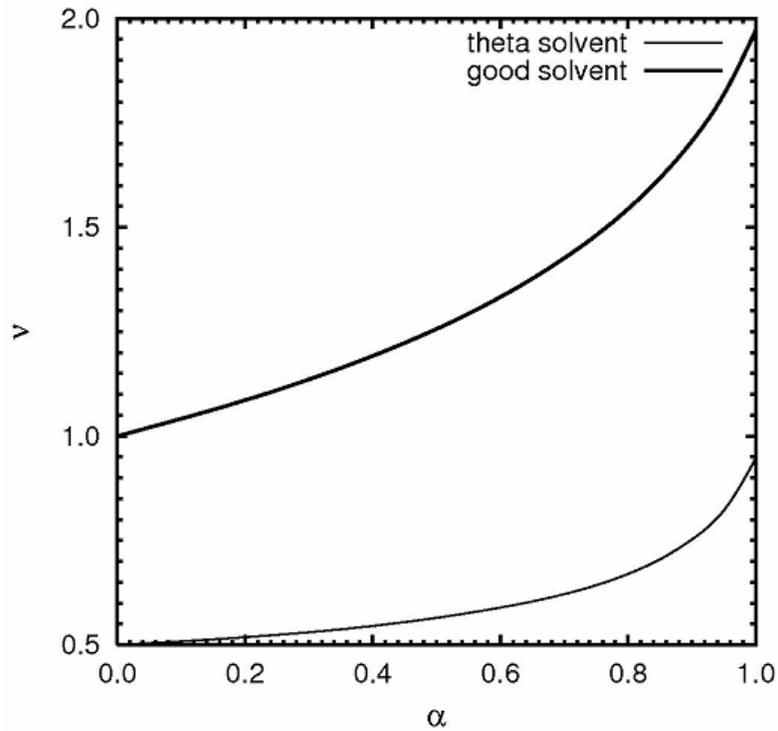


Fig.3: Scaling exponent ν as a function of barrier strength α in theta and good solvents.

References

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