

SINGLE-FILE DIFFUSION, DRIFT, AND COLLISIONS IN ONE-DIMENSIONAL POLYMER SOLUTIONS

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SUMMARY

Research into the dynamics of polymer chains in tightly confined spaces is a crucial aspect of microfluidic device transport studies. Single-file diffusion remains one of the most under-explored topics in this field, yet it holds potential for various applications and further research.

In this thesis, I focus on the dynamics of polymer molecules under narrow tube confinement. These projects mainly aim to simulate various systems' behaviors over time and understand the collective movement mechanism of polymer chains.

A good part of the work is related to first-passage issues within these systems. For example, we analyze the time to first separation for polymer fragments to reach clear separation in DNA mapping related problems. The system's initial conditions significantly affect how fragments are spatially and temporally separated. We investigate the effect of randomness as well as segmental ordering on separation times. As a complement, we also briefly investigate how the initial random fragmentation of a polymer molecule affects its final fragment order, highlighting the importance of the blob theory in our study.

In addition, we also study collisions between polyelectrolytes and uncharged polymer chains under strong confinement. Non-monotonic velocity behaviour, collision duration, collision type and gel electrophoresis-like conditions may all contribute to the successful separation of polymer chains. However, building practical separation devices may require further modifications to the system, such as applying pulsed fields with asymmetric time periods or artificially creating asymmetric tube diameters. Ultimately, it should be possible to manipulate polyelectrolytes using the ideas presented in this thesis.

We also study the single-file diffusion of polymer chains using molecular dynamics (MD) simulations. By comparing the motion of long polymer chains with the predictions of known theories for hard particles, we can gain a better understanding of the multiple time regimes that exist. In addition, with well-designed algorithms, we are able to simulate the same problems using simple Monte Carlo (MC) methods, thus increasing computational speed. Finally, we demonstrate that it is possible to establish a link between these two simulation methods (MD and MC) by mathematically calculating their key parameters.

SOMMAIRE

La recherche sur la dynamique des chaînes de polymères dans des espaces étroitement confinés est un aspect crucial des études de transport des dispositifs microfluidiques. La diffusion en file unique reste l'un des sujets les moins explorés dans ce domaine, alors qu'elle présente un potentiel pour diverses applications et pour des recherches plus approfondies.

Cette thèse se concentre sur la dynamique des molécules de polymères dans un tube étroit. Mes projets visent principalement à simuler les comportements de divers systèmes dans le temps et à comprendre le mouvement collectif des chaînes de polymères.

Une partie du travail est liée à des questions de premier passage. Ainsi, nous analysons le temps nécessaire à la séparation des fragments de polymères pour obtenir une séparation nette en cartographie de l'ADN. Les conditions initiales du système affectent la séparation des fragments. Nous examinons l'effet du hasard et de l'ordre segmentaire sur les temps de séparation. En complément, nous étudions brièvement comment la fragmentation aléatoire d'une molécule de polymère affecte l'ordre final des fragments, soulignant ainsi l'importance de la théorie des blobs dans notre étude.

En outre, nous étudions également les collisions entre les polyélectrolytes et les chaînes de polymères non chargées dans des conditions de confinement sévère. Le comportement non monotone de la vitesse, la durée des collisions, le type de collision et les conditions semblables à celles de l'électrophorèse sur gel peuvent tous contribuer à la réussite de la séparation des polyélectrolytes. Cependant, la construction de dispositifs de séparation pratiques peut nécessiter d'autres modifications du système, telles que l'application de champs pulsés avec des périodes de temps asymétriques ou la création artificielle de diamètres de tubes asymétriques. En fin de compte, il devrait être possible de manipuler les polyélectrolytes en utilisant les idées présentées dans cette thèse.

Nous étudions également la diffusion en file unique de polymères à l'aide de dynamique moléculaire. En comparant le mouvement des longues chaînes avec les prédictions des théories connues pour les particules dures, nous expliquons les multiples régimes temporels qui existent. En outre, grâce à nos propres algorithmes, nous pouvons simuler ces mêmes problèmes à l'aide de méthodes de Monte Carlo, ce qui augmente la vitesse de calcul. Enfin, nous démontrons qu'il est possible d'établir un lien entre ces deux méthodes de simulation en liant leurs paramètres clés.

AUTHOR CONTRIBUTIONS

I declare that the work presented in this thesis is, to the best of my knowledge, original. My work comes from my PhD training under the supervision of Prof. Gary Slater.

This thesis includes two papers published in peer-reviewed journals (Chapters 2 and 4), and one manuscript that will be submitted for publication (Chapters 3). In addition, four smaller and exploratory projects are included in Chapter 5.

As the first author of all papers (the only other co-author is my supervisor), all simulation results were generated by me. The data analysis, the theoretical work and the writing of the manuscript were shared with my supervisor. My supervisor was a tremendous help throughout the project and thesis, which includes, but is not limited to, critical thinking about theory, suggestions for analyses, help in improving manuscripts, and revisions of writing. We co-edited the manuscripts using the online LaTeX platform *Overleaf*, whose writing tools also greatly assisted in the writing process.

All Langevin Dynamics and Lattice Boltzmann simulation results presented in this thesis are the result of my work, and these programs used the *ESPResSo* simulation package. All Monte Carlo simulation codes were written by me in *python* and *C++* languages.

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INTRODUCTION

The purpose of this introduction is, on the one hand, to provide some information about the motivation behind the work and the history of the field at the centre of the thesis and, on the other hand, to give a brief overview of the background knowledge of the research topic of the thesis. This introduction is written so that (most of) it can be read not only by experts but also by non-experts who want to understand the main concepts of the thesis. While it is too early to delve into the specifics of the projects on page one, I will provide a concise overview of my Ph.D. work, emphasizing my achievements and the techniques employed.

This thesis investigates the dynamics of polymer chains in dilute solutions, where the polymer molecules are constrained within quasi-one-dimensional geometries. In subsequent sections, we will delve into the specifics of polymer chains, the confinement conditions, and the interactions and forces involved. For now, we address a fundamental question: what is

the rationale behind pursuing this line of research?

The study of flexible polymer chains in dilute conditions constitutes a foundational aspect of the entire field of polymer physics. While classical approaches [1] describe the conformations and dynamics of polymer chains in three-dimensional dilute solutions for various types of solvents, there is a growing interest in systems with reduced dimensionality, especially quasi-one-dimensional systems (in which the chains are confined in narrow tubes or channels)[2, 3]. Although the study of individual polymer chains under confinement is extensively covered in academic literature, much less research has been done on polymer solutions under such conditions.

Indeed, many research groups have proposed theories to describe the physics of an individual polymer chain in a narrow channel. The stiffness of the polymer chain, the hydrodynamic interactions, the solvent conditions, various liquid flows, the effect of electrostatic interactions, etc. A multitude of possible factors have been explored, and their effects summarized, when considering a single polymer chain in a narrow channel. However, this is not the case for multi-chain systems, which are a relatively unexplored subject.

My doctoral research involves a theoretical and computational examination of certain issues that fall within this category of polymer-related problems. Unlike similar studies performed on 3D dilute solutions, interactions between polymer chains are unavoidable in most cases, even in the dilute limit. The chains are unable to diffuse independently and are forced to arrange themselves along the channel's axis, resulting in strong steric interactions.

Placing polymer molecules in such confined environments is a simple but important experimental setup for many polymer-related experiments. Such devices can be used to probe, separate, purify, sense, or manipulate polymer molecules. Nature also has such narrow tubes, for example in blood vessels, where red blood cells and various macromolecules have to move. The diffusion coefficients of the polymer chains are influenced by the system parameters, so that large physical effects can be expected in multiple-chain systems. Thus, understanding the movement of objects in narrow tubes helps in biophysical research.

But what is a polymer molecule? Simply said, polymer molecules are made of many repeating molecular units (monomers) linked by chemical bonds. They are a part of modern human materials integrated into daily life.

The polymer molecules and narrow tubes that interest us are extremely small, measuring in the micron (10^{-6} m) or even nanometre (10^{-9} m) range. That's thousands of times smaller than the diameter of the average Ph.D. student's hair, assuming they haven't gone bald by the end of their PhD work. Care must be taken when handling polymer molecules and tiny tubes on such a small length scale. Before building an experimental setup, the experimentalists may want to know how to design the setup to maximize the success and accuracy of the experiment. Natural nanoscale systems, such as chemical transport in living cells, are also challenging to study. Therefore, numerical simulations are excellent tools to understand these delicate systems.

Experimental and theoretical studies have been the two main approaches to scientific research for a millennium. Since the last century, computational modelling has become the third component of research approaches, and it is a rapidly growing field as the processing power of computers has increased dramatically over the last few decades. Computational simulations build virtual worlds guided by theoretical models to perform virtual measurements. These virtual measurements serve as a basis for physicists to test new ideas or possible approximations relatively quickly and cheaply.

My simulations are run on desktop computers and supercomputer servers. No one expects virtual simulations to perform better than experimentation, but it is a reasonable strategy to guide the research. For instance, long-range interactions between polymer chains, such as hydrodynamic interactions (HI), are not considered in most of my simulation models. Neither are the atomistic details of the molecules. While there are good reasons to ignore these considerations, it is worth pointing out that HI is a real factor and is closely related to actual experimental results.

In practice, our simulations do not aim for a perfect one-to-one model and do not construct the target object from the most detailed level (atomic structure, for example).

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Instead, I cut out unnecessarily complex parts in order to complete the simulations in a reasonable amount of time.

In the following parts of the Introduction, I give some basic background information about my work, starting with what polymers are (Section 1.1); how they move (Section 1.2); special polymer-related problems of interest (Section 1.3), including electrophoresis, polymer collisions, and single-file diffusion; and the simulation methodologies I used (Section 1.4). Finally, this chapter ends with a short overview of the thesis (Section 1.5).

1.1 THE PHYSICS OF POLYMERS

The word polymer consists of two parts: *poly* meaning *many*, and *meros* meaning *parts*; polymer means many repeating units joined together. This is the physical structure of polymer molecules: the monomers are connected to form chains, rings, or complex configurations.

In a sense, the history of polymers is the history of materials science. The development of polymers has greatly affected our civilization and life. Today, polymer materials are inseparable from our daily lives, from plastic sunglasses to shoe soles; from the cover layer of space stations on an inclined orbit to the floating plastic bags inside the ocean, all aspects of our life have been affected by these materials. No matter good or bad, polymers are an unavoidable part of life. The examples of polymers around us are obvious, but the fact that our bodies are full of them is also amazing: Human genes are written on a polymer called deoxyribonucleic acid, or to use its more common name, DNA. Polymers are not only the blueprints for most organisms on Earth; they are also the building blocks of these organisms, forming the complex structures in our bodies that support our activities.

Polyethylene is one of the most common and simplest examples of polymers, with CH_2 as the monomer, and each monomer being linearly connected to its neighbours, leaving two CH_3 end groups. Except for these two CH_3 groups, each unit is connected by covalent bonding to two neighbouring units. Each CH_2 unit can be treated as one *monomer* along

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the backbone of the polyethylene molecule, and, of course, the CH_3 groups are the two end monomers.

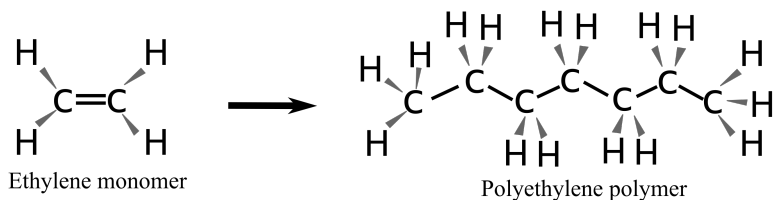


Figure 1.1: Polyethylene is generated by a polymerization process involving ethylene molecules.

Polymers have a wide range of sizes. The magicians in the lab (I adore and respect lab members, they're all very capable), often use the molecular weight of a molecule or other related quantities (the average molecular weight for a mixed sample, for instance) to characterise their samples. For us, doing mainly theoretical calculations or simulations, the polymer size is expressed in terms of the number of repeating units, N , also called the degree of polymerisation. In general, the degree of polymerisation can range from dozens to millions $N \in [10^1, 10^6+]$, and some giants can reach billions. The value of N varies depending on the problem.

Most of our simulated polymers are simple, with N monomers per polymer chain, linearly connected without any branching. We also need to simulate the environment of these polymer chains, such as obstacles or walls. In addition, we need to simulate the thermal baths, which contain solvent molecules that collide with the monomers. In this thesis, we assume that all solvents are good solvents, which means that the monomers interact the same with the solvent molecules and with the other monomers.

By admitting defeat in solving this many-body problem and predicting the motion of the polymers, one can turn to thermodynamic averaging. Certain properties of a single polymer chain can be well characterized when the number of units N , i.e. the degree of polymerization, is sufficiently high. In the remainder of this chapter, I will introduce some of the most important and well-known results for a single polymer chain in a good solvent.

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1.1.1 IDEAL POLYMER CHAINS AND THEIR SIZE

The question that comes before "how to characterize a specific polymer" is: What kind of polymer are we dealing with? Polymer characterization results vary with the polymer type. Imagine a single linear polymer chain inside a liquid heat bath environment. The chain consists of N connected repeating units. It is constantly moving and deforming due to collisions with the solvent molecules. In this subsection, it is assumed that such deformation and motion are constrained solely by the connectivity of the monomers and the lengths of the bonds. The effects of monomer excluded volume are ignored, and the presence of a good solvent is assumed.

In the simplest model of this polymer chain, its segments are free to orient themselves in any direction they choose. This model chain is called a freely-jointed chain (FJC).

The FJC model can be treated as a random walk of $N - 1$ steps of length b . This walker has no memory such that the direction of its next step is totally random; this is known as a **Markovian process**. Therefore, the walker can return to any position (or positions) it previously occupied. The trajectory of such a walker resembles a polymer chain of N connected points or beads; the size of the beads is ignored and the restriction on overlapping segments is removed. A polymer model with this property is considered an ideal chain, distinct from other relatively complex polymer models.

To characterize this N -bead ideal chain, we first need to define the chain's position and the size of its conformation. The position of the i -th bead is noted as $\mathbf{r}_i$, with $i \in [0, N - 1]$. The set of bead positions $(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{N-1})$ gives both the polymer molecule conformation and the 3D position of its centre of mass. Figure 1.2 shows an example of a FJC polymer conformation. The chain position is the average position of its beads:

$$\mathbf{r}_{cm} = \frac{1}{N} \sum_{i=0}^{N-1} \mathbf{r}_i \quad (1.1)$$

Technically, this expression gives the position of the *centre of mass* only if the polymer

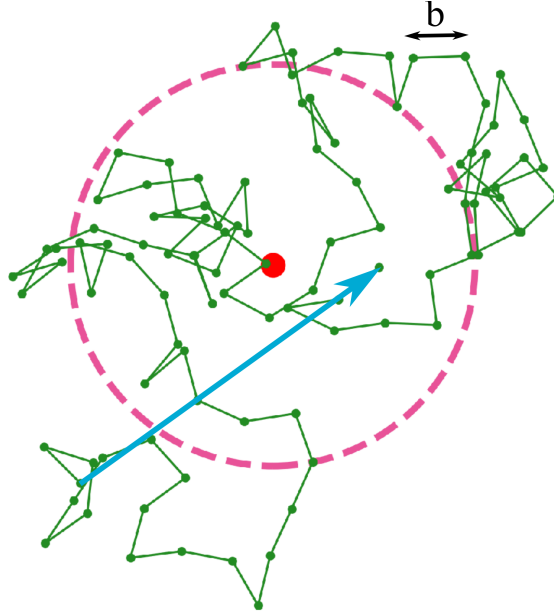


Figure 1.2: A 2-dimensional ideal linear polymer chain, constructed as a random walk of 100 steps with a fixed bond length b . The red dot is the position of the centre of mass. A dashed red line outlines the circle having a radius equal to the instantaneous radius of gyration R_g . The cyan arrow indicates the end-to-end vector.

chain is uniform. Since this thesis only examines homopolymers, Eq. 1.1 represents the centre of mass of the polymer in all discussions. The red dot in Fig. 1.2 is an example.

The next issue is the spatial size of the polymer conformation. If we imagine the polymer chain as a straight line, its length from one end to the other is called the *contour length*, $L_c = (N - 1)b$. Since no such polymer exists in the natural environment, this information is useful but not sufficient. Our polymer has a total of N monomers (or beads), which together occupy a certain volume of space; this implies that the conformation of the entire polymer group can be described with a certain length scale. However, the polymers cannot hold their shape because they are constantly changing and moving in the heat bath. We need an 'average' concept to describe the mean size of the polymer conformations.

As previously noted, a polymer chain's natural conformation resembles a random walk.

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It is easy to notice the start and end points of random walks. The distance between these two endpoints can describe their size, aka the size of the conformation of the linear polymer chain. The end-to-end vector of this random walk is

$$\mathbf{R}_{ee} = \mathbf{r}_{N-1} - \mathbf{r}_0 \quad (1.2)$$

The average value of this vector $\langle \mathbf{R}_{ee} \rangle = 0$ since random walks have no directional biases. Note that we do not consider this random walk to be a self-avoiding walk (SAW); bond overlapping is acceptable for now.

Starting from the same point, considering a large number of random walks, the aggregate vectors will form a sphere and there will always exist another vector $-\mathbf{R}_{ee}$ towards the opposite direction, hence the fact that $\langle \mathbf{R}_{ee} \rangle = 0$. However, the radius of this sphere of trajectories is a nonzero value; this is an obvious measure of the average size of the polymer/random walk and can be easily estimated.

Let us not treat this polymer as a collection of point-like monomers, $(\mathbf{r}_0 \dots \mathbf{r}_{N-1})$, but instead as a series of bonds, $(\mathbf{s}_0 \dots \mathbf{s}_{N-2})$, of length b , with $\mathbf{s}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$. Thus the end-to-end vector can be rewritten as the vector summation

$$\mathbf{R}_{ee} = \sum_0^{N-2} \mathbf{s}_i, \quad (1.3)$$

while the mean square end-to-end distance is

$$\begin{aligned} \langle \mathbf{R}_{ee} \cdot \mathbf{R}_{ee} \rangle &= \left\langle \sum_0^{N-2} \mathbf{s}_i \cdot \sum_0^{N-2} \mathbf{s}_j \right\rangle \\ &= \sum_{i=j}^{N-2} \langle \mathbf{s}_i \cdot \mathbf{s}_i \rangle + \sum_{i \neq j}^{N-2} \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle \\ &= Nb^2 = L_c b. \end{aligned} \quad (1.4)$$

Note that in the limit where $N \gg 1$, when the polymer is really large, the difference

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between $N - 2$ and $N - 1$ is negligible. Since $\mathbf{s}_i \cdot \mathbf{s}_i = b^2$, the first term of Eq. 1.4 equals $\sum b^2 = Nb^2$. For two uncorrelated vectors, the dot product is $s_i \cdot s_j = s_i s_j \cos(\psi)$, where ψ is the angle between these two vectors. For $\psi \in (0, \pi)$, we have that $\langle \cos(\psi) \rangle = 0$. Thus the second term equals zero. The typical end-to-end distance is thus given by:

$$\sqrt{\langle \mathbf{R}_{ee}^2 \rangle} = N^{1/2} b. \quad (1.5)$$

We now consider an ideal random walk in one dimension. The value of $|\mathbf{R}_{ee}| = x(N)$ is its final position after N steps. Assuming that n steps are in the $+$ direction and $(N - n)$ in the $-$ direction, the final position is $x = nb + (N - n)(-b) = b(2n - N)$. The probability of being at that position is a binomial distribution with $P_N(n) = \frac{1}{2^N} \frac{N!}{n!(N-n)!}$. To predict $P_N(n)$ in the $N \rightarrow \infty$ limit, we use Stirling's formula approximation; this binomial distribution then approaches the normal distribution

$$P(|\mathbf{R}_{ee}| = x) = \frac{1}{\sqrt{2\pi N b^2}} e^{-\frac{x^2}{2Nb^2}} \quad |x| \ll Nb. \quad (1.6)$$

This is the probability density for a one-dimensional *Gaussian* random-walk *polymer* chain [4], with similar expressions for the other dimensions. The three-dimensional probability density is the product of the probability densities in each dimension, which leads to

$$P(|\mathbf{R}_{ee}| = r) = \left(\frac{3}{2\pi N b^2} \right)^{3/2} e^{-\frac{3r^2}{2Nb^2}}, \quad (1.7)$$

where $|\mathbf{R}_{ee}| = r$ is the magnitude of the end-to-end vector in 3D, with $r^2 = x^2 + y^2 + z^2$.

Describing ideal polymer dimensions using $\sqrt{\langle \mathbf{R}_{ee}^2 \rangle}$ has limitations, as it focuses only on the end monomers, neglecting other details. End-to-end vectors also do not provide useful insights into non-linear polymers, such as ring polymers or branched polymers.

In most polymer studies, we use an alternative measure of conformational size, the

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radius of gyration [1]:

$$R_g^2 = \frac{1}{N} \sum_{i=0}^{N-1} (\mathbf{r}_i - \mathbf{r}_{cm})^2 . \quad (1.8)$$

The calculation involves the relative positional information for all monomers to determine the effective radius of the conformation. This length scale is more useful because it can be used to calculate the size of all configurations (e.g., ring polymers have no ends). The radius of gyration of an ideal polymer linear chain is given by [4]:

$$\langle R_g^2 \rangle = \frac{1}{6} N b^2 \quad (1.9)$$

The value of $\langle R_g^2 \rangle^{1/2}$ offers an alternative way to characterize the mean size of a polymer conformation inside a given environment. For ideal linear polymers in 3D **free** solution, the ratio between the two averaged length scales introduced above is $\langle \mathbf{R}_{ee}^2 \rangle / \langle R_g^2 \rangle = 6$. The radius of gyration is a useful length scale for representing the size of a polymer, and in this thesis, we use R_{go} (or other symbols similar to it) to denote its value in free solution.

We can now characterize ideal polymers and view them from another perspective. Equation 1.7 can also be thought of as the probability of a state, specifically a state with an end-to-end distance $\mathbf{R}_{ee}$ and a free conformational energy U . In statistical mechanics, the probability of such a state is weighted by the Boltzmann factor $e^{-U/k_B T}$, where T is the temperature of the heat bath and k_B is the Boltzmann constant. We can consider that Eq. 1.7 includes the free energy $U(\mathbf{R}_{ee}) = \frac{1}{2} k \mathbf{R}_{ee}^2$, similar to the expression for a harmonic spring with a spring constant

$$k = \frac{3k_B T}{N b^2} . \quad (1.10)$$

We can thus map the ideal polymer onto a harmonic spring with an extension $\mathbf{R}_{ee}$ and a spring constant k . This is effectively a *harmonic entropic spring* that pulls two ends. The conformational entropy acts as this spring, and the concept of entropy plays an important role in polymer studies. In fact, any subsection of an ideal polymer chain can be replaced by such a spring – this is the idea behind the various bead-spring models.

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1.1.2 REAL POLYMERS

The previous section introduced the ideal polymer model, which is useful for anyone to understand the physical properties of polymers, but it does not include the actual size of the monomers. All real polymers exhibit inherent self-avoidance characteristics, thus enhancing the model is essential.

Real polymer chains are subject to excluded volume interactions between the monomers. This is known as the “swelling” effect since real polymer chains will naturally occupy more space than the equivalent ideal chains. We can start by considering a set of ideal polymer chains with dimensions $R_{go} \propto N^{1/2} b$. If we replace each point-like monomer with a finite-size sphere, some of the monomers of the ideal polymer will inevitably overlap with other monomers in a way that is not permitted for real polymers. Therefore, we eliminate these overlapping conformations from all of the conformations of an ideal polymer. The size of the remaining conformations are larger because, on average, the conformations with an overlap are smaller.

Similarly to the scaling law in the ideal polymer model $R_{go} \sim N^{1/2} b$, the real chain size R_{go} has its own scaling law. According to Flory [1], the following is more consistent with the physical properties of real polymer chains in free solution:

$$R_{go} \propto N^\nu b . \tag{1.11}$$

Flory predicted that $\nu = 3/(d + 2)$ in d -dimensional ($d \leq 4$) space, with $\nu = 3/5$ in three dimensions (a more accurate value would be $\nu = 0.588$ [4]). It is worth noting that the values of $\nu = 1$ and $3/4$ are exact in one and two dimensions, respectively. Not surprisingly, $\nu = 1$ is correct in one dimension: once the random walker decides to take the first step, it cannot go back to its previous position, so the magnitude of the end-to-end vector of such a polymer chain would be $|\mathbf{R}_{ee}| = Nb$. As the dimensionality d increases, we obtain $\nu = 1/2$ when $d = 4$, which implies that real polymers behave similarly to ideal chains in 4D. This is because the probability of re-visiting the same volume of size $\simeq b^d$ decreases

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with increasing dimensionality: at higher dimensions (≥ 4) there exists a huge amount of space for the polymer to occupy.

The size exponent ν is known as the Flory exponent. Flory's derivation of ν looks for the equilibrium between the above-mentioned polymer swelling and the entropic effects opposing swelling. Flory used a simple method to estimate ν by expressing the free energy of a real chain as a function of the entropy resulting from the different chain conformations and the excluded volume interactions between the monomers.

The polymer chain length scale is $r = \mathbf{R}_{ee}$, where $\mathbf{R}_{ee}$ is the end-to-end distance of the polymer. We assume that each monomer is surrounded by a uniform cloud of monomers inside the polymer coil. Although not indicative of actual polymer conformations, this assumption is a reasonable mean-field approach.

On the one hand, the probability density for the end-to-end distance of a 3D Gaussian chain is given by Eq. 1.7. Its entropy can be estimated as $S_c \simeq k_B \ln(P) \simeq -k_B r^2 / Nb^2$ (c stands for 'conformation'). Its contribution to the Helmholtz free energy A is thus $A_c = -TS_c$, where T is the temperature. Note that this expression remains constant across all dimensions. This entropic contribution can be considered as an entropic spring: as we introduced in the previous section, the free energy is $U(\mathbf{R}_{ee}) = \frac{1}{2}k\mathbf{R}_{ee}^2$. The spring constant k is given by Eq. 1.10. Note that this argument is for an ideal polymer.

On the other hand, each monomer of size b occupies a volume $v_d \simeq b^d$, and the space they occupy is $V_d \simeq r^d$. In thermal equilibrium, the energy due to a monomer-monomer interaction is of order $k_B T$. The probability of one monomer interacting with another one is equal to the total volume of the N beads over the total volume $\frac{Nb^d}{r^d}$. There are N monomers in total; thus, the free energy due to the excluded volume is given by $A_e \simeq k_B T \times N \times \frac{Nb^d}{r^d}$.

The sum of these two contributions is Flory's estimate of the free energy of the polymer chain. These free energies have opposing dependencies on r : increasing r reduces the monomer density and weakens the excluded volume interactions, but A_c increases as the entropic spring is stretched. The value of r that optimizes $A_e + A_c$ is the most appropriate

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value of r for a given N in d dimensions:

$$\frac{d}{dr} (A_e + A_c) = 0 \quad , \quad (1.12)$$

$$k_B T \frac{d}{dr} \left(N^2 \frac{b^d}{r^d} + \frac{r^2}{N b^2} \right) = 0 \quad .$$

Solving Eq. 1.12, we find the scaling law for the polymer size r :

$$r \sim N^{3/(d+2)} b \quad . \quad (1.13)$$

In d dimensions, the Flory exponent is thus approximately

$$\nu = \frac{3}{d+2} \quad . \quad (1.14)$$

Note that Eq. 1.14 is not exact in 3D, but the numerical value (0.588) is close to $3/5$ [4].

Another factor is the solvent condition [4]. Depending on how likely the polymer molecules are to interact favourably with the solvent molecules, the solvent condition can be classified into poor, theta, and good solvent. Poor solvents cause polymer molecules to collapse ($\nu \rightarrow 1/3$), with stronger attraction between polymer segments than solvent-segment attraction (an example is polystyrene in methanol). On the other hand, good solvents cause molecules to swell ($\nu \rightarrow 3/5$) because of the excluded volume interactions. The polymer segments interact more with the solvent than the other segments, leading to the expanded conformation in the solution, i.e. polystyrene in toluene. Theta solvents are characterized by the fact that $\nu = 1/2$. It is important to note that $\nu = 1/2$ does not imply polymer chains are ideal in these solvents; rather, it indicates that the polymer's radius-of-gyration scales like that of an ideal chain, despite its segments not overlapping, which is unlike an ideal polymer. In this thesis, we assume that all solvents are good solvents, and that $\nu = 3/5$.

1.1.3 POLYMER RIGIDITY

So far, we have discussed freely jointed, flexible polymer models. Now, we explore models incorporating bond angle restrictions and rigidity. Note that excluded volume interactions are neglected in this section.

We have already talked about the bond vector $\mathbf{s}_i$; now we look at its immediate neighbour, $\mathbf{s}_{i+1}$. These two consecutive bonds form an arbitrary angle ψ . In the FJC model, ψ can take any value between 0 and π . In a revised model, we fix ψ for all bond vector pairs along the chain but allow unrestricted rotation along the direction of $\mathbf{s}_i$ (the different positions along the cone have the same probability).

The complementary angle of ψ is $\theta = \pi - \psi$ such that $\mathbf{s}_i \cdot \mathbf{s}_{i+1} = \cos(\theta) b^2$ (see Fig. 1.3). Projecting the next bond vector, $\mathbf{s}_{i+2}$, will reduce the $\cos(\theta)$ by another similar amount $\cos(\theta)$, and propagation to further bonds will build up through such multiplication. We are interested in this projection because of this question: "How many more bonds will be needed before the effects of the orientation of the first bond wear off?"

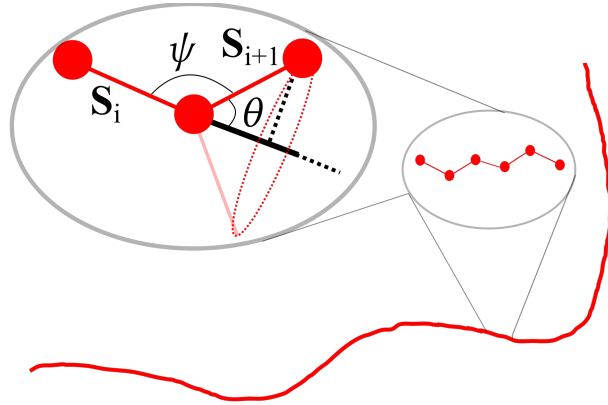


Figure 1.3: Bond vectors in the bead-stick model with a bond angle ψ in a zoomed-in plot. The red curve around the zoomed-in image is a worm-like chain sketch.

The memory of the original bond vector $\mathbf{s}_i$ will decay after sufficient additional projections. By taking the ensemble average, we can thus conclude that the orientation correla-

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tion between bonds i and $i + j$ is $\langle \mathbf{s}_i \cdot \mathbf{s}_{i+j} \rangle = \cos^{|j|}(\theta) b^2$, so that

$$\begin{aligned} \frac{\langle \mathbf{s}_i \cdot \mathbf{s}_{i+j} \rangle}{b^2} &= \cos^{|j|}(\theta) = e^{\ln[\cos^{|j|}(\theta)]} = e^{|j| \ln[\cos(\theta)]} \\ &= e^{-|j|b/L_p} \end{aligned} \quad (1.15)$$

where the characteristic decay length is

$$L_p = \frac{-b}{\ln[\cos(\theta)]} . \quad (1.16)$$

Bond correlation thus decays exponentially over a length scale L_p or over L_p/b monomers.

If we want to introduce extreme rigidity into the model (corresponding to $L_p \gg b$), much like the rigidity that double-stranded DNA molecules have, we can consider that the value of θ is small. When $\theta \ll 1$, the small angle approximation gives $\cos(\theta) \simeq 1 - \theta^2/2$. Since we then have $\ln[1 - \theta^2/2] \simeq -\theta^2/2$, Eq. 1.16 becomes:

$$L_p = 2b/\theta^2 . \quad (1.17)$$

In the limit where $L_c \gg b$, the conformation of the chain is not zigzag but a smooth curve in a 3-D space. This polymer model is called the Kratky-Porod model or the wormlike chain, and L_p is called the persistence length [5]. The wormlike chain model can be described using two parameters, L_p and the contour length $L_c = Nb$.

In the wormlike chain model, the mean square end-to-end distance $\langle R_{ee}^2 \rangle$ is given by:

$$\langle R_{ee}^2 \rangle = 2L_p [L_c + L_p(\exp(-L_c/L_p) - 1)] \quad (1.18)$$

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The ratio of L_p/L_c suggests two different limits here:

$$\langle R_{ee}^2 \rangle = \begin{cases} L_c^2 \left[1 - \frac{L_c}{3L_p} + \dots \right] & L_p \gg L_c , \\ 2L_c L_p \left[1 - \frac{L_p}{L_c} + \dots \right] & L_p \ll L_c . \end{cases} \quad (1.19)$$

When $L_p/L_c \gg 1$, the polymer chain has an extremely long persistence length and behaves as a solid rod with $\langle R_{ee}^2 \rangle = L_c^2$. When $L_p/L_c \ll 1$, on the other hand, the polymer chain acts like a flexible string with $\langle R_{ee}^2 \rangle = 2L_c L_p$. Since we have $\langle R_{ee}^2 \rangle = Nb^2 = L_c b$ for a freely jointed chain, these two results are identical if the effective bond length of the worm-like chain is $b_K = 2L_p$; this effective bond length is called the Kuhn length.

Similarly, the radius-of-gyration of the worm-like chain is [4]:

$$\langle R_{go}^2 \rangle = \frac{1}{3} L_p L_c - L_p^2 + 2 \frac{L_p^3}{L_c} \left[1 - \frac{L_p}{L_c} (1 - \exp(-L_c/L_p)) \right] \quad (1.20)$$

In the two limits, we have:

$$\langle R_{go}^2 \rangle = \begin{cases} \frac{1}{12} L_c^2 \left[1 - \frac{L_c}{5L_p} + \dots \right] & L_p \gg L_c , \\ \frac{1}{3} L_c L_p \left[1 - \frac{3L_p}{L_c} + \dots \right] & L_p \ll L_c . \end{cases} \quad (1.21)$$

In the limit $L_p \ll L_c$, we recover the FJC result $\langle R_g^2 \rangle = \frac{1}{3} L_c L_p = \frac{1}{6} N b_K^2$. In the other limit where $L_p \gg L_c$, the polymer chain acts like a rigid rod and we obtain $\langle R_g^2 \rangle = \frac{1}{12} L_c^2$, the well-known result for the moment of inertia of a rod.

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1.1.4 TOPOLOGICAL POLYMERS: RINGS

While previous sections focused on linear polymer chains, this thesis also explores a different topology: polymer rings. Here, I will introduce their main characteristics.

The structure of a ring polymer is just like what its name suggests: N monomers are connected, joined end to end to form a circle. In other words, ring polymers can be considered as two parallel linear polymer chains, and the size of the ideal cyclic polymers reflects this metaphor:

$$R_{go}^2 = \frac{1}{12} N b^2 . \quad (1.22)$$

Equation 1.22 is exactly $\frac{1}{2}$ of Eq. 1.9. Not only is the average size of the ring polymer reduced, but its conformational entropy drops too. By connecting the two end monomers of a linear polymer, its original ends lose their conformational freedom. Another way of looking at this problem is that random walkers are limited to $R_{ee} = 0$, and many possible conformations are not achievable for this reason. Therefore, ring polymers have reduced conformational entropy compared to linear polymers of the same molecular weight.

This means that cyclic polymers are more compact compared to linear polymers, and this fact plays a crucial role in some size-related problems. Note that we assumed $L_c \gg L_p$ cases (the polymer is flexible) and possible knots on the polymer chains are not considered in our studies.

For a real ring polymer, its radius of gyration is $R_{go} \sim N^{3/5}$. The topological structure of the ring polymer yield a different prefactor, but the scaling is the same as that of the linear real polymer chain (the Flory exponent is unaffected).

1.1.5 CONFINED POLYMER CHAINS: TUBES AND BLOBS

I have covered some of the basics about the statistical properties of polymer chain conformations, discussing their size and scaling laws. Thus far, the discussion has been on

1.1. THE PHYSICS OF POLYMERS

polymer chains in a free solution, the simplest situation. The properties of polymers become more challenging when they are in a confined space.

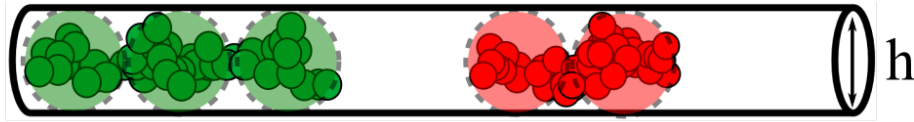


Figure 1.4: Two polymer chains confined inside a cylindrical tube of diameter h . Also shown is a representation of the blobs (light coloured circles) used in the theoretical description.

Figure 1.4 illustrates two flexible polymer chains within a tube of diameter h . Deformation occurs when the polymer size in free solution exceeds the channel size ($R_{go} > h$). In general, we use the blob theory to help us understand the conformation of polymers in such situations.

Let's consider a random walker starting inside the tube; how many steps might it take to reach the wall of the tube? According to Eq. 1.13, the end-to-end distance for a polymer chain in a free solution is proportional to $N^\nu b$. Therefore, we can expect that the walk will intersect the wall after g steps, with $h \simeq g^\nu b$. The theoretical description models a long flexible chain (with N monomers and a Kuhn length comparable to b) inside a tube of diameter $b \ll h \ll R_{go}$ as a series of $M = N/g$ blobs of size h that contain $g \simeq (h/b)^{1/\nu}$ monomers each. Below the tube length scale h , the random walk blobs simply follow the scaling rules and statistical laws for chains in free solutions. The key point here is that these blobs do not overlap or intersect each other (unlike in the case of ideal chains). The length of the polymer conformation along the tube axis is then that of a series of M blobs

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placed end to end:

$$L(N, h) \simeq M(N, h) h \simeq N \left(\frac{b}{h} \right)^{1/\nu} h \sim N h^{1-1/\nu}. \quad (1.23)$$

The length scale L introduced here is similar to the concept of polymer chain *span*. The latter is defined as the maximum distance between parallel planes normal to the cylinder axis which contain segments of the chain.

When a polymer chain is confined within a narrow tube, its entropy is reduced: moving a polymer chain from a free solution (where its radius of gyration is R_{go}) into a narrow tube restricts its possible conformations. We can start this problem by asking: how much free energy is required to squeeze a free polymer chain in a cylinder of size $h < R_{go}$?

Why is there a cost in free energy? The very act of 'squeezing' is energy-intensive and we can think back to preparing the Christmas turkey dinner: stuffing the turkey is hard work! Similarly, if we force a polymer coil into a narrow tube, its size is reduced from R_{go} to h in two directions, while it is increased to L in the other direction. The conformational entropy of the polymer chain acts like a spring that resists this change, and it takes energy to overcome it. We can use a simple scaling argument to understand this process. In this problem, we have two length scales (R_{go} and h) and a single energy, namely $k_B T$. Thus the free energy difference must scale like $\Delta A \sim k_B T \times \left(\frac{R_{go}}{h} \right)^y$. The exponent y is unknown at this moment. However, we know that the free energy is directly proportional to the loss in entropy, $\Delta A = -T \Delta S$. In addition, the entropy is an extensive concept: losses in entropy are linearly proportional to N . Therefore, we must have $\Delta A = -T \Delta S \sim T N^1$. We can thus conclude that $\left(\frac{R_{go}}{h} \right)^y \sim N$. Since $R_{go} \sim N^\nu$ according to Eq. 1.11, we find that $y = 1/\nu$, and thus we have:

$$\Delta A \simeq k_B T \left(\frac{N^\nu b}{h} \right)^{1/\nu} \simeq N k_B T (b/h)^{1/\nu}. \quad (1.24)$$

Note that Eq. 1.24 is a scaling relation. Without an exact pre-factor, we can't find the

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exact entropy difference, but it provides the right physics insight: the larger the polymer chain, the harder it is to squeeze it into a narrow tube. In the extreme condition $h = b$, the monomers align along the tunnel, incurring a free energy cost of $k_B T$ per monomer.

Since we have assumed that the polymer chains are flexible on the length scale of the tube width, the above discussion must be treated with caution, especially if the Kuhn length of the chain is not negligible compared to the tube width. The discussion in this section encompasses the main methodology we use when trying to characterize the size of confined polymers: find the blobs!

1.1.6 DILUTE POLYMER SOLUTIONS

Our previous discussions focused solely on a single polymer chain. It takes two to tango, and most interesting physics problems involve many polymer chains. Therefore, we need to introduce the concept of polymer solutions.

A polymer solution is a system in which polymer molecules are dissolved in a solvent. The mixture's volume is denoted by $\mathbb{V}$, and it contains n polymer chains. The concentration of polymer chains is then $C = \frac{n}{\mathbb{V}}$. In this thesis, we focus on dilute polymer solutions, the concentration conditions under which there is "sufficient space" between the polymer chains. The term "sufficient space" is ambiguous; what does it mean? To clarify this, we need to introduce the overlap concentration C^* .

In short, we can think of C^* as the reference concentration where the polymer molecules start to touch each other. Assuming all polymers share the same degree of polymerization, each chain has an average radius of gyration $R_{go}(N)$ in free solution. At C^* , the volume of the solution is packed with polymer coils, $\mathbb{V} \simeq nR_{go}^3(N)$, so that $C^* \simeq R_{go}^{-3}(N)$. When $C < C^*$, the polymer molecules are separated from each other; this solution is called a dilute solution. The other limit is when $C > C^*$; the polymer chains then interact with one another, and the system is said to be semi-dilute. The physics vary significantly in these situations. The top row of Fig. 1.5 illustrates three scenarios when varying polymer

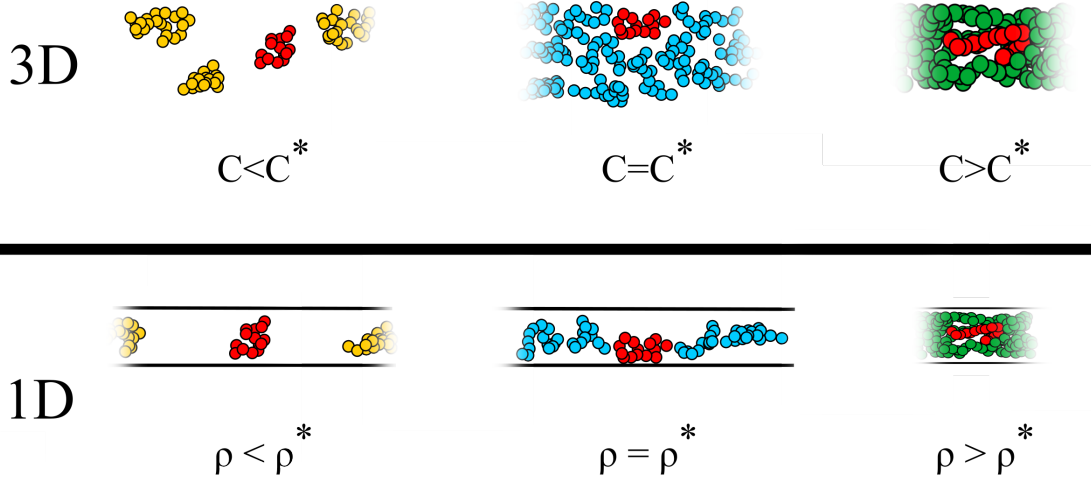


Figure 1.5: Concentration regimes for solutions of linear flexible polymers: dilute solutions (left), solution at the overlap concentration (centre), and the semi-dilute solution (right). The three-dimensional (top row) and one-dimensional (bottom) cases are shown.

chain concentration in a 3D solution.

However, in the case of cylindrical constraints, we use a slightly different way to define the overlap concentration. We now place n polymer chains, each with an axial size $L(N, h)$ given by Eq. 1.23, in a cylindrical system of length $\mathbb{L}$. The resulting linear concentration is $\rho = n/\mathbb{L}$. Again, the concentration at which the polymer molecules begin to touch is defined as the overlap concentration, and it is given by $\rho^* \simeq 1/L(N, h)$. Similar to the discussion in 3D, we have a dilute polymer solution when $\rho < \rho^*$. Figure 1.5 also shows the transition to the demi-dilute regime; however, our main interest remains in dilute polymer solutions.

1.2 POLYMER DYNAMICS AND HYDRODYNAMICS IN A TUBE

1.2.1 EINSTEIN THEORY OF DIFFUSION FOR SOLID PARTICLES

This section introduces polymer dynamics, starting with the fundamental unit: the monomer. Imagine a single monomer in a heat bath where solvent molecules collide with it, exerting random forces in various directions. The monomer will move or slow down as a result of these collisions. These forces cause the monomer to undergo what is known as Brownian motion. Brownian motion is named for the botanist Robert Brown [6], who was the first to systematically describe this type of motion in the early 19th century.

These solvent molecules are not only a source of random collisions but also a source of viscous damping effects. For example, let's consider an object moving at velocity $\mathbf{v}$ in a liquid. The solvent molecules are moving around this object and slow it down with a drag force $\mathbf{F}_f = -\zeta\mathbf{v}$. This force is in the opposite direction of the object's velocity. A large value of ζ means a high-resistance solvent; a zero ζ means a vacuum-like environment, where objects experience no drag forces because of their motion.

In 1851, Stoke [7] determined that for a sphere with radius R in a liquid with viscosity η , its friction coefficient is

$$\zeta = 6\pi\eta R . \tag{1.25}$$

An object in a liquid moves at a velocity $\mathbf{v}$ if a force $\mathbf{F}_k$ is applied to it. The flow around this object yields a drag force $\mathbf{F}_f = -\zeta\mathbf{v}$. This object dissipates energy into the surrounding liquid over a volume $\simeq R^3$. In an overdamped system, the object's acceleration is zero at steady state, requiring forces to satisfy $|\mathbf{F}_k| = |\mathbf{F}_f|$.

The full-fledged theory of Brownian motion was not established until Albert Einstein completed his work in 1905 [8]. Einstein demonstrated that the time-dependence of the mean square displacement (MSD) of a spherical particle of radius R , inside a liquid with

1.2. POLYMER DYNAMICS AND HYDRODYNAMICS IN A TUBE

viscosity η at temperature T , can be written as

$$\langle \Delta x^2(t) \rangle = 6Dt , \quad (1.26)$$

where

$$D = \frac{k_B T}{\zeta} = \frac{k_B T}{6\pi\eta R} \quad (1.27)$$

is the particle's diffusion coefficient. We note that Einstein thus showed that D is the ratio of the thermal energy of a particle ($k_B T$) to its dissipative friction coefficient ζ . The relation $D = \frac{k_B T}{\zeta}$ is known as the Einstein-Smoluchowski relation; it basically says that diffusion is powered by thermal energy and constrained by friction.

In addition, Einstein derived the diffusion equation (here in one dimension)

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2} , \quad (1.28)$$

where $P(x, t)$ is the probability of finding a particle at position x at time t . The solution of the diffusion equation with an initial condition $P(x, t = 0) = \delta(x)$ is:

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left[-\frac{x^2}{4Dt} \right] . \quad (1.29)$$

This theory links the random motion of particles to their thermal energy $k_B T$, and to their friction coefficient [8], a beautiful masterpiece indeed. This work is as beautiful as all the other papers by Einstein published in the same year – often called *annus mirabilis*.

As mentioned above, the solvent molecules are the source of random fluctuations. In fact, the solvent molecules are both the source of resistance during diffusion and the source of the random forces that cause it, leading to the fluctuation-dissipation theorem Eq. 1.27. The environment sets the value of $k_B T$, whereas the non-trivial value of ζ holds particular interest when studying polymer molecules. In the next section, I will introduce several commonly used models in this area.

1.2.2 POLYMER DIFFUSION: THE ROUSE AND ZIMM MODELS

Obviously, the coefficient of friction ζ of a polymer chain in solution results from the contributions of all of its parts. An initial assumption might be that it is simply the sum of the friction coefficients of its N monomers. This assumption is known as the *Rouse* model [1]. Rouse dynamics thus assumes that $\zeta_R = N\zeta_o$, where the quantity ζ_o is the friction coefficient of a single monomer, such that

$$D = \frac{k_B T}{\zeta_R} = \frac{k_B T}{N\zeta_o} \sim N^{-1}. \quad (1.30)$$

The diffusion coefficient of a Rouse polymer is predicted to be inversely proportional to its degree of polymerization, $D \sim 1/N$.

Assuming that each bead contributes **independently** to the diffusion process is generally not valid because of the non-trivial role of the solvent molecules. In experiments measuring the diffusion coefficient of long polymer chains in good solvents, results scale with molecular weight (or monomer number) as [1]

$$D \sim N^{-3/5}. \quad (1.31)$$

What explains the discrepancy between the Rouse assumption and reality is the presence of long-range hydrodynamic interactions (HI).

The Rouse model neglects HI, meaning it ignores the secondary effects on a bead resulting from the movements of other beads. Imagine a sphere moving in a fluid. This sphere must push fluid molecules around it as it moves, and since that fluid is incompressible, the repositioning of the sphere indirectly exerts a force on other objects in its vicinity. These collective effects actually diminish the net friction on the monomers. The solvent molecules around the monomers are mobile and can be mobilized by the motions of all of the other monomers. These effects build up to affect the coefficient of friction of the polymer chain. Zimm demonstrated that the hydrodynamic interactions between the monomers make a

1.2. POLYMER DYNAMICS AND HYDRODYNAMICS IN A TUBE

diffusing polymer behave like an impervious solid ball with a radius comparable to the polymer's effective radius in free solution R_{go} . The corresponding Zimm friction coefficient is thus $\zeta_z \simeq 6\pi\eta R_{go} \sim N^\nu$ and the resulting scaling law $D_z = k_B T / \zeta_z \sim N^{-\nu}$ is consistent with Eq. 1.31 if we use the Flory exponent $\nu = 3/5$ suggested by Eq. 1.14. Zimm's model can be summarized by the simple scaling law $D \sim k_B T / R_{go}$.

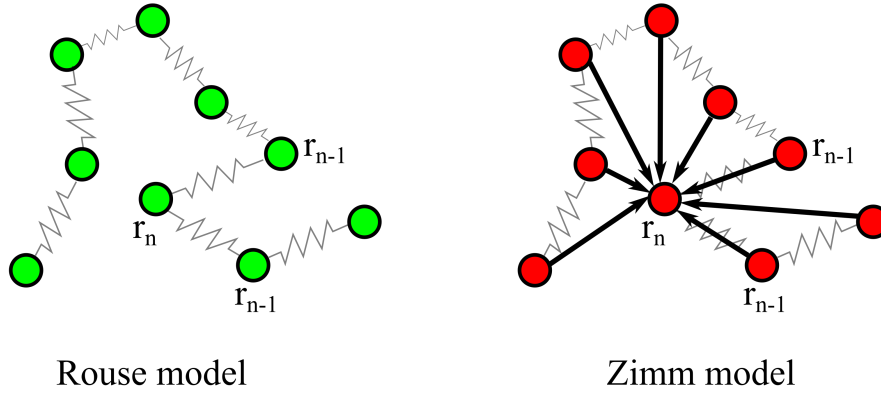


Figure 1.6: In the mathematical treatment of the Rouse model, the chain is modelled as a collection of beads connected by entropic springs. The random and drag forces are applied to the beads, while the springs replace the conformational entropy of the monomers on length scales smaller than the mean spring extension. In the Zimm model, the motion of a bead depends on the motion of all the other beads through hydrodynamic interactions.

Let us examine the Rouse and Zimm models in a more quantitative way. In order to be able to carry out analytical calculations, it is necessary to simplify the problem to its most basic elements. To do so, we replace the monomers by a bead-spring model, i.e. a series of beads connected by long entropic springs – see Fig. 1.6. Each spring replaces several monomers and has a mean-square extension a^2 in equilibrium. The advantage of this model is that it correctly incorporates the physics of the different parts of the chain (i.e., the friction forces, the random forces, and the conformational entropy), while still following the physical principles of the Rouse or Zimm models.

The reader can take a moment to imagine such a bead-spring chain in free solution. The chain is composed of N beads. The position $\mathbf{r}_n$ of the n -th bead is affected by the

1.2. POLYMER DYNAMICS AND HYDRODYNAMICS IN A TUBE

position of all the other beads. Figure 1.6 shows bead n connected to two adjacent beads by springs. The Langevin dynamics equation of motion for $\mathbf{r}_n$ is given by [4]

$$\frac{d\mathbf{r}_n}{dt} = \sum_{m=0}^{N-1} \mathbf{H}_{nm} [k_s(\mathbf{r}_{m-1} + \mathbf{r}_{m+1} - 2\mathbf{r}_m) + \mathbf{F}_{Bm}] \quad (n = 0, 1, \dots, N-1) \quad (1.32)$$

where $\mathbf{r}_{-1} = \mathbf{r}_0$ and $\mathbf{r}_N = \mathbf{r}_{N-1}$ are the boundary conditions. The quantity $\mathbf{F}_B$ represents the random forces due to thermal noise from the environment and $k_s = 3k_B T/a^2$ is the entropic spring constant between two beads (see Eq. 1.10). Note that this model implicitly uses a random walk model instead of the SAW model, since there are no excluded volume interactions between the different parts of the chain. The symbol H is a second-rank tensor, the so-called "Oseen tensor". The Oseen tensor describes how the velocity of the m th bead affects the velocity of n th bead through the solvent between them.

Without hydrodynamic interactions, the interaction tensor reduces to the diagonal elements $H_{nm} = (\delta_{nm}/\zeta_o)$, and the equation of motion then reduces to

$$\zeta_o \frac{d\mathbf{r}_n}{dt} = k_s(\mathbf{r}_{n-1} + \mathbf{r}_{n+1} - 2\mathbf{r}_n) + \mathbf{F}_{Bn} \quad (n = 0, 1, \dots, N-1). \quad (1.33)$$

It can be solved to obtain the normal modes of the chains and their relaxation times. The longest (or terminal) relaxation time of the Rouse scales like $\tau_1 \sim N^2$ [4]. More importantly for this thesis, the solution for the diffusion coefficient is $D = k_B T/N\zeta_o$, as given in Eq. 1.30.

The non-local contributions of the Oseen tensor depend on the conformation of the polymer chain and are therefore time-dependent. To simplify the calculation, Zimm decoupled H_{nm} from the main part of the equation of motion and replaced it with its average value at equilibrium (the *pre-averaging approximation*),

$$\frac{d\mathbf{r}_n}{dt} = \sum_{m=0}^{N-1} \langle H_{nm} \rangle_{eq} [k_s(\mathbf{r}_{m-1} + \mathbf{r}_{m+1} - 2\mathbf{r}_m) + \mathbf{F}_{Bn}] \quad (n = 0, 1, \dots, N-1), \quad (1.34)$$

1.2. POLYMER DYNAMICS AND HYDRODYNAMICS IN A TUBE

where $\langle H_{nm} \rangle_{eq}$ is the average hydrodynamic coupling term between monomers n and m in equilibrium (Gaussian) conformations. This approximation allowed Zimm to solve the equation of motion of the Rouse chain in the presence of HI. Zimm's solution for the diffusion coefficient includes the mean value of the pre-averaged coupling $\langle H_{nm} \rangle_{eq}$ over all pairs of monomers:

$$\left\langle \langle H_{nm} \rangle_{eq} \right\rangle_{nm} = \frac{1}{6\pi\eta} \left\langle \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right\rangle_{nm} = \frac{1}{6\pi\eta R_H} . \quad (1.35)$$

and $R_H = \langle |\mathbf{r}_n - \mathbf{r}_m|^{-1} \rangle_{nm}^{-1}$ is called the hydrodynamic radius of the polymer chain. In fact, R_H is nothing but the radius of a solid sphere that has the same friction coefficient as the polymer chain, i.e. $\zeta_z = 6\pi\eta R_H$.

It is clear that R_H depends on the chain conformation. The conformations of the polymer chains in the Zimm model do not differ from those in the Rouse model. The average can be computed exactly for a Gaussian chain (random walk conformations) to give $R_H/R_{go} = (3/8)\sqrt{\pi} = 0.665$ [4].

After rigorous calculations, Zimm reached one key conclusion: in the presence of hydrodynamic interactions, the scaling law for the diffusion coefficient is

$$D = \frac{k_B T}{\zeta_z} \sim \frac{k_B T}{\eta R_H} \sim \frac{k_B T}{\eta R_{go}} . \quad (1.36)$$

In the absence of the excluded volume interactions, the diffusion coefficient of polymer chains in the Zimm model thus scales as $D \sim 1/R_{go} \sim 1/\sqrt{N}$.

If we extend this discussion to SAWs, where the Flory exponent is $\nu = 3/5$, the scaling argument becomes $D \sim k_B T / \eta N^{3/5}$, which agrees with the experimental scaling law Eq. 1.31. In this scenario, we have $R_H/R_{go} = 0.640$ (see reference [4], section 3.2.7).

Comparing the two models, the Rouse model overestimates the friction coefficient of the polymer chains. However, in most of the studies in this thesis, we abandon the *Zimm* model, not because it is not true, but because the essentialness of using it is low. For

1.2. POLYMER DYNAMICS AND HYDRODYNAMICS IN A TUBE

polymers in a narrow channel of width $h < R_{go}$, which is the most common situation of our study, the hydrodynamic interactions only contribute a small amount.

1.2.3 POLYMER DIFFUSION: HYDRODYNAMIC INTERACTIONS IN TUBES

We have introduced the hydrodynamic interactions (HI) that act on a polymer chain in a free solution. In a weak confinement situation, when the tube size is larger than the polymer chain size ($h \gg R_{go}$), we could consider that the HI works just like it does in a free solution, except near the walls.

The presence of channel walls becomes more important as the width of the tunnel decreases. We need to revisit the blob theory introduced in Section 1.1.5. For moderate confinement, monomers within a blob influence each other through hydrodynamic coupling. Thus, on the blob scale, the hydrodynamic interactions do play a role and Zimm scaling should apply. Beyond the length scale of a blob, however, the hydrodynamic interactions cannot spread very far. Most of the effects are shielded by the walls beyond distances larger than the width of the tube, h . In other words, the hydrodynamic disturbances are not exchanged between blobs. Therefore, we can simply add the friction coefficients of the blobs as they are independent from each other, just like in the Rouse model.

Due to the blobs, our polymer chain is no longer a Rouse chain with a diffusion coefficient $D \sim 1/N$. Instead, it is a Rouse polymer chain with M blobs, each blob having its own diffusion coefficient D_b , so that $D \sim D_b/M$. In Section 1.1.5 we showed that $M = N/g$, where $g \sim (h/b)^{1/\nu}$. We can conclude that each blob under confinement has a diffusion coefficient $D_b \sim 1/h \sim g^{-\nu}$. Therefore, the whole chain has a diffusion coefficient:

$$D \sim g^{-\nu}/M \sim h^{1/\nu-1}/N, \quad (1.37)$$

with a tube width dependence $h^{1/\nu-1}$ and a number of monomer dependence $1/N$. Considering the high computational requirements of HI, and its minor impact in most of our

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simulation system set-ups (narrow tubes), we ignore HI in our study. Therefore, we use Rouse dynamics in our simulations and theoretical descriptions.

Both *Zimm* and *Rouse* models are fundamental tools in polymer physics. Many possible extensions can be considered in different physics problems; for instance, charged polymers, topological polymers, etc. The models used in the subsequent chapters will be discussed in the context of each chapter.

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1.3.1 ELECTROPHORESIS AND POLYELECTROLYTES

The movement of charged polymer molecules (polyelectrolytes), ions and colloidal particles in a fluid under the action of an electric field is called electrophoresis. Usually, the solvent contains salt, and the dissolved salt produces free ions, like the green and yellow charges in Fig. 1.7. An immersed charged object attracts some of these oppositely charged ions/counterions, and the latter form a layer around it. The width of this layer, called the *Debye length* λ_D , is given by

$$\lambda_D^{-2} = \frac{\sum \rho_i (q_i)^2}{\epsilon_o \epsilon_r k_B T} \quad , \quad (1.38)$$

where $\epsilon_o \epsilon_r$ represents the product of vacuum permittivity ϵ_o and the relative permittivity of the medium ϵ_r , while q_i and ρ_i are the charge and number concentration of the i -th ionic species, respectively. The Debye length depends on the solvent condition (including the ion concentration and the solvent permittivity ϵ_r) and the temperature.

Suppose now that there is an external electric field $\mathbf{E}$ acting on the system. The charged object and the counter-ions in its Debye layer then move in opposite directions. We saw previously (see Section 1.2.1) that an uncharged particle moving in a fluid under the action of an external force dissipates its energy by disturbing the fluid over a length scale comparable to its hydrodynamic radius R_H . However, Fig. 1.7 suggests that in the

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presence of electric forces, the dissipation would occur over a length scale λ_D instead. In fact, depending on whether the size of the charged object is less than or greater than λ_D , its electrophoretic behaviour will be different. More precisely, energy dissipation occurs over the smaller of the two length scales, R_H or λ_D .

For instance, when the particle size is small compared to the Debye length, $R_H < \lambda_D$, the cloud of counterions is not involved in energy dissipation because the concentration of ions is basically uniform over distances $\sim R_H$. In other words, the electric forces then act just like purely mechanical forces (such as gravity).

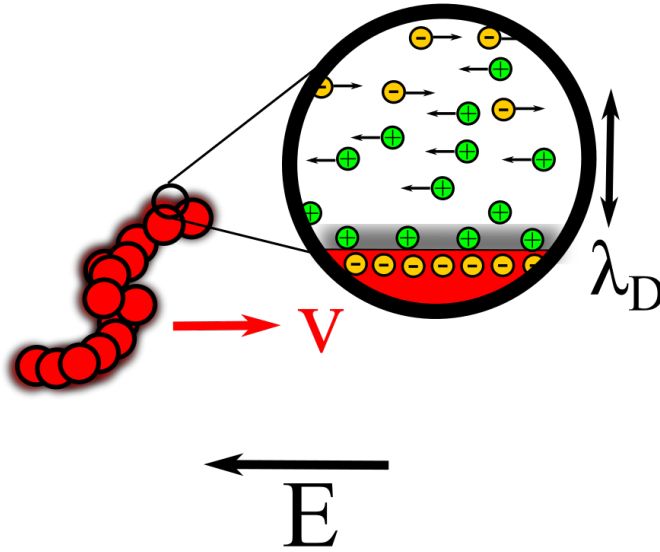


Figure 1.7: Schematic plot of a charged object in solution, with counterions (green dots) and ions (yellow dots). The counter-ions accumulate over a distance λ_D near the surface of the object. The charged object and the ions in solution move when an electrical field $\mathbf{E}$ is applied. In this particular case, the object is a polyelectrolyte.

Our focus, though, is on large negatively charged polymer chains, like DNA. In these cases, the size of the polymer is greater than the Debye length, $R_H \gg \lambda_D$. The Debye

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length is in the range of a few nanometres [9, 10] in a typical electrophoresis buffer, much smaller than the size of DNA chain fragments of interest (for example, a double-stranded 5000 base pairs long DNA molecule has a radius-of-gyration of order 100 nm. The localized aggregation of counterions along the backbone shields the Zimm hydrodynamic interactions (HI) between the monomers. The counterions near the polymer chain drag the rest of the fluid with them when applying an external electrical field $\mathbf{E}$. Without the HI between the polymer parts, the fluid can penetrate through the charged polymer chain conformation; the molecule is free-draining and comparable to that in the Rouse model.

The problem with this shielding effect is that the velocity of the charged polymer is independent of its size. Therefore, in the $R_H \gg \lambda_D$ limit, the velocity is the same for all molecular sizes. Simple electrophoresis cannot separate large polymer chains, and we need an auxiliary effect that affects the velocity of different-sized molecules in different ways.

1.3.2 DRIVEN POLYMER CHAINS COLLIDING WITH OBSTACLES

Since polyelectrolytes exhibit size-independent velocities in free solution, a different method is required for their separation via electrophoretic forces. Historically, this has been done mostly using the sieving properties of hydrogels, which has led to gel electrophoresis, a workhorse of the molecular biology labs.

Let's start with an example: cooking a pot of spaghetti and using a sieve to strain the water out of the pasta. If some spaghetti is broken (*mi dispiace, amico mio*), smaller pieces may fall through the sieve, while larger ones remain. This is basically how gel electrophoresis works, not in an Italian way.

The basic principle of gel electrophoresis is that when polyelectrolyte chains undergo electrophoresis in a porous environment (such as a gel), they slow down depending on their size. The gel itself can be permanent or temporary; organized or randomly linked; fluctuating or stiff, as long as it filters the polymer chain segments in different ways. Like spaghetti pieces passing through the holes of a sieve, smaller polyelectrolyte fragments tend

to move faster through the gel network, while larger polymer chains are left behind.

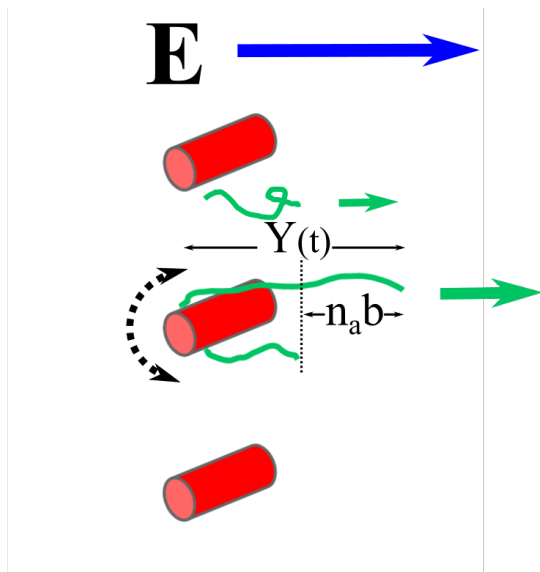


Figure 1.8: A simple schematic showing polymer chains colliding with poles. Under external forces, the smaller polymer chains may miss the obstacle, while the longer polymer chains generally undergo J-shaped collisions. The larger the polymer, the longer the escape time.

Gel electrophoresis is a powerful tool for separating charged polymer chains. We observed similar effects in Chapter 2. It is thus important to understand the basic theory of polymer-obstacle collisions [11]. Several previous group members have studied various types of collisions [12, 13].

Figure 1.8 shows the most frequent type of collision, known as the J-type collision. The posts are strategically arranged to allow small polymer chains to bounce off them without becoming trapped. However, large polymer molecules are more likely to wrap around a post and take a long period of time to escape from the collision. This size-dependent effect is crucial for separating polymer chains.

Let's estimate the molecular-size dependence of the escape time from a J-type collision using the simplest possible model – see Fig. 1.8. We thus ignore the hydrodynamic

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interactions and treat the problem as a mechanical one. We further focus on long chains (the size of the post is neglected) and the high field limit where both arms of the J are essentially fully stretched. The chain is made of N beads of size b , each bead having charge q_b and friction coefficient ζ_b . The collision is driven by an electric field $\mathbf{E}$. We define the difference in the number of beads between the two arms at time t as $n_a(t)$, while $y(t)$ is the length of the longest arm (in the direction of $\mathbf{E}$). Because the longest arm contains n_a more charges than the shorter one, it will dominate the tug-of-war, expanding from its initial length $y(0)$ to $y(t = \tau_e) = Nb$. This implicitly defines the escape time τ_e , as the shortest arm vanishes at $t = \tau_e$. Since $n_a(t)b = 2y(t) - Nb$, the equation of motion for this pulley-like overdamped problem is:

$$N\zeta_b \frac{\partial y(t)}{\partial t} = n_a(t) q_b E = \left[\frac{2y(t) - Nb}{b} \right] q_b E \quad (1.39)$$

Given an initial condition $y(0)$, the solution of this differential equation is

$$y(t) = \frac{1}{2} Nb + \left(y(0) - \frac{1}{2} Nb \right) \exp\left(\frac{2q_b E}{Nb\zeta_b} t \right) \quad (1.40)$$

The escape time is the solution of $y(\tau_e) = Nb$:

$$\tau_e(y(0)) = \frac{Nb\zeta_b}{2q_b E} \ln \left[\frac{Nb/2}{y(0) - Nb/2} \right] \quad (1.41)$$

The extreme case of J-collisions happens when the polymer chain is folded evenly, like the letter ‘U’. Both arms pull in the same direction with no net force driving the escape until random forces make one arm win the tug-of-war. Indeed, the escape time calculated above diverges when $y(0) = Nb/2$. If we average $\tau_e(y(0))$ over all possible values of the initial condition $y(0) \in (\frac{N}{2}, N)$ using a uniform distribution function, we obtain

$$\langle \tau_e \rangle = \frac{1}{Nb/2} \int_{Nb/2}^{Nb} \tau_e(y(0)) dy(0) = \frac{Nb\zeta_b}{2q_b E} \sim N. \quad (1.42)$$

The mean escape (or collision) time is thus increasing linearly with the polymer size.

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Although this is a simple example, it demonstrates that collisions can lead to size-dependent effects.

In Chapter 2 we explicitly investigate polymer-polymer collisions in narrow channels. In some cases, such as when ring polymer chains are involved, the two polymer molecules can become entangled for extremely long times (see Section 5.1).

1.3.3 SINGLE FILE DIFFUSION

In three-dimensional dilute polymer solutions, the polymer chains can easily diffuse around and change position with their neighbours. In this thesis, however, our polymer chains are in narrow channels that severely limit their movement, even along the tube axis. For instance, adjacent polymer chains cannot easily switch positions. This situation is reminiscent of a phenomenon called Single-File Diffusion (SFD).

The most outstanding characteristic of SFD is its scaling law, found by Harris in 1965 [14]. Harris showed that the mean squared displacement of a tagged particle grows with time as $\langle \Delta x^2 \rangle \propto \sqrt{t}$, instead of the standard diffusion law $\langle \Delta x^2 \rangle \propto t$. The diffusion process slows down considerably as collisions with adjacent particles impede the movement of tagged particles.

The original idea of SFD was introduced in 1955 in the field of biophysics and concerned the transport of ions through molecular-sized channels in membranes [15]. Other SFD examples have been found since then, including 1D conductors [16], and colloid motion in 1D [17, 18]. Hard-core, spherical particles inside narrow channels represent the most common SFD scenario. The diameter of the tube h is slightly larger than the diameter of the particles d , yet smaller than $2d$. The shape of the particles is not strictly limited; rod or square particles [19] have similar physical properties if their sizes are chosen appropriately.

In a standard SFD situation, the particles are not only confined by the tube, but also feel the inter-particle hard-core repulsive interactions, making it impossible to switch positions or to pass through each other. Our interest was in SFD of polymer chains in dilute polymer

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solutions in a tube since polymer chains can pass through each other. However, the main purpose of this section is not to give an introduction to polymer SFD, but rather to provide some basic knowledge about SFD for hard particles, as shown in Fig. 1.9.

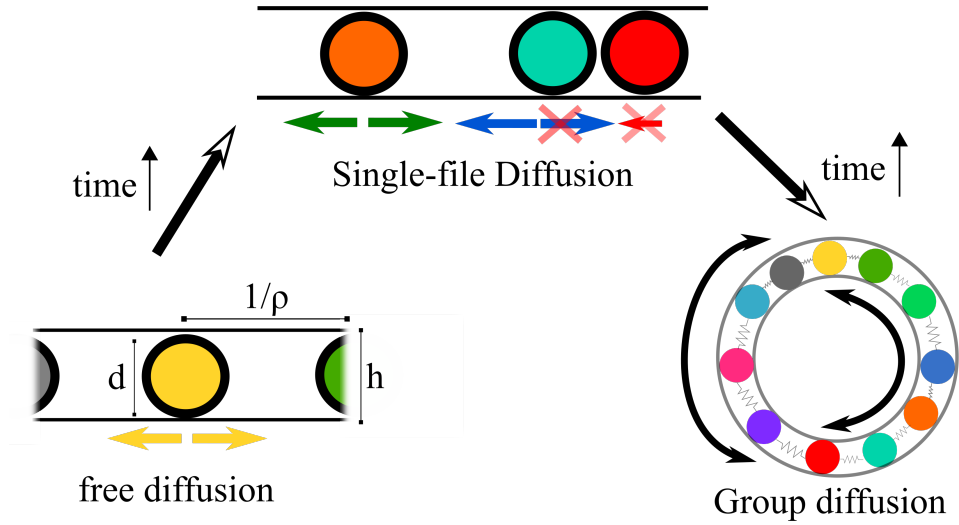


Figure 1.9: Schematic evolution of single-file diffusion over time. The diameter of the hard-sphere particles is d , which is slightly less than the width of the torus, h . All N particles are initially separated uniformly with a distance of $1/\rho$ between their centres of mass. Particle overlap is prohibited, so hard particles must diffuse in a single file once they begin to come into contact. In the long time limit, particles are like pearls on a necklace, connected by virtual springs with a negligible spring constant and moving as a group.

Let's consider a periodic system (a torus) containing $N \gg 1$ particles with a linear density ρ , so that the total system size (the torus circumference) is N/ρ . The width of the tunnel is labelled as h , and the size of the hard particles is defined as d , as shown in Fig. 1.9. We start with the simple case of $h = d$. To simplify the discussion, we assume that the initial distance between adjacent particles is $1/\rho$. Note that the distance between two adjacent particle hard boundaries is $S = 1/\rho - d$.

First, we randomly select a tagged particle and track its motion. Since the initial condition is that the collision-free distance between particles is S , there will be no "neigh-

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bourhood problem” until it diffuses over a distance $\simeq S$. This regime persists until the particle collides with one of its two neighbours at time t_o so that

$$\langle x^2(t) \rangle = 2D_o t \quad t < t_o, \quad (1.43)$$

$$t_o \approx \frac{S^2}{2D_o},$$

where D_o is the free diffusion coefficient of the hard particles along the channel axis.

When adjacent particles come into contact, the system enters the SFD regime. The motion of the tagged particle is then limited by the presence of its neighbours, as demonstrated in the top part of Fig. 1.9. This results in a slowdown of the spreading of the tagged particle probability distribution function (PDF), compared to the case of free diffusion. Between the collision time t_o and some characteristic time t_λ , the particle is in the SFD regime:

$$\langle x^2(t) \rangle = 2F\sqrt{t} \quad t_o < t < t_\lambda, \quad (1.44)$$

$$F = S \sqrt{\frac{D_o}{\pi}},$$

where F is the diffusivity of the particles while doing SFD [20]. The estimated exit time from the SFD regime, t_λ , will be discussed later. Despite this anomalous diffusion behaviour, the tagged particle’s PDF is still given by a Gaussian:

$$p(x, t) \sim \frac{1}{\sqrt{2\pi\langle x^2(t) \rangle}} e^{-x^2/2\langle x^2(t) \rangle}. \quad (1.45)$$

This expression is true regardless of whether the tagged particle undergoes SFD or normal diffusion. Equations 1.44 and 1.45 are the most important results of the SFD theory and have been confirmed in various experiments and computer simulations.

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At longer times ($t > t_\lambda$), a closed periodic boundary condition (PBC) system like a torus will slowly transition to another regime where the particles behave like monomers of a long polymer and the whole population moves as a whole, like a one-dimensional Rouse chain of beads. Figure 1.9 shows a schematic of this movement, with the group of particles resembling a discrete snake biting its own tail. Its Rouse diffusion coefficient is $D_R = D_o/N$, so that

$$\langle x^2(t) \rangle = 2 D_R t = 2 \frac{D_o}{N} t \quad t > t_\lambda \quad . \quad (1.46)$$

This type of Rouse regime has been reported by several research groups (it is often referred to as 'compound diffusion' [21–23]). The crossover time between single-file diffusion and Rouse diffusion is given by an equality between Eqs 1.44 and 1.46:

$$t_\lambda = \frac{\lambda^2}{2D_R} \quad , \quad (1.47)$$

$$\lambda = \sqrt{\frac{2}{\pi}(NS)(S)} \quad .$$

The distance $\lambda \sim N^{1/2}S$ is the geometric mean of the mean inter-particle spacing S and the *effective system size* NS . Since $\lambda \ll NS$ in large systems, particles only need to diffuse over relatively small displacements to exit the SFD regime. We note that in the Rouse regime ($t > t_\lambda$), the MSD of the system is again proportional to time, rather than the square root of time. In other words, the dominant transport process changes its scaling behaviour again at long times.

We can also compare SFD to the motion of a monomer that is part of a polymer chain. At very short times, the monomer does not feel the constraints of being part of a chain. After some time, the monomer begins to feel the constraints imposed by neighbouring monomers. Logically, these two processes can be compared to the SFD states before and after t_o , and indeed they share the same time scaling laws [1].

In a more complicated situation, these particles can switch positions. In particular, we

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can ask ourselves what happens when the motion of a particle is no longer strictly limited by its neighbours? How can particle switching influence the system's dynamics?

This switching requires space for both particles to pass each other. In other words, we need $\delta_c = (h - 2d)/d > 0$. Defining the hopping time t_w that measures the average time for two particles to pass one another, hundreds of times longer than it takes for a particle to diffuse its own size, Mon et al [24] found the scaling law for non-rotating spherical particles scales like:

$$t_w \sim \delta_c^{-\mu}, \quad \delta_c \ll 1 \quad . \quad (1.48)$$

In the regime where exchanging two particles is difficult, they found that the exponent $\mu = 2$. The larger the gap, the less time it takes for particles to switch places, and vice versa. Sane et al [25] showed that the effective diffusion D_w is then inversely proportional to the switching time t_w :

$$D_w \sim t_w^{-1/2} \quad . \quad (1.49)$$

On the other hand, if t_w decreases to the point where it becomes comparable t_o , then the SFD picture fails and D_w will approach the free diffusion coefficient D_o . For Eq. 1.49 to be effective, t_w must be much greater than t_o , implying a small δ_c value is necessary, generally $\delta_c \leq 0.1$. Furthermore, if $t_w > t_\lambda$, the system would still be doing the Rouse diffusing before any possible switch can occur, giving $\langle x^2(t) \rangle \sim D_R t$ instead of $D_w t$.

Our research has identified similar expressions in the study of polymer SFD, supporting the validity of our work and paving the way for its representation within a simpler model. This leads to an important inquiry of this thesis: can the complex molecular dynamics of the polymer be simplified into a symbolic particle-like system? These questions are addressed in Chapter 4.

1.4 SIMULATION METHODS

1.4.1 LANGEVIN DYNAMICS

The molecular dynamics simulations presented in this thesis were all performed using the simulation package *ESPResSo* 4.04 [26]. *ESPResSo* is an open source simulation tool developed mainly at the University of Stuttgart, but with contributions from all over the world. It is a sophisticated code for simulating the dynamics of coarse-grained soft matter systems. In this thesis, we mainly use the Langevin equations of motion to model the dynamics of polymer chains, with and without constraints.

The position and velocities of the simulation beads are integrated in time based on the Langevin equation of motion [27]

$$m\ddot{\mathbf{r}} = \mathbf{F}_e + \mathbf{F}_B - \zeta \dot{\mathbf{r}}, \quad (1.50)$$

where $\mathbf{F}_e$ is the sum of all conservative forces, $\mathbf{F}_B$ is a random Brownian force, $\mathbf{r}$ is the position vector of a simulation bead having a mass m , and ζ is the friction coefficient of this bead. The solvent is implicitly present via the last two terms of Eq. 1.50.

The fluctuation-dissipation theorem links the random Brownian force and the frictional force, both of which are due to the solvent. When an object moves through a liquid, it experiences a viscous drag force $-\zeta\dot{\mathbf{r}}$, which *dissipates* energy into the environment. The surrounding liquid molecules randomly collide with this moving object, leading to an associated *fluctuating* Brownian force $\mathbf{F}_B$. To construct this connection, we use an uncorrelated random force vector $\mathbf{F}_B$ with zero mean and variance $\langle \mathbf{F}_B^2 \rangle = \frac{2\zeta k_B T}{\Delta t} = \frac{2\zeta^2 D}{\Delta t}$. The variance is selected to satisfy the fluctuation-dissipation relation $D = k_B T / \zeta$ in each dimension.

Our focus is on determining the trajectories of particles and polymers in the simulations. In practice, at each time step Δt , the numerical integration of point-like particle positions

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is discretized as follows:

1. Calculate the velocity at the half-step, $\mathbf{v}(t + \frac{\Delta t}{2}) = \mathbf{v}(t) + \frac{\mathbf{F}(\mathbf{r}(t), \mathbf{v}(t - \Delta t/2), t)}{m} \cdot \frac{\Delta t}{2}$
2. Calculate the new position, $\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t + \frac{\Delta t}{2})\Delta t$
3. Calculate the force based on the new position, $\mathbf{F}(\mathbf{r}(t + \Delta t), \mathbf{v}(t + \frac{\Delta t}{2}), t + \Delta t)$
4. Calculate the new velocity, $\mathbf{v}(t + \Delta t) = \mathbf{v}(t + \frac{\Delta t}{2}) + \frac{\mathbf{F}(\mathbf{r}(t + \Delta t), \mathbf{v}(t + \Delta t/2), t + \Delta t)}{m} \cdot \frac{\Delta t}{2}$

This is called the "Velocity Verlet algorithm" [28].

In general, Langevin dynamics contains no hydrodynamic interactions between particles or between the particles and the walls. However, in the situation where hydrodynamics do matter, we use the Lattice-Boltzmann method to simulate the motion of the monomers.

1.4.2 LATTICE BOLTZMANN

Our goal is to describe hydrodynamic effects. Obviously, we are working on complex problems, which means that a lot of computational resources are needed. In order to avoid overly detailed calculations as much as possible, we need a large-scale, long-duration hydrodynamic modelling method without molecular details. The best choice for this is the Lattice Boltzmann (LB) method. We use a GPU-based LB code to simulate the solvent behaviour. The fluid interacts with the polymer molecules by linking the LB fluid to the Langevin equation for the monomers.

In the LB method, the use of a cubic lattice to discretise both the position and the momentum of the fluid elements greatly simplifies the problem [29, 30]. There are several LB simulation modes, such as 'D3Q19', 'D2Q9' and 'D3Q15'. In the package tool *ESPResSo*, we use the D3Q19 LB implementation, where 'D3' stands for dimension and 'Q19' stands for the number of discrete velocity vectors $\mathbf{c}_i$ (i.e., $i \in [1, 2, \dots, 19]$).

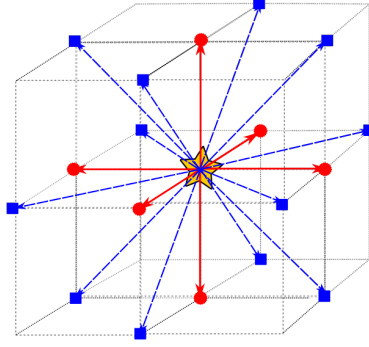


Figure 1.10: The 19 velocity vectors $\mathbf{c}_i$ for a D3Q19 lattice. From the centre point of a grid cell, the velocity vectors point towards all 18 nearest neighbours marked by circles and squares. The zero velocity is the 19th vector.

In mode D3Q19, there are 19 independent velocity vectors $\mathbf{c}_i$ emerging from every lattice position $\mathbf{r}$, as shown in Fig. 1.10. The velocity vectors include: 1 zero velocity; 6 velocity vectors pointing to the nearest lattice site (red circle) and 12 velocity vectors pointing to the next nearest neighbour site (blue square). The discretized velocity vectors are selected such that each new position $\mathbf{r} + \mathbf{c}_i \Delta t$ is also a lattice site.

The LB algorithm can be summarized by the equation

$$n_i(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t) = n_i(\mathbf{r}, t) - [n_i(\mathbf{r}, t) - n_i^{eq}(\mathbf{r}, t)] \frac{\Delta t}{\tau_B}, \quad (1.51)$$

where $n_i(\mathbf{r}, t)$ is the distribution function for the number of solvent particles with velocity $\mathbf{c}_i$ at lattice site $\mathbf{r}$ at time t . The parameter τ_B is the phenomenological time for the relaxation of the actual particle distribution $n_i(\mathbf{r}, t)$ toward its local equilibrium function

1.4. SIMULATION METHODS

n_i^{eq} , which needs to be solved for every lattice site at each time step.

The particle distribution function $n_i(\mathbf{r}, t)$ can be used to obtain other key quantities, including the equilibrium function n_i^{eq} . The local mass density Φ and momentum density $\mathbf{j}$ can be directly calculated from n_i 's as follows:

$$\Phi(\mathbf{r}, t) = \sum_{i=0}^{18} n_i(\mathbf{r}, t) , \quad \mathbf{j}(\mathbf{r}, t) = \sum_{i=0}^{18} n_i(\mathbf{r}, t) \mathbf{c}_i . \quad (1.52)$$

The local fluid velocity is then given by:

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) / \Phi(\mathbf{r}, t) \quad (1.53)$$

This result is needed to calculate the local equilibrium distribution [31]:

$$n_i^{eq}(\Phi, \mathbf{u}) = \omega_i \Phi \left[1 + \frac{\mathbf{u} \cdot \mathbf{c}_i}{c_s^2} + \frac{(\mathbf{u} \cdot \mathbf{c}_i)^2}{2c_s^4} - \frac{\mathbf{u}^2}{2c_s^2} \right] , \quad (1.54)$$

where c_s is the speed of sound, which takes on a value that depends on the properties of the mesh. The weight parameters ω_i are chosen such that the LB model recovers the macroscopic Navier-Stokes equations¹. It is easy to iterate the calculation of the distribution function $n_i(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t)$ at each time step Δt using Eq. 1.51.

The last step is to couple the fluid dynamics to the Langevin dynamics described in Section 1.4.1. Particles are coupled to the LB fluid via the so-called force coupling method: given the fluid velocity $\mathbf{u}(\mathbf{r})$ and the particle velocity $\dot{\mathbf{r}}$, the effective friction force acting on the particle is simply

$$\mathbf{F}_H = -\zeta (\dot{\mathbf{r}} - \mathbf{u}), \quad (1.55)$$

where ζ is the friction coefficient of the particle in the liquid. We then add $\mathbf{F}_H$ as an extra force in Eq. 1.50, which leads to $m\ddot{\mathbf{r}} = \mathbf{F}_e + \mathbf{F}_B - \zeta \dot{\mathbf{r}} + \zeta \mathbf{u}$. The additional force is the result of the hydrodynamic flow $\mathbf{u}$ around that particle. In practice, in our simulations,

¹The values of the parameters ω_i for D3Q19 can be found in reference [30].

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we use grid size σ_w equal to 1 monomer diameter (i.e. σ), $\tau_B = \Delta t$, and $c_s = \frac{1}{\sqrt{3}} \frac{\sigma_w}{\tau_B}$ is the default constant for a given grid size and relaxation time.

Up to this point, we have outlined the simulation methods used during our research for modelling particles, with or without hydrodynamic interactions. Now, we need to simulate polymer chains.

1.4.3 KREMER-GREST POLYMER CHAINS

We are not interested in the detailed structure of the polymer/DNA chains that we simulate. A bead-spring polymer chain can thus be used in our molecular dynamic simulations. In order to model polymer chains consisting of N beads linked by springs, it is necessary to choose particular mathematical expressions for the excluded-volume potential U_{ev} and the spring potential U_s .

To replace the point monomers by beads with a finite size, the repulsive Weeks-Chandler-Andersen (WCA) potential

$$\frac{U_w(r)}{4\epsilon} = \begin{cases} \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} & r < r_m \\ 0 & r \geq r_m \end{cases} \quad (1.56)$$

is used to model excluded volume interactions between beads; here, r is the distance between the centres of two monomers. When their centres are apart by $r = \sigma$, the repulsive potential is $U_w(\sigma) = \epsilon$. The WCA energy parameter in the simulations is set to match the monomer's thermal energy: $U_w(r = \sigma) = \epsilon = k_B T$. Therefore, the effective bead diameter σ and the potential depth ϵ define the simulation units of length and energy.

This potential is actually a shifted Lennard-Jones (LJ) potential with a cutoff distance $r_m = 2^{1/6}\sigma \approx 1.1224\sigma$, which corresponds to the minimum of the LJ potential, ensuring it acts as a purely repulsive potential. The cutoff distance r_m has been carefully chosen to remove the discontinuities in energy and force at $r = r_m$.

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The interactions between the beads and the geometrical constraints (walls) are also modelled using this WCA potential. In this case, r in Eq. 1.56 is the shortest distance between the centre of the bead and the surface. We should be particularly careful when defining the effective wall position. Although the radius of the beads is $\simeq \sigma/2$, we cannot naively take it as the distance from the bead centre to the wall surface. The WCA potential effectively adds another exclusion length $\sigma/2$ to the distance where the surface is nominally defined. Thus the distance between the wall and the bead centre is effectively σ .

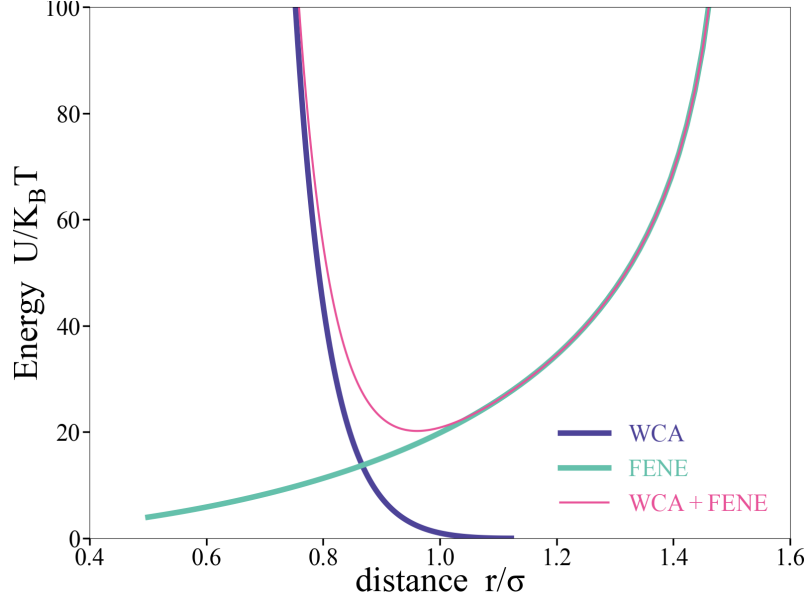


Figure 1.11: Combining the FENE and WCA potentials and using the Kramer-Grest parameters yields a sharp, asymmetric energy well. The minimum is located at $r = 0.961 \sigma$.

Along the chain backbone, beads are connected with the Finitely Extensible Nonlinear Elastic (FENE) spring potential

$$U_{FENE}(r) = -\frac{1}{2} K_{FENE} \Delta r_{max}^2 \ln \left[1 - \left(\frac{r}{\Delta r_{max}} \right)^2 \right], \quad (1.57)$$

where r is again the distance between the centres of the two connected beads. In this

1.4. SIMULATION METHODS

thesis, the maximum extension is chosen to be $\Delta r_{max} = 1.5\sigma$ while the spring constant is $K_{FENE} = 30\epsilon/\sigma^2$. Equation 1.57 is widely used in polymer physics. The parameters above can be used as a convenient combination of potentials to prevent bond-crossing. [32]

These potentials are plotted in Fig. 1.11 as a function of the distance r between two connected beads. The sum of U_W and U_{FENE} yields a minimum at $r_{min} = 0.961\sigma$. Since the potential is asymmetric, the mean value of the bond length has a temperature dependence. When $k_B T = 1\epsilon$, the mean value is $\langle r \rangle \simeq 0.968\sigma$ (numerically obtained), close to the value minimizing the potential energy. As a result, the bead-to-bead distances are very stable. Even under the relatively strong external potentials, this bond length is not affected too much, thus avoiding any constraint violation.

As mentioned before, σ will be the unit of length in this thesis, while the energy $\epsilon = k_B T$ defines the energy units. The units of force will thus be ϵ/σ . The last simulation parameter is the friction coefficient of a monomer, ζ_σ . The diffusion coefficient of a single monomer is then given by $D_\sigma = k_B T / \zeta_\sigma$, and it is used to measure diffusion coefficients. Finally, the time simulation unit is defined as the time scale for one bead to diffuse over its own size $\tau_\sigma = \sigma^2 / D_\sigma = \sigma^2 \zeta_\sigma / k_B T$.

1.4.4 LATTICE MONTE CARLO

Lattice Monte Carlo (LMC) simulation methods are commonly used to study diffusion-related problems, especially when the latter cannot be solved analytically. For example, we can use point-like particles moving on a 1D lattice. Every step is of fixed length a , the lattice parameter. In all of our LMC simulations, particles perform unbiased random walks on a lattice; Fig. 1.12 shows the lattice and a particle.

To illustrate the simulation method, we start with one particle. This point-like particle may represent an ion, a colloidal particle, or even a polymer coil. In the basic unbiased LMC algorithm, the particle moves either right or left by one lattice site per step, with

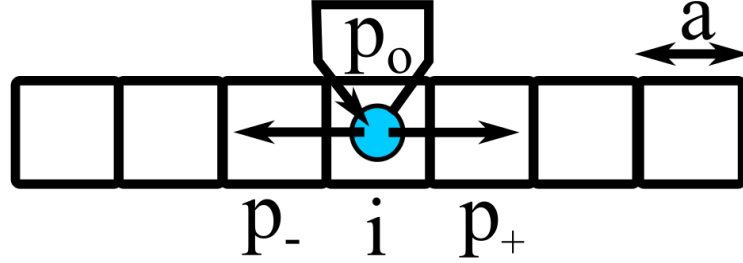


Figure 1.12: Schematic of the 1D Lattice Monte Carlo algorithm used in this thesis. The particle on site i can move to one of the two neighbouring sites during a time step. The particle can also remain in its original lattice site i . For unbiased diffusion, we use $p_{\pm} = \frac{1}{6}$ and $p_o = \frac{2}{3}$.

equal probabilities

$$p_+ = p_- = 1/2 \quad . \quad (1.58)$$

The associated time step τ for this jump is the average first-passage time required to reach the subsequent lattice site:

$$\tau = \frac{a^2}{2D} \quad , \quad (1.59)$$

where D is the diffusion coefficient of the particle in the system. The time step τ is identical for all sites, and the value of τ is also history-independent.

Lattices are discrete and the smaller the mesh, the closer the system is to a continuous space, hence the smaller the lattice step size, the more realistic the results will be. On the other hand, smaller mesh sizes increase the computational cost of the simulation, so a balance between resources and accuracy needs to be established.

We use an improved LMC version for enhanced accuracy. My supervisor developed this algorithm with former group members Michel G. Gauthier and Mykyta V. Chubynsky [33, 34]. We label the position of particle i at time t as $x_i(t)$. The probability of jumping

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between sites is given by:

$$\begin{cases} x_i(t + \tau_s) = x_i(t) - a & , & p_- = \frac{1}{6} \\ x_i(t + \tau_s) = x_i(t) & , & p_o = \frac{2}{3} \\ x_i(t + \tau_s) = x_i(t) + a & , & p_+ = \frac{1}{6} \end{cases} . \quad (1.60)$$

Compared to the simple LMC approach in Eq. 1.58, a probability to stay still, p_o , is introduced, as shown in Fig. 1.12. This algorithm is superior to the simple method because its distribution function for one particle is more precise, i.e., it is closer to being a Gaussian distribution – an important property for simulation of first-passage problems.

Since the jump probabilities are reduced by a factor of 3 from $p_{\pm} = 1/2$ to $p_{\pm} = 1/6$, the diffusion coefficient is also (apparently) reduced threefold. The new jump probability set thus requires a new time step τ_s . Here are the first 5 moments of the particle displacement distribution:

$$\begin{cases} \langle x(t) \rangle & = 0 \\ \langle x^2(t) \rangle & = \frac{1}{3} \frac{t}{\tau_s} a^2 \\ \langle x^3(t) \rangle & = 0 \\ \langle x^4(t) \rangle & = \frac{1}{3} \left(\frac{t}{\tau_s} \right)^2 a^4 \\ \langle x^5(t) \rangle & = 0 \end{cases} . \quad (1.61)$$

We can define the new diffusion coefficient for this algorithm to be $D_s = \frac{a^2}{2t_n}$, where $t_n = \frac{\tau_s}{p_+ + p_-} = 3\tau_s$. This means that the particle makes on the average three attempts before a successful jump, compared with the simple method. If we replace $\frac{a^2}{\tau_s}$ by D_s , we have $\langle x^2(t) \rangle = 2D_s t$, as expected.

The Kurtosis is a measurement of the degree of flatness or sharpness of a distribution when compared to a Gaussian distribution. It is defined by:

$$Ku = \frac{\langle x^4(t) \rangle}{\langle x^2(t) \rangle^2} - 3 . \quad (1.62)$$

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Gaussian distributions have a zero Kurtosis by construct. This is also the case for our algorithm, but it is not for the simple method in Eq. 1.58. This suggests that the probability sets in Eq. 1.60 can provide a more accurate algorithm in LMC simulations. However, note that neither algorithm gives the correct higher moments of the distribution.

Our LMC method can be flexibly modified to study multi-particle problems. In practice, at each simulation time step, we randomly select a particle from the population of particles in the system. The motion of this particle is based on Eq. 1.60. With the standard algorithm, there is an additional term $\sim t$ in the expression for the fourth moment. If the next lattice position is already occupied by another particle, the move attempt is rejected and the selected particle remains stationary in its original position (Chapter 3). In the special case of allowing particles to overlap (Chapter 4), the attempt to move can be accepted with a certain probability. Then the next iteration of jumping starts. More detailed discussion will be addressed later in the chapters.

1.5 THESIS OVERVIEW

This thesis explores the dynamics of polymer solutions in quasi-one-dimensional geometries. It uses scaling arguments, polymer physics theories, and various computer simulation methodologies.

Chapter 2 focuses on field-driven collisions between a polyelectrolyte and an uncharged polymer chain. The essence of gel electrophoresis, capillary electrophoresis, and microfluidics lies in field-induced collisions between the target polyelectrolyte and chosen obstacles. Yet, this approach has received limited attention in one dimension. Our motivation is to investigate the possibility of separating and manipulating polymer chains in narrow channels, based on the size of the polymer chains involved in field-driven collisions. We provide a careful study of the parameters that can be used to characterize polymer collision events. We conclude that the nature of the collisions, the duration of the collisions, and the non-monotonic function of one of the parameters in the system, offer the possibility

1.5. THESIS OVERVIEW

of manipulating or separating polyelectrolytes in similar systems, possibly with the use of pulsed electric fields and ratcheting effects.

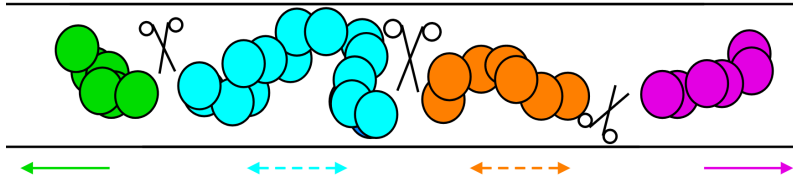


Figure 1.13: A long, flexible chain is confined in a narrow channel or tube. While the chain is under equilibrium conditions, an enzyme (the symbolic scissors) is used to cut it into small pieces. Due in part to entropic repulsion, the pieces diffuse away from each other. Experimentally, the number of pieces and the order in which they are observed helps researchers establish a map of the genetic information contained in the original DNA molecule.

Chapter 3 is motivated by the DNA mapping problem, a necessary step in order to understand the location of information along DNA molecules. One approach is to break a long DNA chain into pieces in a narrow channel so that the relative position of the pieces is maintained after they move away from each other (this would not be the case in solution). Figure 1.13 gives a schematic description of the process. The final order, as well as the size of the fragments thus generated, contributes to the mapping exercise. We focus on one specific problem: how much time does it take for the fragments to be clearly separated (so that they can be visualized in a laboratory environment)? We also examine the space occupied by the population of molecules after the final state is reached. In the supplementary study presented in Section 5.4, we use a different and more detailed simulation approach to validate our conclusions about the separation time, and we investigate the condition under which the final order could be wrong despite the presence of the constraint.

The third manuscript (Chapter 4) discusses the issue of single-file diffusion (SFD) in dilute polymer solutions in narrow channels. We introduced the problem of SFD for hard particles in Section 1.3.3. In this study, however, we use linear polymer chains. The system is entropy-driven and, to the best of our knowledge, has not yet been studied.

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Polymer chains can interpenetrate, adding a crucial and novel element of 'exchange' to the SFD issue. The project uses two different simulation approaches: Langevin dynamics and Monte Carlo. In a system with periodic boundary conditions, we examine all four possible regimes for polymer dynamics. We plot the phase diagram of polymer diffusion behaviour as a function of system parameters. We also investigate the exchange mechanism and establish its limits. The two simulation techniques agree and offer the potential to simplify the method, enhancing simulation speed.

During my research project, I studied many problems involving polymer chains diffusing in narrow tubes. Some of these problems didn't get a chance to be completed for a range of reasons. We included some results related to these projects in Chapter 5. They have not yet become manuscripts, either because they were too small or, on the contrary, because they turned out to be larger than expected. They may be excellent choices for future work and theses.

Following Section 1.4, I trust the reader has grasped the key aspects of the simulation methods used in this thesis. For example, the lattice Monte Carlo method is the fastest approach with the smallest amount of molecular details, while Molecular Dynamics driven by the Langevin equation demands more computational resources.

Figure 1.14 shows a schematic of the hierarchy of simulation methods one can use, from the most detailed atomic structures of polymer chains, to Langevin dynamics of molecules with/without solvents, to Monte Carlo methods, and finally to continuum models. When the level of model refinement is decreasing, the speed of computer simulation is increasing. A secondary motivation of this thesis is to bridge the gap between different simulation approaches while correctly modeling these different physical phenomena. We want to keep the computational cost as low as possible while maintaining the validity of the physics. Good examples are given in Chapters 3 and 4 as well as in the supplementary material in Section 5.4.

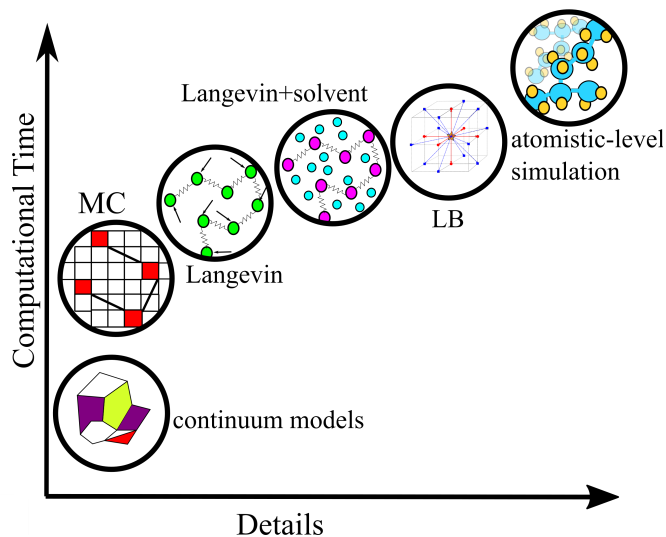


Figure 1.14: Simple schematic depiction of the time-consuming level of simulation methods versus the level of detail for different types of algorithms. From the most detailed atomic structures of polymer chains, to Lattice Boltzmann method, to Langevin dynamics of molecules without/with solvents, to Monte Carlo methods, and finally to continuum models, the level of model refinement is decreasing but the speed of computer simulation is increasing.

FIELD-DRIVEN
POLYELECTROLYTE-POLYMER COLLISIONS
IN NANOCANNELS

H. Y. Wang, and G. W. Slater, "Field-driven polyelectrolyte-polymer collisions in nanochannels," J. Chem. Phys. 160, 194902, 2024. <https://doi.org/10.1063/5.0195302>

RESEARCH ARTICLE | MAY 15 2024

Field-driven polyelectrolyte–polymer collisions in nanochannels

H. Y. Wang  ; G. W. Slater 

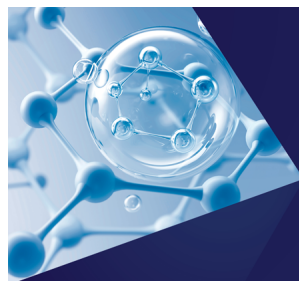


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ABSTRACT

Even though dilute (unentangled) polymer solutions cannot act as gel-like sieving media, it has been shown that they can be used to separate DNA molecules in capillary electrophoresis. The separation then comes from sporadic, independent DNA–polymer collisions. We study polymer–polymer collisions in nanochannels (i.e., channels that are smaller than the normal size of the polymers), a situation where a polyelectrolyte is forced to migrate “through” isolated uncharged molecules during electrophoresis. We use Langevin dynamics simulations to explore the nature of these collisions and their effect on the net motion of the two polymer chains. We identify several types of collisions, including some that are unique to nanochannels. When the uncharged polymer is much larger than the polyelectrolyte, the system is reminiscent of gel electrophoresis, and we propose a modified empirical reptation model to explain the data, with an orientation factor that depends on the tube diameter. We also observe that the duration of a collision is a non-monotonic function of the polymer size ratio when the two chains are of comparable size, a surprising resonance-like phenomenon, which, combined with the asymmetric nature of molecular conformations during collision, suggests possible ratchet-like mechanisms that could be used to sort polyelectrolytes in nanodevices.

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I. INTRODUCTION

It is nearly impossible to separate polyelectrolytes, such as DNA, using free solution electrophoresis.¹ Over the last few decades, numerous strategies have been used to separate ever-larger DNA molecules by electrophoresis. These methods generally use gels or other types of sieving media (e.g., entangled polymer solutions, microchannels with various topologies, and arrays of posts^{2–4}), sometimes with pulsed fields.⁵ Surprisingly, Barron *et al.*⁶ showed in a seminal 1994 paper that ultra-dilute polymer solutions can be used in capillary electrophoresis to separate large DNA molecules, forcing us to revisit the concept of sieving.⁷ Polymer collisions have thus been extensively studied; examples include DNA molecules colliding with cylindrical poles,^{2–4} gel fibers,⁵ various types of obstacles,^{8,9} and uncharged polymers.¹⁰ Excellent review articles have covered this field.^{11,12}

In this article, we investigate field-driven polymer–polymer collisions in narrow cylindrical channels. A polymer chain is said to be confined if its free-solution radius-of-gyration R° exceeds the channel diameter, h . Unlike in dilute bulk polymer solutions, a

polyelectrolyte cannot avoid colliding with an uncharged polymer chain if at least one of them is in a confined state inside the channel. This is the situation of interest here. Confinement also changes the nature of collisions since confined chains are not in random coil conformations. Our goal is to investigate and characterize such collisions in order to determine whether they can potentially be used to design new separation devices or explain natural phenomena.

The physics of polymer chains confined to narrow channels is itself an active field.^{11–14} Among the elements being studied, we note the following: the effects of excluded volume interactions and confinement on chain conformations, hydrodynamic interactions and their effect on diffusion, the coupling between the polymer conformation and liquid flow, the behavior of confined semiflexible polymers, the impact of wall coatings, and the electrohydrodynamic interactions that control the electrophoresis of polyelectrolytes in bulk solutions.^{15–17}

Our understanding of polymer physics in narrow tubes is largely based on de Gennes’ concept of blobs,^{18,19} with the hydrodynamic interactions being screened between blobs due to the presence of the walls. However, the short-ranged hydrodynamic interactions

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are not eliminated within the blobs.^{20,21} The hydrodynamics of collisions between uncharged polymers have been studied before,²² but we are not aware of similar studies in confined environments. Although polyelectrolytes are free-draining in free solution electrophoresis, this is no longer the case if they are also subjected to mechanical forces (such as the friction coming from a collision or an uncharged label); a good example of this is when an uncharged polymer is attached to a polyelectrolyte.^{23,24}

Although it is possible to simulate electrophoretic polymer-polymer collisions while taking into account hydrodynamic and electrostatic interactions (including explicit counter-ions²⁵), we have chosen as a first step to make use of the simplest possible numerical model, the Langevin Dynamics (LD) of a Rouse chain. This allows us to derive some analytical results, optimize the simulation times, and simulate larger systems while keeping the key physical effects.

This paper is structured as follows. In Sec. II, we present our thoughts on polymer-polymer collisions inside a channel, a description of the different stages of a collision, and the regimes that can exist. The simulation approach is outlined in Sec. III. Section IV presents our results in several subsections covering the following topics: the equilibrium properties of single chains; the different phases of a collision; how the collision parameters are distributed and how they affect collision dynamics; the various types of collision; the velocity of the two chains during a collision; the gel electrophoresis limit; and finally an overview of polymer compression/stretching during a collision. Our conclusions, including possible future extensions of these results, are found in Sec. V.

II. THEORETICAL CONSIDERATIONS

We consider a collision between a flexible polyelectrolyte of contour length $L_e = N_e b$ (subscripts e) and a flexible uncharged polymer of contour length $L_p = N_p b$ (subscripts p), where $N_{e,p}$ is the number of monomers of size b . We focus on cases where the polymers' free-solution radii-of-gyration R° exceeds the channel width h : $\{R_{e,x}^\circ, R_{p,x}^\circ\} > h$. As shown in Fig. 1(a), the polymer chains have equilibrium axial radii-of-gyration $R_{e,x}^\circ$ and $R_{p,x}^\circ$ before the collision, and there is a distance of ℓ_0 between their two closest monomers. A force F_e is applied to all charged monomers. Most collisions belong to one of the following four groups: side-by-side [Fig. 1(b)]; J- or U-conformations²⁶ (C); gel-like (D); and glancing (E).

A. Rouse dynamics of a polymer chain in free solution

We use the Rouse model of polymer dynamics,²⁷ in which hydrodynamic interactions are neglected. Therefore, friction is additive: if a monomer has a friction coefficient ζ_1 in a liquid, the total friction coefficient of a chain with N monomers is $\zeta(N) = N\zeta_1$ and its diffusion coefficient is given by

$$D(N) = \frac{k_B T}{\zeta(N)} = \frac{k_B T}{N \times \zeta_1} = \frac{k_B T / \zeta_1}{N} = \frac{D_1}{N}, \quad (1)$$

where $D_1 = k_B T / \zeta_1$ is the diffusion coefficient of a single monomer. If a force $\vec{F}_e$ is applied to each monomer, the velocity of the center-of-mass (CM) of the chain is given by

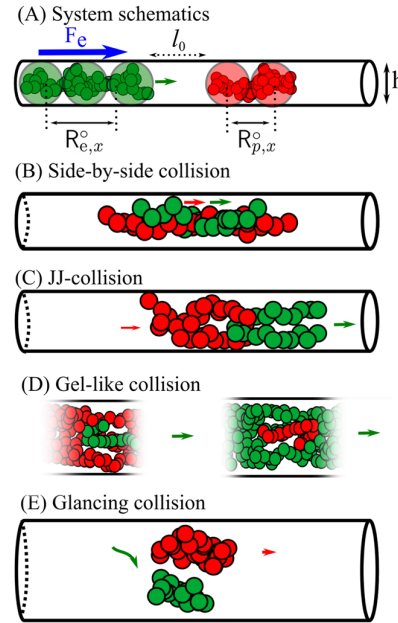


FIG. 1. Schematics of the simulation system. (a) The two polymer chains, with equilibrium axial radii-of-gyration $R_{e,x}^\circ$ and $R_{p,x}^\circ$, are separated by an initial distance ℓ_0 . The diameter of the tube is h , as is the size of the polymer blobs. An external force F_e is applied to all charged monomers. Four types of collisions are shown: (b) in tight tubes, the chains move side by side and the polyelectrolyte drags the neutral chain via contact friction; (c) in wider tubes and with chains of comparable sizes, the final disentanglement process often involves a double-pulley effect, with the polyelectrolyte pulling the other chain, while their conformations are J- or U-shaped; (d) when $R_{e,x}^\circ \ll R_{p,x}^\circ$, the uncharged chain acts as a gel that the polyelectrolyte must traverse (in the opposite case where $R_{e,x}^\circ \gg R_{p,x}^\circ$, the picture is identical if you interchanged the colors and reverse the field); and (e) in a wide tube, we mainly observe glancing collisions between two random coils.

$$\vec{v}(N) = \frac{N \times \vec{F}_e}{\zeta(N)} = \frac{N \times \vec{F}_e}{N \times \zeta_1} = \frac{\vec{F}_e}{\zeta_1} \equiv \vec{v}_0, \quad (2)$$

which is independent of the polymer size N .

B. Describing a collision

Our analysis will use the following notation and arguments:

Before a collision: Neglecting diffusion, the equation of motion for the polyelectrolyte's CM along the tube axis $\hat{x}$ is

$$x_e(t) = v_0 t, \quad (3)$$

where we assumed that $x_e(0) = 0$. Of course, the velocity of the uncharged polymer is trivially zero, $v_p(t) = 0$, both before and after the collision; its initial location is denoted as $x_p(0)$.

After a collision: For the polyelectrolyte, we now have

$$x_e(t) = v_0 t - \Delta x_r = v_0(t - \tau_r), \quad (4)$$

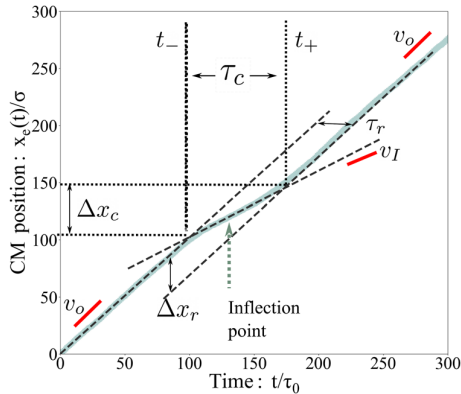


FIG. 2. Detailed trajectory plot defining the collision parameters introduced in Sec. II B. The simulation conditions are $N_e = 60$ beads, $N_p = 100$, tube diameter $h = 6$, and external force $F_e = 1$. For this trajectory, we obtain the collision parameters: $\tau_r = 33(2)$, $\tau_c = 74(7)$, $\Delta x_r = 34(3)$, $\Delta x_c = 42(4)$, $v_o = 1.03(1)$, $v_I = 0.57(1)$, $t_- = 97(2)$, and $t_+ = 172(7)$.

where Δx_r is the lost displacement due to the collision and

$$\tau_r = \Delta x_r / v_o \quad (5)$$

is the retardation (hence the subscript r) time. Note that τ_r is not the duration of the collision; it is rather the time that a free polyelectrolyte would have to stop moving to satisfy Eq. (4). The different parameters used in this section to characterize a collision are described in Fig. 2. The uncharged polymer is “pushed” forward by the polyelectrolyte during the collision; the corresponding displacement Δx_p is not expected to be equal to Δx_r since these values depend on the details of a given collision.

Independent collisions: There are two reasons why consecutive collisions may not be independent:

- (1) *Multi-collisions:* The polyelectrolyte collides with ≥ 1 additional uncharged polymer chains before the previous collision is completed. This happens if

$$v_I \tau_c > \ell_p, \quad (6)$$

where τ_c is the true duration of a collision (i.e., the time between the first and last polymer–polymer contacts), v_I is the mean velocity of the polyelectrolyte during the collision, and ℓ_p is the distance between two adjacent uncharged polymers.

- (2) *Non-equilibrium conformations:* Although collisions are individual events when $v_I \tau_c < \ell_p$, the time between collisions may not be sufficient for the polyelectrolyte to fully relax before the start of a new collision, which may alter the physics of the latter. In order to recover an equilibrium conformation, we need to satisfy the stricter condition

$$v_I \tau_c < \ell_p - v_o \tau_R, \quad (7)$$

where τ_R is the relaxation time of the polyelectrolyte chain.

The chains’ velocities during a collision: The $x_e(t)$ vs t curve has an inflection point at time t_I and position $x_I = x_e(t_I)$ during a collision [see Fig. 3(a)]. As a measure of the polyelectrolyte velocity during the collision, we simply use

$$v_I \equiv \left. \frac{dx_e(t)}{dt} \right|_{t=t_I}. \quad (8)$$

As for the uncharged polymer, we use $v_{Ip} = v_p(t_I)$.

The duration of a collision: The equation of the tangent line at the inflection point of the polyelectrolyte trajectory is

$$x_e(t) = x_I + v_I(t - t_I). \quad (9)$$

The intersection between this line and the pre-collision trajectory $x_e(t) = v_o t$ defines the beginning of the collision,

$$t_- = \frac{x_I - v_I t_I}{v_o - v_I}. \quad (10)$$

Similarly, the end of the collision is defined as the intersection between the tangent and $x_e(t) = v_o t - \Delta x_r$ [i.e., Eq. (4)],

$$t_+ = \frac{x_I - v_I t_I + \Delta x_r}{v_o - v_I}. \quad (11)$$

The duration of the collision is thus given by

$$\tau_c = t_+ - t_- = \frac{\Delta x_r}{v_o - v_I} = \frac{\tau_r}{1 - v_I/v_o}, \quad (12)$$

while the distance traveled during the collision is

$$\Delta x_c = v_I \tau_c = \frac{\Delta x_r}{v_o/v_I - 1}. \quad (13)$$

We note that $\tau_c \geq \tau_r$ and $\Delta x_c \geq \Delta x_r$ (see Fig. 2). The simplest estimate (and lower bound) for the collision distance is

$$\Delta x_c \approx 2(R_{e,x}^o + R_{p,x}^o) \quad (14)$$

since the two chains change position during a collision.

Extrema of the collision velocities: If the two polymers are entangled with U-shaped conformations [Fig. 1(c)], neither chain slides around their point of contact;²⁴ it is as if they were attached to each other. Their velocity v_U is then given by

$$v_U = \min[v_I] = \max[v_{Ip}] = \frac{N_e}{N_e + N_p} v_o \quad (15)$$

because forces and frictions add linearly in Rouse models. In practice, U–U collisions should be both rare and long-lasting.

Increased dispersion due to collisions: So far, we have used deterministic Rouse dynamics and neglected diffusion. Between collisions, the polymers diffuse along the channel axis with Rouse diffusion coefficients $D_{e,p} \sim 1/N_{e,p}$. In particular, we can write that for the polyelectrolyte before a collision

$$\langle \Delta x_e^2(t) \rangle = \langle x_e^2(t) \rangle - (v_o t)^2 = 2D_e t. \quad (16)$$

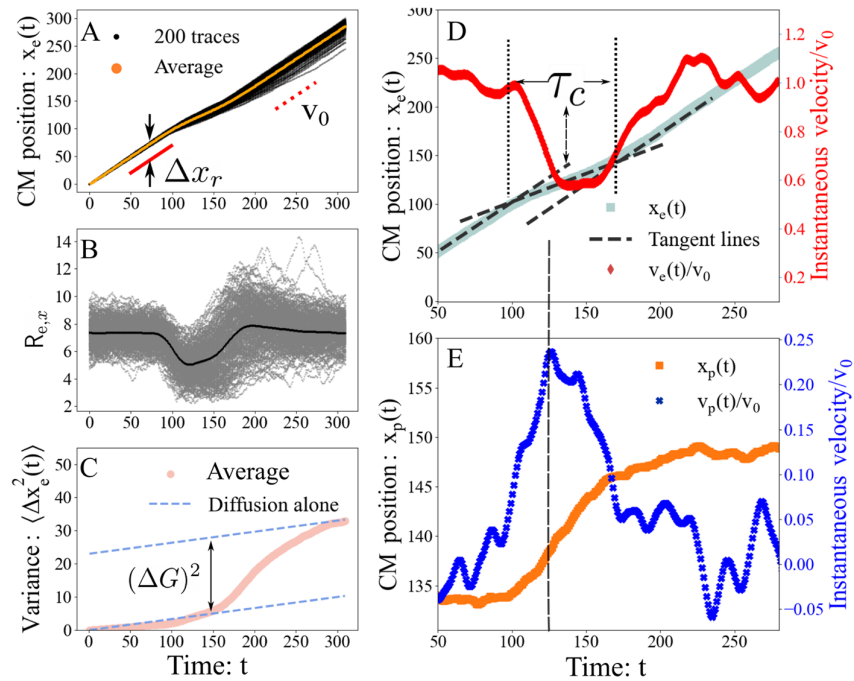


FIG. 3. Analyzing the collision between a polyelectrolyte ($N_e = 60$ beads) and an uncharged polymer ($N_p = 100$) separated by a distance $\ell_0 = 50$ at $t = 0$. The tube diameter is $h = 6$, and the external force is $F_e = 1$ on each charged bead. (a) 200 different polyelectrolyte trajectories; also shown are the mean trajectory, the free solution velocity $v_0 = 1$, and the retardation distance Δx_r . (b) The polyelectrolyte axial radius-of-gyration $R_{e,x}(t)$ decreases and then increases during a collision. (c) The variance of the trajectories jumps by $(\Delta G)^2$ due to the collision. (d) A polyelectrolyte trajectory with its derivative (the instantaneous velocity); see Fig. 2 for the notation. The tangent at the inflection point $t = t_i = 124$ (the vertical black arrow) defines the collision velocity v_i . The tangent and the fits before and after the collision determine the collision duration τ_c . (e) Similar to (d), but for the uncharged polymer. The vertical dotted line at $t = 122$ shows when v_p is maximum.

In other words, the width of a population of identical polyelectrolytes migrating freely inside a tube will broaden as described above (assuming that $\langle \Delta x_e^2(0) \rangle = 0$). The wide range of retardation times τ_r will lead to a jump ΔG^2 in the variance of the distribution so that after a collision, we should have

$$\langle \Delta x_e^2(t) \rangle = 2D_e t + \Delta G^2. \quad (17)$$

Such increases play a key role in separation science.

The relevant parameters: In principle, a complete theory needs, as an input of the polyelectrolyte collision, the mean values and variances of the collision parameters τ_r , τ_c , Δx_r , Δx_c , v_0 , v_i (all of which are described in Fig. 2), and ΔG^2 .

C. The different collision regimes

Equation (6) indicates that the **single-collision regime (S)** is found when the distance between uncharged polymers is

$$\ell_p > \Delta x_c = v_i \tau_c, \quad (18)$$

while Eq. (7) implies that the **equilibrium regime (E)** requires

$$\ell_p > \Delta x_c + v_0 \tau_R. \quad (19)$$

In principle, we can thus have four main regimes depending on the (uncharged) polymer axial concentration $\rho_p = 1/\ell_p$:

1. The **ES regime**: We expect isolated collisions between two relaxed chains if Eq. (19) is satisfied, which means a dilute polymer solution. If we also have $N_e \ll N_p$, the polyelectrolyte spends most of its collision time inside the space occupied by the uncharged polymer [see left part of Fig. 1(d)]: the latter then acts as a slowly drifting sieving gel until the polyelectrolyte escapes.
2. The **~~E~~S regime**: In more concentrated solutions with $\Delta x_c < \ell_p < \Delta x_c + v_0 \tau_R$, we expect isolated collisions and polyelectrolytes still deformed by the last collision.
3. The **~~ES~~ regime**: When $\ell_p \lesssim \Delta x_c$, the polyelectrolyte almost always drags more than one uncharged polymers.
4. We expect a **steady-state regime** if $\ell_p \ll \Delta x_c$ where the polyelectrolyte always drags multiple chains. When one chain escapes at the back, a new one collides at the front and a steady-state is maintained because the escape and collision rates become equal after a transient period.

In this article, we focus on single-collision systems, leaving other situations for future studies.

III. METHODS

We use a simple bead-spring model to simulate the dynamics of our polymers. The beads are considered as point particles and interact with each other via the purely repulsive shifted Weeks–Chandler–Andersen (sWCA) potential,²⁸

$$\frac{U_w(r)}{4\epsilon} = \begin{cases} \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4}, & r < r_m, \\ 0, & r \geq r_m, \end{cases} \quad (20)$$

where r is the distance between the two beads, ϵ is the magnitude of the potential, and σ is the sWCA length-scale. The potential is truncated at $r = r_m \equiv 2^{1/6}\sigma$ so that its derivative is continuous, while $U_w(r_m) = 0$. The nominal bead size R is defined as the position where $U_w(R) = k_B T$; since we use a temperature $k_B T = \epsilon$, it is given by $R = \sigma$. The wall–polymer interactions are also purely repulsive and modeled using the same $U_w(r)$ potential.

The N beads of a chain are connected using the finitely extensible nonlinear elastic (FENE) potential,²⁹

$$U_{FENE}(r) = -\frac{1}{2}K_{FENE}\Delta r_{\max}^2 \ln\left[1 - \left(\frac{r}{\Delta r_{\max}}\right)^2\right], \quad (21)$$

with $\Delta r_{\max} = 1.5\sigma$ and $K_{FENE} = 30\epsilon/\sigma^2$. The resulting average bond length is $b \approx 0.97\sigma$.

We use Langevin Dynamics³⁰ (LD) to simulate the dynamics of the chains. A bead is thus subjected to four types of forces: (1) the external axial force $\vec{F}_e$; (2) the random Brownian force $\vec{F}_B$ and the dissipative force due to the fluid; (3) the repulsive forces $\vec{F}_w$ near walls and other beads; and (4) the FENE force that connects it to adjacent beads along the chain. The corresponding equation of motion for a bead is

$$m\dot{\vec{v}} = -\vec{\nabla} U(\vec{r}) + \vec{F}_B + \vec{F}_e - \zeta_\sigma \vec{v}, \quad (22)$$

where m is its mass, ζ_σ is its friction coefficient, and $\vec{v} = \dot{\vec{r}}$ is its velocity. The term $\vec{\nabla} U(\vec{r}) = \vec{\nabla}[U_w(\vec{r}) + U_{FENE}(\vec{r})]$ is the sum of the conservative forces (i.e., the FENE and sWCA forces), while the term $-\zeta_\sigma \vec{v}$ represents the damping effects of the liquid. The random force $\vec{F}_B$ is a Gaussian random variable with zero mean, $\langle \vec{F}_B \rangle = 0$, and variance $\langle F_B^2 \rangle = 2\zeta_\sigma k_B T / \Delta t$ in each spatial dimension.³¹ Note that the external field is uniform inside the channel and that the field lines are parallel to the walls. We neglect the electrostatic repulsive forces between the beads and do not explicitly include counter ions.

The LD simulations are implemented using the ESPReSo package,³² version 4.2. In Sec. IV, lengths are in units of σ , ϵ acts as our unit of energy, forces are in units of ϵ/σ , and times are in units of the Brownian time $\tau_o \equiv \sigma^2/D_\sigma$ ($D_\sigma = k_B T/\zeta_\sigma$ is the diffusivity of a single bead). The integration time step is $\Delta t = 0.01\tau_o$. The polymers' diffusion coefficient along the tube axis is simply $D(N, h) = D_\sigma/N = 1/N$, independent of the tube diameter h . The velocity of a charged chain between collisions is simply $v_o = F_e$. Unless otherwise indicated, ensemble averages are based on 500 to 1000 simulations, and each simulation is sufficiently long to allow the polyelectrolyte to reach a distance of 150σ beyond the collision.

IV. RESULTS

A. Single polymer chains

In free solution, the radius-of-gyration and relaxation time of long flexible chains with $N \gg 1$ beads scale like $\mathbb{R}_g^\circ(N) \sim N^\nu$ and $\tau_R^\circ(N) \sim N^{1+2\nu} \sim \mathbb{R}_g^\circ(N)^{2+1/\nu}$, respectively, where the Flory exponent³³ is $\nu \approx 3/5$. Simulations give a value of ν that decreases with N , slowly converging toward the asymptotic theoretical value (data and fits not shown). For example, in the range $50 \leq N \leq 150$, our results give

$$\begin{aligned} \mathbb{R}_g^\circ(N) &= 0.409(8) (N-1)^{0.626(4)}, \\ \tau_R^\circ(N) &= 0.012(3) (N-1)^{2.4(2)} \\ &= 0.62(1) \mathbb{R}_g^\circ(N)^{3.5(2)}. \end{aligned} \quad (23)$$

Note that $[6D\tau_R^\circ]^{1/2} \approx \frac{2}{3} \mathbb{R}_g^\circ(N)$, showing that long polymers diffuse over distances comparable to their own size when they relax. For shorter chains ($8 \leq N \leq 20$), however, we obtain

$$\begin{aligned} \mathbb{R}_g^\circ(N) &= 0.319(2) (N-1)^{0.699(3)}, \\ \tau_R^\circ(N) &= 0.0069(7) (N-1)^{2.62(4)} \\ &= 0.49(2) \mathbb{R}_g^\circ(N)^{3.8(2)}. \end{aligned} \quad (24)$$

According to polymer physics,¹⁹ a long chain confined to a narrow channel with $h \ll \mathbb{R}_g^\circ(N)$ forms a series of $M(N, h) = N/g$ non-overlapping undisturbed blobs of size $\approx h$ [see Fig. 1(a)] containing $g(h)$ monomers each, with $\mathbb{R}_g^\circ(g) \approx h$. The resulting axial radius-of-gyration is $R_{gx} \approx Mh = \frac{N}{g}h$. If h is large enough for the Flory exponent $\nu = 3/5$ to be valid, we obtain $g \sim h^{1/\nu} \sim h^{5/3}$, leading to $R_{gx} \sim Nh^{1-1/\nu} \sim Nh^{-2/3}$ and a monomer density $\rho_\sigma \sim g/h^3 \sim h^{-4/3}$. The relaxation time of a confined Rouse chain is $\tau_R \sim M^2 \tau_g = (N/g)^2 \tau_g$, where $\tau_g \sim g^{1+2\nu}$ is the blob relaxation time.^{16,18,19,34} We thus obtain $\tau_R \sim N^2 g^{2\nu-1} \sim N^2 h^{2-1/\nu} \sim N^2 h^{1/3}$.

As our blobs generally contain $8 \leq g \leq 20$ monomers, we must use Eq. (24) to make predictions here. We also use the effective diameter $H \equiv h - 2$ instead of h since the bead size is not negligible. This leads to the approximate scaling laws $g \sim H^{1/0.699(3)} \sim H^{1.431(6)}$, $R_{gx} \approx MH = (N/g)H \sim NH^{-0.431(6)}$, $\tau_g \sim g^{2.62(4)}$, and finally $\tau_R \sim N^2 g^{0.62(4)} \sim N^2 H^{0.89(6)}$. Our data (not shown) are consistent with these predictions,

$$\begin{aligned} R_{gx}(N, H) &= 0.22(1) (N-1)^{1.02(2)} H^{-0.47(3)}, \\ \tau_R(N, H) &= 0.0051(3) (N-1)^{1.97(2)} H^{1.01(5)}. \end{aligned} \quad (25)$$

Since the axial radius-of-gyration of a rod of length $\mathcal{L}$ is $R_{gx} = \mathcal{L}/\sqrt{12}$, a polymer chain constrained inside a tube of diameter H can also be seen as a polymer plug of length $\mathcal{L} = \sqrt{12} R_{gx}$, with $\mathcal{L} > H$. By definition, the blobs have a size H in the tube; therefore, this polymer chain is made of $M = \mathcal{L}/H$ blobs, each containing $g(H) = N/M = NH/\mathcal{L} = NH/\sqrt{12} R_{gx}$ monomers. This implies that polymer chains with fewer than $g(H)$ monomers are not fully

constrained in a tube of width H : this defines the *critical polymer size* $N^*(H) = g(H)$. Using Eq. (25), the number of monomers in a blob (or the critical polymer size) is given approximately by

$$g(H) = N^*(H) \approx 1.3 H^{3/2}. \quad (26)$$

This will be quite useful when analyzing collision data.

B. Anatomy of a collision

We place the center-of-mass (CM) of a polyelectrolyte chain of size N_e in an equilibrium conformation at axial position $x_e(0) = 0$ in a tube of diameter $H = h - 2$. The uncharged polymer of size N_p is placed at $x = x_p(0)$ such that there is a distance of ℓ_0 between their two closest beads. If both N_e and N_p are larger than $N^*(H)$, the collision is effective between a polyelectrolyte “plug” of length $\mathcal{L}_e = \sqrt{12} R_{e,x}(N_e)$ made of $M_e = \mathcal{L}_e/H$ blobs each containing $g(H)$ beads and a polymeric plug of length $\mathcal{L}_p = \sqrt{12} R_{p,x}(N_p)$ made of $M_p = \mathcal{L}_p/H$ blobs each containing $g(H)$ beads as well. The two CMs are thus initially separated by a distance $\ell_0^* \approx \ell_0 + \frac{1}{2}(\mathcal{L}_e + \mathcal{L}_p) = \ell_0 + \sqrt{3}(R_{e,x} + R_{p,x})$. An external force $\vec{F}_e = F_e \hat{x}$ is applied to all charged beads at $t = 0$, and the tube length is $\gg \ell_0^*$. The collision would take place at time $t_0 = \ell_0^*/v_0$ if we had two non-diffusing, point-like objects.

Figure 3 shows simulation data for $h = 6$, $F_e = 1$ (implying that $v_0 = 1$), $N_e = 60$, $N_p = 100$, and $\ell_0 = 50$. With $R_{p,x}(100) = 12.17$ and $R_{e,x}(60) = 6.95$, we expect the collision to start around time $t_0 \approx 84$. Our chains have $M_e \approx 6$ and $M_p \approx 10$ blobs containing $g(H = 4) \approx 10$ beads each.

Figure 3(a) shows 200 different $x_e(t)$ vs t polyelectrolyte trajectories and their average. The CM velocity is v_0 before and after the collision. The collision has two main effects. First, the trajectory is shifted down by a distance Δx_r , or equivalently, it is shifted right by a time Δt_r , in agreement with Eq. (4). Second, the spread of trajectories increases dramatically. Not only is the trajectory of the polyelectrolyte affected, but Fig. 3(b) shows that its conformation is as well: its instantaneous axial radius-of-gyration $R_{e,x}(t)$ first decreases at the beginning of the collision (starting around the predicted collision time $t_0 \approx 84$), but then goes through a maximum before relaxing to its equilibrium (pre-collision) value.

Figure 3(c) illustrates the fact that the large spread of post-collision trajectories in (a) leads to a sharp increase in the variance ΔG^2 defined in Eq. (17). Before and after the collision, the variance increases linearly with time, as per normal diffusion; the dashed lines have slopes $2D_e = 2/N_e = 1/30$.

Single trajectories allow us to extract several collision parameters using the equations in Sec. II B (see also Fig. 2). Figure 3(d) shows an example: the instantaneous polyelectrolyte CM velocity is minimum at the inflection point $t = t_I$ of the $x_e(t)$ vs t curve; this defines the velocity v_I —see Eq. (8). The trajectory of the uncharged polymer [Fig. 3(e)] shows that it diffuses freely before and after the collision and is dragged by the polyelectrolyte during the collision; further, it reaches its maximum velocity roughly when the polyelectrolyte reaches its minimum velocity. We use the inflection point to define the polymers’ collision velocities v_I and $v_{Ip} = v_p(t_I)$.

C. Statistical distributions

Figure 4 represents distribution functions for several collision parameters for the case presented in Sec. IV B. Figure 4(a) shows the minimum and maximum radii-of-gyration of the polyelectrolyte during a collision, scaled by the mean equilibrium value $R_{e,x}^0$. We see two well-separated asymmetric peaks, with the equilibrium distribution (centered on 1.0) located between them. These broad peaks suggest that each collision is unique and that compression is more severe than stretching, consistent with Fig. 3(b) where a rapid, intense compression process is followed by a weaker and slower stretching process. We show the same distributions for the uncharged polymer chain in Fig. 4(b); because it is larger, this polymer is less compressed or stretched during the collision.

Figure 4(c) gives the distribution of scaled instantaneous velocities for the charged (v_I/v_0) and uncharged (v_{Ip}/v_0) polymers at collision time $t = t_I$. The extreme value v_U given by Eq. (15) (dashed line) separates the two peaks; the rare cases near this line thus correspond to U-U collisions. Finally, Fig. 4(d) studies the collision distances Δx_c ; the most likely value is roughly given by Eq. (14). The peak is asymmetric and has a short tail, indicating that the polyelectrolyte is able to pass through the uncharged chain relatively easily in most cases.

D. Parameters that affect a collision

The degree of deformation of the polymer during a collision is expected to depend on the external force F_e . Figure 5 shows how the velocity ratios v_I/v_0 and v_{Ip}/v_0 change as F_e increases from low ($F_e = 0.4$) to high ($F_e = 5$) for the case studied in the previous sections ($N_e = 60$, $N_p = 100$, $h = 6$). We note that v_I/v_0 is a weak function F_e , approaching the theoretical limit at low force and leveling off at high force. In contrast, v_{Ip}/v_0 is essentially flat over the entire range. Furthermore, the standard deviations increase as F_e decreases. These results are consistent with the fact that unlike the uncharged polymer, the polyelectrolyte conformation is field-dependent below $F_e \approx 2$ (results not shown).

A collision can also be characterized by its duration τ_c , as defined in Eq. (12). First, let us make some theoretical predictions regarding τ_c , given the results obtained so far. We see in Fig. 5 that v_I/v_0 reaches a constant plateau value (to be denoted as V_∞) in the large force limit, while Fig. 4(d), together with Eqs. (13) and (14), indicated that $v_I \tau_c \approx 2[R_{e,x}^0 + R_{p,x}^0]$. Since our axial radii-of-gyration scales roughly like $R_{gx}(N) \sim N/H^{1/2}$ [see Eq. (25)] while $v_0 = F_e$, we can write that

$$\tau_c \approx \frac{2[R_{e,x}^0 + R_{p,x}^0]}{v_0 V_\infty} \sim \frac{N_e + N_p}{H^{1/2} F_e}. \quad (27)$$

In fact, the $1/F_e$ scaling should be decent even in the low force limit because v_I/v_0 is a weak function of F_e (see Fig. 5).

Figure 6 shows our data for several values of h , N_e , and F_e ; the axes allow us to directly check the validity of Eq. (27) when it is rewritten as

$$\tau_c \times \sqrt{H} F_e \sim N_e \times \left(1 + \frac{N_p}{N_e}\right). \quad (28)$$

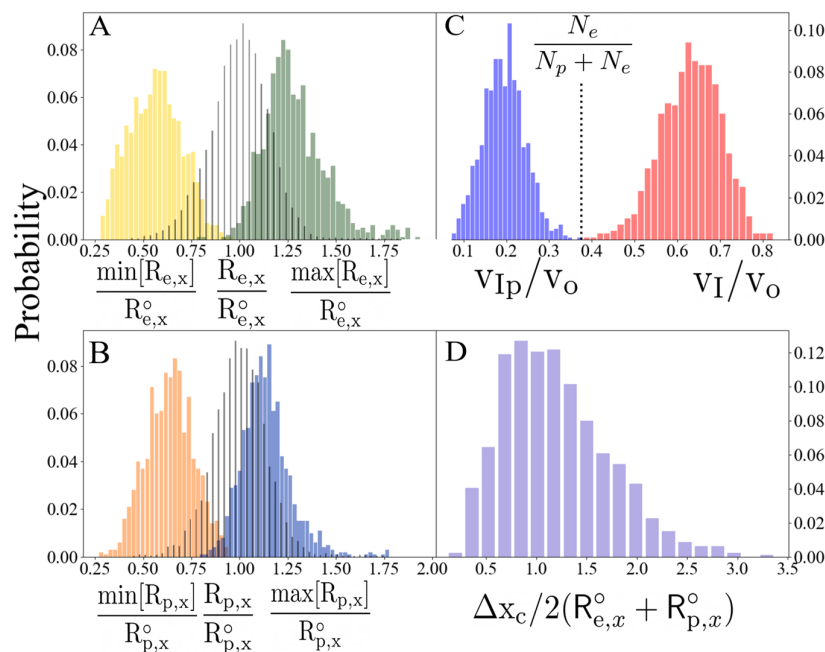


FIG. 4. Probability distribution functions for the case studied in Fig. 3. (a) $\min [R_{e,x}]$ is the minimum value of the axial radius-of-gyration of the polyelectrolyte during a collision (gold) and $\max [R_{e,x}]$ is its maximum value (green), while the black histograms give the data before a collision. The radii-of-gyration are scaled by the mean equilibrium value $R_{e,x}^0$. (b) Same data for the uncharged polymer chain. (c) Reduced velocity at time $t = t_i$ for the polyelectrolyte (red) and the uncharged polymer (blue); the (vertical) dashed line shows the theoretical limit given by Eq. (15). (d) The distance traveled during the collisions, Δx_c , is normalized by the value proposed in Eq. (14).

Since the relevant critical sizes are $N^*(h=6) \approx 10$ and $N^*(8) \approx 19$, all three polyelectrolytes ($N_e = 30, 60, 90$) are constrained here. The data points collapse on universal curves for $N_p/N_e > 1$, and the slope of the linear fits indeed increase like $\sim N_e$. When $N_p \gg N_e$, the

uncharged polymer is essentially a long gel-like network; the linear increase $\tau_c \sim N_p$ is then due to the fact that the length of this porous region is $\approx R_{p,x}^0 \sim N_p$.

When $N_p < N_e$, however, the situation is fundamentally different: it is now the smaller, uncharged polymer that has to migrate through the polyelectrolyte chain. We can see that the data points collapse on a universal curve for the whole range of size ratios when $h=6$; note that for some $N_p/N_e < 1$ data points, the uncharged polymer is smaller than the critical size $N^*(h=6) = 10$. Although we also observe data collapse for the $h=8$ case when $N_e = 90$, this is no longer the case for shorter polyelectrolytes. Interestingly, the duration of the collision decreases as N_p increases in this regime, a somewhat counter-intuitive result that leads to τ_c reaching a minimum value when $N_p \approx N_e$, a somewhat unexpected finding.

The presence of this minimum can be explained as follows. When the two polymers are of very different sizes (i.e., when $N_p \gg N_e$ or $N_p \ll N_e$), the smaller one must migrate through the other (the latter forming a plug in the tube). This process is essentially a (somewhat inefficient) sieving effect, with the smaller of the two trying to work its way through a long gel-like plug. The collision time is then directly proportional to the size of the longer polymer. When the two polymers are of similar size, neither really migrate through the other; instead, the disentanglement process starts immediately after the entanglement process is completed. The polymers only have to migrate over a distance equal to their own size to

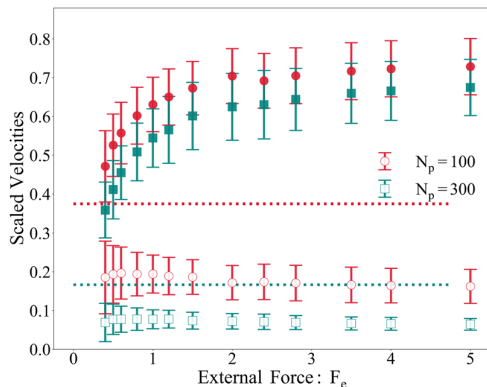


FIG. 5. Mean scaled collision velocities v_i/v_0 (solid symbols) and v_{ij}/v_0 (hollow symbols) vs the external force F_e for a polyelectrolyte of size $N_e = 60$ and a tube diameter $h = 6$. Data for $N_p = 100$ and 300 are shown. The (horizontal) dashed lines give the theoretical limits predicted by Eq. (15). The error bars are standard deviations.

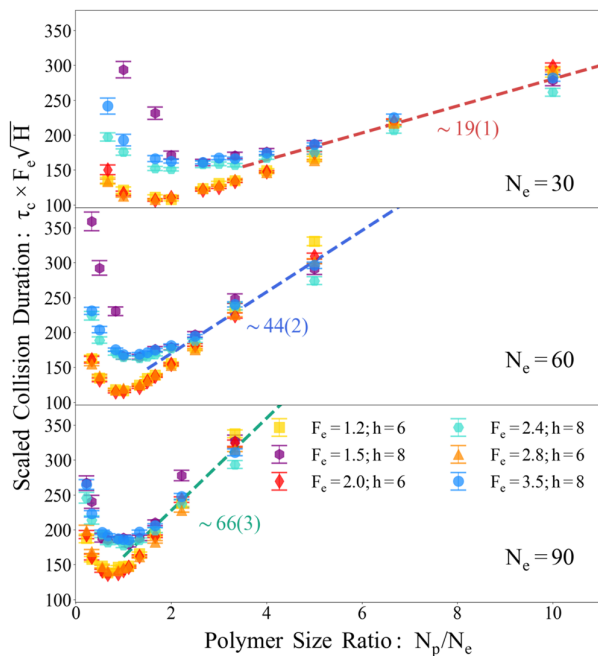


FIG. 6. Scaled collision duration, $\tau_c \times F_e \sqrt{H}$, vs polymer size ratio N_p/N_e for various external forces F_e and tube widths $h = H + 2$. The dashed lines show the linear fits (and slopes) for the $N_p/N_e > 1$ data.

disentangle. The resulting disentanglement process is more efficient than the sieving process, and we observe the shortest collision times when $N_p \approx N_e$.

E. The different types of collision

Since the polyelectrolyte drags the uncharged polymer during a collision, their velocities must be anti-correlated. For instance, while the polyelectrolyte's minimum velocity and the uncharged polymer's maximum velocity are both given by v_U in Eq. (15), we have $v_{lp} = 0$ when $v_l = v_o$ (no collision). Figure 7 shows v_l/v_o vs v_{lp}/v_o for several cases (each point represents one collision). Remarkably, there is an approximate linear relationship between the two velocities in all regimes. The linear function $v_{lp}/v_o = \alpha \times (1 - v_l/v_o)$, with $\alpha = v_U/(v_o - v_U) = N_e/N_p$, satisfies the two limits mentioned above—see the diagonal solid lines in Figs. 7(a) and 7(b). For reference, the tubes' critical molecular sizes (or blob sizes) are $N^*(h = 5) \approx 7$, $N^*(7) \approx 15$, and $N^*(20) \approx 99$.

We can assign collision types to particular regions in Fig. 7. For instance, glancing collisions dominate when neither polymer is large enough to obstruct the tube—see Fig. 1(e): this is the case for $h = 20$ in the lower right of Fig. 7(a) where $v_{lp} \ll v_o$ and $v_p \approx v_o$ (see the histogram distributions). Collisions are inevitable in narrower tubes as in Fig. 7(a) for $h = 7$. The two dashed lines show $v_U/v_o = 1/2$: the few data points near the intersection thus correspond to U-U collisions. In most cases, however, the polyelectrolyte drags the uncharged polymer, while the latter slips away. This leads

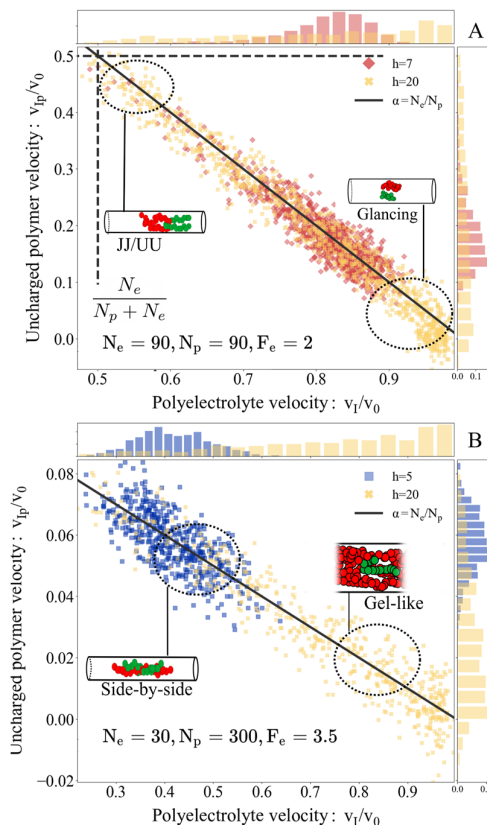


FIG. 7. Scaled velocity of the uncharged polymer vs scaled velocity of the polyelectrolyte at collision time $t = t_l$ for at least 500 different collisions. The histograms show the distributions. (a) The simulation parameters are $F_e = 2$, $h = [7, 20]$, and $N_p = N_e = 90$, giving a limit velocity $v_U/v_o = 1/2$ (dashed lines). The solid (diagonal) line is the function $v_{lp}/v_o = 1 - v_l/v_o$. (b) The parameters are $F_e = 3.5$, $h = [5, 20]$, $N_p = 300$, and $N_e = 30$, giving $v_U/v_o = 1/11$. The solid (diagonal) line shows the linear function $v_{lp}/v_o = (1 - v_l/v_o)/10$.

to broad velocity distributions centered around $v_l/v_o \approx 0.84$ and $v_{lp}/v_o \approx 0.14$.

Figure 7(b) examines the case of a short polyelectrolyte colliding with a large uncharged polymer ($N_e = 30 = N_p/10$ and $v_U/v_o = 1/11$) in the presence of a stronger field and a narrow tube ($h = 5$). The two velocities never get close to v_U ; instead, the polyelectrolyte essentially moves parallel to the uncharged polymer, and the latter is slowly pushed forward via friction. In the $h = 20$ case, on the other hand, the polyelectrolyte must migrate through an almost immobile ($v_{lp} \ll v_o$) gel-like plug.

F. The velocity of the polymers during a collision

Free polymer chains dissipate the energy supplied by an external force via friction with the liquid. Polymer-polymer collisions provide a second dissipation mechanism: conformational deformation. The extent to which a polyelectrolyte can pull an

uncharged chain during a collision is obviously correlated with their degree of entanglement; for instance, a collision ultimately ends because the chains slide around each other, thereby eliminating the entanglements—see Ref. 24.

Figure 8 examines how the collision velocities vary with the size ratio N_p/N_e for three different polyelectrolyte sizes N_e and forces F_e when using a narrow ($h = 5$) and a wide ($h = 10$) tube. Since the corresponding critical polymer sizes are $N^*(h = 5) \approx 7$ and $N^*(10) \approx 26$, the $N_e = 30$ polyelectrolyte is barely constrained in the wider tube; note that some values of N_p used for this plot are smaller than these critical sizes.

The top six plots in Fig. 8 show (first row) the scaled collision velocities v_l/v_o (filled symbols) and v_{lp}/v_o (empty symbols) as well as (second row) the scaled velocity differences $(v_l - v_{lp})/v_o$ vs the polymer size ratio N_p/N_e for three different external forces F_e (the three columns) in the narrow $h = 5$ tube. The dashed lines show the minimum (maximum) polyelectrolyte (uncharged polymer) velocity v_U given by Eq. (15). Although $v_l \geq v_U \geq v_{lp}$ in all cases, as expected, we note that $v_l \approx v_U$ for $N_p \lesssim 2N_e$ when $F_e = 0.5$: the polymers are then minimally deformed, which maximizes the number of contact points as well as the duration of the collision—see Fig. 6. This is no longer the case when $N_p/N_e \gg 1$ or when the force is high. Interestingly, v_{lp}/v_o is a rather weak function of F_e and N_e for a fixed ratio N_p/N_e , whereas our data for v_l/v_o lie on a universal curve at a low field.

The relative velocity $(v_l - v_{lp})/v_o$ nearly falls on a universal curve when the force is low, and it reaches a minimum value around $N_p/N_e \approx 1$ for all three forces. The physics of polymer-polymer collisions again leads to non-monotonic, resonance-like behavior. Of course, $(v_l - v_{lp})/v_o$ plateaus when $N_p/N_e \gg 1$ as we then have small polyelectrolytes traversing large, almost stationary uncharged polymer plugs.

The last two rows of Fig. 8 show similar data for a wider tube, $h = 10$. Although we still have $v_l \geq v_U \geq v_{lp}$ (third row), both velocities are now far from v_U . Here, however, the data points fall on universal curves in all cases. The last row shows the relative velocity $(v_l - v_{lp})/v_o$. At low field, the data again fall on a universal curve, but there is no minimum over the range of N_p/N_e studied here. A shallow minimum can be observed at $F_e = 2$, and a much deeper one is clearly seen for $F_e = 5$ in the range $1 \leq N_p/N_e \leq 4$. The position of the minimum now depends on both N_e and F_e , which leads to the curves crossing each other (this was not the case for $h = 5$).

In order to better understand the last row of Fig. 8, Fig. 9 examines the effect of the force when the relative velocity is plotted vs N_p . Remarkably, not only is the relative velocity a function of N_e at low force only, but smaller polyelectrolytes are actually slower than larger ones; this is somewhat similar to band inversion in DNA gel electrophoresis.²⁴ The data fall on nearly universal curves at higher forces, showing co-migration, also similar to DNA gel electrophoresis.⁵ This limit is further investigated in Sec. IV G.

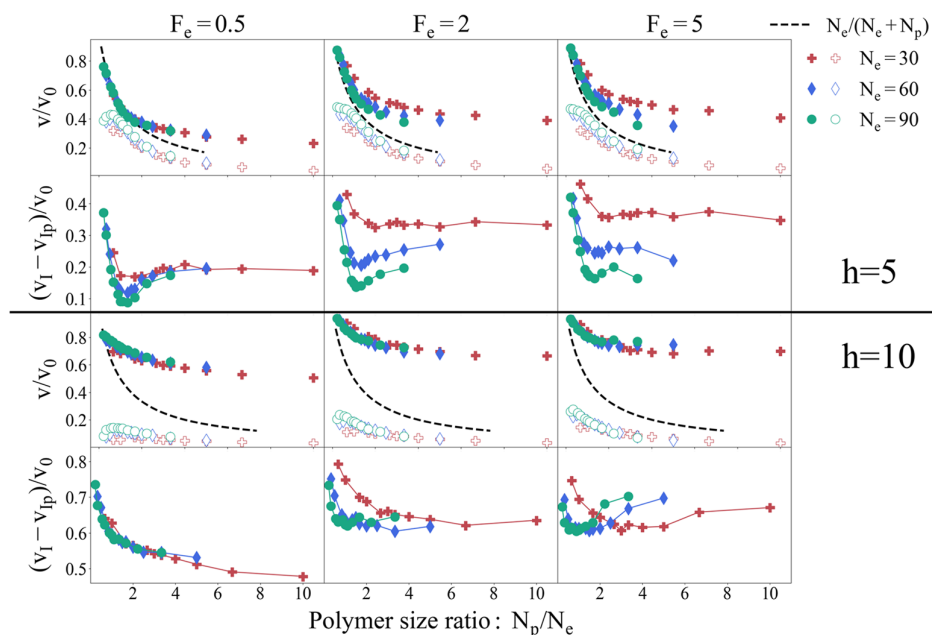


FIG. 8. Scaled collision velocities vs polymer size ratio N_p/N_e for polyelectrolytes of size $N_e = 30, 60, 90$ in a narrow $h = 5$ (top two rows) and a wide $h = 10$ (bottom two rows) tube. Left column: low external force $F_e = 0.5$. Middle column: intermediate force $F_e = 2$; right column: high force $F_e = 5$. The first and third rows give both v_l/v_o (solid markers) and v_{lp}/v_o (hollow markers). The second and fourth rows give the relative velocity $(v_l - v_{lp})/v_o$. The size of the uncharged polymers vary between $N_p = 20$ and $N_p = 300$. The dashed lines show the theoretical limit v_U given by Eq. (15).

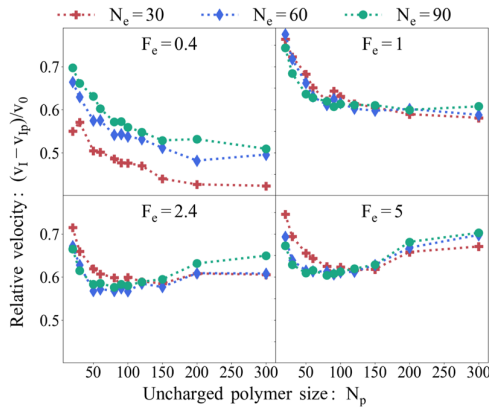


FIG. 9. Scaled relative collision velocity $(v_l - v_{ip})/v_0$ vs uncharged polymer size N_p for polyelectrolytes of size $N_e = 30, 60, 90$ in a $h = 10$ tube. Four different values of the external force F_e are shown.

G. Toward gel electrophoresis

In the $N_p \gg N_e$ limit, the uncharged polymer plug is essentially an immovable (i.e., $v_{ip} \rightarrow 0$) gel-like region. Moreover, the combined time taken by the polyelectrolyte to enter and leave this region is then negligible compared with the time taken to cross it. In order to study this limit, we have estimated the extrapolated dimensionless mobility $\hat{\mu}_e(N_e, F_e) \equiv \lim_{N_p \rightarrow \infty} \frac{(v_l - v_{ip})}{v_0}$ from our data and, inspired by the work of Viovy on the reptation model of DNA gel electrophoresis [see Eq. (5.25) in Ref. 5], we fitted the results using the expression

$$[\hat{\mu}_e(N_e, F_e)]^2 = \frac{1}{[F_h/F_e + 1/\hat{\mu}_e^\infty]^2} + \left[\frac{N_h}{N_e}\right]^2, \quad (29)$$

where the fitting $\hat{\mu}_e^\infty$, F_h , and N_h , which are functions of the pore size in a gel, may be expected to vary with h here. Clearly, F_h is the critical force separating weak and strong forces, while N_h is the critical size separating small and large polyelectrolytes. Consequently, $\hat{\mu}_e^\infty = \lim_{N_e \rightarrow \infty} \lim_{F_e \rightarrow \infty} \hat{\mu}_e(N_e, F_e)$ is the asymptotic mobility of large polyelectrolytes at high field (empirically, we have $\hat{\mu}_e^\infty \approx 1/3$ in gels⁵).

In order to estimate the fitting parameters, we used the following systematic three-step approach:

- (1) Since the zero-force limit of Eq. (29) reads $\hat{\mu}_e(N_e) = N_h/N_e$, we estimated the value of $\hat{\mu}_e(N_e, F_e \rightarrow 0)$ by extrapolation and used it to find N_h for each value of N_e .
- (2) Similarly, as the infinite force limit of Eq. (29) reads $[\hat{\mu}_e(N_e, F_e \rightarrow \infty)]^2 = [\hat{\mu}_e^\infty]^2 + [N_e/N_h]^2$, where the last term is known after step (1), we estimated $\hat{\mu}_e(N_e, F_e \rightarrow \infty)$ from our data to obtain the value of the fitting parameter $\hat{\mu}_e^\infty$.

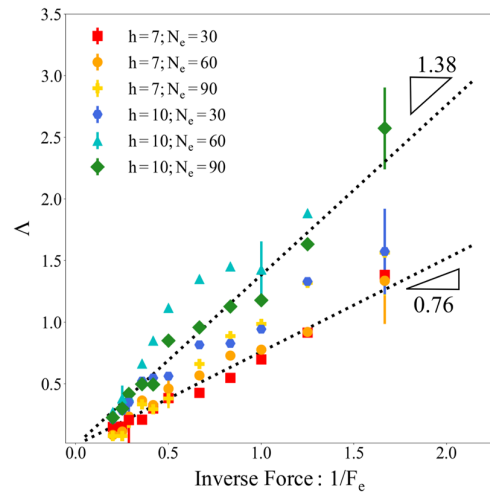


FIG. 10. The value of $\Lambda(F_e)$, as defined in Eq. (30), is plotted vs $1/F_e$ for polyelectrolyte sizes $N_e = 30, 60, 90$ and tube diameters $h = 7, 10$. To avoid cluttering the graph, only the smallest and largest error bars are shown for each dataset. The slope of the linear fits gives the value of the fitting parameter $F_h(h)$ (since F_h should not depend on N_e , all three datasets were fitted together for a given value of h). The Pearson correlation coefficient is ≥ 0.82 for all the cases shown here.

- (3) Finally, given these values of N_h and $\hat{\mu}_e^\infty$, we fitted the $\hat{\mu}_e(N_e, F_e)$ vs F_e data to obtain F_h . In order to do that, though, we rewrote Eq. (29) as

$$\Lambda(F_e) \equiv \left([\hat{\mu}_e(N_e, F_e)]^2 - \left[\frac{N_h}{N_e} \right]^2 \right)^{-1/2} - \frac{1}{\hat{\mu}_e^\infty} = \frac{F_h}{F_e} \quad (30)$$

and plotted $\Lambda(F_e)$ vs $1/F_e$. If Eq. (29) applies, we should obtain straight lines with slopes $F_h(h)$. Figure 10 shows that this is roughly the case.

The value of the fitting parameters is given in Table I for three different values of N_e and four values of h . Both $\hat{\mu}_e^\infty$ and F_h were found to not depend on N_e given the error bars (not shown). As expected, all three fitting parameters vary with the tube diameter h . Since the density of monomers inside the gel-like plug is predicted to scale like $\rho \sim (h - 2)^{-4/3}$, the effective pore size of the plug increases

TABLE I. The value of the three fitting parameters in Eq. (29) for different choices of tube diameter h and polyelectrolyte size N_e . Note that N_h is the only parameter that appears to depend on N_e .

h	$\hat{\mu}_e^\infty$	F_h	$N_e = 30$	$N_e = 60$	$N_e = 90$
			N_h	N_h	N_h
6	0.64(1)	0.77(3)	3.4(7)	13.2(9)	24.8(4)
7	0.66(1)	0.76(3)	6.5(2)	21.0(8)	36(2)
8	0.74(1)	1.28(15)	8.4(5)	25(1)	39(3)
10	0.75(2)	1.38(12)	10.3(5)	27(2)	40(2)

with h . Larger pores (wider tubes) are expected to lead to higher mobilities μ_e^∞ ; similarly, N_h being essentially the size of a polyelectrolyte that fills a pore in the reptation theory,⁵ it has to increase with h . Our results agree with these qualitative predictions.

However, our results differ from the predictions of the reptation model in two respects. First, F_h (which is the minimum external force needed to orient a long polyelectrolyte along the field direction in the reptation model) should decrease when h increases since it is inversely proportional to the pore size in a gel.⁵ However, long polymers are oriented along the tube axis even at zero-force in a tube. Since the degree of orientation of a constrained chain, e.g., the ratio $R_{e,x}(N)/R_{e,g}(N) \sim N^{2/5}h^{-2/3}$, decreases when h increases, the force needed to induce orientation actually increases with h . Second, N_h varies with N_e here, which is not the case in the reptation model. In our case, though, when both polymers occupy the same section of the tube, the very high local monomer density changes the effective pore size, an effect that appears to weaken in larger tubes, i.e., when the monomer density is small.

H. Collision-driven compression and stretching

As we see in Fig. 3(b), a polyelectrolyte first contracts when it collides with an uncharged chain and then stretches before escaping and relaxing back to its equilibrium size. Figure 11 examines the correlation between the minimum (x axis) and maximum (y axis) values of the axial radius-of-gyration $R_{e,x}$ during a collision; each point corresponds to one simulation, and the corresponding distribution functions are shown on the sides. The critical polymer sizes for the three tube diameters used here are $N^*(h=5) \approx 7$, $N^*(7) \approx 15$, and $N^*(20) \approx 99$.

The two chains are identical in size (90 beads each) in Fig. 11(a). In the narrower $h=5$ tube, side-by-side motion leads to a skewed $\min[R_{e,x}]$ distribution with a mean $\approx 0.43 R_{e,x}^\circ$. The $\max[R_{e,x}]$ distribution is peaked near the equilibrium value $R_{e,x}^\circ(90,5) \approx 5.3$, but with a long tail that contains a second peak around $\approx 1.5 R_{e,x}^\circ$. The reason for the presence of two peaks is that the polyelectrolyte sometimes fold. Finally, we remark that the distribution of points in the plane indicates virtually no correlation between $\min[R_{e,x}]$ and $\max[R_{e,x}]$.

When $h=7$, both distributions remain fairly narrow. However, the data points are clearly aligned along a diagonal direction, indicating a correlation between $\min[R_{e,x}]$ and $\max[R_{e,x}]$. This is not surprising with two polymers of the same size since the details of the collision, including the late stages, depend on the details of the conformation in the early stages.

In the larger cylinder, $h=20$, the $\min[R_{e,x}]$ distribution has a single peak, a long tail, and a mean not far from the equilibrium value. The distribution of $\max[R_{e,x}]$ values also has a single peak, but the long tail now extends to about six times the equilibrium value with the largest values, $\max[R_{e,x}] \approx 23$, corresponding to near full extension. However, the peak remains centered around the equilibrium value, indicating a high probability of having glancing collisions with minimal impact on the polyelectrolyte conformation (the weak diagonal distribution in this area supports this conclusion).

Figure 11(b) represents a case where the uncharged polymer is large enough to fully obstruct the tube, and since the polyelectrolyte is much smaller, we basically have collisions with a gel-like plug.

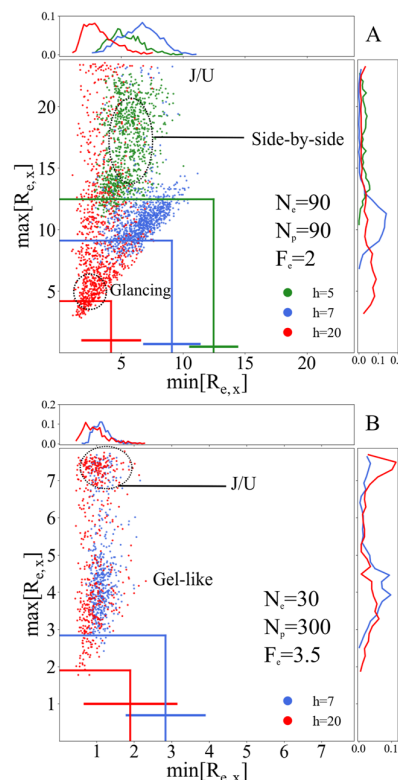


FIG. 11. A study of the correlation between the minimum and maximum values of the polyelectrolyte axial radius-of-gyration $R_{e,x}$. The distribution functions are also shown. (a) $F_e = 2$ and $N_p = N_e = 90$; 1000 collisions. The means and standard-deviations of the $\min$ distributions are 5.4 ± 1.3 , 6.5 ± 1.5 , and 3.3 ± 1.3 for tubes with diameters $h = 5, 7, 20$, respectively. For the $\max$ data, we have 17 ± 3 , 11 ± 2 , and 10 ± 5 . (b) $F_e = 3.5$ and $N_p = 10N_e = 300$; 500 collisions. The means and standard-deviations of the $\min$ distributions are 4.7 ± 1.3 and 5.2 ± 1.8 for $h = 7, 20$, respectively; for the $\max$ data, we have 1.14 ± 0.22 and 0.96 ± 0.33 . The square boxes give the mean equilibrium values $R_{e,x}^\circ$ with the horizontal lines showing the corresponding standard-deviations.

There is essentially no correlation between $\min[R_{e,x}]$ and $\max[R_{e,x}]$ because the charged polymer has lost memory of its initial, compressed conformation by the time it has traversed the entire polymer plug. While the $\min[R_{e,x}]$ distribution is featureless, the $\max[R_{e,x}]$ distribution is clearly bimodal when $h=20$. The latter phenomenon shows that there are two escape modes from the gel, one of which leads to elongated J-shaped conformations just before escape.

V. CONCLUSION

We have studied force-driven polymer-polymer collisions in narrow channels, an extension of the bulk solution problem first examined experimentally by Barron *et al.*⁶ and theoretically by Hubert *et al.*⁷ We began by describing a single collision and the parameters that control the different regimes, leaving the issue of multi-polymer collisions to future work. We proposed a method

for characterizing collisions using trajectory inflection points and collision and retardation times and distances; these parameters will be essential for the design of collision-based nanofluidic devices.

In the limit of large uncharged polymers with $N_p \gg N_e$, the system is somewhat similar to gel electrophoresis, except for the fact that the polyelectrolyte is oriented (by the tube walls) even in the absence of an external force. We proposed a modified reptation equation to explain the relative velocity of the two polymers during a collision and highlighted the fact that the orientation parameter F_h increases with tube diameter h , a counter-intuitive result due to the tube constraints.

We used different approaches to investigate the link between conformational changes, the different types of collision, and the parameters that can be used to characterize a collision (such as its duration). Undoubtedly, the most remarkable finding is that of resonance-like effects leading to non-monotonic behavior, echoing similar phenomena in gel electrophoresis. For instance, the shortest collisions happen when $N_p \approx N_e$ and not when one of the chains is much larger than the other.

In this article, we have only studied isolated collisions and used the simplest polymer model—that of the Rouse chain. Clearly, many details are missing from our model. For example, the stiffness of the charged polymer is not taken into account, a feature that would certainly be necessary if the experiments involved dsDNA. As mentioned before, we have neglected the hydrodynamic and electrostatic interactions at this stage of our investigation. Although all of these effects would impact our quantitative results, they probably would not affect qualitative findings, such as the non-monotonic dependence of the collision time on the polymer size ratio N_e/N_p . We thus believe that our results represent a useful first step toward understanding this class of problems. Logically, the next step is to study collisions involving more than two polymer chains, a regime we briefly touched on in Sec. II C. The addition of electrohydrodynamic interactions should also be considered.

Finally, another important result is that the collision time τ_r does not appear to be a strong function of the size N_e of the polyelectrolyte. The design of a nanofluidic device to manipulate or separate polyelectrolytes should therefore be based either on the strong conformational asymmetry of the collision process, or on the above-mentioned non-monotonic behavior, or on both. This points heavily in the direction of ratchet mechanisms, a methodology that is ideal in a one-dimensional system of this type.^{15–17,26}

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

H. Y. Wang: Conceptualization (supporting); Data curation (lead); Formal analysis (equal); Software (lead); Visualization (lead); Writing – original draft (lead). **G. W. Slater:** Conceptualization (lead); Formal analysis (supporting); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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DIFFUSIVE SPREADING OF A
POLYDISPERSE POLYMER SOLUTION IN A
CHANNEL

Diffusive spreading of a polydisperse polymer solution in a channel

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Long DNA molecules can be mapped by cutting them with restriction enzymes inside a narrow channel. Once cut, the individual fragments thus produced move away from each other due to diffusion and entropic effects. We investigate how long it takes for these fragments to travel distances large enough for an experimental device to distinguish them and (possibly) estimate their size. In essence, this is a single-file diffusion process in which molecules of different sizes and hence different diffusion coefficients spread out from an initially dense configuration. We use Monte Carlo methods to investigate this class of problems and define the time taken to reach the required final state as a first-passage *spreading time*. Our results demonstrate that the stochastic nature of the diffusion process is as significant as the specifics of the molecular size distribution in determining the spreading time. We examine the relationship between the spreading time and the final space occupied by the fragments as a function of the experimental parameters and determine the fundamental length scale governing this process. We introduce a molecular sequence randomness parameter, Z , which is linearly correlated with the final spreading time. Finally, we show that the distribution function of spreading times follows a well-known form for first-passage time problems, and that its variance decreases linearly with the number of fragments.

I. INTRODUCTION

Nanofluidic channels are becoming very powerful instruments in laboratories [1], especially for studying and analyzing DNA molecules. For example, Schwartz et al. [2, 3] introduced the idea of using nanochannels to map long DNA molecules [4, 5]. Since then, the methodologies used for DNA imaging and data analysis, as well as the implementation of mapping techniques, have advanced [6, 7].

This approach to DNA mapping typically involves extending a long DNA chain within a narrow channel, cutting it using restriction enzymes [2], and imaging the distribution and order of the resulting fragments in the channel [8]. Restriction enzymes target short, specific DNA sequences and cut the DNA chain into smaller fragments in a very precise and reproducible way. Because the cutting process is performed within a narrow channel, the order of the restriction fragments is maintained (fragments cannot change position due to excluded volume interactions), allowing molecular mapping once the fragments can be imaged.

The objective of this study is to explore a particular dimension of this problem. Specifically, we are interested in investigating the dynamics of a linear polymer chain confined within a channel after it has been cut into several fragments. The fundamental question we seek to address is the time required for these fragments to become visibly separated from each other to a degree that allows for their unambiguous detection. This process is influenced by two key factors: entropic repulsion and diffusion. We will focus on understanding the parameters that control the necessary separation time; in doing so, we will use parameters that roughly match the conditions used for DNA mapping in channels (e.g. $N = 5 - 20$ fragments) while also investigating the (admittedly more theoretical) asymptotic limits (e.g., $N \gg 1$). Of course, the size and order of the molecular fragments are also important factors; for example, very large fragments can block the diffusion process of smaller ones if located near the ends of a sequence of fragments.

The paper is organized as follows. In Section II, we describe our Monte Carlo model and the necessary parameters for analyzing simulation data. Section III presents our results in several subsections covering the following topics: the properties of monodisperse systems; a study of some simplified bimodal systems; a comparison between random and monodisperse systems, leading to the introduction of a parameter Z to characterize the molecular arrangement; the role of permutations in random systems; and finally, a look at extreme situations and distribution functions of spreading times. Our conclusions, including possible future extensions of these results, are found in Section IV.

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II. THE LATTICE MONTE CARLO MODEL

The top part of Fig. 1 shows a molecular view of the system. A long polymer chain of mass M is cut into N pieces at time $t = 0$, after which the pieces start to move away from each other. The diameter of the channel, h , is smaller than the free-solution radius of gyration R_g of all the pieces; as a result, the molecular fragments form blobs of diameter h that are aligned along the channel axis. We denote by $\tilde{X}$ the minimum gap size that can be detected between two adjacent fragments; in other words, the distance between two fragments must be $\geq \tilde{X}$ so that we can confirm the presence of two fragments instead of a single, longer one. For example, this minimum gap may have to be of order h (e.g., the X_2 gap in Fig. 1).

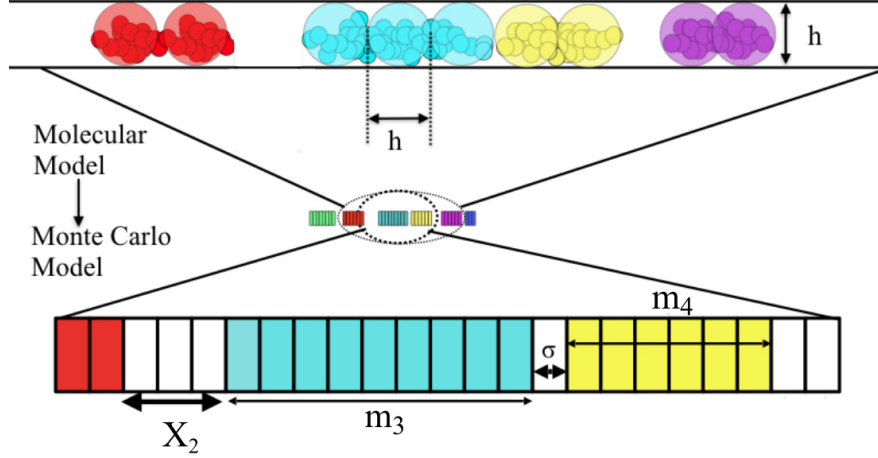


FIG. 1. Diagram of the molecular model and its mapping onto the simulated system. Top panel: A long polymer chain inside a narrow tube of diameter h was cut into 4 fragments. The fragments form blobs of size h aligned along the tube axis. Middle panel: The system is then mapped onto a one-dimensional Monte Carlo model with rigid objects. Bottom panel: The i^{th} object comprises $m_i \geq 1$ lattice cells of size $\sigma = 1$. The target state is reached when all gaps X_i are simultaneously larger than a threshold value $\tilde{X}$ for the first time.

We map this molecular system onto a one-dimensional Lattice Monte Carlo model, also shown in Fig. 1. The lattice cell size, $\sigma = 1$, is smaller than both h and the smallest gap, $\tilde{X}$. The system thus consists of N rigid molecules diffusing in the single-file diffusion (SFD) regime; the fluctuations in the axial length of the molecules are neglected. Because hydrodynamic interactions are screened between blobs [9, 10], we use a Rouse model for the polymer chains; the diffusion coefficient of molecule i is then $D(m_i) = D_1/m_i$, where $m_i \geq h$ refers to its size (i.e., number of lattice cells occupied). The total molecular size is thus $M = \sum_{i=1}^N m_i$. We use the optimized Monte Carlo moves described in ref. [11].

We denote by X_i ($i = 1..N-1$) the spacing or gap between molecules i and $i+1$. At time $t = 0$, the molecules are equally spaced by a single lattice cell: $X_i(0) = 1, \forall i$. We simulate the evolution of this system until *all* gaps are simultaneously greater than a certain target value $\tilde{X}$ *for the first time*,

$$X_i(t = \tau_f) \geq \tilde{X} \quad \forall i, \quad (1)$$

which defines the *spreading time* τ_f . Our main goal is to understand how the mean first passage time τ_f depends on the total molecular size M , the number of molecular fragments, N , the minimum final gap size, $\tilde{X}$, and especially the details of the distribution of molecular sizes, $(m_i) \equiv (m_1, m_2, \dots, m_N)$.

In addition to the spreading time τ_f , the span of the system (i.e., the difference between the largest and smallest axial coordinates of the M lattice cells that constitute the molecular fragments), $S(t) = M + \sum_{i=1}^{N-1} X_i(t)$, is also of interest. As we chose $X_i(0) = 1$, its initial value is $S(0) = M + N - 1$. We will look at the mean increase of the span, $\Delta S_f = \langle S(\tau_f) - S(0) \rangle = \sum_{i=1}^{N-1} [X_i(\tau_f) - 1]$, during the process. The minimum value of ΔS_f compatible with the desired final state is

$$\Delta s \equiv \min[\Delta S_f] = (N-1)(\tilde{X} - 1). \quad (2)$$

As we shall see, Δs turns out to be a key length scale. Finally, the links between ΔS_f , τ_f and the final mean square center-of-mass (CM) displacement of the population, $\langle \Delta x_{\text{CM}}^2(\tau_f) \rangle$, are studied to understand what controls $\tau_f(N, h, (m_i))$.

The (dimensionless) simulation data will be given in units of σ for distances and $\tau_1 = \sigma^2/2D_1$, where $D_1 \equiv D(m=1)$, for times. The ensemble averaged results will be denoted $A(a)$, where a is the statistical error on the mean. In some cases, we will use the notation $A[\alpha]$ to give the standard-deviation α of the distribution of values for A .

III. RESULTS

A. Monodisperse solution of molecules

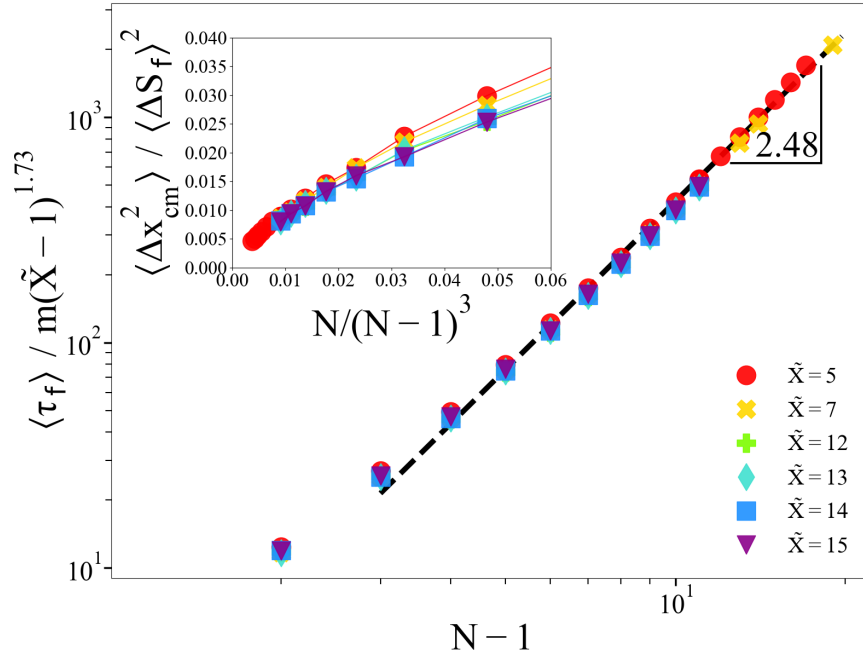


FIG. 2. Scaled mean spreading time $\langle \tau_f \rangle / m(\tilde{X} - 1)^{1.73}$ vs. $N - 1$ for an ensemble of 10000 monodisperse systems made of N molecules of size m . The data for different final gaps $\tilde{X}$ collapse; the linear fit uses the range $N \in [10, 20]$. The exponent 1.73 was found to collapse the data for the different values of $\tilde{X}$. Inset: Relative displacement ratio $\langle \Delta x_{\text{CM}}^2(t = \tau_f) \rangle / \langle \Delta S_f \rangle^2$ vs. $N/(N - 1)^3$.

We first study how a group of identical molecules of size m reaches the desired final state. Since $D \sim 1/m$, the value of m only affects the spreading time via a trivial pre-factor. We thus expect a scaling law of the form

$$\langle \tau_f(N, \tilde{X}) \rangle \sim m (N - 1)^{\eta_\tau} (\tilde{X} - 1)^{\chi_\tau}, \quad (3)$$

where the $(N - 1)$ comes from the fact that we have $N - 1$ gaps growing simultaneously, while the $(\tilde{X} - 1)$ represents the necessary increase in gap size. Our results (see Fig. 2) for the ranges $N \in [10, 20]$ and $\tilde{X} \in [8, 20]$ are consistent with

$$\langle \tau_f \rangle \sim m (N - 1)^{2.48(2)} (\tilde{X} - 1)^{1.73(1)}. \quad (4)$$

Extrapolating our results (data not shown), we find that $\eta_\tau(N \rightarrow \infty) \approx 2.93(5)$ and $\chi_\tau(\tilde{X} \rightarrow \infty) \approx 1.99(4)$, suggesting the asymptotic behavior

$$\langle \tau_f \rangle \sim m N^3 \tilde{X}^2 \sim M \times [\Delta s]^2 \sim [\Delta s]^2 / D(M). \quad (5)$$

Interestingly, the mean spreading time scales like the time required for the uncut molecule of size M to diffuse over a distance equal to the minimum span increase compatible with the desired final state, Δs . We also note that $\langle \tau_f \rangle \sim MN^2 \sim mN^3$ increases very rapidly with the number of fragments.

Similarly, the final mean square displacement of the CM was fitted using the scaling form

$$\langle \Delta x_{\text{CM}}^2(\tau_f) \rangle \sim N(N-1)^{\eta_x} (\tilde{X}-1)^{\chi_x}. \quad (6)$$

Our results give (data not shown)

$$\langle \Delta x_{\text{CM}}^2(\tau_f) \rangle \sim N(N-1)^{0.6(1)} (\tilde{X}-1)^{1.8(1)}, \quad (7)$$

as well as $\chi_x(\tilde{X} \rightarrow \infty) \approx 2.0(1)$ and $\eta_x(N \rightarrow \infty) \approx 0.9(1)$ for an asymptotic limit

$$\langle \Delta x_{\text{CM}}^2(\tau_f) \rangle \sim N^2 \tilde{X}^2 \sim [\Delta s]^2. \quad (8)$$

The CM of the group diffuses over a distance comparable to the minimum increase Δs , consistent with Eq. 5.

Finally, the increase of the span was fitted using the form

$$\Delta S_f \sim (N-1)^{\eta_s} (\tilde{X}-1)^{\chi_s}, \quad (9)$$

leading to (data not shown)

$$\Delta S_f \sim (N-1)^{1.54(1)} (\tilde{X}-1)^{0.975(6)}. \quad (10)$$

In this case, our extrapolations give $\eta_s(N \rightarrow \infty) \approx 1.96(1)$ and $\chi_s(\tilde{X} \rightarrow \infty) \approx 1.01(3)$, suggesting the asymptotic scaling law

$$\Delta S_f \sim N^2 \tilde{X} \sim N \Delta s. \quad (11)$$

Thus, the final span is $\sim N$ times its minimum value.

There are several key asymptotic scaling results here. First, the *diffusion ratio* scales like $\langle \Delta x_{\text{CM}}^2(\tau_f) \rangle / \tau_f \sim 1/M$, as one would expect. Second, the *relative displacement ratio* $\langle \Delta x_{\text{CM}}^2(\tau_f) \rangle / \Delta S_f^2 \sim N^{-2}$ vanishes when $N \gg 1$, indicating that CM diffusion is not relevant. Third, the *spreading velocity* $v_s \equiv \Delta S_f / \tau_f \sim ND(M) / \Delta s \sim 1/M\tilde{X}$ is entirely controlled by the parameter $\tilde{X}$. Finally, the key parameter Δs , which is determined by the experimental conditions N and $\tilde{X}$, controls the spreading time τ_f for a given molecular size M .

The distribution of $[\tau_f, \Delta S_f]$ data points, shown in Fig. 3 for 20 000 different simulations with $N = 11$ fragments of size $m = 10$ and a final gap size of $\tilde{X} = 15$, demonstrates that there is wide variety of cases – looking at mean values is not sufficient. For example, we have long times but small final spans in the bottom right quadrant, while the points in the top left quadrant correspond to rapid spreading accompanied by large spans. The power-law fit having a small slope of 0.218(1), the correlation between τ_f and ΔS_f is rather weak.

It is possible to estimate the missing asymptotic coefficients in Eqs. 5 and 11 using the fact that $\langle \tau_f \rangle \approx 10^6$ and $\Delta S_f \approx 300$ in Fig. 3. Since $M = mN = 10 \times 11 = 110$ while $\Delta s = (N-1)(\tilde{X}-1) = 14 \times 10 = 140$, we obtain

$$\begin{aligned} \langle \tau_f \rangle &\approx \frac{1}{2} M [\Delta s]^2 \\ \Delta S_f &\approx \frac{1}{5} N \Delta s \end{aligned} \quad (12)$$

Although this example is not in the asymptotic limit, these approximate relations will be useful guides later.

B. Bimodal distributions of molecules

We now study a bimodal system with N_1 fragments of size m_1 and N_2 fragments of size m_2 , for a total molecular size $M = N_1 m_1 + N_2 m_2$. As the number of ways to distribute $N = N_1 + N_2$ molecules along the tube is very large, we only study a few cases, including the simple one where the $N_1 - 1$ pairs of type 1

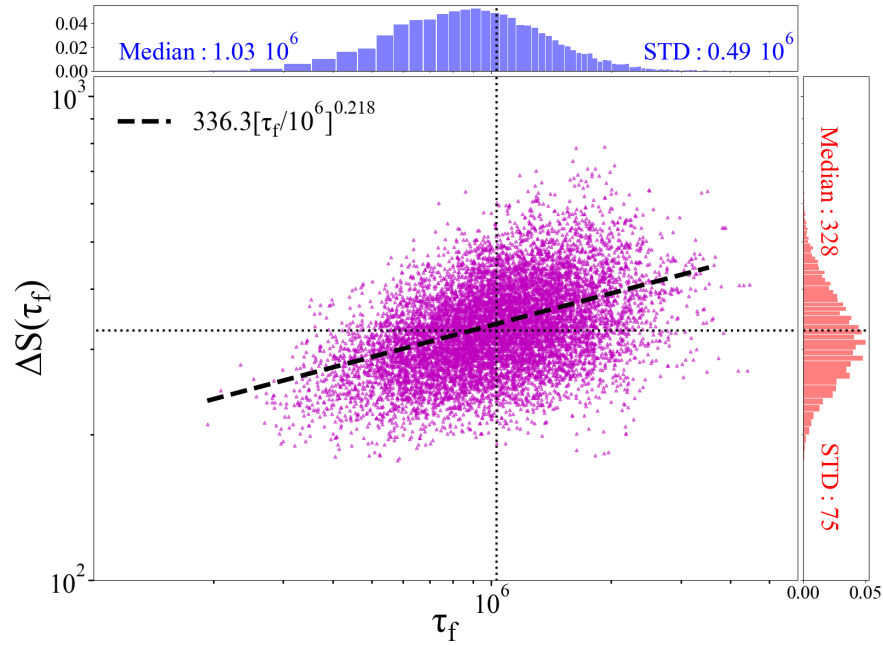


FIG. 3. The data points $[\tau_f, \Delta S_f]$ for 20 000 simulations with $N = 11$ molecular fragments of size $m = 10$ and a final minimum gap of $\bar{X} = 15$. The histograms on top and right show the distributions, with the median (also shown as thin dotted lines) and standard deviations. The dashed line is a power-law fit.

molecules are separated by P type 2 molecules each, with the remaining δN type 2 molecules placed at the end(s).

An example with $M = 72$, $m_1 = 12$, $m_2 = 3$, $N_1 = 4$, $N_2 = 8$ and $P = 0$ is shown in Fig. 4 (a); as $P = 0$, the two types of molecules form separate groups. We show $\langle \tau_f \rangle$ vs N_2 data for such segregated systems in panels (b–d) for $N_1 = 1, 3$ and 5 , respectively; we keep $m_2 = 10$ and $\bar{X} = 5$ fixed, and examine three values of $m_1 > m_2$ (note that M is not kept fixed here). To better understand the results, we also show data for three limit cases: 1) the lowest line is for $N_1 = 0$; 2) the horizontal dashed lines are for $N_2 = 0$; 3) the dotted line is for $[N_1 = 1; m_1 \rightarrow \infty]$ (a single type-1 molecule acts as a fixed wall on the left).

As shown in Figs. 4 (c–d), the spreading time plateaus at a value $\langle \tau_f(N_1) \rangle$ when $N_2 < N_1$ because the N_1 large molecules then limit the spreading process. Conversely, when $N_2 \gg N_1$, all data sets must converge to the lowest line $\langle \tau_f(N_2) \rangle$, which corresponds to having only type-2 molecules. Although this convergence is visible for $m_1 = 20$ in Fig. 4 (b), it is much slower in the other cases. Interestingly, the data sets first converge towards the dotted line, then cross it before converging towards the lowest line. This intermediate regime corresponds to a small group of $N_1 \ll N_2$ type-1 molecules of size $m_1 \gg m_2$ acting as an immobile wall from which the N_2 smaller molecules must move away. It is only when the relaxation time of the N_1 molecules has become negligible compared to that of the N_2 molecules that the data sets can converge towards the lowest line. We can also see this double-convergence process in Fig. 4 (b), but there is no plateau when $N_2 \rightarrow 0$ since we then have a single (large) molecule. The transition between the two asymptotic regimes can be defined as the point where $\langle \tau_f(N_1) \rangle = \langle \tau_f(N_2) \rangle$, as shown in Figs. 4 (c–d); Eq. 3 predicts that this happens for a critical population size

$$N_2^* = N_1 \times \left(\frac{m_1}{m_2} \right)^{1/\eta_\tau}. \quad (13)$$

This rough approximation, which works well for our data here with $\eta_\tau \approx 2.75$ (not shown), indicates that the transition point is a rather weak function of the size ratio m_1/m_2 , especially given the asymptotic exponent $\eta_\tau = 3$.

Figure 4 showed data for segregated bimodal systems ($P = 0$). The opposite limit is when $N_2 = (N_1 -$

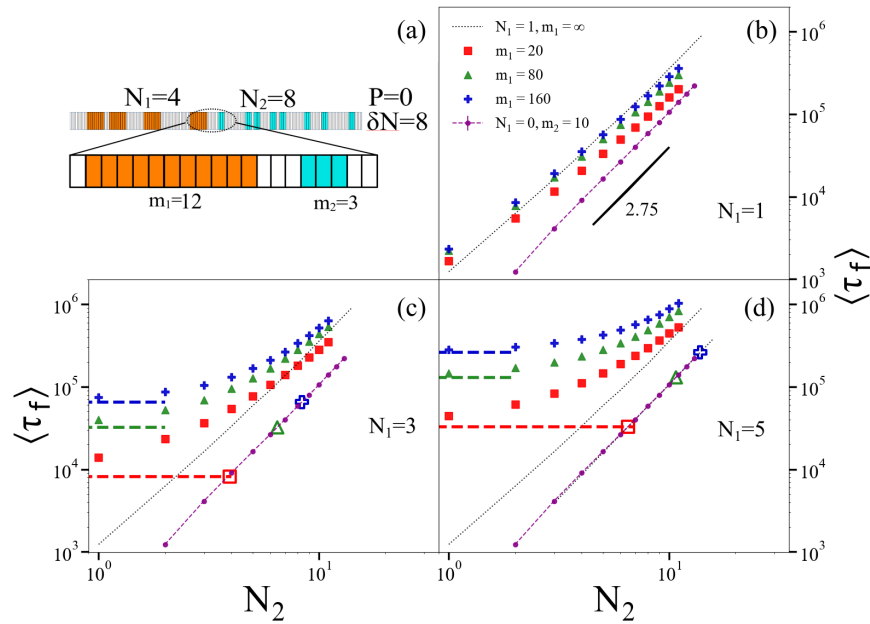


FIG. 4. (a) A schematic view of a segregated bimodal system with $N_1 = 4$ fragments of size $m_1 = 12$ and $N_2 = 8$ fragments of size $m_2 = 3$. The next three panels show the mean spreading time $\langle \tau_f \rangle$ vs the number N_2 of type 2 molecules of size $m_2 = 10$ for three different values of m_1 ; the final minimum spacing is $\bar{X} = 5$ and the ensemble size is 12 000. In all three cases, the lowest data set is for $N_1 = 0$, the dashed horizontal lines correspond to $N_2 = 0$, while the dotted lines present the $[N_1 = 1; m_1 \rightarrow \infty]$ limit. (b) $N_1 = 1$; there is no horizontal line since τ_f is not defined when $N_2 = 0$ and $N_1 = 1$. (c) $N_1 = 3$. (d) $N_1 = 5$. The hollow markers along the lower ($N_1 = 0$) line show the transition points $N_2^*(m_1)$ between the two asymptotic regimes.

$1) \times P$: all of the type-2 molecules are then located between the larger type-1 molecules. Given Eq. 4, it is not surprising that we recover a scaling form $\tau_f(P \gg 1) \sim P^{\eta_\tau}$ (data not shown) in the limit where the type-2 molecules dominate.

As described previously, the total mass M is fixed when the molecule is cut into N pieces in an experimental situation. We thus finish this section by looking at simple bimodal systems with a fixed M but varying mass ratios $\mu \equiv m_2/m_1$. The questions here include: 1) Is τ_f smaller in the presence of several small molecules or a few large ones? 2) Does having large molecules at both ends of the sequence slow down spreading? 3) What is the effect of the mass asymmetry μ ?

Figure 5 (a) shows $\langle \tau_f \rangle$ vs. the mass ratio μ for a system where $N_1 = 3$, $N_2 = 2$, $M = 648$ and $P = 1$ are kept fixed (this sequence thus reads **12121**). Interestingly, the mean spreading time $\langle \tau_f(\mu) \rangle$ is not a monotonic function; instead, it peaks at about $\mu = 0.45(3)$ and plateaus in both limits (the two horizontal dashed lines mark the limits when the smallest molecules are of size $m = 1$). Since $\langle \tau_f \rangle \sim m(N-1)^{\eta_\tau}$ with $\eta_\tau > 2$ according to Eq. 4, we do expect molecular spreading to take more time with three large molecules of size $m_1 = 215$ rather than two large molecules of size $m_2 = 322$. Moreover, as we shall see, large molecules at (or near) the ends have a greater impact than those in the middle. Equation 12 predicts a mean value of $\langle \tau_f \rangle \approx 0.83 \cdot 10^5$, close to the lowest plateau; unsurprisingly, the dependence of the mean spreading time $\langle \tau_f \rangle$ on the mass ratio μ is not captured by Eq. 12.

Data for similar systems but different P values are shown in Fig. 5 (b): these sequences read **1[2]_P1[2]_P1** (the $P = 2$ case is shown in the top right corner). The non-monotonic curves move up and drift towards smaller values of μ when P increases. These results clearly show the effect of having more, albeit smaller, molecules in the system.

In Fig. 5 (c), we start with the $P = 3$ case and systematically move the type-1 molecules towards the centre while preserving the left-right symmetry. Clearly, having large molecules near the ends increases the spreading time. In this case, Eq. 12 predicts $\langle \tau_f \rangle \approx 3.3 \cdot 10^5$, an excellent estimate overall.

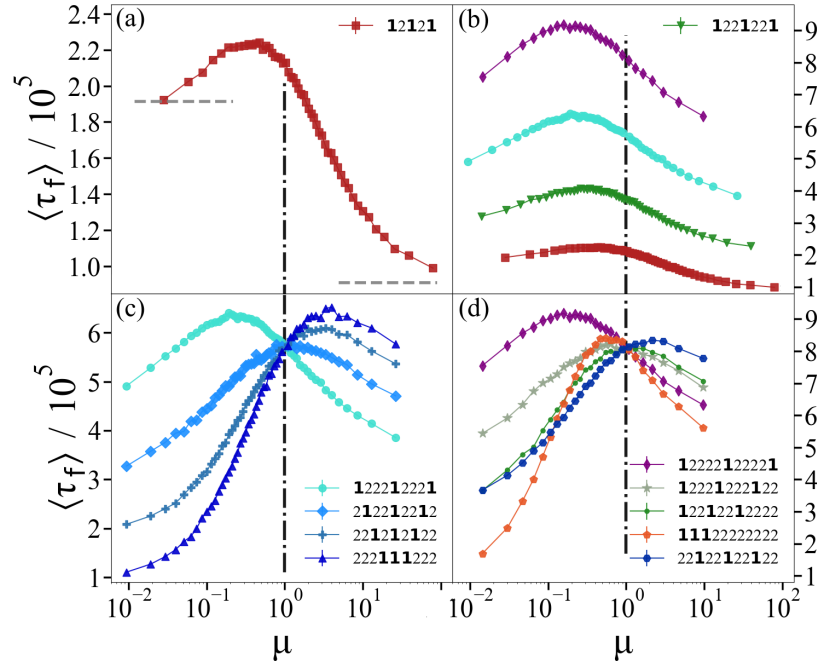


FIG. 5. Mean spreading time $\langle \tau_f \rangle$ vs mass ratio $\mu = m_2/m_1$. The systems are described symbolically as series of 1 and 2. The total molecular weight is fixed at $M = 648$, while $\tilde{X} = 5$ and $N_1 = 3$. (a) $N_2 = 2$ and $P = 1$; (b) $N_2 = 2P$ with, from top to bottom, $P = 4$ (◆), 3 (●), 2 (▼), 1 (■). The $P = 2$ sequence is shown. (c) Four systems with $N_2 = 6$ are compared: the type-1 molecules are systematically moved towards the centre of the $P = 3$ sequence of panel B; (d) Five systems with $N_2 = 8$ are compared.

Finally, in Fig. 5 (d) we start with the $P = 4$ case and move the type-1 molecules towards one of the ends. Segregating the larger molecules generally decreases the spreading time, mostly because the smaller molecules can then move more freely. We also show data for the sequence 22122122122 : this curve converges with that of the 12212212222 sequence in the $\mu \ll 1$ limit. These two sequences share the same 1221221 core; when $\mu \ll 1$, the type-2 molecules outside this core play a minor role. Equation 12 predicts $\langle \tau_f \rangle \approx 5.2 \cdot 10^5$ for panel D, again an excellent estimate overall.

We thus conclude that having a large number of small molecules generally leads to a longer spreading process, while large molecules placed at the end tend to act as slow-moving walls. We also notice that for a given sequence, the spreading time is a non-monotonic function of the size ratio μ . All of these results suggest that the precise location of the molecules in a random sequence $(m_1, m_2, \dots, m_N)$ can affect the mean spreading time, an effect that Eq. 12 cannot capture.

C. Random distributions: main results

We now study the central problem of this article, i.e., that of a molecule of size $M = \sum_{i=1}^N m_i$ randomly cut into N pieces of size m_i inside a narrow channel. This process generates an ordered sequence of molecular sizes (m_i) along the channel. Since we assumed that $\tilde{X}$ is the minimum gap that can be measured, we also use $\tilde{X}$ as the minimum molecular size that can be visualized; therefore, all m_i 's $\in [\tilde{X}, M - (N-1)\tilde{X}]$.

We first address the question of the mean spreading time for random sequences. Our data (not shown) indicate that Eq. 3 now reads (R stands for Random):

$$\begin{aligned} \langle \tau_f \rangle &\sim \bar{m} (N-1)^{\eta_t^R} (\tilde{X}-1)^{\chi_t^R}, \\ &\sim \bar{m} (N-1)^{2.60(1)} (\tilde{X}-1)^{1.70(5)}. \end{aligned} \quad (14)$$

Extrapolating our results, we find $\eta_\tau^R(N \rightarrow \infty) \approx 2.91(3)$ and $\chi_\tau^R(\tilde{X} \rightarrow \infty) \approx 1.97(3)$, suggesting the asymptotic behavior

$$\langle \tau_f \rangle \sim \bar{m} (N-1)^3 (\tilde{X}-1)^2 \sim M \times [\Delta s]^2, \quad (15)$$

identical to Eq. 5, the relation for monodisperse systems, except that $m \rightarrow \bar{m}$. Similarly,

$$\begin{aligned} \Delta S_f &\sim (N-1)^{\eta_s^R} (\tilde{X}-1)^{\chi_s^R}, \\ &\sim (N-1)^{1.52(3)} (\tilde{X}-1)^{0.88(1)}, \end{aligned} \quad (16)$$

with the extrapolated values $\eta_s^R(N \rightarrow \infty) \approx 2.0(1)$ and $\chi_s^R(\tilde{X} \rightarrow \infty) \approx 0.97(3)$. We thus conclude that Eq. 11, for $\Delta S_f \sim N \Delta s$, is also unaffected by randomness. Even though random distributions behave like monodisperse ones on average, it does not mean that the average behavior is a good description of specific cases (this was also true in the previous section for bimodal mass distributions).

Three questions come to mind here. First, given that the distribution of spreading times is broad even for monodisperse systems (e.g., see Fig. 3), does the random cutting process add further variability to τ_f ? Second, what are the differences between the most likely random sequences (m_i) and the extreme ones – e.g., the monodisperse ones? Finally, since molecular order matters, what is the impact of simply permuting elements in a given sequence (m_i)?

The randomness of a sequence (m_i) can be described by the ratio $\lambda = \text{STD}[(m_i)]/\bar{m}$ between the standard-deviation (STD) and the mean $\bar{m} = M/N$ of its N elements. Figure 6 (a) presents τ_f vs λ data for 10^4 molecules of size $M = 600$ randomly cut into $N = 9$ pieces with $\tilde{X} = 8$. The mean values are $\bar{\lambda} = 0.764(2)$ and $\langle \tau_f \rangle = 1.110(6) 10^6$, while Eq. 12 predicts $\langle \tau_f \rangle \approx 0.94 10^6$, consistent with our data. The weak correlation between τ_f and λ decreases rapidly when N increases (data not shown). The data points on the left (in grey) correspond to the monodisperse case $\lambda = 0$; we then have $\langle \tau_f \rangle = 1.271(5) 10^6$, larger than the mean value for random cuts.

The distribution of λ values narrows as N increases, while $\bar{\lambda}$ increases toward an asymptotic value (data not shown). Moreover, λ does not provide information on the location of the largest molecules in an ordered sequence (m_i), which is an important factor, as shown in previous sections. Thus, we need another parameter to characterize (m_i), a parameter that measures how much mass is located near the two ends. We propose to use (defined here for N odd):

$$Z = \frac{\left[\sum_{i=1}^n (n-i) m_i \right] \times \left[\sum_{i=n}^N (i-n) m_i \right]}{\left[\frac{M/N}{8} (N^2 - 1) \right]^2} \quad (17)$$

where $n = \frac{1}{2}(N+1)$ marks the central molecule of the sequence. The two terms in the numerator are basically torque-like quantities from the two halves of the sequence. The denominator, which is used to normalize the Z parameter, is the value of the numerator for a monodisperse system. Larger values of Z indicate the presence of large molecules near both ends (indices $i = 1, N$), while a small Z means that most large molecules are located near the center (index $i = n$).

We colored the data points in Fig. 6 (a) based on their Z values; the horizontal dashed lines give the mean spreading times $\langle \tau_f \rangle$ for each of the three colors. We note that $\langle \tau_f \rangle$ increases from blue to green, and that the $Z = 1$ monodisperse case is in the middle. Although these results confirm that having large molecules near *both* ends slow down spreading, there is substantial overlap between the three groups.

Figure 6 (b) shows that τ_f tends to increase with Z , confirming that the location of the largest molecules matters. We also note that the monodisperse system is located in the red region, at $Z = 1$, and that the binned data can be fitted with a straight line. We added data sets for two extreme cases. The sequence (272 [8] 272), which has the maximum possible value of $Z = 2.904$, has a mean time $\langle \tau_f \rangle = 1.705 10^6$, while the sequence ([8]₄536[8]₄), with the minimum possible value of $Z = 0.014$, gives $\langle \tau_f \rangle = 0.166 10^6$. In both cases, the STD of the distribution of spreading times is $\approx 45\%$ of its mean (this is also true for $Z = 1$). The fit does not extrapolate to these two limits, pointing to a change in behavior for extreme cases; however, it nearly captures the monodisperse case.

The inset of Fig. 6 (b) shows that there is an overall nonmonotonic relationship between the randomness parameters λ and Z . This is not surprising since, for any given value of λ , it is possible to reduce (increase) the value of Z by moving the larger molecules toward the center (ends) of the sequence.

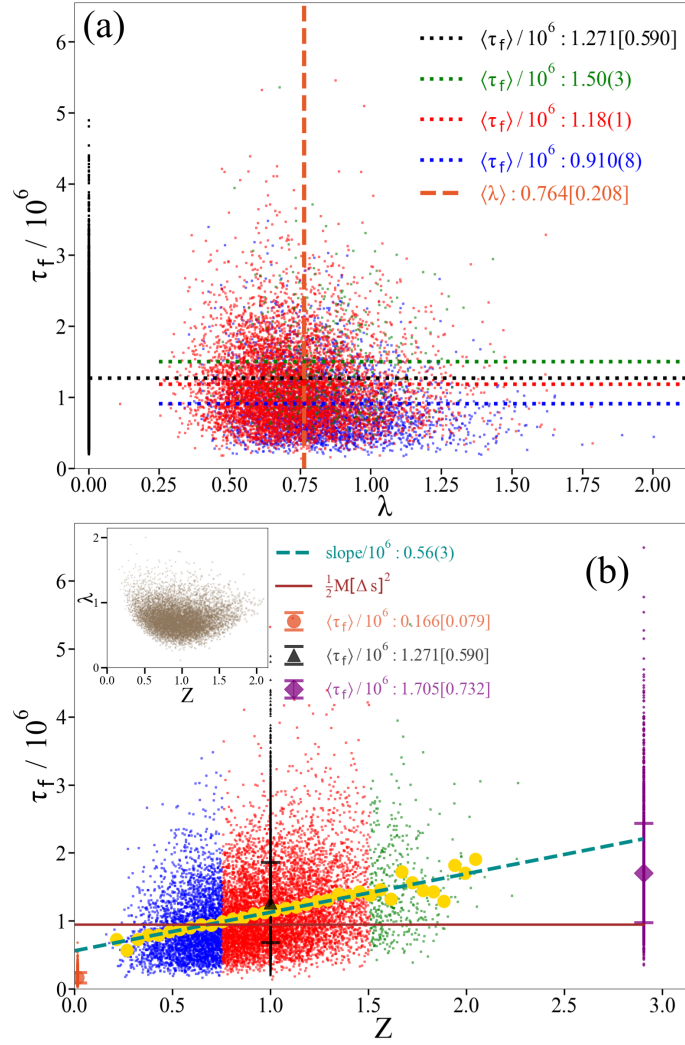


FIG. 6. (a) Spreading time τ_f vs λ for 10^4 molecules of size $M=600$ randomly cut into $N=9$ pieces of minimum size $\bar{X}=8$. The means and standard-deviations (in $[\cdot]$) are $\langle \tau_f \rangle = 1.110 [0.563] 10^6$ and $\bar{\lambda} = 0.764 [0.208]$. The data for the monodisperse system (in grey at $\lambda = 0$) has a mean of $\langle \tau_f \rangle = 1.271 [0.590] 10^6$. The points are colored based on their Z values, as defined in Eq. 17. The maximum value of Z being $Z_m = 2.26$ here, the color code is as follows: green for $\frac{2}{3}Z_m \leq Z \leq Z_m$; red for $\frac{1}{3}Z_m \leq Z < \frac{2}{3}Z_m$; and blue for $0 \leq Z < \frac{1}{3}Z_m$. (b) Spreading time τ_f vs Z . The cyan dashed line (---) is a linear fit to the binned data (large golden dots $\bullet$). The three vertical distributions (2,000 data points each) correspond to $Z = 0.014$ (the theoretical minimum Z value), $Z = 1$ (the monodisperse case) and $Z = 2.904$ (the theoretical maximum Z value). Insert: λ vs Z .

The main conclusion comes directly from Fig. 6 (b): while the mean spreading time increases from about $0.5 10^6$ to $2 10^6$ over the full range of Z values, the standard deviations are of order 10^6 . In other words, the correlation between the spreading times and the details of the (m_i) sequence is roughly comparable to the randomness of the Brownian spreading process itself.

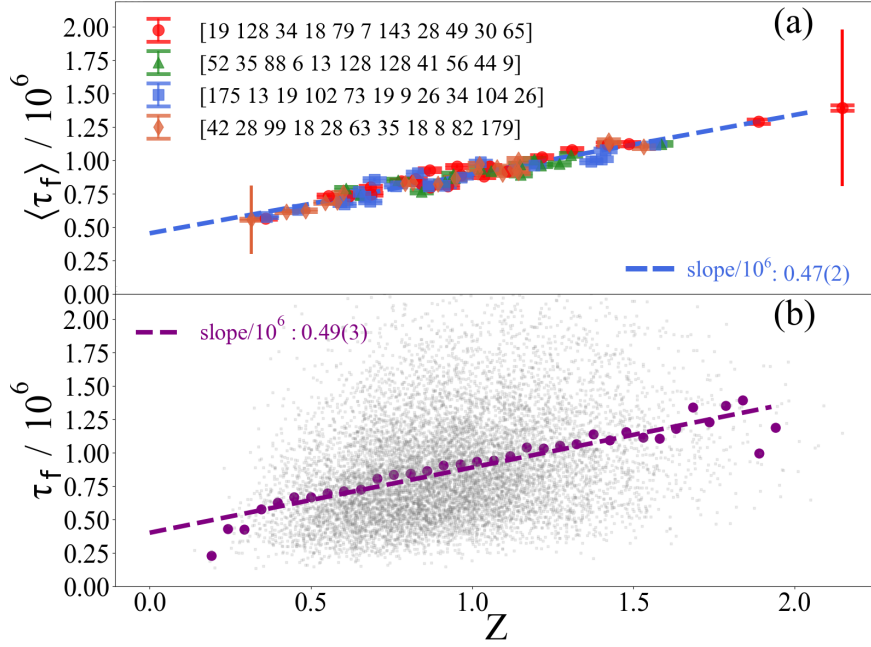


FIG. 7. (a) Mean spreading time $\langle \tau_f \rangle$ vs Z for systems of size $M=600$ cut into $N=11$ pieces of minimum size $\tilde{X}=6$. Four random sequences with the following λ values are presented: 0.792 (red $\bullet$), 0.757 (green $\blacktriangle$), 0.924 (blue $\blacksquare$), and 0.875 (orange $\blacklozenge$). Each one was shuffled 20 times – thus generating sequences with 20 different values of Z . Each data point is an average over 1000 simulations; the error bars are comparable to the size of the symbols (the vertical lines mark the standard-deviations for the two end points). (b) Spreading time τ_f vs Z for 10000 random systems (no permutations) with the same parameters as in (a). The dashed line is a linear fit to the binned data (large dots).

D. Random distributions: permutations

Although shuffling the elements in a sequence (m_i) does not affect λ , it does change the value of our Z parameter. In this section, we examine how such permutations affect the spreading time.

There are $\Omega = N!/2$ ways of placing N different objects on a line. For example, there are $\Omega \approx 20$ million possible permutations for a given molecular sequence (m_i) containing $N = 11$ molecules (Ω is smaller if some molecules happen to have the same size). As Ω is very large, we use the following sampling process. We first generate a random sequence $\Lambda = (m_i)$ for a given total molecular weight M , number of fragments N , and minimum molecular size $\tilde{X}$. We then choose a random subset of $\Omega_\Lambda^* = 20$ permutations. The latter are simulated 1000 times each in order to obtain their mean spreading times. Finally, the process is repeated for different initial sequences Λ .

Figure 7 (a) shows $\langle \tau_f \rangle$ vs Z data for four initial sequences. The linear increase observed in Fig. 6 (b) is recovered in all cases. In fact, these four systems give essentially identical data (except that the largest and smallest values of Z strongly depend on the initial sequence). The four data sets were fitted together to obtain a slope of $0.47(2) 10^6$. Figure 7 (b) shows the data for 10 000 random systems (no permutations), similar to what we presented in Fig. 6 (b); the linear fit gives a slope of $0.49(3) 10^6$, indicating that the relation between Z and the spreading time is universal.

Our data, for both random *and* shuffled sequences, show that Brownian noise is as important as the details of the molecular sequence. In fact, the latter only shifts, usually rather slightly, the center of a broad distribution of spreading times.

E. Random Distributions: Extreme Cases

To better understand our results, we now focus on extreme cases, specifically the outliers in Fig. 8 (a). A total of 15 cases were selected for further analysis, and each case was simulated 2000 times. The distribution of spreading times τ_f for the 5 cases with the shortest (longest) times is shown in panel (c) (panel (d)), while panel (b) shows the distributions for the 5 cases with the largest values of Z .

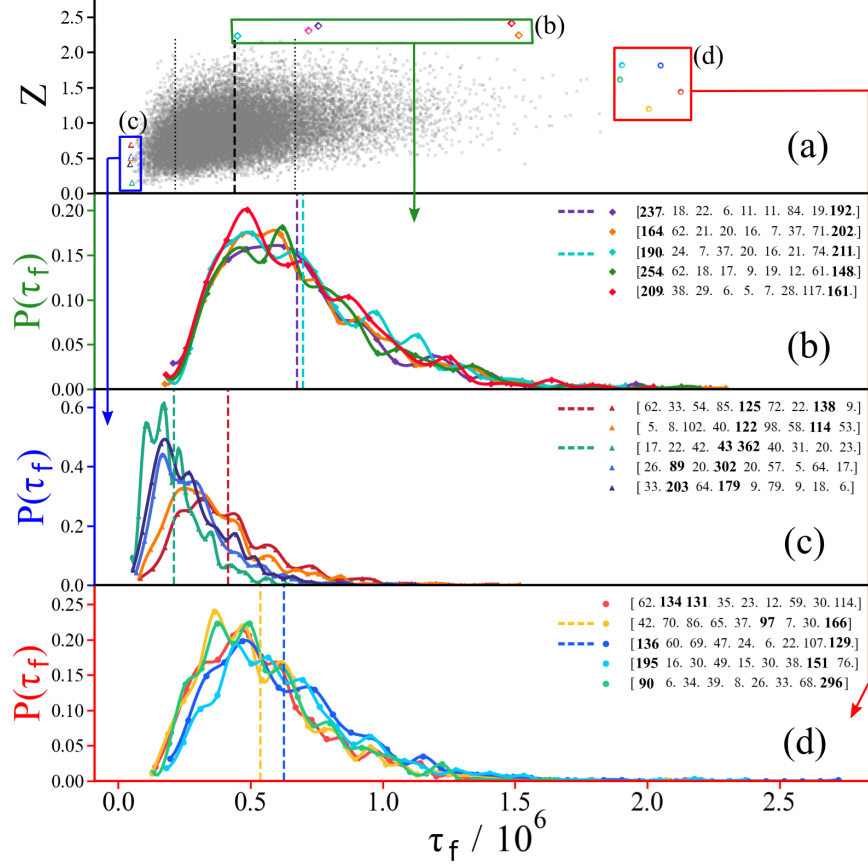


FIG. 8. Data for a molecule of size $M = 600$ randomly cut into $N = 9$ pieces of minimum size $\bar{X} = 5$. (a) Spreading time τ_f vs Z for 10 000 random systems; the dashed lines give the mean and width (STD) of the distribution of points. (b) The distribution function of spreading times for the 5 sequences with the largest values of Z in (a). (c-d) The distribution function of spreading times for the 5 sequences with the shortest (largest) values of τ_f in (a). In panels (b-d), the dashed lines give the maximum and minimum values of the means of the five distributions shown. The chosen sequences are given in the legend, with the two largest molecules in bold.

The distribution functions in Fig. 8 (d) are similar to each other; unsurprisingly, their means are larger than the global mean separation time shown in Fig. 8 (a). All but one of these sequences have large molecules near their ends; the exception has a molecule of size 97 in the middle and possesses the shortest separation time in this group. All five of these outliers are found far in the high- τ_f tail of their distributions.

Figure 8 (c) shows that the distributions do not overlap for the low- τ_f outliers, all of which have large objects near their midpoints. The shortest times are found for the smallest Z value (in green): the central molecule (size 362) is over 50% of the total weight. The largest value of Z (in red) corresponds to the longest times: this case has a large molecule in the middle, but the largest one is close to an end. All 5 of these outliers are found far in the low- τ_f tail of their distributions.

As Fig. 8 (a) shows, the Z values of the high- τ_f outliers are larger than those of the low- τ_f outliers. Yet, there is a substantial amount of overlap between the distribution functions found in panels (c) and (d),

demonstrating that Brownian variability is at least as important as the Z factor.

The distributions for the five outliers with the highest values of Z are similar to each other in Fig. 8 (b), and even share the same mean and standard deviation. All five sequences feature very large molecules at both ends, a factor we identified as responsible for slowing down the spreading process.

Figures 8 (b-d) suggests that one could collapse all distribution functions by rescaling τ_f by its mean value $\langle \tau_f \rangle$ in each case. Figure 9 (a) shows that it is indeed so for the 15 outlier cases studied above. The standard-deviation of these rescaled curves is 0.466(7) [0.027]. We thus conclude that rescaled distribution functions are not affected by the initial sequence (however, the mean values $\langle \tau_f \rangle$ are). A good description of these curves is obtained using the following empirical normalized function, inspired by the problem of a Brownian particle's first-passage time [12]

$$P(t) = \frac{\sqrt{t_0/\pi}}{t^{3/2}} e^{-(t-1)^2/(t/t_0)}, \quad (18)$$

where $t \equiv \tau_f / \langle \tau_f \rangle$. This function has a mean of 1 and a variance of $1/2t_0$. Given that the standard deviation of our data is 0.466(7), this predicts $t_0 = 2.30(7)$ and a maximum at $t = 0.726(7)$. As Fig. 9 (b) shows, this function is excellent over the entire range of spreading times.

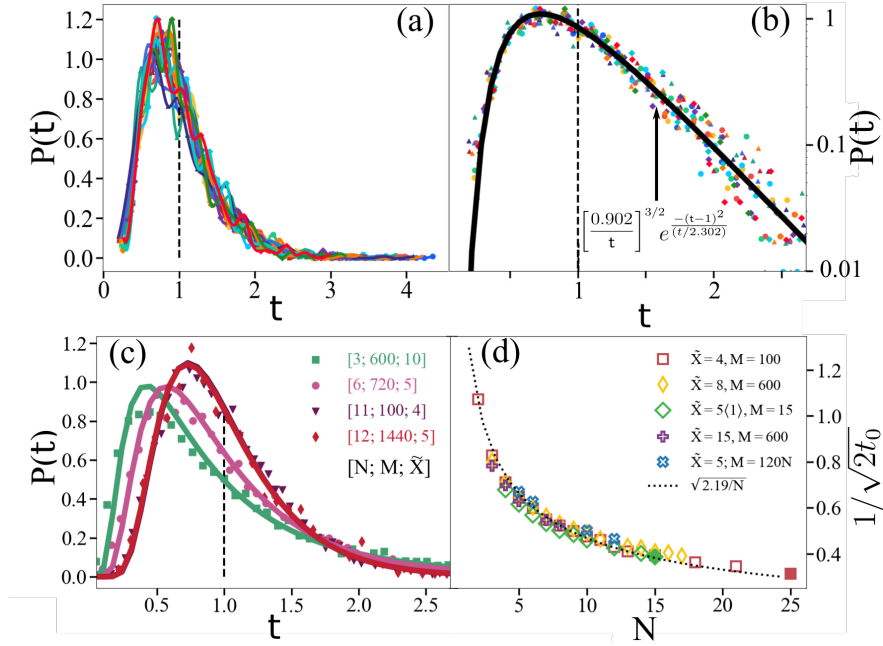


FIG. 9. (a) Distribution function of rescaled spreading times $t \equiv \tau_f / \langle \tau_f \rangle$ for the 15 outlier cases chosen in Fig. 8. The bin width is 0.1135. (b) Same data in a semi-log format; the solid line is the function $P(t) = [0.902/t]^{3/2} e^{-(t-1)^2/(t/2.302)}$. (c) Data for four systems with different parameters. (d) The STD of the distributions, $1/\sqrt{2}t_0$, as a function of N for 5 different systems; the filled markers correspond to the largest value of N allowed (i.e., a monodisperse system), while the dashed lines show the fit $(2.19/N)^{1/2}$. Note that for the green diamonds ($\diamond$ and $\blacklozenge$) we used $\tilde{X} = 5$ for the minimum final gap, but $\tilde{X} = \langle 1 \rangle$ for the minimum fragment size.

Equation 18 provides an excellent description of the distribution functions for all the systems we have examined (four more examples are shown in panel (c) for different choices of N , M and $\tilde{X}$). As panel (d) shows, the standard deviation of the scaled distributions (related to t_0 in Eq.18) varies with N but not with $\tilde{X}$, suggesting that Eq. 18 may be a convenient tool for describing this problem. The fit in Fig. 9 (d) shows that the STD decreases as $1/\sqrt{N}$, with the limit being that of a monodisperse system (see the filled markers). Interestingly, the transition from a random to a monodisperse population of fragments does not affect the validity of Eq. 18.

In this paper, we chose to have the minimum final gap and the minimum fragment size equal to each other (denoted $\tilde{X}$). To demonstrate that our results do not depend on this choice, Fig. 9 (d) includes a data set (green diamonds) with $\tilde{X} = 5$ as the minimum final gap, but $\tilde{X} = 1$ for the minimum fragment size. The data points fall on the very same universal curve.

IV. CONCLUSION

Mapping a long DNA molecule by cutting it in a narrow channel is a well-defined experimental situation that can be seen as a first-passage problem involving multiple moving components coupled by the single-file diffusion constraint. We used a discretized Monte Carlo simulation algorithm to investigate the relationship between the spreading time τ_f (defined as the time required to achieve the desired final state for the first time after the enzymes have cut the DNA) and the experimental parameters related to the molecule (specifically, the total molecular weight M and the number of fragments generated by the cutting process, N) and the device (the limited lateral resolution $\tilde{X}$). A variety of monodisperse, bimodal, and random systems with increasing system complexity were examined.

In order to better understand how these parameters influence the spreading time τ_f , we must also consider the increased span of the system, i.e. the increase of the linear space occupied by the population of DNA fragments during the process, ΔS_f . A scaling analysis of the problem begins with the characteristic length scale $\Delta s \equiv \min[\Delta S_f] \sim N\tilde{X}$. The mean square displacement of the center-of-mass of the population during the spreading process should scale as $\Delta x_{\text{CM}}^2(\tau_f) \sim [\Delta s]^2 \sim N^2\tilde{X}^2$ giving a spreading time $\tau_f \sim \Delta x_{\text{CM}}^2(\tau_f)/D(M) \sim M[\Delta s]^2 \sim MN^2\tilde{X}^2$. The outward entropy-driven velocity of the molecules should scale as $v_s \sim D(m)/\Delta s \sim 1/M\tilde{X}$ since they have an average molecular size of $m = M/N$. As a result, we expect the final span of the population to scale as $\Delta S_f \sim v_s \tau_f \sim N\Delta s \sim N^2\tilde{X}$. Our simulation data validated these scaling laws in the asymptotic limit. However, we observed strong finite-size effects for any experimentally meaningful value of N , as well as sequence-dependent effects.

While ensemble averages over random sequences corroborate the scaling laws presented above, we observed considerable variability in the observed spreading times (more precisely, the standard deviations are $\approx 50\%$ of the means). In order to shine light on this, we studied a toy bimodal system of fragments. The results clearly indicated that the placement of the largest molecules plays a major role in determining the expected spreading time. In particular, large molecules placed near the ends slow the spreading, while spreading tends to be rapid if most of the mass is located in the middle.

The results we obtained for bimodal systems of molecules prompted us to pose a fundamental question: To what extent does the polydispersity of a random molecular sequence (m_i) affect the variability of its spreading time? Is this additional source of variability as important as Brownian motion?

We first showed that the standard deviation of the molecular size distribution of a given sequence (m_i) is a very weak predictor of its mean spreading time $\langle \tau_f \rangle$. This outcome was to be expected, given that the value of the STD does not consider the location of the largest fragments along the channel.

We then proposed a new parameter, denoted Z , that describes the "weight torque" of the molecular system around its central element. We observed a positive correlation between Z and τ_f for random systems, including extreme cases and shuffled sequences. However, we have also found that the impact of the Z parameter is comparable to that of the Brownian motion. In other words, although mean spreading times do increase with Z , we cannot reliably use Z to predict the spreading time of a given molecular system.

Finally, our results indicate that the distribution of the rescaled spreading times $t = \tau_f/\langle \tau_f \rangle$ is a universal function with a standard deviation that decreases like $\sim 1/\sqrt{N}$, independent of the other system parameters. An excellent fit is provided by a function suggested by the theory for single-particle first-passage problems.

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IMPERFECT SINGLE-FILE DIFFUSION OF POLYMER CHAINS: A PHASE DIAGRAM

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Note: Equation 17 should read $m\dot{\vec{v}} = -\vec{\nabla} U(\vec{r}) + \vec{F}_B - \zeta_\sigma \vec{v}$.

Imperfect single-file diffusion of polymer chains: A phase diagram

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We use Langevin dynamics (LD) simulations to investigate single-file diffusion (SFD) in a dilute solution of flexible linear polymers inside a narrow tube with periodic boundary conditions (a torus). The transition from SFD, where the time (t) dependence of the mean-square displacement scales like $\langle x^2 \rangle \sim t^{\frac{1}{2}}$, to normal diffusion with $\langle x^2 \rangle \sim t$, is studied as a function of the system parameters, such as the size and concentration of the polymer chains and the width of the tube. We propose a phase diagram describing different diffusion regimes. In particular, we highlight the fact that there are two different pathways to normal long-time diffusion. We also map this problem onto a one-dimensional lattice Monte Carlo model where the diffusing object represents the polymer's center of mass. Possible extensions of this work to polydisperse polymer solutions, one-dimensional electrophoresis, and DNA mapping are discussed.

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I. INTRODUCTION

Single-file diffusion (SFD) generally refers to the Brownian motion of hard-core particles in a narrow channel, whose cross-section is too small to allow two adjacent particles to switch positions. Since the initial order of the particles cannot change with time, diffusion is constrained and the asymptotic (long-time) mean-square displacement $\langle x^2(t) \rangle$ of a given particle does not scale linearly with time t . The original SFD concept was proposed decades ago to describe phenomena such as ion transport through pores in biomembranes [1]. More recently, the SFD concept has been used to understand molecular diffusion inside zeolites [2], biological systems such as blood vessels [3,4], and molecular dynamics inside nanotubes [5].

In a pure SFD regime, the long-time mean-square displacement scales $\langle x^2(t) \rangle \sim t^{\frac{1}{2}}$. Two different effects can limit the duration of the SFD regime. First, if particles can switch position (e.g., if the tube width is slightly more than twice the particles' width), we expect a transition from $\langle x^2 \rangle \sim t^{\frac{1}{2}}$ to "normal diffusion" $\langle x^2 \rangle \sim t$ at long time [6]. Secondly, if the particles are located inside a torus (equivalent to using periodic boundary conditions), then they will move as a group at long time, a phenomenon sometimes called compound diffusion [7,8].

In this paper, we examine the dynamics of dilute solutions of monodisperse polymer chains diffusing along the axis of a narrow tube of width h with periodic boundary conditions. We use the simplest possible model: the Langevin dynamics of a Rouse polymer chain. This allows us to derive some analytical results and optimize the simulation times while keeping the key physical effects. In particular, our study does not consider hydrodynamic interactions (HIs). While HIs are not eliminated on length scales shorter than the tube width, they are known to be screened over longer distances [9–13]. To put it briefly, hydrodynamic interactions are important between pairs of monomers that are closer to each other than to the walls; since the presence of walls does not shield HIs

over such short distances, Zimm scaling is then expected to be applicable. However, since the HI are screened by walls at distances greater than h , the different parts of the chain are independent from each other and the total axial friction coefficient of the chain increases linearly with its molecular weight, which is the key assumption of the Rouse model. To simplify matters, we have employed the Rouse model to study the diffusion of the center of mass of the polymers and disregarded the minor impact of HI.

Unlike hard particles, polymer chains can switch position even if the tube is narrow; however, this process means that two chains must become entangled in order to share the same tube section, then possibly diffuse together before disentangling and moving away from each other. Thus, we expect the duration of the SFD regime to strongly depend on the properties of the polymer molecules, as spontaneous entanglement of two free chains is strongly hindered by entropic factors.

Figure 1(a) illustrates the problem at hand. A dilute solution of N flexible chains (each made of M monomers) is placed in a square-section tube (width h and length $L = N\ell_o$) with periodic boundary conditions. In principle, if the channel width h exceeds twice the monomer size, two polymer chains can pass through each other. The figure also defines the mean polymer axial span $S_x(M, h)$, which is a measure of the footprint of a chain along the tube. In order to be in the dilute regime, the chains must be separated by a mean distance $\ell_o > S_x$. Figure 1(b) shows a lattice Monte Carlo model of the same system: the lattice cells are of size $a = S_x$ so that a polymer chain occupies a single cell. Figure 1(b) also depicts two chains occupying the same cell, representing the entangled chains in Fig. 1(a). We study the model of Fig. 1(a) using Langevin dynamics and the model of Fig. 1(b) using Monte Carlo simulations.

This paper is organized as follows: Section II examines both SFD theory and Rouse chain dynamics within a tube. The two simulation models are introduced in Sec. III. Section IV describes our results, followed by the final discussion in Sec. V, including possible extensions of this study.

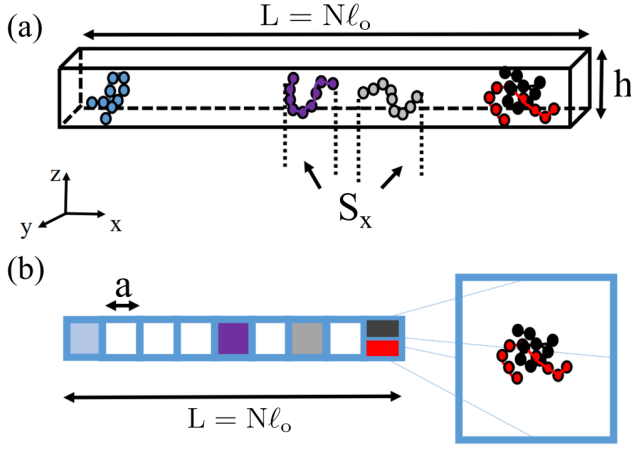


FIG. 1. A schematic view of the two simulation models. (a) N flexible polymer chains with M monomers each diffuse along a square-section tube of width h and length L (with periodic boundary conditions). The mean distance between the molecules is $\ell_0 = L/N$ while their mean axial span is S_x . (b) A lattice Monte Carlo model of the same system: the cells have a size $a = S_x$ and can be either empty or occupied by one or more molecules.

II. THEORY

A. Single-file diffusion for hard particles

We first consider a system of N hard colloidal particles of diameter β inside a tube of width $\beta < h < 2\beta$ and length $L = N\ell_0$. Although $\ell_0 > \beta$ is the mean distance between the particles, the actual mean free space between two neighboring particles is $\ell = \ell_0 - \beta$. In fact, β is not important here, and the system can be seen as a set of point-like objects on a line of effective length $L_e = N\ell$. We can distinguish three different regimes for this system. In the short time regime, i.e., before the particles have diffused over a distance $\approx \ell/2$, their motion is essentially unhindered and we have

$$\langle x^2(t) \rangle = 2D_0 t, \quad t < t_0, \quad (1)$$

where D_0 is the free diffusion coefficient of the particles along the tube axis. This regime persists until the particles start to collide, which occurs around time

$$t_0 \approx (\ell/2)^2 / 2D_0 = \ell^2 / 8D_0. \quad (2)$$

Between the collision time t_0 and some characteristic time t_λ , the particle is in the SFD regime with [14,15]

$$\langle x^2(t) \rangle = 2F t^{1/2}, \quad t_0 < t < t_\lambda, \quad (3)$$

where the SFD mobility F is given by

$$F = \ell \sqrt{\frac{D_0}{\pi}} = D_0 \sqrt{\frac{8t_0}{\pi}}. \quad (4)$$

If the particles are trapped in a closed circular system, the SFD regime ends when the entire population moves as a whole, like a one-dimensional Rouse chain of beads, so that

$$\langle x^2(t) \rangle = 2D_R t, \quad t > t_\lambda, \quad (5)$$

where

$$D_R = D_0 / N \quad (6)$$

is the Rouse diffusion coefficient of the population of N particles. The time t_λ and the corresponding length scale λ define the conditions that lead to an equality between Eqs. (3) and (5):

$$\lambda = \sqrt{\frac{2}{\pi}} N \ell^2, \quad (7)$$

$$t_\lambda = \frac{\lambda^2}{2D_R} = \frac{8}{\pi} N^2 t_0. \quad (8)$$

Interestingly, λ is essentially the geometric mean of the inter-particle spacing ℓ and the system's effective length $L_e = N\ell$; this implies that $\lambda \ll L_e$ for large systems so that relatively small displacements are sufficient to exit the SFD regime.

In short, we expect the diffusion sequence $D_0 \rightarrow F \rightarrow D_R$ for such systems. However, the displacement probability distribution function remains Gaussian in all three regimes,

$$P(x, t) = \frac{1}{\sqrt{2\pi \langle x^2(t) \rangle}} \exp\left(-\frac{x^2}{2\langle x^2(t) \rangle}\right), \quad (9)$$

where $\langle x^2(t) \rangle$ is given by Eq. (1), (3), or (5).

Another regime can exist if we allow neighboring particles to switch position (for example, if the tube width h is slightly larger than 2β or if we use polymer chains instead of hard particles). In essence, the effect of the collisions is then similar to that of an increased viscosity, and we expect that the mean-square displacement of a particle will be given by

$$\langle x^2(t) \rangle \approx \langle x^2(t_s) \rangle \times \frac{t}{t_s}, \quad t \gg t_s, \quad (10)$$

where t_s is the mean time between “switching” events involving a given particle and $\langle x^2(t_s) \rangle$ is the distance traveled by that particle between two events.

In the trivial case where $t_s \ll t_0$, Eq. (1) gives $\langle x^2(t_s) \rangle = 2D_0 t_s$ and Eq. (10) then reduces to Eq. (1): frequent switching renders their impact negligible, allowing particles to diffuse freely.

The most interesting case is found when $t_0 \ll t_s \ll t_\lambda$. Using Eq. (3), we then find a new switching regime with

$$\langle x^2(t) \rangle \approx 2F t_s^{1/2} \frac{t}{t_s} = 2\left(\frac{F}{t_s^{1/2}}\right) t, \quad t_\lambda > t > t_s, \quad (11)$$

which implies that the diffusion coefficient of a particle in the switching regime is given by

$$D_s = \frac{F}{t_s^{1/2}} = \left(\frac{8t_0}{\pi t_s}\right)^{1/2} D_0. \quad (12)$$

The predicted diffusion coefficient is independent of the value of N , an expected result since collisions are local events. Using Eqs. (6) and (7), we can rewrite this result as follows:

$$D_s = \left(\frac{t_\lambda}{t_s}\right)^{1/2} D_R. \quad (13)$$

Since $t_\lambda > t_s$ in this regime, the system will first transition from free diffusion (for $t < t_0$) to SFD (for $t_0 < t < t_s$), and then from SFD to this switching regime ($t > t_s$), where $D_s > D_R$. In fact, we expect the switching regime to extend to times $t > t_\lambda$ as well because $D_s > D_R$ (in other words, the Rouse

regime does not exist anymore). Obviously, the sequence $D_o \rightarrow F \rightarrow D_s$ would also exist in an infinite system.

Finally, it is also possible to have $t_s \gg t_\lambda$; this leads to

$$\langle x^2(t) \rangle \approx 2D_R t_s \frac{t}{t_s} = 2D_R t, \quad t \gg t_s. \quad (14)$$

The diffusion sequence $D_o \rightarrow F \rightarrow D_R$ is recovered, and the particle switching process is too rare to have a major impact.

B. Polymer Rouse dynamics

We consider a dilute solution of N polymer chains (with M monomers of size b each) confined in a tube [16,17], as shown in Fig. 1. Free polymers can be characterized by their radius of gyration $R_g^\circ(M) \sim M^\nu$, where $\nu = 3/5$ is Flory's exponent [18]. Since we use Rouse chains, the polymer diffusion coefficient is given by [18–20] $D_o(M) = D_1/M$, where $D_1 \equiv D_o(M = 1)$ is the diffusion coefficient of one monomer. Importantly, the diffusion coefficient of a Rouse chain is still given by $D_o(M)$ in a tube. Although free polymers have aspherical shapes [21], their span scales like the radius of gyration: $S_o \sim R_g^\circ(M) \sim M^\nu$.

There are two key differences between particles and polymer chains in this system: (1) The particle size β must be replaced by the span $S_x = S_x(M, h)$; (2) polymers can, in principle, switch positions even if their size exceeds the tube width $R_g^\circ(M) > h$. These differences will affect the various regimes described above for particles.

III. METHODS

In both simulation approaches, we place particles or polymer chains along a one-dimensional channel with a uniform initial separation ℓ_o . The number concentration of molecules is thus $\phi_N = 1/\ell_o$ and we use periodic boundary conditions.

A. Langevin dynamics simulations

We use a simple bead-spring model for the polymer chains. The beads are treated as point particles, and the interaction between them is the purely repulsive shifted Weeks-Chandler-Andersen (sWCA) potential [22]

$$\frac{U_w(r)}{4\epsilon} = \begin{cases} \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4}, & r < r_m \\ 0, & r \geq r_m, \end{cases} \quad (15)$$

where r is the distance between the two beads, ϵ is the magnitude of the potential, and σ is the sWCA length-scale. The potential is truncated at $r = r_m \equiv 2^{\frac{1}{6}}\sigma$ so that both its value and derivative are zero at this point. We use the same potential for the wall-bead interactions.

The N beads of a chain are connected using the finitely extensible nonlinear elastic (FENE) potential [23]

$$U_{\text{FENE}}(r) = -\frac{1}{2}K_{\text{FENE}}\Delta r_{\text{max}}^2 \ln \left[1 - \left(\frac{r}{\Delta r_{\text{max}}} \right)^2 \right], \quad (16)$$

with $\Delta r_{\text{max}} = 1.5\sigma$ and $K_{\text{FENE}} = 30\epsilon/\sigma^2$. The resulting nominal bond length, $b = 0.9679\sigma$, minimizes the potential energy between two beads. Since we use a temperature $k_B T = \epsilon$, the nominal bead size R , which is the solution of $U_w(R) = k_B T$, is given by $R = \sigma$.

Langevin dynamics [24] (LD) is used to simulate polymer dynamics. A bead is thus subjected to three types of forces: (1) a random Brownian force $\vec{F}_B$ and a dissipative force due to the fluid; (2) repulsive forces $\vec{F}_w$ near walls and other beads; (3) the FENE force that connects it to its neighbors along the chain. The corresponding equation of motion for a bead is

$$m\dot{\vec{v}} = \vec{\nabla}U(\vec{r}) + \vec{F}_B - \zeta_\sigma \vec{v}, \quad (17)$$

where m is its mass, ζ_σ its friction coefficient, and $\vec{v} = \dot{\vec{r}}$ its velocity. The term $\vec{\nabla}U(\vec{r}) = \vec{\nabla}[U_w(\vec{r}) + U_{\text{FENE}}(\vec{r})]$ is the sum of the conservative forces (i.e., the FENE and sWCA forces), while the term $-\zeta_\sigma \vec{v}$ represents the damping effects of the liquid. The random force $\vec{F}_B$ is a Gaussian random variable with zero mean, $\langle \vec{F}_B \rangle = 0$, and variance $\langle F_B^2 \rangle = 2\zeta_\sigma k_B T / \Delta t$ in each spatial dimension [25].

The LD simulations are implemented using the ESPReSo package [26]. In the Results section, lengths are in units of σ , ϵ acts as our unit of energy, forces are in units of ϵ/σ , and times are in units of the Brownian time $\tau_o \equiv \sigma^2/D_o$ ($D_o = k_B T / \zeta_\sigma$ is the diffusivity of a single bead). The integration time step is $\Delta t = 0.01\tau_o$. The polymers' diffusion coefficient along the tube axis is simply $D_o(M) = D_o/M = 1/M$, independent of the tube width h . Unless otherwise indicated, ensemble averages are based on 500 to 1000 simulations each.

B. Lattice Monte Carlo simulations

We also simulate this system using a one-dimensional (1D) lattice Monte Carlo method. Lattice particles replace the confined polymer chains: each of the N polymer chains thus occupies a lattice cell of size a , which corresponds to the average axial span of a confined chain, S_x . The lattice has a length $L = N\ell_o$ composed of L/a lattice cells. One MC step (MCS) is one attempted jump per particle: this defines the unit of time τ_c (a defines the unit of distance).

At the beginning of each time step of duration τ_c/N , we randomly select one lattice particle and the type of jump to be attempted: forward to the next lattice site with a probability p_+ , backward by one site with a probability p_- , or stay put with a probability $p_o = 1 - p_+ - p_-$. The unbiased probabilities for a free particle are chosen to be [27] $p_o = 2/3$ and $p_\pm = 1/6$. The free diffusion coefficient is thus $D_o = a^2/6\tau_c$.

The MC algorithm should allow for polymer chains to collide, overlap or entangle, disentangle, and switch position. This is equivalent to allowing two (or more) lattice particles to share the same lattice site for a period of time, with probabilities that take into account the entropy cost associated with multiple occupancy. In this algorithm, because neither the tube width h nor the molecular weight M are directly involved, we need to simulate the physics of polymer collisions through indirect MC parameters. In order to reduce the number of free parameters to a strict minimum, we use only two parameters, the probabilities P and Q to control these polymer-polymer interactions: while P controls the probability for particles to overlap, Q controls the disentanglement process.

Collision dynamics must take into account the occupancy n_f of the site chosen as a possible final (subscript f) destination, as well as the occupancy n_i of the site where the particle is initially (subscript i) located. When $n_i = 1$ and $n_f = 0$, the

simple rules for a free particle, as described above, can be used. Our Monte Carlo algorithm thus follows these steps:

(1) We start by randomly choosing one of the N particles.
 (2) Then a jump ($p_{\pm}$ or p_o) is selected randomly. If p_o is chosen, the particle stays put.

(3) If a $\pm$ jump is chosen, we check the values of n_i and n_f to determine whether the jump will be accepted. The following tests are then applied, in this order:

(1) If $n_i = 1$ and $n_f = 0$, the jump is accepted.

If $n_i = 1$ and $n_f \geq 1$, the entropic cost of joining a group of n_f molecules represents a potential barrier. We accept this jump with a probability P^{n_f} since entropy is an extensive variable.

(2) If $n_i \geq 2$ and $n_f = 0$, we have three options:

(i) a probability $1/n_i$ that all n_i particles move together to the chosen destination. The $1/n_i$ factor reflects the fact that the Rouse diffusion coefficient of a group of n_i polymer chains is reduced by a factor $1/n_i$ compared to that of a single chain (i.e., $n_i = 1$);

(ii) a probability $Q \leq 1 - 1/n_i$ that the particle moves alone, leaving the other $n_i - 1$ particles behind.

(iii) if options (i) and (ii) fail, the jump is simply rejected.

(3) Finally, if $n_i \geq 2$ and $n_f \geq 1$, two cases are considered:

(i) when $n_i > n_f$ the particle does not have to overcome a potential barrier, and we accept the jump with a probability Q (otherwise the jump is simply rejected);

(ii) if $n_i \leq n_f$, on the other hand, the molecule must both leave the initial site and overcome a barrier: the jump is then accepted with a probability $QP^{n_i-n_f+1}$ (otherwise the jump is simply rejected).

We neglect the unlikely situation where ≥ 2 particles on a lattice site move together and merge with ≥ 1 particles on a neighboring site.

IV. RESULTS

A. Langevin dynamics: Single polymer chains

As mentioned above, the axial diffusion coefficient of a confined Rouse chain with M monomers should be given by $D_o(M) = 1/M$ in our units. Our data (not shown) give $D_o(M) = 0.998(2)/M$, thus confirming this prediction.

The free-solution radius of gyration of a polymer chain scales like $R_g^o(M) \sim M^\nu$, where ν is Flory's exponent. When confined to a narrow channel with $R_g^o(M) \gg h$, it forms a series of $n(N, h) = M/g$ nonoverlapping blobs of size $\simeq h$ containing $g(h)$ monomers each [28], with $R_g^o(g) \simeq h$. The axial extension of this series of blobs is $R_{gx} \simeq nh = (M/g)h$. These expressions imply that $g \sim h^{1/\nu}$, leading to $R_{gx} \sim Mh^{1-1/\nu}$.

In a previous paper [29], we showed that due to finite-size effects, the Flory exponent [30] is $\nu \approx 0.68$ in this LD model for this range of parameters, instead of $3/5$. As a result, our data gave

$$R_{gx}(M, h) = 0.22(1)(M - 1)^{1.02(2)}(h - 2)^{-0.47(3)}, \quad (18)$$

where we use the effective width $h - 2$ instead of h because the bead size is not negligible. Furthermore, the number of monomers in a blob was found to be given by

$$g(h) \approx 1.3(h - 2)^{3/2}. \quad (19)$$

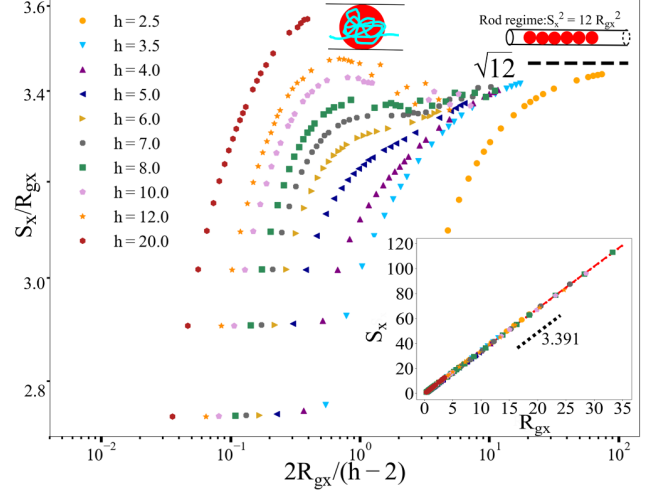


FIG. 2. Log-log plot of the polymer size ratio S_x/R_{gx} vs the blob size ratio $2R_{gx}/(h - 2)$. Inset: Span S_x vs radius of gyration R_{gx} . The red dashed line is a linear fit with a slope of 3.391.

Since the axial radius of gyration of a rigid rod of length $\mathcal{L}$ is $\mathcal{L}/\sqrt{12}$, a polymer chain constrained inside a tube of width h can also be seen as a (porous and fluctuating) polymer rod of length $\mathcal{L} = \sqrt{12}R_{gx}$, when $\mathcal{L} > h$. However, we suggest that it is the axial span of the polymer chains, S_x , that matters here, and not their effective rod length $\mathcal{L}$, because a collision between two chains starts as soon as the first monomers touch. Therefore, we will use S_x as a measure of the effective SFD axial polymer size.

The inset of Fig. 2 shows that we (nearly) have a linear relationship between the axial span and the axial radius of gyration for all tube widths h and polymer lengths M :

$$S_x \simeq 3.391(1)R_{gx}. \quad (20)$$

Equation (20) is convenient, but it obscures subtle effects, as the main part of Fig. 2 reveals. The ratio S_x/R_{gx} increases towards the asymptotic value of $\sqrt{12} = 3.4641$ as we increase M , but this increase is monotonic only for very tight tubes ($h < 7$). In fact, S_x/R_{gx} reaches a maximum that exceeds $\sqrt{12}$ when $h > 10$. These effects occur because a cigar-shaped polymer conformation orients under weak constraints before blob formation begins. A detailed examination of the balance between orientation and compression is outside this article's scope.

B. Langevin dynamics results—polymer chains

We begin simulations by placing N polymer chains, each with M monomers, in a tube of width h , ensuring their centers of mass are initially separated by a distance ℓ_o large enough to prevent contact at $t = 0$. All N chains were individually pre-simulated to achieve relaxed conformations. The position of the chains' center of mass (c.m.) (and other output parameters as needed) is tracked throughout the simulations, and the mean-square displacements (MSD) are computed as a function of time.

Figure 3(a) shows a log-log plot of the time evolution of the MSD ($\langle x^2(t) \rangle$) for $N = 5$ polymer chains of size $M = 15$

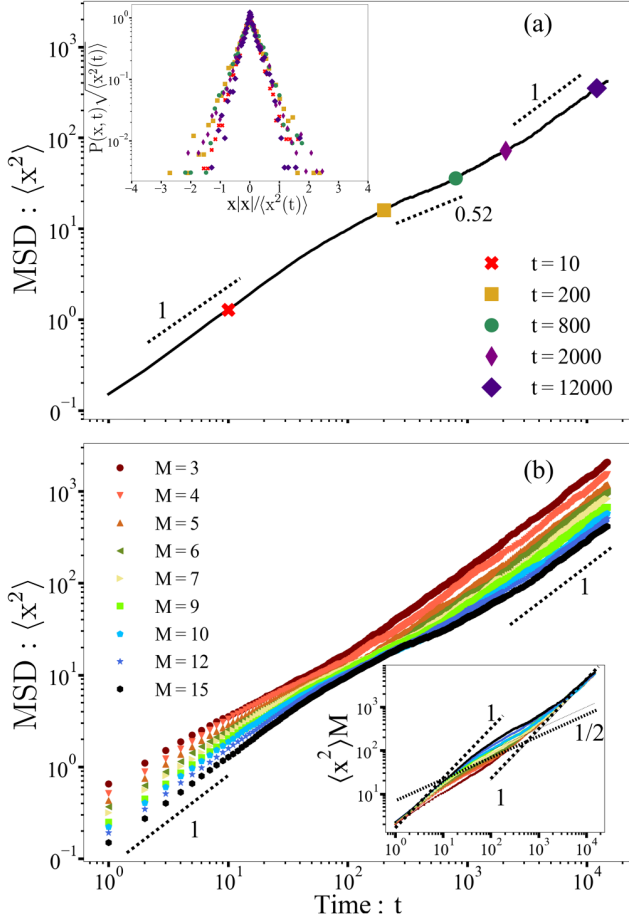


FIG. 3. (a) Mean-square displacement (MSD) *vs* time *t* for the $M = 15$ case presented in panel (b). Inset: scaled probability distribution function *vs* scaled position for the five different times highlighted in the main plot. (b) MSD *vs* time *t* for several molecular weights M . The tube width is $h = 3.5$, the number of polymer chains is $N = 5$, and the initial separation $\ell_0 = M + 1$. Inset: Same data with the y axis multiplied by M . The two dashed lines with a unit slope differ (along the time axis) by a factor of $N^2 = 25$, as predicted by theory. We also show a dotted line with a slope of $\frac{1}{2}$, the value expected in the SFD regime.

diffusing in a tube of width $h = 3.5$. We clearly see the normal diffusion regimes, as predicted by Eqs. (1) and (5) for short and long times, respectively. We also observe the intermediate SFD regime described by Eq. (3). The slope in the SFD regime, $\alpha = 0.52(1)$, is consistent with the value of $\frac{1}{2}$ predicted by Eq. (3). The inset gives the distribution function for the five different times marked in the main plot; in agreement with Eq. (9), the distribution is Gaussian in all cases.

Similar data are presented in Fig. 3(b) for sizes $3 \leq M \leq 15$. Although we see the same three regimes in all cases, the intermediate regime starts earlier for smaller sizes. Because $D_0 \sim 1/M$ and $D_R \sim 1/NM$ while $F \sim D_0^{\frac{1}{2}} \sim 1/M^{\frac{1}{2}}$, the curves get closer to each other in the intermediate regime: the difference between the $M = 3$ and $M = 15$ curves is a factor of 5 at both ends but only a factor of $\sqrt{5}$ in the middle, leading to a visible narrowing. The inset shows the same data

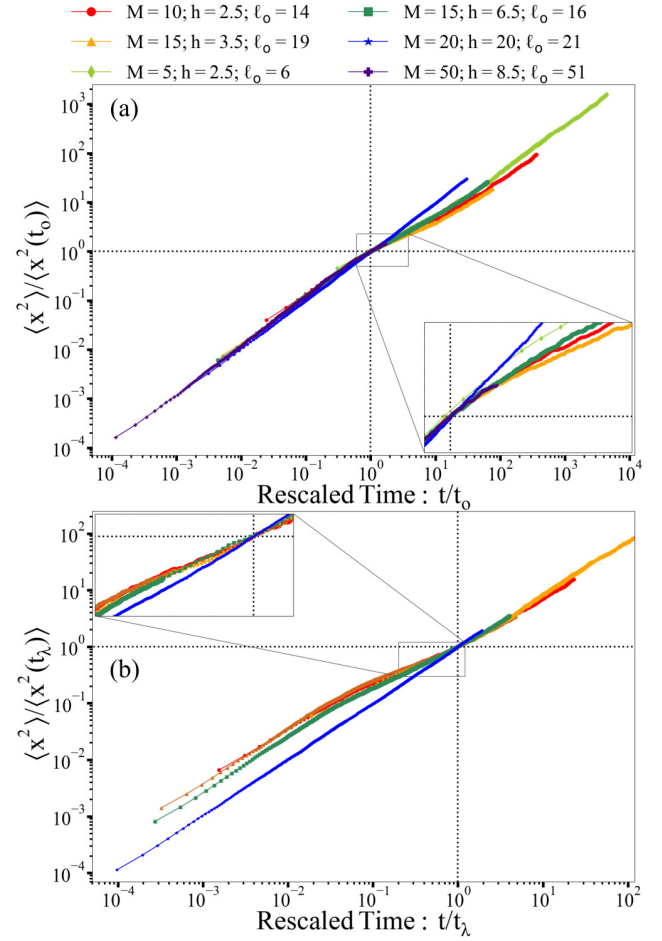


FIG. 4. (a) Mean-square displacement (MSD) *vs* time *t* showing the transition between the free diffusion and SFD regimes. The time axis is scaled using the predicted transition time t_0 given by Eq. (21) while the y axis is scaled using the MSD values at $t = t_0$. (b) Similar data showing the transition between the SFD and Rouse regimes. The time axis is scaled using the predicted transition time t_λ given by Eq. (22) while the y axis is scaled using the MSD values at $t = t_\lambda$.

when we multiply the y axis by M in order to remove the trivial $1/M$ dependence of D_0 and D_R . The different datasets then overlap at short and long times, while the SFD regime forms a bubble. The gap between the two asymptotic dashed lines (with slopes of 1) is a factor of $D_R/D_0 = 1/N = 1/5$ here.

The ratio $M/g(h)$, which gives the number of blobs formed by a chain of size M in a tube of width h , determines how difficult it is for this chain to change position with one of its neighbors. Polymer chains rarely change position (if at all) when $M/g(h) \gg 1$, so the system then exhibits strong SFD characteristics. The time required for a chain to collide with a neighbor is given by Eq. (2); for the current system, it reads

$$t_0 = \frac{\ell^2}{2D_0(M)} = \frac{M(\ell_0 - S_x)^2}{8D_\sigma}. \quad (21)$$

Beyond this timescale, the chains enter the SFD regime because their motion is constrained by their two neighbors and we expect $\langle x^2(t) \rangle \sim t^{\frac{1}{2}}$. Figure 4(a) shows that if we rescale

both axes using this predicted time, the curves collapse up to $t = t_0$ and diverge at longer times. The slope changes from unity to about $\frac{1}{2}$ in all cases, the only exception being the $[h = 20, M = 20]$ system (blue stars) because the polymer chains remain in the free diffusion regime at all times.

The SFD regime ends when the cooperative motion of the polymer chains leads to a global Rouse regime. Equation (8) gives the following transition time

$$t_\lambda = \frac{\lambda^2}{2D_R(M, N)} = \frac{\frac{2}{\pi} N \ell^2}{2D_o(M)/N} = \frac{MN^2(\ell_o - S_x)^2}{4\pi D_o}. \quad (22)$$

Figure 4(b) shows that if we now rescale both axes using this predicted transition time, the curves collapse at the transition point. The slope changes from about $\frac{1}{2}$ to unity in all cases, with the same exception.

Polymer SFD thus shows properties similar to hard particle SFD when chain order is maintained. The next section examines what happens when the conditions are such that the chains can and do change position, which is obviously expected to compete with SFD and cooperative Rouse dynamics.

C. Polymer chains switching positions

The notion of positional exchange can be ambiguous in the context of polymers. Unlike rigid particles that possess well-defined spatial boundaries, polymer chains continuously undergo deformation and can entangle (or overlap) for extended periods of time. Our primary interest here lies in understanding how the frequency of these events varies with system parameters. In order to do this, we chose to measure the time it takes for the first such event to be observed in a simulation.

We track the distance $\Delta x_{i,i+1}$ between the centers of mass of each pair $(i, i+1)$ of adjacent polymer chains (with $i \in 1 \dots N-1$) as a function of time. We start the system with a uniform distance $\Delta x_{i,i+1}(0) \equiv \ell_o = M + 3$ between neighbors, and we record the time t_1 at which we observe two chains changing position for the first time. We repeat this process for 891–1000 times for each combination of tube width h and chain length M , with $N = 5$ chains in each case. In some cases, no polymer switching was observed during a simulation, hence the smaller ensemble. Some range of parameters, for example $M = 15$ and $h \leq 4.5$, did not produce any chain switching event.

Figures 5(a) and 5(b) show examples with $M = 8$ and $h = 6$; the time evolution of the $N = 5$ chain-chain gaps is shown, and we see that two chains change positions at times $t_1 = 250$ (in A) and $t_1 = 1401$ (in B). Figure 5(c) shows the mean time $\langle t_1 \rangle$ as a function of the tube width h for four different chain lengths M . These times diverge when $(h-2) \rightarrow 0$ because two monomers cannot be side by side in the tube. In the opposite wide tube limit, $\langle t_1 \rangle$ eventually plateaus because we simply have free diffusing chains. We can estimate the switching time in the large h and M limits using the simple approximation

$$\langle t_1 \rangle_\infty \approx \frac{\ell_o^2}{2D_o(M)}. \quad (23)$$

Since $\ell_o = M + 3$ and $D_o \sim 1/M$, the mean time should then scale approximately as $\langle t_1 \rangle_\infty \sim M^3$. We thus scaled the y

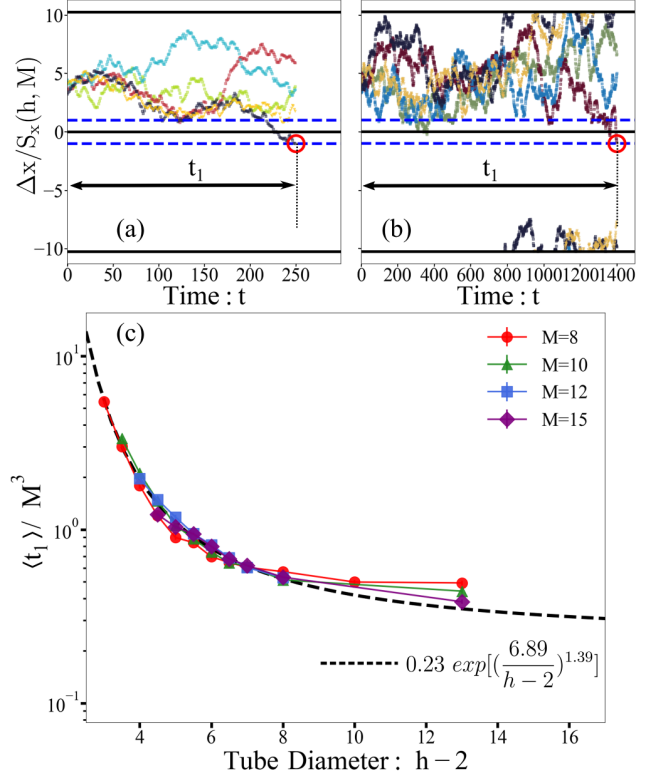


FIG. 5. (a), (b) Simulation examples showing the time dependence of the scaled distance $\Delta x(t)/S_x$ between all five pairs of nearest-neighbor chains. The system parameters are $N = 5$, $M = 8$, $h = 6$, $\Delta x(0) = M + 3 = 11$, and $S_x = 2.67$. The first two polymer chains to change positions do so at times $t_1 = 250$ and $t_1 = 1401$. (c) Scaled mean first switching time $\langle t_1 \rangle / M^3$ as a function of the effective tube width $h - 2$. The dashed line shows the fitting function Eq. (25).

axis in Fig. 5(c) accordingly, which indeed results in the near collapse of all four datasets.

The entropy [28] of a long chain in a tube (i.e., a chain that forms blobs) scales like $S \sim Mh^{-1/\nu}$. Equation (19) indicates that we need molecules of size

$$M > g(h) = 1.3(h-2)^{\frac{3}{2}} \quad (24)$$

to be in this regime. For the four molecular weights used in Fig. 5(c), this means tubes of width $h(M = 15) < 7$, $h(M = 12) < 6.4$, $h(M = 10) < 6$, and $h(M = 8) < 5$. Since several data points are in this regime, we fitted the four datasets for $h < 7$ using an exponential function to obtain

$$\frac{\langle t_1 \rangle}{M^3} = 0.23(4) \exp[6.9(8)/(h-2)]^{1.4(1)}. \quad (25)$$

This form is compatible with the fact that the potential barrier is of entropic origin. Since we have $\nu \approx 0.68$ here due to finite-size effects, this implies that $S \sim h^{-1.47}$, in fair agreement with Eq. (25). The range of polymer sizes we could simulate is not large enough to fully study the M -dependence of $\langle t_1 \rangle$. The critical tube size obtained in Eq. (25) is $h = 8.9$, in decent agreement with our estimates above.

The theory in Sec. II A for the transition regime with switching times in the range $t_\lambda \gg t_s \gg t_0$ predicts two

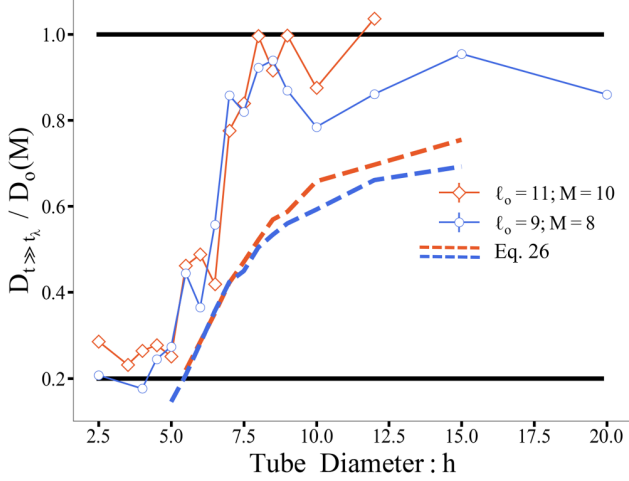


FIG. 6. Scaled asymptotic diffusion coefficient $D_{t \gg t_\lambda} / D_0$ vs tube width h for $\ell_0 = 11$, $N = 5$, and $M = 10$. The corresponding free diffusion coefficient is $D_0(M) = 1/M = 1/10$ (shown as the upper solid line). The lower solid line gives the Rouse diffusion of the group of molecules, $D_R = D_0/N = D_0/5$. The dashed line comes from Eq. (26).

properties for the asymptotic diffusion coefficient D_s . First, Eq. (12) indicates that $D_s \sim t_s^{-1/2}$ because polymer switching is more efficient than Rouse cooperative behavior, leading to $D_s > D_R$. Second, Eq. (12) also predicts that D_s should be independent of the number of molecules, N , because polymer switching is a local phenomenon. The second of these predictions will be tested using the Monte Carlo method in the next section.

The MSD lines diverge after converging at $t = t_\lambda$ in Fig. 4(b). Figure 6 shows how the asymptotic diffusion coefficient $D_{t \gg t_\lambda}$ increases from $D_R = D_0/N$ to D_0 as we increase the tube width h for $N = 5$ polymer chains of sizes $M = 8$ and $M = 10$. The diffusion coefficient increases as we transition from the Rouse regime (narrow tubes) to the free diffusion regime (wide tubes). Polymer switching occurs roughly in the narrow range $6 \leq h \leq 9$. We can obtain an estimate the h dependence of the diffusion coefficient in this transition regime using Eq. (12), replacing t_s with the value of $\langle t_1 \rangle$:

$$\frac{D_s}{D_0} \approx \left(\frac{8t_0}{\pi \langle t_1 \rangle} \right)^{1/2} = \frac{\ell_0 - S_x}{[\pi D_0 \langle t_1 \rangle]^{1/2}}, \quad (26)$$

with $S_x(h) = 7.02(h - 2)^{-0.47}$, $\ell_0 = 13$, and $D_0(M = 10) = \frac{1}{10}$. In spite of all the approximations needed for this estimate, the corresponding dashed line in Fig. 6 is in decent agreement with the general trend.

D. Phase diagram

Figure 7(a) presents a M - h phase diagram (for a system with $N = 5$ chains) based on the exponent α found when the scaling law $\langle x^2(t) \rangle \sim t^\alpha$ is used to fit the MSD data in the SFD regime. Systems with the strongest SFD regime (α near $1/2$) are located on the left, shown in blue hues. Conversely, the conditions under which SFD does not play a major role (α close to 1) are found on the right (orange).

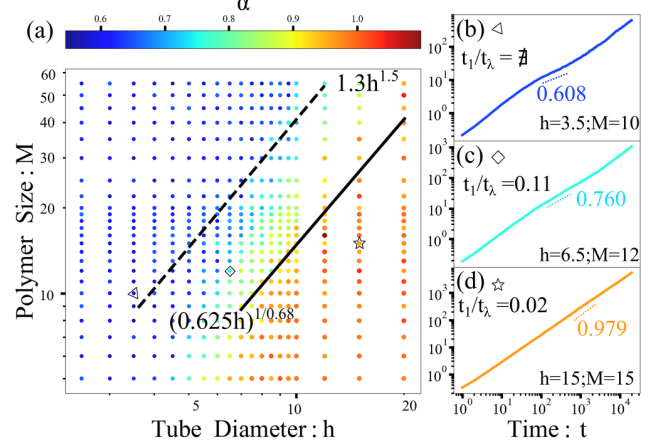


FIG. 7. (a) M - h phase diagram based on the value of the exponent α (see color code at the top) in the scaling law $\langle x^2(t) \rangle \sim t^\alpha$ when applied to intermediate times. The initial polymer separation is $\ell_0 = M + 1$, and the number of polymers is $N = 5$. The two diagonal lines are the theoretical boundaries described in the text. Panels (b), (c), and (d) show the MSD vs time t plots from which the value of the exponent α was obtained for the three marked points (∇ , $\diamond$, and $\star$) in panel (a). The ratio t_1/t_λ is given as well.

We added two solid lines to this phase diagram. The higher one, $M = 1.3(h - 2)^{3/2}$, is suggested by Eq. (19); on the left of this line, the chains form strings of blobs and the switching time increases very rapidly, thereby leading to strong SFD behavior. The second line, $h = 5 R_g^2(M) = 1.6(M - 1)^{0.68}$, corresponds to a tube wide enough that two random coil chains should easily pass each other (the factor of 5 is arbitrary). The points on the right of this second line correspond to cases where the polymers rarely collide with each other and essentially diffuse freely in a wide tube. Systems between these lines exhibit intermediate exponents α as both polymer switching and SFD coexist.

Figures 7(b)–7(d) show three examples marked by empty symbols in the phase diagram. The Fig. 7(b) case is in the SFD part of the phase diagram, and we observe that $\langle x^2(t) \rangle \sim t^{0.608}$ in the intermediate time regime. We were unable to observe polymer switching in this case. The Fig. 7(d) case is clearly in the wide tube regime, and indeed the intermediate time regime has an exponent close to unity and very short switching times. Finally, Fig. 7(c) is in the middle regime where both SFD and polymer switching coexist.

The next section revisits these issues using a very efficient Monte Carlo scheme that is informed by our LD results.

E. Monte Carlo results—particles vs polymer chains

As described in Sec. III B, our LMC simulations use periodic boundary conditions and four parameters: the number of particles, N , the initial spacing ℓ_0 between them, and finally the collision parameters P and Q . As the molecular weight M is irrelevant in MC simulations, all particles share the same free solution diffusion coefficient D_0 . A particle replaces a polymer chain and occupies a single lattice site. While P governs the probability of chain entanglement, Q dictates the disentanglement rate. For example, $P = 0$ corresponds to

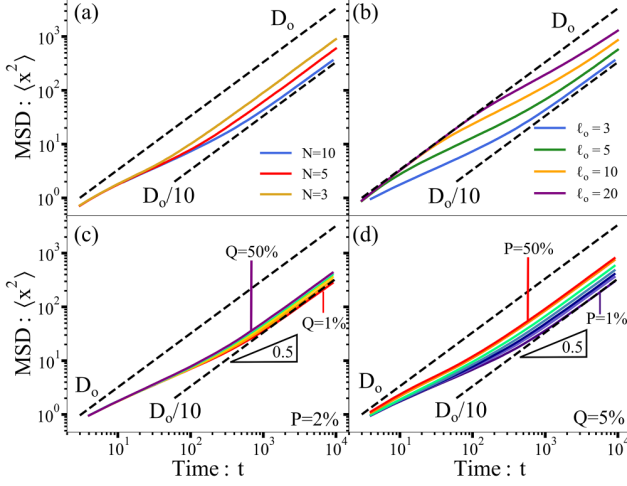


FIG. 8. Mean-square displacement $\langle x^2(t) \rangle$ vs time t for various combinations of Monte Carlo parameters. The dashed lines have a unit slope and show the theoretical limits $D = D_0$ and $D = D_0/10$ for the $N = 10$ case. (a) $\ell_0 = 3$, $P = 2\%$, and $Q = 5\%$ for $N = 3, 5$, and 10 particles. (b) $N = 10$, $P = 2\%$, and $Q = 5\%$, with mean spacings $\ell_0 = 3, 5, 10$, and 20 . (c) $N = 10$, $P = 2\%$, $\ell_0 = 3$, and different values of Q . (d) $N = 10$, $Q = 5\%$, $\ell_0 = 3$, and different values of P .

pure SFD dynamics, the combination $[P = 1, Q = 0]$ leads to molecular aggregation, and we have a gas of lightly interacting chains if both parameters are large.

As usual, we have to be careful with lattice Monte Carlo algorithms since small systems can be affected by important lattice discretization effects. On the plus side, we can now simulate larger systems, large ensembles, and longer periods of time (indeed, our MC results are for ensemble sizes of 20 000).

Figure 8 shows a range of typical simulation results [mean-square displacement $\langle x^2(t) \rangle$ vs time t] where we systematically vary each of the four system parameters (i.e., N , ℓ_0 , P , and Q). Figure 8(a) shows the impact of the number of particles, N . At short times $t < t_0$, the particles have yet to be affected by collisions and Eq. (1) applies; indeed, the different curves then overlap and converge towards the free-solution diffusion coefficient D_0 . This is followed by an SFD regime between times t_0 and t_λ , and a long-time regime for $t > t_\lambda$, with

$$\begin{aligned} t_0 &= (\ell_0 - 1)^2 / 8D_0, \\ t_\lambda &= \frac{8}{\pi} N^2 t_0. \end{aligned} \quad (27)$$

While $t_0 \approx 3$ is the same for all three curves, the transition to the last regime shifts to longer times $t_\lambda \sim N^2$ as N increases. The $N = 10$ dataset almost converges with the Rouse prediction $D_R = D_0/10$ at long times; the small difference is due to particles being able to switch position when $P \neq 0$.

Figure 8(b) examines the role of the initial spacing ℓ_0 . The same three regimes are found, but the transition times t_0 and t_λ both increase like $(\ell_0 - 1)^2$. The most interesting feature is the fact that the asymptotic diffusion coefficient slowly increases from $D_0/10$ to D_0 as we increase ℓ_0 ; this is due to the fact that the time between collisions scales like $t_0 \sim (\ell_0 - 1)^2$

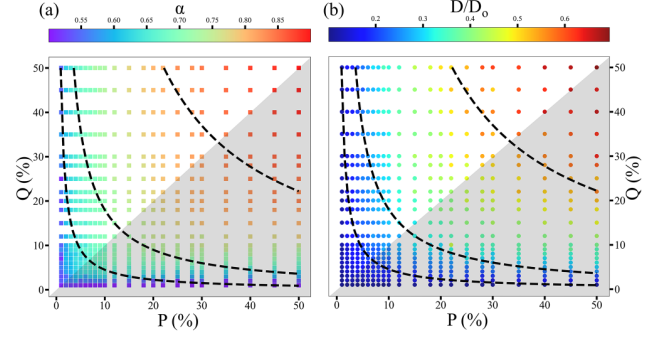


FIG. 9. Q - P phase diagrams showing (a) the value of the SFD exponent α , and (b) the reduced long-time diffusion coefficient D/D_0 . The initial separation between the $N = 10$ particles is $\ell_0 = 3$. The dashed lines show that the function $Q = C/P$ can be used to separate the regimes; from left to right, the values of C are 45, 180, and 1110 (these choices will be explained later because they relate to Fig. 11).

while the time required to complete a switching event is independent of the density of particles. When ℓ_0 is very large, the limiting factor is the diffusion time between collisions, and we recover the free-solution diffusion coefficient D_0 .

Figures 8(c) and 8(d) show how P and Q affect the dynamics of the particles. Large values of either Q or P lead to a fast switching process as long as the other parameter is not negligible. The presence of particle switching increases the asymptotic diffusion coefficient, in agreement with Eq. (12). We note that the intermediate SFD regime disappears when particles can easily change position, which is also as expected. While the different curves collapse at short times in Fig. 8(c), they do not in Fig. 8(d). This is due to the fact that this regime is controlled by the time to the first collision, t_0 : when P is large, these collisions have very little or no impact on the diffusion of a particle, hence the increase towards the D_0 limit.

Figure 8 shows that we can reproduce the key aspects of the physics of this polymer system with a realistic MC model. To get a better idea of the subtle impacts of P and Q , we now present two phase diagrams.

The first one, Fig. 9(a), describes how these parameters impact the exponent α in the SFD regime and is thus the MC equivalent to Fig. 7(a). Strikingly, there is a nearly symmetric distribution of points, with the value of the exponent α growing with both P and Q , producing a rainbow effect. The reason for this comes from the MC rules described in Sec. III B; if we consider only two-particle interactions and neglect the diffusion of particle aggregates, the duration of an event during which two particles change position is $t_s \sim 1/PQ$. The $Q \sim 1/P$ dashed lines separate the three regimes, just like the two straight lines did in Fig. 7(a). The second phase diagram, Fig. 9(b), shows the impact of these parameters on the particles' asymptotic diffusion coefficient. We again observe the quasisymmetry along the diagonal.

Together, these two phase diagrams demonstrate that SFD survives if particle-particle collisions rarely lead to switching events. SFD “survival” means that we keep these two elements: (1) the exponent α , which describes the MSD in the SFD regime $\langle x^2(t) \rangle \sim t^\alpha$, is close to $\frac{1}{2}$; (2) the asymptotic diffusion coefficient of the particles is close to D_0/N because

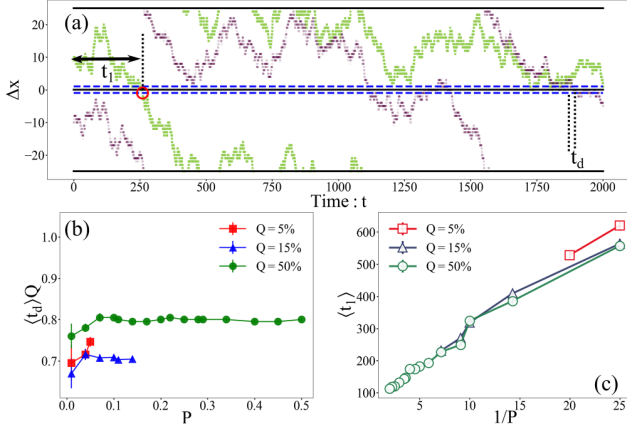


FIG. 10. (a) Simulation examples showing the time dependence of the distance $\Delta x(t)$ between two pairs of nearest neighbor particles. The system parameters are $P = 12\%$, $Q = 15\%$, $\Delta x(0) = \ell_o = 10$, $N = 5$. The first particles to change positions do so at time $t_1 = 260$. The duration of the event starting at time $t = 1885$ is $t_d = 19$. (b) Scaled mean event duration $\langle t_d \rangle Q$ vs P . (c) Mean first switching time $\langle t_1 \rangle$ vs $1/P$. The ensemble size for B and C is 1000.

SFD leads to cooperative motion of the particles at long times. Both phase diagrams clearly show these two limits.

Note that we shadowed the $P > Q$ areas in both phase diagrams because we consider this situation to be unrealistic. In this hypothetical region, particles (polymer chains) would have a high probability to overlap (P) and a low probability to separate (Q), which seems to make little sense unless there are attractive interactions leading to stable aggregates, a situation that is beyond the scope of this paper.

In order to investigate the switching mechanism, we repeated the study that led to Fig. 5 using our MC algorithm. An example is shown in Fig. 10(a). From these trajectories, we extracted the time to the first switching event, $\langle t_1 \rangle$, and the mean duration of successful switching events, $\langle t_d \rangle$ [both are defined in Fig. 10(a)]. Note that we will focus on the $Q \geq P$ part of the phase diagram for the reasons given above.

Figure 10(b) shows that the mean duration of successful switching events, t_d , is essentially independent of the parameter P but inversely proportional to Q . This is as expected since t_d is in fact the disentanglement time of two particles, a process that is controlled by Q in our MC algorithm; the small residual Q and P dependencies come from multiparticle interactions. Figure 10(c) shows that the mean first switching time $\langle t_1 \rangle$ grows linearly with $1/P$, while exhibiting a very weak dependence on Q . This result is also expected since P controls the first switching event in the MC algorithm. As $t_d \sim 1/Q$ and $t_1 \sim 1/P$, we can conclude that t_s , which includes both of these processes, should scale roughly like $t_s \sim 1/PQ$, in agreement with the structure of the phase diagrams in Fig. 9.

Equations (12) and (13) indicate that the diffusion coefficient scales as $D \sim t_s^{-1/2}$ when the switching time falls within the range $t_o < t_s < t_\lambda$. This transition regime is shown in Fig. 6, where D rises from the Rouse value $D_R = D_o/N$ (when $t_s > t_\lambda$) to the free diffusion value $D = D_o$ (when $t_s < t_o$) as polymer switching frequency increased (h was increased). Since we have roughly $t_s \sim 1/PQ$ in our MC algorithm, we

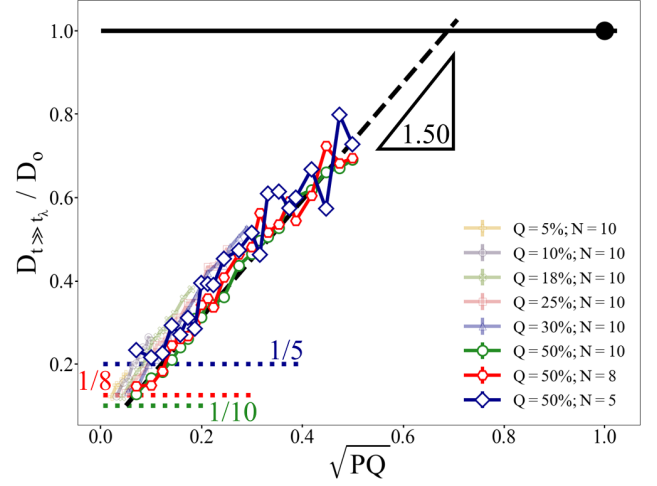


FIG. 11. Scaled asymptotic diffusion coefficient $D_{t \gg t_s} / D_o$ vs. $\sqrt{PQ}$ for various combinations of Q and N ; the system parameters are on the figure, and the fixed separation is $\ell_o = 3$. The lower dotted lines give the Rouse prediction $D_R = D_o/N$ for the group, while the solid line at the top (in black) shows the free-solution diffusion coefficient D_o . The (1,1) point is the theoretical free-diffusion case. The dashed line is a linear fit for the $N = 10$ and $Q = 50\%$ dataset.

should expect $D \sim \sqrt{PQ}$ here. Figure 11 confirms that this is the case in the intermediate regime for various parameter combinations. The data points approach the $D_R = D_o/N$ limit as PQ decreases. Because we restricted our parameters to $P \leq Q \leq 1/2$, the product PQ is not large enough to reach the free-diffusion limit $D = D_o$. The theoretical $D(P = Q = 1) = D_o$ point on the top line demonstrates that the linear intermediate regime does not extend to this point. Our MC model is unsuitable for modeling the regime where particles barely interact (corresponding to $h \gg R_g^o(M)$ for polymer chains).

The dashed line in Fig. 11 is the linear fit $D/D_o = 1.50(2)\sqrt{PQ}$ to the $[N = 10; Q = 50\%]$ dataset. The fact that this fit also agrees with the other datasets demonstrates that the diffusion coefficient does not depend on the number of particles N in this intermediate regime, an important prediction of Eq. (12). For the $N = 10$ case, this fit predicts that $D = D_R = D_o/10$ when $Q \approx 0.45/P$, which should be interpreted as marking the hard limit for SFD dynamics (no particles exchanging position); similarly, it predicts that $D = D_o/2$ when $Q \approx 11.1/P$, which should be the point beyond which particle switching dominates. Finally, it gives $D = D_R = 2D_o/10$ when $Q \approx 1.8/P$, possibly pointing to a condition where SFD and particle switching play equal roles. These three lines are shown in the phase diagrams, Fig. 9; we can clearly see that they indeed correspond to the description given above.

V. DISCUSSION AND CONCLUSION

We investigated the dynamics of one-dimensional dilute polymer solutions in a closed continuous system resembling a toroidal tube, a configuration that is amenable to experimental study in the laboratory. The polymer molecular weight M and tube width h influence the polymers' ability to swap posi-

tions. The main theoretical predictions regarding the different regimes to be expected were presented, and two different simulation methods were used to model the system: Langevin dynamics and Monte Carlo, with the aim of establishing the link between these approaches.

The Monte Carlo algorithm was designed to minimize the number of parameters (we used only two, denoted P and Q) while properly accounting for the various features of the polymer systems, such as the entanglement and disentanglement processes. The Q parameter is actually unique to polymer systems since it is decoupled from P . For instance, it could allow us to study aggregating systems. In practice, we restricted the study to $Q \geq P$, which seems to be realistic for noninteracting polymer chains in good solvents.

The LD study confirmed the existence of the many time regimes predicted in the theory section, namely free diffusion, single-file diffusion, polymer switching, and Rouse regimes. Both the tube width h and the polymer size M play a role in determining whether polymer switching will displace the Rouse regime at long times. In fact, the key parameter is the number of blobs formed by the polymer chains in the tube, since chains with multiple blobs are unlikely to interpenetrate and change position on a timescale that would alter the long-term behavior of the polymer solution. Consequently, the tube width range where polymer switching plays a role is relatively narrow.

Polymer chains changing position compete with single-file dynamics at intermediate times and with Rouse dynamics at longer times. We therefore proposed to use the α exponent, which describes the time evolution of the mean square displacements (MSD) at intermediate times, as a way of characterizing the effect of polymer switching. This has led to the M - h phase diagram in Fig. 7, where we can see that the system transitions smoothly between the different regimes predicted by the theory. However, modeling these systems with LD is challenging due to the long simulation times needed to gather sufficient polymer switching events for statistical analysis. For this reason, we have also had a look at this problem with the help of an MC algorithm.

The results of the MC method are in agreement with the LD data and theoretical predictions. We thus proposed two phase diagrams in Fig. 9 based on the α exponent and the asymptotic diffusion coefficient. Importantly, Fig. 11 validated the theoretical description of the competition between SFD and particle exchange. We thus conclude that the MC algorithm can be used to study this class of problems. Clearly, the entanglement and disentanglement process is influenced by both h and M , which means the MC parameters (P, Q) need to be related to the LD parameters (M, h). The relation between the two sets of parameters is not trivial because there is no *a priori* reason to assume that two MC parameters are sufficient to model the dynamics of polymer switching events. Nevertheless, we will describe a simple method for establishing an approximate connection between the parameters in the next paragraph.

In order to connect the LD and MC parameters, $[M, h]$ and $[P, Q]$, respectively, we first use the fact that the disentanglement time of two overlapping chains in a tube [31] scales like $t_d \sim M^2 h^{2-1/\nu}$. The MC result $t_d \sim 1/Q$ implies that $Q \sim 1/Mh^{2-1/\nu}$, where we removed one power of M

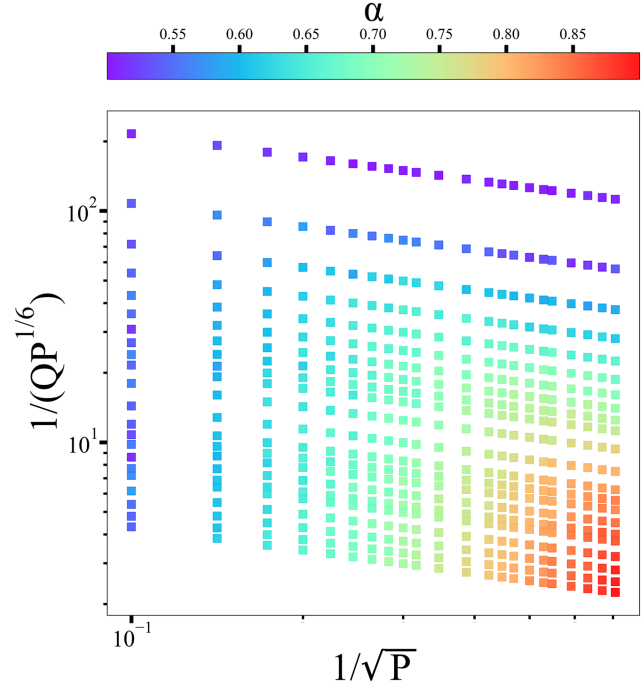


FIG. 12. Phase diagram presented in Fig. 9(a) with both axes replaced by the variables defined in Eq. (28).

because the duration of one MCS scales as $\tau_c \sim M$. We then note that while the different regimes in the LD phase diagram are separated on the basis of the number of blobs (hence the dashed diagonal lines $Mh^{-1/\nu} = \text{const}$), these regimes are separated on the basis of the combined parameter $1/PQ = \text{const}$ in the MC phase diagrams. We will thus assume that $Mh^{-1/\nu} \sim 1/PQ$. Using these two relations, we get

$$\begin{aligned} h &\sim 1/\sqrt{P}, \\ M &\sim 1/QP^{1-1/2\nu} \sim 1/QP^{1/6}, \end{aligned} \quad (28)$$

where the last result is obtained using Flory's exponent $\nu = 3/5$. Figure 12 shows the phase diagram presented in Fig. 9(a) with the two axes modified using these two expressions. The similarity with Fig. 7(a) suggests that it is indeed possible to connect the two simulation methods. The approach used here is not the only option; further research will be necessary in order to fully exploit the MC methods and obtain a better connection between the parameters of the two models.

The polymer SFD problem studied in this paper suggests a number of interesting extensions. For example, it would be interesting to study how the regimes described in our work would evolve as the concentration of the polymers is increased towards the semidilute limit. On a different note, it would also be of interest to study bimodal polymer solutions (e.g., linear and ring polymers with identical molecular weights M) to see if the different switching times can lead to SFD-triggered phase separation along the torus.

As for our MC approach, it can be modified to study a much broader range of one-dimensional problems, including bimodal (or polydisperse) dilute polymer solutions and polymer aggregation. Adding a bias to the movement of one of

the lattice particles could also allow us to investigate one-dimensional electrophoresis [29].

Our investigations used LD and MC simulations, as well as simple analytical theory. These analytical and computational methods did not account for the influence of hydrodynamic interactions and polymer rigidity, in addition to various other factors. While hydrodynamics likely wouldn't qualitatively alter the results, polymer stiffness might, as the Kuhn length introduces a new scale, potentially leading to new regimes. For instance, the rigidity of the polymer, such as dsDNA, would certainly add to the dynamical intricacy of the switching mechanism, possibly allowing rapid polymer exchange because of the smaller cross-sectional area. These associated subjects are promising avenues for upcoming research.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are openly available [32], embargo periods may apply.

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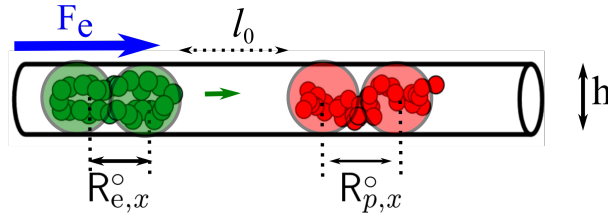
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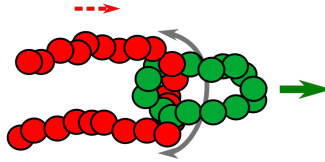
ADDITIONAL PROJECTS

5.1 COLLISIONS INVOLVING RING AND LINEAR CHAINS

Chapter 2 raises an interesting question: does changing the shape of the polyelectrolyte affect collisions? In particular, what if a ring polyelectrolyte collides with an uncharged linear polymer chain in a narrow channel? Figure 5.1 (A) depicts such a situation. This raises fundamental questions and could potentially differentiate ring from linear polyelectrolytes.



(A) System schematics



(B) U-O collision

Figure 5.1: (A) A ring polyelectrolyte will soon collide with an uncharged polymer chain in a narrow channel under the action of an external field. (B) A particular type of collision where the linear chain passes through the 'hole' of the ring polyelectrolyte, which pulls the linear chain.

Similar to the setup in Chapter 2, we apply an external force on the monomers of the ring polyelectrolyte, causing it to collide with the neutral linear polymer chain. Throughout the simulations, we track the CM positions, radii of gyration, and spans of the two polymer molecules at each time step.

In some simulation video recordings, we observed a particular type of collision, which is schematically shown in Fig. 5.1 (B). The linear polymer chain is threaded through the hole of the ring polyelectrolyte and carried by it. This is somewhat analogous to the U-U

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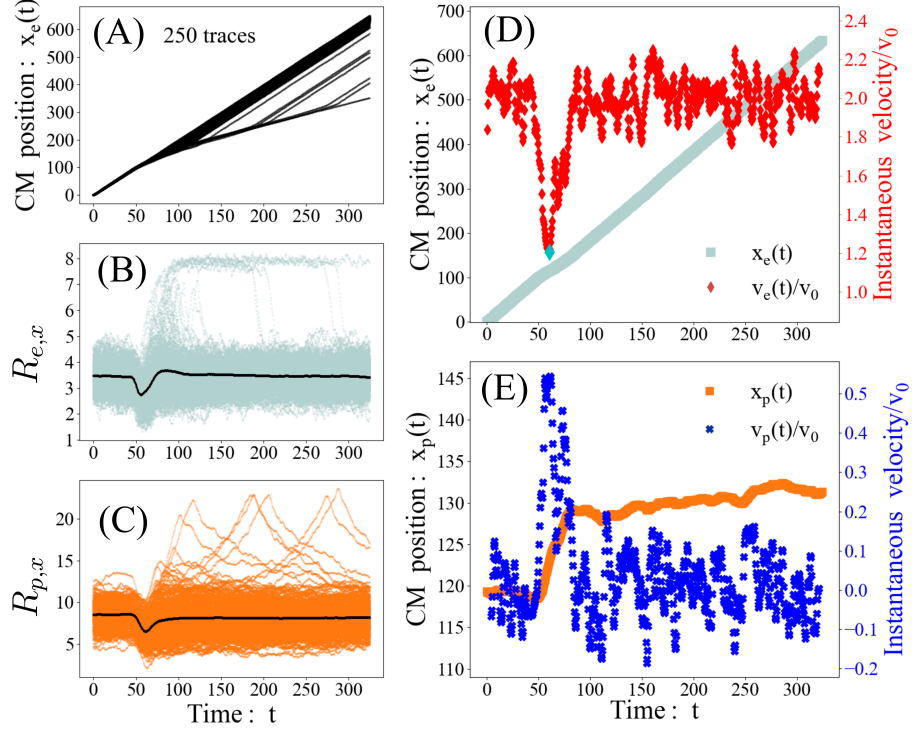


Figure 5.2: Analyzing the collision between a ring polyelectrolyte ($N_e = 60$ beads) and an uncharged linear polymer ($N_p = 100$) separated by a distance $\ell_o = 50$ at $t = 0$. The tube diameter is $h = 8$, and the external force is $F_e = 2$ on each charged bead. (A) 250 different polyelectrolyte trajectories. (B) The ring polyelectrolyte axial radius-of-gyration $R_{e,x}(t)$ decreases and then increases during a collision. (C) The linear polymer axial radius-of-gyration $R_{p,x}(t)$ changes as a function of time. The outliers are due to the linear uncharged polymer being stretched into a rod-like shape. (D) The ring polyelectrolyte trajectory with its derivative (the instantaneous velocity). The tangent at the inflection point $t = t_I = 56$ defines the collision velocity v_I . (E) Similar to (D), but for the uncharged polymer.

and J-J collisions that we observed between two linear chains; we thus call them U-O and J-O collisions. The next question is what effects U-O collisions will have on the collision

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velocities of the two molecules. When the two chains are linear, they both slide around their point of contact, and one of them eventually escapes. Here, however, since only one of them slides, we can expect much longer escape times, especially if the starting configuration is U-O instead of J-O.

The 3 plots in the left column of Fig. 5.2 show the time evolution of (A) the CM position $x_e(t)$ of the ring polymer, (B) the radius of gyration $R_{e,x}$ of the ring polymer, and (C) the radius of gyration $R_{p,x}$ of the linear uncharged polymer (there are 250 traces in total in each plot). The most striking phenomenon is the presence of spectacular outliers, which are due to the special U-O collisions described above. Some centre of mass trajectories keep a very low velocity for unusually long periods of time, a measure of the duration of U-O collisions. Both polymers being highly stretched during these particular collisions, we observe isolated orange peaks in Fig. 5.2 (C); these peaks are about 3 times higher than the equilibrium value of $R_{p,x}$ and mark the point where the linear chain escapes (indeed, we observe the relaxation of the linear chain immediately after the peak). Similarly, the higher plateau in panel (B) shows that ring polymers are also highly stretched during the collision. The above description is typical of U-O collisions, which last much longer than other types of collisions.

How do we quantify the number and impact of U-O collisions? To answer these questions, we start with the analytic process shown in Figs. 5.3 (A)-(B). The distribution of ring polyelectrolyte final positions is very asymmetric, with a long tail of outliers on the short side (the expected impact of U-O collisions). In order to quantify their importance, we chose to estimate the number of cases that are at least three standard deviations, σ_x , below the mean, $\bar{x}$, of the distribution – see Fig. 5.3 (B). Of course, we expect this to underestimate the number of U-O collisions, but it has the advantage of being a simple approach. The results, in % of cases in this situation, are presented in Fig. 5.3 (C) as a function of the polymer size ratio N_p/N_e for three different ring sizes. Remarkably, roughly $\sim 3 - 10$ % of the collisions can be considered U-O collisions using this simple criterion. How to utilize U-O collisions, unique to ring polyelectrolytes, as the basis to build a separation method is an interesting question for further research.

5.1. COLLISIONS INVOLVING RING AND LINEAR CHAINS

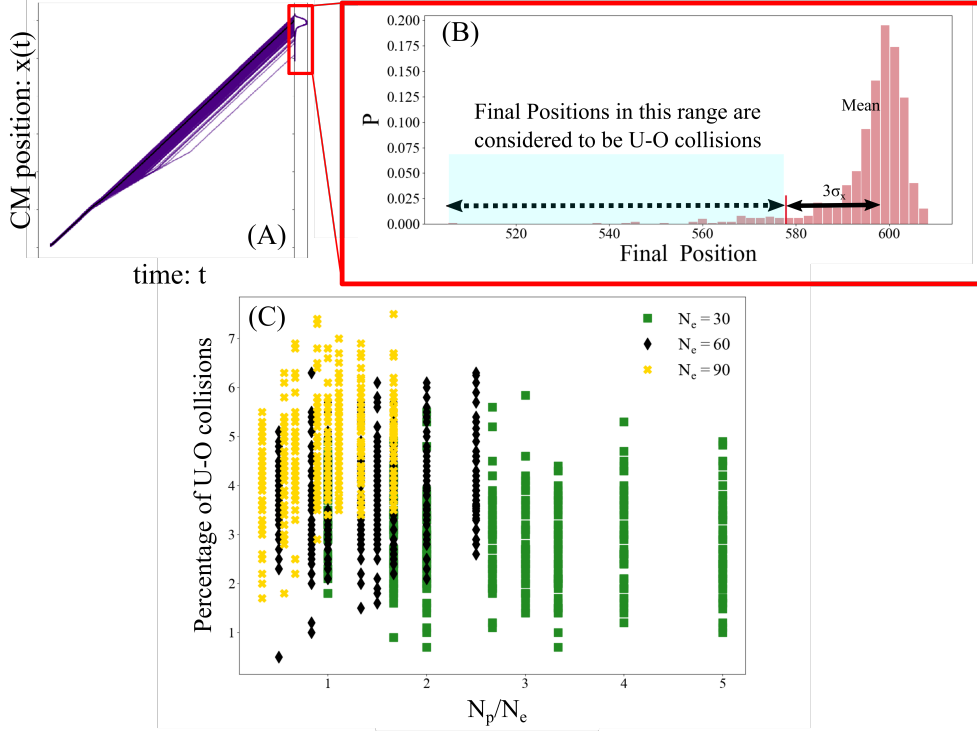


Figure 5.3: (A) The CM trajectory of a ring polymer with $N_e = 60$ monomers colliding with an uncharged linear polymer of size $N_p = 80$. The applied force is $F_e = 2.0$ on each monomer and the tube width is $h = 7.0$. The distribution of final positions is shown at the top right. The ensemble size is 1000. (B) A zoomed version of the distribution function in panel (A). (C) Probability of observing a U-O collision using our criterion. Data for ring polyelectrolytes of size $N_e = 30, 60$, and 90 are presented. The vertical distribution of data points corresponds to the same ratio N_p/N_e under different tube diameters h and external forces F_e . The ensemble size for each data point is 1000.

There is no doubt that the physics of U-O collisions need more modelling and testing, but one conclusion we can draw is that the larger the ring polyelectrolyte, the higher the chance that a collision will be recognized as of the U-O type. This is a reasonable conclusion because the larger the ring, the greater the chance that the uncharged polymer will pass through the ‘hole’ in the ring, leading to J-O or U-O collisions.

In order to better understand the differences between ring and linear polyelectrolytes,

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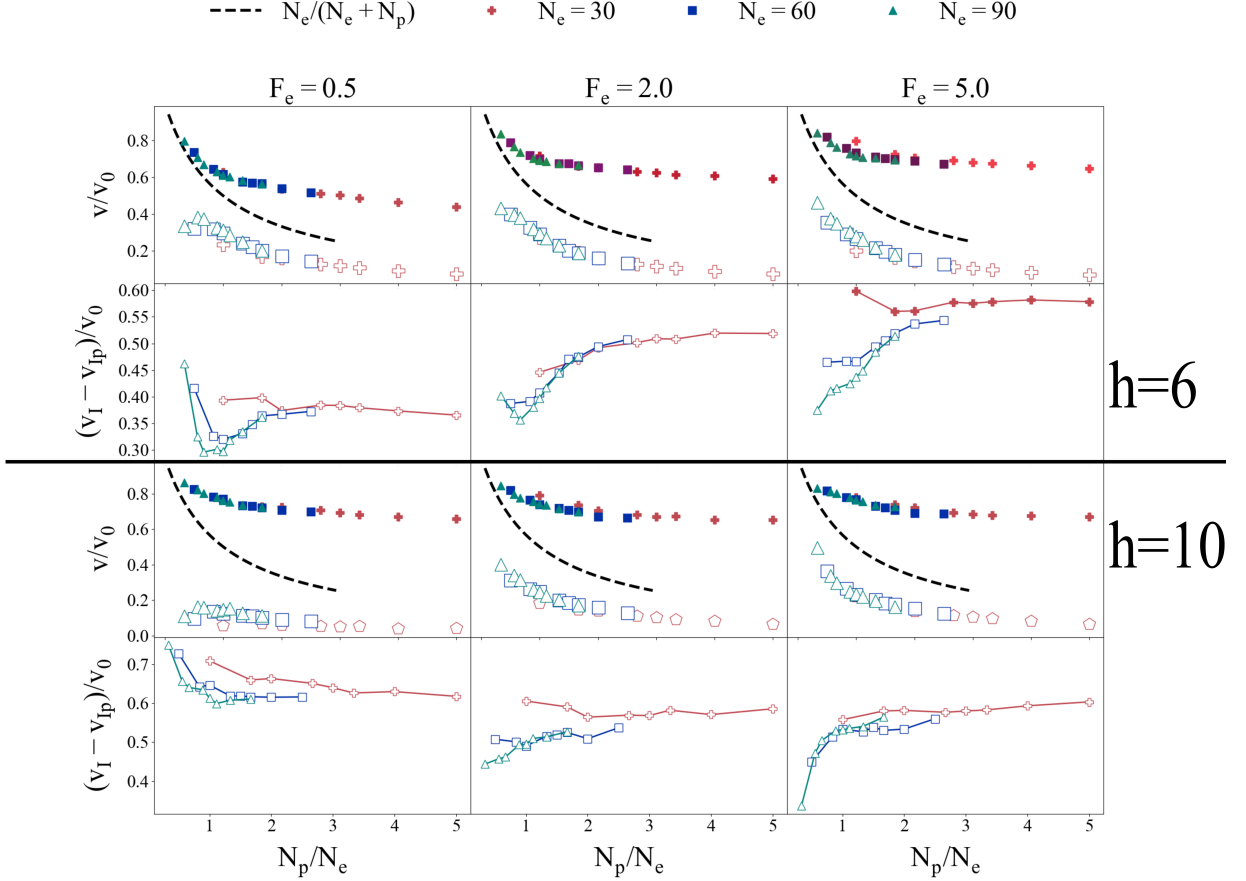


Figure 5.4: Scaled collision velocities vs polymer size ratio N_p/N_e for ring polyelectrolytes of size $N_e = 30, 60, 90$ in a narrow $h = 6$ (top two rows) and a wide $h = 10$ (bottom two rows) tube. Left column: low external force $F_e = 0.5$. Middle column: intermediate force $F_e = 2$; right column: high force $F_e = 5$. The first and third rows give both v_I/v_0 (solid markers) and v_{Ip}/v_0 (hollow markers). The second and fourth rows give the relative velocity $(v_I - v_{Ip})/v_0$. The size of the uncharged polymers varies between $N_p = 20$ and $N_p = 150$.

we now repeat the simulations that led to Fig. 8 of Chapter 2. In Fig. 5.4, we look at the collision velocity of the ring polymer chain, v_I , the collision velocity of the uncharged polymer, v_{Ip} , and finally the relative velocity between the two, as a function of the polymer size ratio N_p/N_e for different forces and tube widths.

5.1. COLLISIONS INVOLVING RING AND LINEAR CHAINS

Compared to linear polymer collisions, there are no significant differences when the external force is weak (the left column). For the narrow channel ($h = 6$), we also observe the non-monotonic behaviour of the relative velocities $v_I - v_{Ip}$, with the minimum located around $N_p/N_e \simeq 1$. For larger tubes ($h = 10$), however, the local minima are not significant.

In the presence of larger forces, the situation changes and we observe that the uncharged polymer chains have a greater velocity v_{Ip} . For both $F_e = 2$ and $F_e = 5$, the collision velocity of the uncharged polymer is closer to the theoretical maximum value $\frac{N_e}{N_e + N_p}$ than what we previously obtained for linear polyelectrolytes. The results also show that the relative velocities of the two polymer chains change significantly. The plateau region remains constant, suggesting that the nature of the collision is the same when the uncharged polymer fills the channel. However, when N_p is small, ring polyelectrolytes are more likely to hit the uncharged polymer than linear polyelectrolytes (ring polymers have a more dense cross-section than linear polymer chains in a tube). In 2nd and 4th rows of Fig. 5.4, when N_p/N_e is small, it is clear that $v_I - v_{Ip}$ is dropping for both $F_e = 2$ and 5 cases, in contrast with the linear collision cases. The most interesting cases are those with $h = 6$ and $F_e = 5$ (row 2; column 3), where the relative velocity splits into two different trends in the limit $N_p/N_e \leq 2$. In short, the smaller ring polyelectrolyte has a larger relative velocity compared to the larger ring polyelectrolyte, and this red curve coincides with the same collision scenario in Fig. 8 in Chapter 2.

This suggests that ‘missing’ collisions dominate in the small uncharged polymer limit. The non-monotonic behaviour in Chapter 2 at that limit is due to the fact that linear-linear polymer collisions are easier to miss, compared to ring-linear polymer collisions. Remember that ring polyelectrolytes have a denser ‘cross-sectional’ area compared to linear polyelectrolytes. This mechanism disappears as the uncharged polymer increases in size. In addition, if the polyelectrolyte moves relatively slowly (e.g., $F_e = 0.5$), the collision rate recovers because the chances of collisions during the same time increase.

In this section, we presented a brief analysis of ring polyelectrolyte-linear polymer

collisions, which supplements Chapter 2. The most important finding is probably the U-O collision, although the ‘missing’ mechanism in some N_p/N_e limits may also be crucial for practical applications.

5.2 MIXTURES OF RING AND LINEAR POLYMER CHAINS

In Chapter 4, we demonstrated that single-file diffusion (SFD) is highly dependent on the number of blobs, and consequently, on the tube width h . This raises an interesting question: can SFD and entropy trigger or allow phase separation in dilute mixtures of ring and linear chains?

We will examine two facets of the ring/linear mixing issue. First, for infinitely long or toroidal systems, do ring/linear polymer chain mixtures spontaneously form phase-separated regions? Secondly, for finite systems with sealed tube ends, do these end walls act as catalysts for phase separation? Indeed, there are entropic reasons to believe that ring molecules may prefer staying near the ends rather than mixing with the linear polymer chains in the middle; Fig. 5.5 describes this hypothetical situation.

Let us first study the mixing process of linear and ring polymer chains, starting from a phase-separated state. If there are entropic reasons that favour phase separation, these polymer molecules should not mix beyond some interfacial region. Figure 5.6 shows such an example. We have five linear polymers on the left and five ring polymers on the right. The polymer size ($N = 10$ monomers) was chosen such that both linear and ring polymers have radii of gyration comparable to the tube width, thus allowing polymer chains to change position with some small but finite probability. The tube is capped at both ends, so mixing can only occur in the middle. This system was studied using Langevin Dynamics simulations. The mixing (the purple area) is progressing in an almost symmetric fashion around (roughly) the middle point of the tube. The small asymmetry is due to the fact that ring polymers have smaller radii of gyration and thus occupy less space. The initial phase-separated state is obviously unstable *vs* mixing.

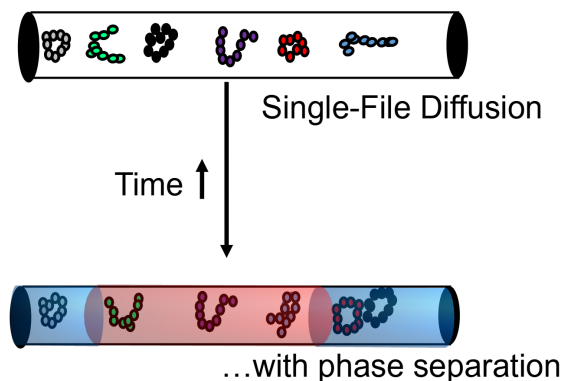


Figure 5.5: Schematic representation of the mixed dilute polymer solution that we study in this section. Three pairs of ring/linear polymer chains are arranged in an alternating pattern in a narrow tube. Will these molecules phase-separate due to the fact that rings have less conformational entropy and occupy less space than linear chains? The two ends of the tube can be connected (thus forming a toroidal system) or capped. In the latter case, the walls may attract the ring polymers because these molecules loose less entropy near walls.

Figure 5.7 shows results of simulations with a slightly wider tube. The total simulation time is the same as in Fig. 5.6. As expected, mixing is much faster. We still observe a slight asymmetry around the mid-point.

Figure 5.8 shows results for a much wider tube. In fact, the chains now have radii of gyration much smaller than the tube width and can thus change position fairly easily. As expected, mixing is fast and, at the end of the simulation, the polymer chains are homogeneously mixed and the system has completely lost any memory of its initial state.

This suggests that entropic segregation due to differences in polymer conformations does not seem to exist. Instead, a different type of entropic pressure may occur, which favours the reduction of ring-ring overlap and thus drives the ring/linear mixing process. A recent paper from Grest’s group [35] showed that ring/linear polymer mixtures evolve to minimize ring/ring interactions. However, their studies, which involved concentrated polymer solutions in three dimensions, are different from our case.

5.2. MIXTURES OF RING AND LINEAR POLYMER CHAINS

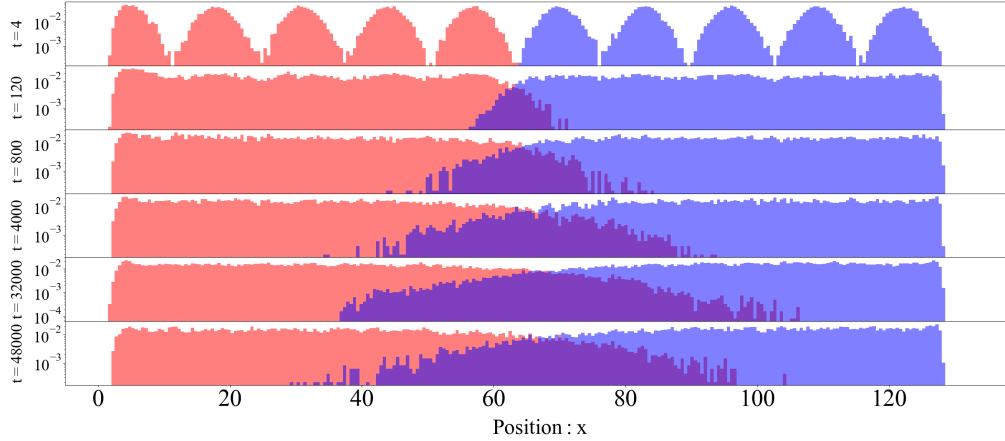


Figure 5.6: Probability distribution function for the CM of the chains *vs* axial position x for a mixture of ring and linear polymer chains (all with $N = 10$ monomers). The tube width is $h = 5$. The free-solution radii of gyration of these molecules are $R_{go}^{lin} = 1.485(1)$ and $R_{go}^{ring} = 0.712(2)$. The 5 linear polymers are initially placed on the left side (red) while the 5 ring polymers are placed on the right side (blue). The initial separation between the centres of mass of the chains is 13, and the length of the (capped) tube is 130. The data is an average over an ensemble of 625 runs and the last five integer values of t (e.g., $t = 4$ means an average over $t = 0, 1, 2, 3, 4$).

The evolution of the interface in Figs. 5.6-5.8 gives us information about the rate at which polymer chains can change position. We note, for instance, that the probability distribution functions are essentially identical at time $t = 120$ and nearly so at $t = 800$. Since the width of the interface at these times is still less than the initial distance between the molecules, very few chains have changed position. The width of the interface at longer times is an indirect measure of the time needed for two polymer chains to change position.

We finish this section with a study of the impact of sealed ends. Figure 5.9 displays data on polymer chain types near the end walls. The system is initially phase-separated, so it takes time for a ring/linear polymer chain to reach the other end. For example, $Z(r)$ is the probability of finding a ring polymer near the wall at the Z (left) end of the tube given that all such polymers start on the right side of the tube. Similarly, $Y(l)$ is the

5.2. MIXTURES OF RING AND LINEAR POLYMER CHAINS

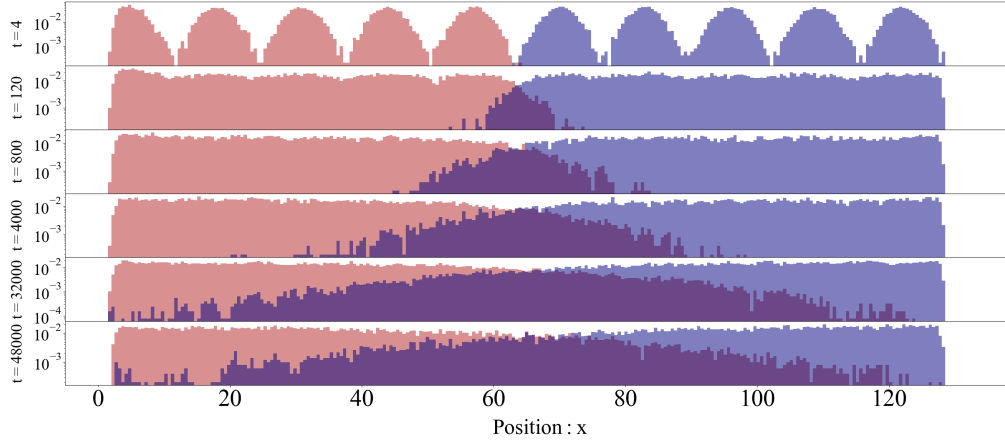


Figure 5.7: Same as Fig. 5.6, now with a tube diameter $h = 5.8$.

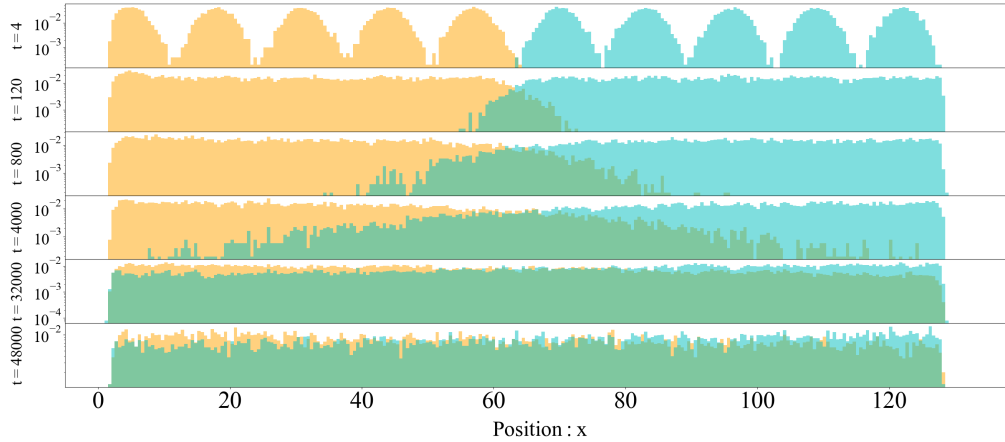


Figure 5.8: Same as Fig. 5.6, now with a tube diameter $h = 8$.

probability of finding a linear polymer near the wall at the Y (right) end of the tube given that all such polymers start on the left side of the tube. In all cases shown in Fig. 5.9, both curves, i.e. $Z(r)$ and $Y(l)$, are growing in the very same manner. This indicates that ring polymers do not appear to be more prone to be at the ends than linear polymers. Clearly

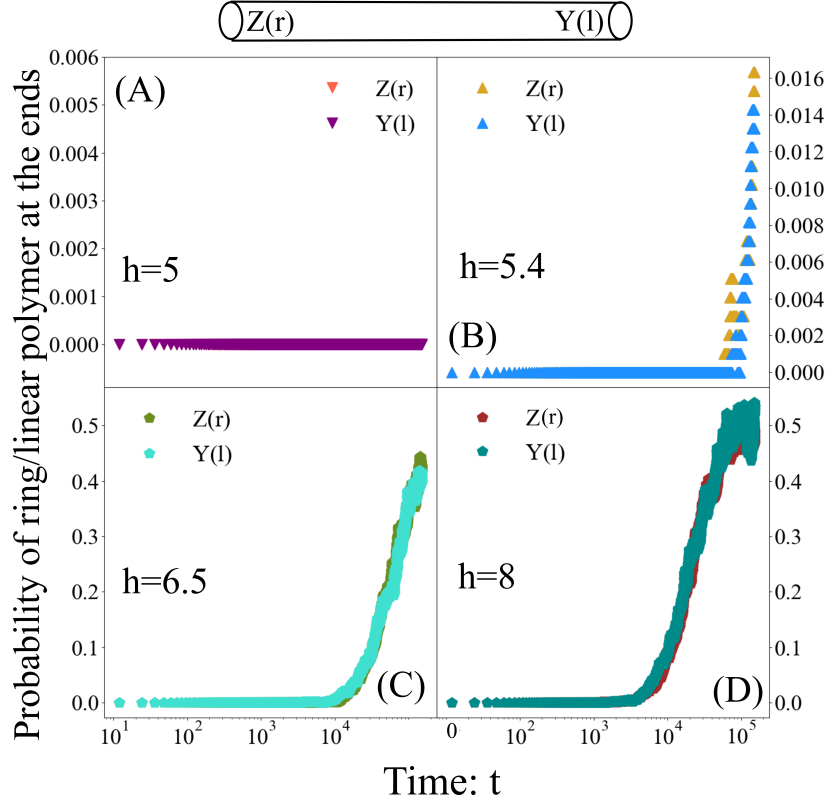


Figure 5.9: Time evolution of the probability of observing a given type of polymer chain near a given end wall. Definitions: $Z(r)$ is the probability of having a (r)ing polymer chain at the Z end of the tube; $Y(l)$ is the probability of having a (l)inear polymer chain at the Y end. The system is like the one used for Fig. 5.6, except that the initial separation between the centres of mass of the chains is 12, and the length of the (capped) tube is 120. The initial phase-separated state implies that $Z(r) = Y(l) = 0$ and $Z(l) = Y(r) = 1$ at time $t = 0$, while $Z(r) = Y(l) = 1/2$ would correspond to perfect mixing. The simulation ensemble size is 500.

though, the tube width very strongly affects the time scale over which SFD-limited chain migration can occur. In the $h = 8$ wide tube case, the simulation reached uniform final states, similar to the last frame of Fig. 5.8.

The different spans and local monomer densities of ring and linear polymer chains

5.3. THE IMPACT OF HYDRODYNAMIC INTERACTIONS

within a tube suggest that there may be intermediate tube diameters h that allow linear chains to pass but prevent ring polymers from swapping positions (or vice versa). We did not observe such situations in our simulations, but we did not systematically scan all possible combinations of N and h . However, if such conditions do exist, their range is likely to be very narrow. Further investigation into phase separations in dilute mixtures of ring and linear polymers is necessary, as this topic remains in its infancy.

5.3 THE IMPACT OF HYDRODYNAMIC INTERACTIONS

In all the simulations presented in this thesis, we used a simple model that ignored hydrodynamic interactions. This is theoretically justified as a first approximation because of the screening effects. However, we must use the LB method to simulate the system in order to insure that the results are indeed similar to those obtained with LD methods. We chose to use a SFD set-up for this test.

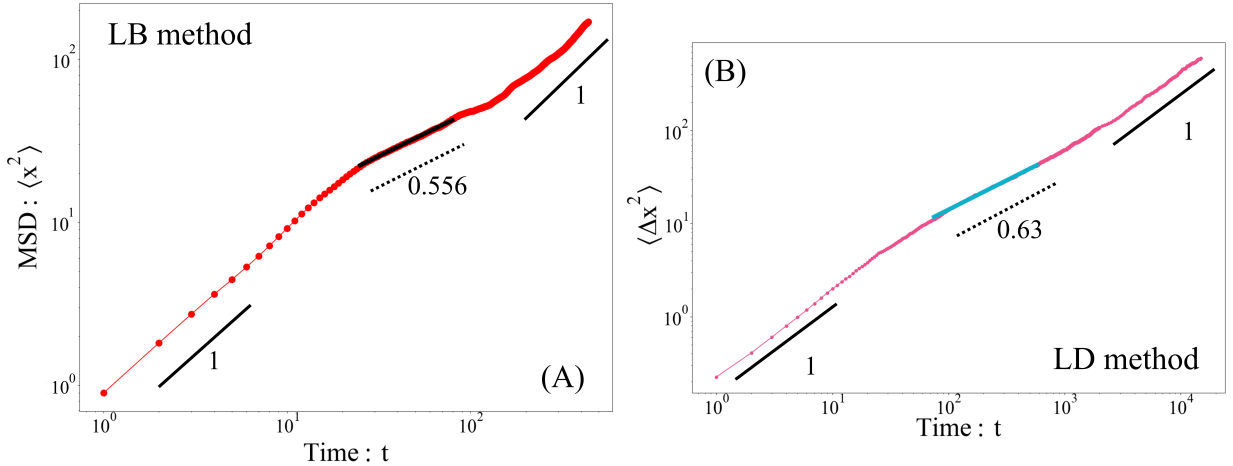


Figure 5.10: MSD vs time t for 5 polymer chains with $M = 10$ monomers each. The tube width is $h = 5$, and the initial separation between adjacent chains is $\ell_o = M + 2$. (A) Lattice Boltzmann simulation results; the ensemble size is 420. (B) Langevin Dynamics simulation results; the ensemble size is 1000.

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We start with a simple test in which 5 linear polymer chains of size $M = 10$ are placed in a narrow toroidal channel of width $h = 5$. According to Eq. 1.23, the number of monomers in one blob is $g(h) \simeq 7$ in this tube, which means that the polymer chains are long enough to undergo proper SFD. This is the same setup as in our SFD project in Chapter 4, the only difference being that the hydrodynamic interactions are activated in the LB simulation. The initial distance between the centres of mass of adjacent chains is $\ell_o = M + 2$. Figure 5.10 shows the time-dependence of the mean square displacement (MSD) of these five chains for both Lattice Boltzmann (left) and Langevin Dynamics (right) algorithms.

We can clearly see two regime changes as time increases, from simple diffusion (slope near unity), to single-file diffusion (slope close to $1/2$), and then the group diffusion regime (slope close to unity again). The SFD exponent is similar in both cases.

Analyzing the LB results further, we note that in the first regime, for $t < 10$, a fit gives an axial diffusion coefficient $D \simeq 0.402(2)$. This value is higher than that predicted by the Rouse model, $D = \frac{1}{M} = 0.1$, as expected for a Zimm chain – see Section 1.2.2.

This shows that the LB method is able to correctly simulate the SFD problem we are interested in. However, this is much more computationally expensive, which is one of the reasons we abandoned the LB approach. The change in diffusion coefficient changes the time scales, but not the fundamental physics.

5.4 DIFFUSIVE SPREADING OF A POLYDISPERSE SOLUTION VIA LANGEVIN DYNAMICS

Our study in Chapter 3 used a simple but efficient Monte Carlo algorithm. However, this approach needs to be validated using a more detailed simulation methodology. In this section, we first use Langevin Dynamics simulations to test a key scaling law we obtained using Monte Carlo simulations. We then examine the assumption that the fragments remain in the initial order after the polymer chain is cut (obviously, this cannot be tested

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using Monte Carlo methods).

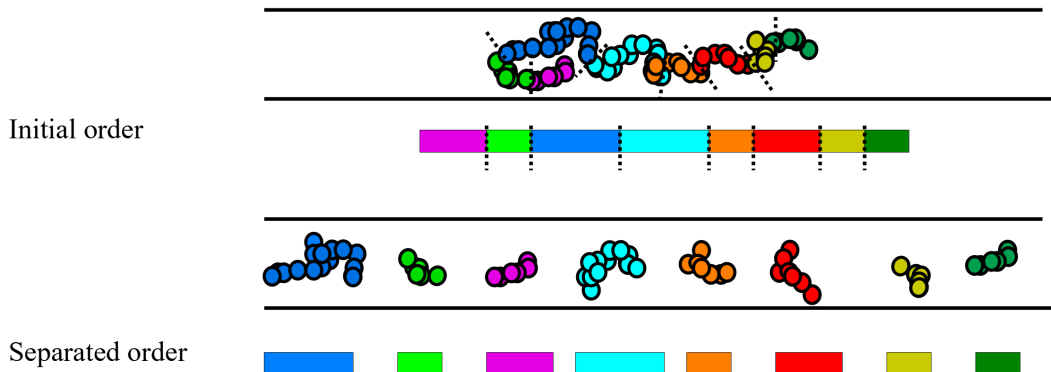


Figure 5.11: Schematic diagram of a polymer chain being cut inside a tube. The order of the fragments in the original molecule is marked by the coloured bars, from left to right. When these segments become well-separated for the first time, the simulation is stopped and the final order is recorded. In this example, the last three fragments on the left end up in the wrong order.

As shown in the upper part of Fig. 5.11, a long polymer chain is initially in equilibrium in a narrow cylindrical channel of width h . At time $t = 0$, $N - 1$ bonds are cut. The N molecular fragments thus created immediately start moving away from each other for entropic reasons. The initial order of these fragments is colour-coded. The third row shows the final state (the fragments are clearly separated). The last row shows the final order, which is not identical to the initial one. We first investigate the time required to achieve the final state and we compare it to the results obtained using Monte Carlo simulations. We then explore the issue of fragments being in the wrong order.

In this first set of Langevin Dynamics simulations, the total size of the polymer chain is $M = 300$ monomers, the tube diameter ranges from $h = 2.5$ to $h = 6$, and the number of fragments N ranges from 3 to 15. The polymer chains are cut into pieces of identical size $m = \frac{300}{N}$ chosen to be large enough to prevent possible positional switching between segments (in other words, the fragments form several blobs). Just like in Chapter 3, we vary both the target separation $\tilde{X}$ and the number of fragments N in this brief study. The

5.4. DIFFUSIVE SPREADING OF A POLYDISPERSE SOLUTION VIA LANGEVIN DYNAMICS

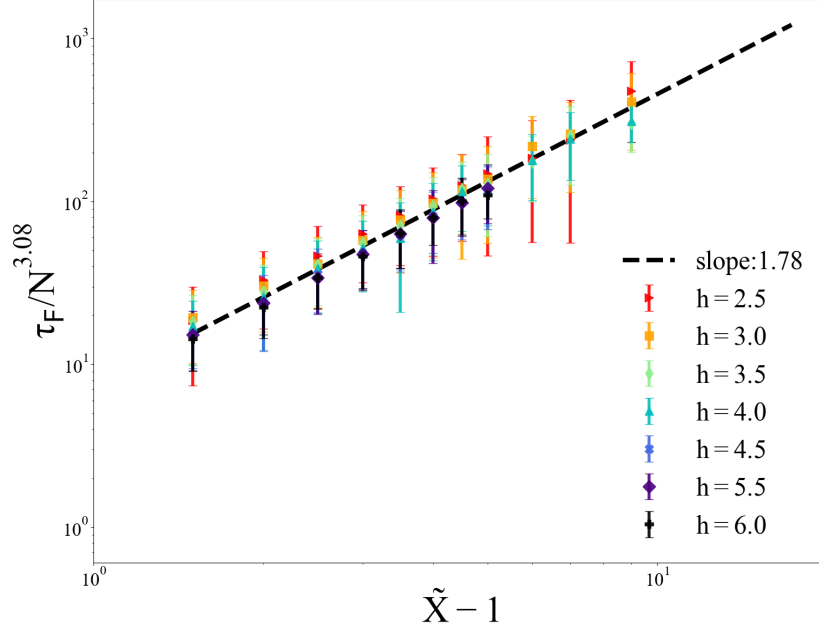


Figure 5.12: Scaled mean spreading time $\tau_F / N^{3.08}$ vs. $\tilde{X} - 1$ for an ensemble of 1 000 monodisperse systems made of N molecules of size $m = \frac{120}{N}$, and various tube diameters h .

results are presented in Fig. 5.12. The dashed line fit is

$$\tau_F = 7.5(8) m (\tilde{X} - 1)^{1.78(5)} N^{3.08(4)} \quad (5.1)$$

These power laws are consistent with what we found in Chapter 3 in the asymptotic limit, i.e. $\tau_F \sim m (\tilde{X} - 1)^2 (N - 1)^3$. This agreement indicates that the very efficient MC method we developed to study this problem is indeed valid.

We now examine the issue of molecular order when the diameter of the tube is not large enough to ensure the formation of blobs and the preservation of the order. Two mechanisms can cause molecular fragments to be in the wrong order after the population has dispersed. The first and most obvious one is SFD: if some of the fragments are less than one blob in size, then they can in principle change position during the dispersion

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process. This situation is symbolically represented by the blue and green fragments at the left end of the chain in Fig. 5.11. The other possibility is for the cuts to be inverted along the tube axis because of the complexity of the polymer conformation; this is symbolically represented by the purple and green fragments (also at the left end of the chain).

To check for such inversions, we cut a polymer chain made of M beads into N blocks and we keep track of the order of these blocks using the sequence $K = \{k_i\}$, where i represents the index of the polymer segment. For example, in the upper part of Fig. 5.11, the order of the polymer sequence is simply $K(t = 0) = \{1, 2, 3, 4, 5, 6, 7, 8\}$; at $t = \tau_F$, i.e. when the blocks are separated, the order is $K(t = \tau_F) = \{3, 2, 1, 4, 5, 6, 7, 8\}$ in this example. We use the disorder parameter S'_p to describe the degree of disorder of the polymer fragments after separation:

$$S'_p = \sum_{i=1}^N |k_i(\tau_F) - k_i(0)| . \quad (5.2)$$

This is simply the sum of the absolute value of the differences between the initial and final orders. We normalize this parameter with the maximum possible value of S'_p for the given N :

$$S_p = \begin{cases} \frac{S'_p}{\max[S'_p]} = \frac{S'_p}{(N^2-1)/2} & N \text{ is odd} , \\ \frac{S'_p}{\max[S'_p]} = \frac{S'_p}{(N^2)/2} & N \text{ is even} . \end{cases} \quad (5.3)$$

As an example, $S'_p = 4$ and $S_p = 4/32 = 1/8$ in Fig. 5.12 since the order of segments 3 and 1 has been switched while $N = 8$. If we average over all 40 320 possible permutations (for $N=8$) of $K(t = 0)$, we obtain $S'_p = 21$ and $S_p = 21/32$.

The normalized parameter S_p will be used to characterize the final sequence $\{k_i(\tau_F)\}$. The initial order $\{1, 2, 3, \dots, N\}$ is preserved (the ideal situation for mapping purposes) if $S_p = 0$. The maximum value $S_p = 1$ means that the order has been reversed, $\{k_i(\tau_F)\} = \{N, \dots, 3, 2, 1\}$, which is obviously very unlikely to happen here. We seek to understand how S_p varies with changes in system parameters, particularly the impact of the number of molecular fragments, N , and the tube diameter, h .

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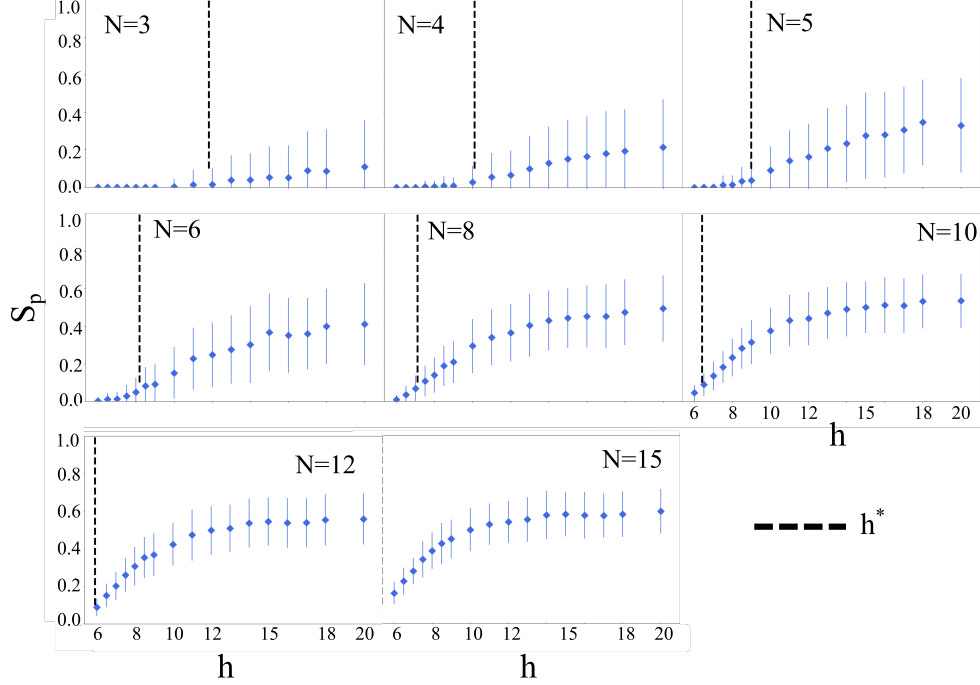


Figure 5.13: Disorder parameter S_p vs tube diameter h for different values of N , the number of pieces obtained by cutting the initial polymer chain. The vertical bars represent the standard deviation of the S_p distributions; each data point is the average of 1000 simulations. All polymer fragments have a size $m = \frac{120}{N}$ in each panel. The vertical dashed lines mark the critical tube diameter h^* defined by Eq. 5.4.

A long flexible polymer with 120 monomers is thus placed in a narrow tube with a diameter h . After the polymer reaches an equilibrium state, it is evenly cut into N pieces. We stop the LD simulation when the distance between all segments is $\tilde{X} = 3$. Figure 5.13 shows that the disorder parameter S_p grows as the tube width h increases or the number of pieces increases (which implies that the uniform fragment size $m = 120/N$ decreases). The larger the fragment size m or the narrower the channel is, the harder it is to change the order of the fragments. We see that $S_p = 0$ if h is very small and N is not too large.

We define the critical tube width h^* as the width that requires precisely m monomers to create a single blob. It is a transformation of Eq. 3.24, representing the critical tube

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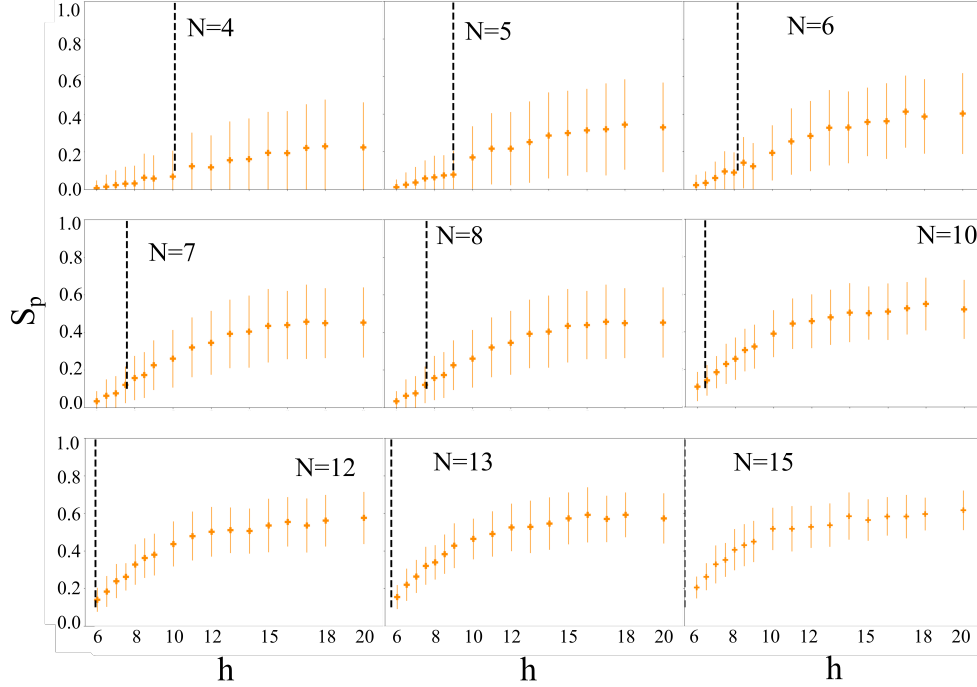


Figure 5.14: Similar to the data in Fig. 5.13, except that the polymer chain was cut randomly.

width as a function of the number of monomers m in one blob:

$$h^* = h(m) = \left(\frac{m}{1.3}\right)^{2/3} + 2 = \left(\frac{120}{1.3N}\right)^{2/3} + 2 \quad (5.4)$$

The value of h^* predicted by Eq. 5.4 is shown as vertical dashed lines in all panels of Fig. 5.13. For tube widths smaller than h^* , the polymer fragments cannot easily switch positions because they form several blobs, which is why we obtain $S_p \simeq 0$. In other words, the time required for fragments to change positions is comparable to, or longer than the separation time τ_F . As the width of the tube increases, the value of S_p reaches a plateau value of $S_p \simeq 0.6$ if $N \geq 10$.

The case of random cuts is the most relevant one for experimental situations. The fragment lengths are now sampled between 3 and $120 - (N - 1) \times 3$, where 3 is chosen

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such that the smallest possible segment equals the minimum separation distance $\tilde{X}$. Figure 5.14 shows our results for randomly cut polymer chains. Clearly, we observe more cases of fragment inversions (larger values of S_p) below the critical tube width h^* . This is to be expected because even below h^* , several fragments are too small to form a single blob. Interestingly, when the x-axis is scaled by the critical tube width h^* , the data for $h \leq h^*$ for different values of N collapses on a universal curve in Fig. 5.15. However, the curves climb to different plateaus for different values of N , approaching the value of S_p expected for random permutations when N is large (for example, this value asymptotically approaches $2/3$ for $N = 9$, which is the exact value determined through numerical calculations by exhaustively enumerating all possible permutations).

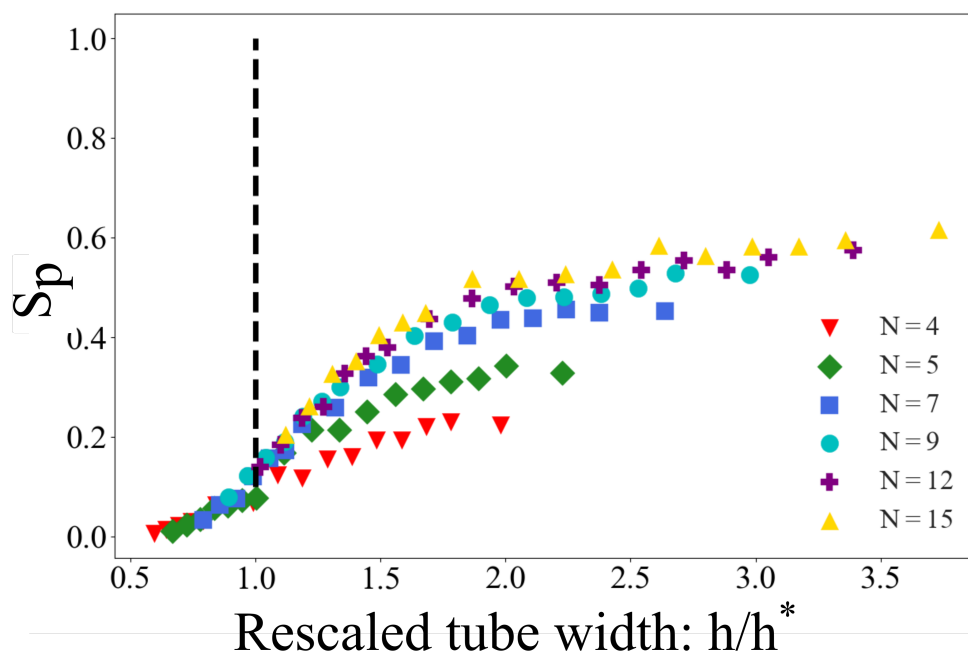


Figure 5.15: Similar to the data in Fig. 5.14, except for the scaled x-axis.

There are many possible extensions to this project, for example, what tube diameter should one use in order to keep the initial fragment order no matter how the polymer chains are cut? Are the ends of the molecule more prone to fragment inversion? Is the

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situation different for stiff polymer chains? And so on and so forth. These issues are good topics for future work.

CONCLUSION

Polymer molecules restricted to narrow channels play an increasingly important role in polymer separation applications. Advancements in technology have now enabled nano-scale experiments with single molecules or dilute solutions in narrow channels. Our focus is directed towards the investigation of dilute polymer solutions problems, as this field remains further explored.

This work was initially motivated by applications concerning single-file diffusion in narrow tubes, and we have broadened this research to address a number of similar issues, both fundamental and practical.

Our work relies on computational models and theoretical analysis. Admittedly, simulations are not as realistic as actual experiments in the laboratory, but we can still claim that simulation studies are useful guides for experimentalists. They are cheaper, faster,

and (generally) easier to carry out. We think that our work could aid in creating innovative experimental designs. To validate the work, promising scenarios should be experimentally tested (and further explored with more detailed simulations).

Our study confirms the crucial role of the blob theory in understanding the physics of long polymer chains in narrow channels. For polymer chains forming a single blob in the channel, this often signifies a system dynamical transition, where physical phenomena notably differ around this subtle boundary. In Chapter 4, for example, the one-blob size threshold distinguishes single-file diffusion from other regimes. In Chapter 2 and Section 5.1, the number of monomers inside a blob determines the nature of the collision. In Section 5.4, the size of this blob primarily dictates the sequence of polymer fragment placement at the end. Those are just a few examples taken from this thesis. Much of our work thus reinforces the importance of the blob theory in this class of problems.

To the best of our knowledge, single-file diffusion of polymer chains has not been fully investigated. Our study successfully identified the diffusion mechanisms for hard particles in periodic or torus systems under conditions prohibiting polymer position exchanges. The complex entropic and excluded volume interactions, along with the polymer chains' physical shape, make it difficult to analyze their switching and entanglement. Nevertheless, the similarities between polymer and hard particle single-file diffusion problems inspired us to ask whether it is possible to simulate the polymer problems using a particle-like lattice model. The latter portion of the SFD project is dedicated to addressing this question, and we have achieved significant results pertaining to our modified Monte Carlo simulation method. We developed a novel Monte Carlo method to simulate the dynamics of long polymer chains in dilute solutions in narrow channels. This approach captures all of the polymer single-file diffusion regimes observed in our Langevin dynamics simulations. The core of both simulation techniques is the polymer switching time, which refers to the typical interval between polymer position exchanges. We established a connection between the free parameters of the two methods. Using Monte Carlo results, we derived an approximate phase diagram that aligns with the Langevin dynamics findings. This work complements fundamental research and offers a method for using simpler simulations to

enhance modelling speed.

Single-file dynamics dominate in quasi-one-dimensional systems, regardless of the presence or absence of external forces. In the case where an external force drives the movement of one of the polymer chains (e.g., if an electric field is used to electrophoresis a polyelectrolyte molecule such as DNA in a dilute solution of uncharged chains), the resulting single-file problem involves polymer-polymer collisions. These collision characteristics—such as their duration, effect on the polyelectrolyte’s velocity, and collision type—provide numerous opportunities for the separation, purification, and manipulation of polymer chains.

The discovery of a gel-like electrophoretic regime is perhaps one of the most important results of the collision project. A modified version of the reptation equation originally proposed by Viovy was used to fit the relative velocities of two polymer chains. Unsurprisingly, the width of the channel plays an important role in this limit. Another significant finding was the variety of collision types achievable, a topic of considerable interest over the past twenty years for the development of two- and three-dimensional separation systems. The J-U and U-U collisions are the most significant types of collision for two linear polymer chains. We presented a detailed study of the parameters that can be used to characterize a collision. By analyzing the velocities at the inflection points, we can discern U-U or J-U collisions and, consequently, hypothesize regarding the probable duration of the collision. Depending on the system parameters, the consequences of a particular collision may be completely different.

The collision type was further explored in another project (Section 5.1) where we introduced ring polyelectrolytes instead of linear ones. The ring topology of the field-driven polymer leads to a U-O collision instead of a U-U collision, resulting in a collision time that can greatly exceed that of a linear-linear collision. Surprisingly, the U-O collision rate is not as low as we may have expected. The U-O collisions, along with the ring’s high monomer concentration in this channel environment, may provide a novel way to differentiate between the ring and linear polymer chains.

In another SFD scenario, we explored the issue of the passive separation or spreading of

disconnected polymer fragments (i.e., molecular fragments resulting from the fragmentation of a long polymer chain in a narrow channel). This project was inspired by DNA mapping studies. In most cases, it is assumed that the polymer fragments are large enough that they cannot exchange positions along the channel. This system is thus a typical example of single-file dynamics. The main aim was to explore the timing and footprint of the final separation, and the effects of the random nature of the fragmentation. The number of fragments was found to be the main parameter that affects the final state of the system. We formulated a scaling law that defines how the final separation time is influenced by the system parameters, and we noted an excellent agreement between theoretical predictions and asymptotic simulation results.

In addition, we found that the order of the fragments also greatly affects the final separation time; the larger the fragments near the ends of the fragment distribution, the longer the separation time. The randomness of the fragment size distribution and the location of the larger fragments thus have a significant impact on the final separation. We proposed a torque-like dimensionless parameter Z to describe the relative size of the end fragments. We showed that the larger the value of Z , which correlates with having larger fragments near the ends, the longer the separation time of the fragments in the tube. Nevertheless, this correlation does not markedly exceed systematic random noise, indicating a limitation in the influence of fragment sequences on separation time. Furthermore, for a specified fragment sequence and parameter Z , a general fitting function we propose can characterize the distribution of separation times. These two factors greatly contribute to understanding the separation time in such systems.

We study a more subtle problem in Section 5.4: indeed, it seems inevitable that some of the fragments generated by the restriction enzymes might exchange position, especially if the tube diameter is increased or some fragments are small. Since this cannot be studied using a Monte Carlo algorithm (the details of the polymer conformation being central to this issue), we used Langevin dynamics simulations to investigate the problem of Chapter 3 with more details. Our findings confirm that fragments that can form at least 1-2 blobs in the channel are not likely to change position during the spreading process. Smaller

fragments, however, may end up at the wrong place and hence lead to wrong mapping conclusions. Again, this is another indication of the importance of the blob theory in this class of problems.

Outlook

As mentioned earlier, we used some fairly simple (and yet very computationally intensive) simulation methods to model the various problems we investigated. Applying more sophisticated numerical methods to the same problems, such as the lattice Boltzmann method employed in section 5.4, would be an improvement. However, there are many more directions for future research throughout the thesis, not limited to improving simulation complexity and testing the whole phase space of free parameters.

Chapter 5 can be seen as a sort of proposed extension of our work. In Section 5.1, we explored ring linear collisions as distinct from the topic of Chapter 2. This type of collision requires further investigation; for example, how would the external force and tube diameter influence the U-O collision rate? What would change if we were to replace the uncharged linear polymer with a star polymer, or with any other polymer that might increase/decrease the chances of being dragged by the ring polyelectrolyte? We observed that the relative velocities of the small ring polyelectrolytes are quite different from those of the large ring polyelectrolytes. This feature could potentially be useful in separation.

In Section 5.4 we discussed the final order of polymer fragments after they reach the final state where they can be visualized. One of the most important extensions here would be to explore the range of tube diameters that can prevent tube segments from becoming disordered. In fact, perhaps more interestingly for physicists, we might ask: which part of the polymer molecule is more prone to fragment inversion, the middle or the ends? Intuitively, the latter seems more likely. Should the experimentalist trust the sequences at the ends in mapping experiments? As it stands, however, our polymer chains are

flexible; what would be the effect of having a stiff polymer (which would be more DNA-like)? Are larger fragments more likely to retain their original sequence than smaller ones? These questions should be considered in future work, although they would require large computational resources.

Unfortunately, we did not obtain any clear conclusion in Section 5.2, largely because of the limited size of the system and the restricted combination of parameters we were able to explore. It's not a bad idea to continue looking for ring-rich regions in sealed tubes. Complete phase separation may be difficult to achieve, but locally separated phases might be achievable.

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APPENDICES

A

SUPPLEMENTARY MATERIAL

A.1. LINEAR POLYMER CHAINS IN FREE SOLUTION

This appendix serves as supplementary material and presents simulations for polymer sizes, relaxation time, and diffusion coefficient. This includes data for linear and ring polymer chains, both in free solution and in tubes. These basic results have been occasionally referred to and used in our manuscripts.

A.1 LINEAR POLYMER CHAINS IN FREE SOLUTION

This short section provides some basic information on polymer chain size and relaxation time in free solution. We used this information in the thesis, but did not show the actual graphs and simulation data. Note that these results are for Rouse chains (no hydrodynamic interactions) in the presence of excluded volume interactions.

We use the autocorrelation function for the polymer chain radius of gyration R_g to estimate its relaxation time. The autocorrelation function $C(t)$ is defined by:

$$C(t) = \frac{\langle (R_g(t) - \langle R_g \rangle) (R_g(0) - \langle R_g \rangle) \rangle}{\langle (R_g(0) - \langle R_g \rangle)^2 \rangle} \quad (\text{A.1})$$

where the averages are over all conformations. The value of $C(t)$ decays approximately exponentially with time, as shown in Fig. A.1. The relaxation time of the polymer chain is thus obtained by using the fitting function $C(t) = e^{-(t/\tau_R)}$ over a time range where the data is approximately linear on a semi-log plot.

Theory says that in free solution, the radius of gyration and relaxation time of long flexible Rouse chains with $N \gg 1$ beads should scale like:

$$\begin{aligned} R_{go}(N) &\sim N^\nu \\ \tau_R^\circ(N) &\sim \frac{R_{go}^2}{D(N)} \sim N^{1+2\nu} \sim R_{go}(N)^{2+1/\nu} \end{aligned} \quad (\text{A.2})$$

where $D(N) \sim 1/N$ and the Flory exponent [36] is $\nu \simeq \frac{3}{5}$ in three dimensions. In other words, we should have

$$R_{go}(N) \sim N^{3/5} ; \quad \tau_R^\circ(N) \sim N^{11/5} \sim R_{go}^{11/3} . \quad (\text{A.3})$$

Our simulation data give a value of ν that decreases with N , slowly converging towards

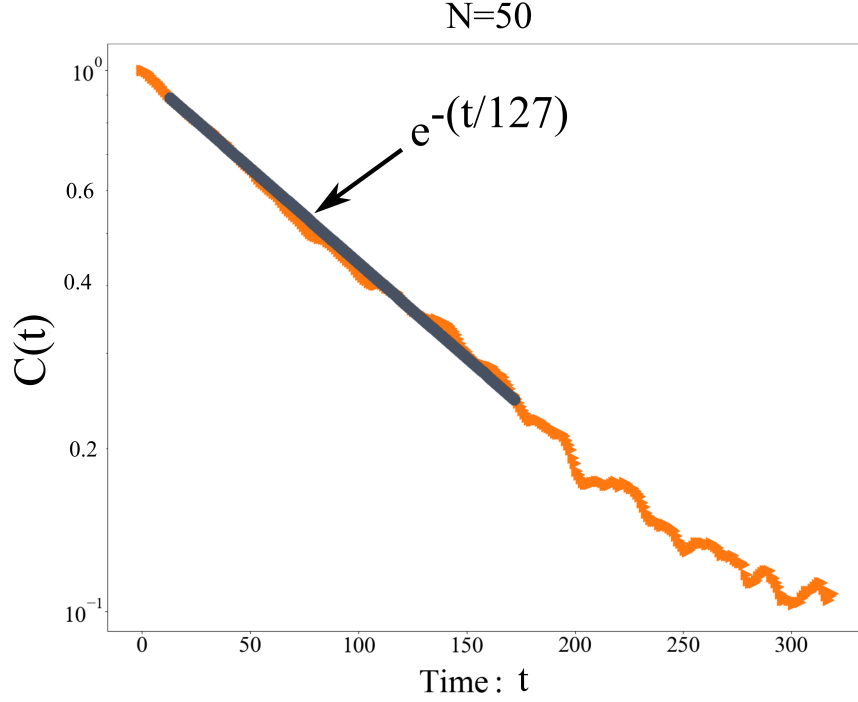


Figure A.1: Semi-log plot of the radius of gyration auto-correlation function $C(t)$ vs time t for an ensemble of 1000 linear polymer chains of size $N = 50$ in free solution. The fit gives a relaxation time $\tau_R = 127.0(4)$.

the asymptotic theoretical value (see Fig. A.2). In the range $50 \leq N \leq 150$, the fit gives

$$\begin{aligned}
 \mathbb{R}_g^\circ(N) &= 0.409(8) (N - 1)^{0.626(4)} \\
 \tau_R^\circ(N) &= 0.012(3) (N - 1)^{2.4(2)} \\
 &= 0.62(1) \mathbb{R}_g^\circ(N)^{3.5(2)} .
 \end{aligned}
 \tag{A.4}$$

A.2. LINEAR POLYMER CHAINS IN TUBES

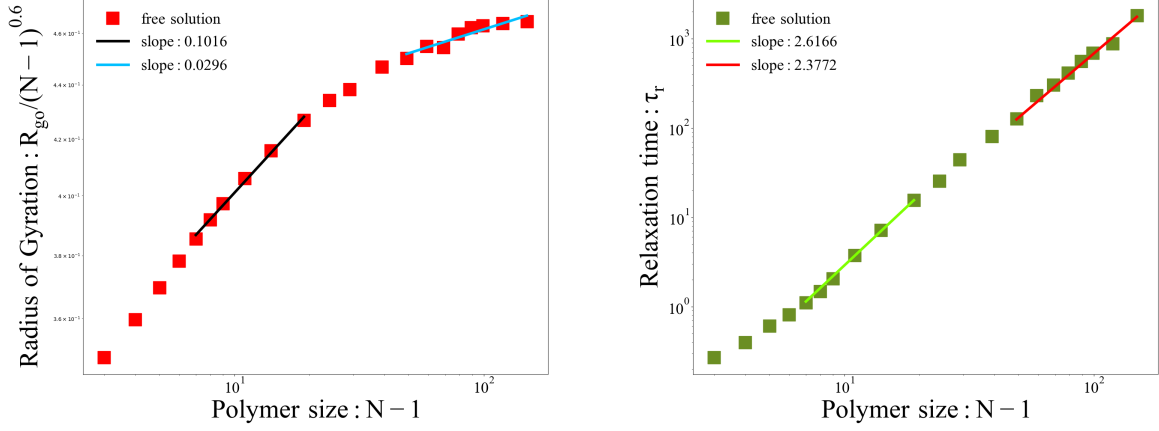


Figure A.2: Left panel: The rescaled radius of gyration of linear polymer chains in free solution divided by $(N - 1)^{0.6}$. Right panel: The relaxation time of linear polymer chains in free solution, with fitting exponents 2.62(4)(green solid line) for short chains ($8 \leq N \leq 20$) and 2.3(2)(red solid line) for longer chains ($50 \leq N \leq 150$).

For shorter chains ($8 \leq N \leq 20$), however, our fit gives

$$\begin{aligned}
 R_g^\circ(N) &= 0.319(2) (N - 1)^{0.702(3)} \\
 \tau_R^\circ(N) &= 0.0069(7) (N - 1)^{2.62(4)} \\
 &= 0.49(2) R_g^\circ(N)^{3.8(2)} .
 \end{aligned}
 \tag{A.5}$$

A.2 LINEAR POLYMER CHAINS IN TUBES

When a long polymer chain is squeezed into a narrow tube, both the average axial size of its conformations and its relaxation time are strong functions of the diameter of the tube, h . Therefore, we now need to fit the radius of gyration and relaxation time with the additional parameter h . Moreover, the scaling laws associated with N also undergo modifications.

But first, we must confirm that the diffusion coefficient of our Rouse chains still scales

A.2. LINEAR POLYMER CHAINS IN TUBES

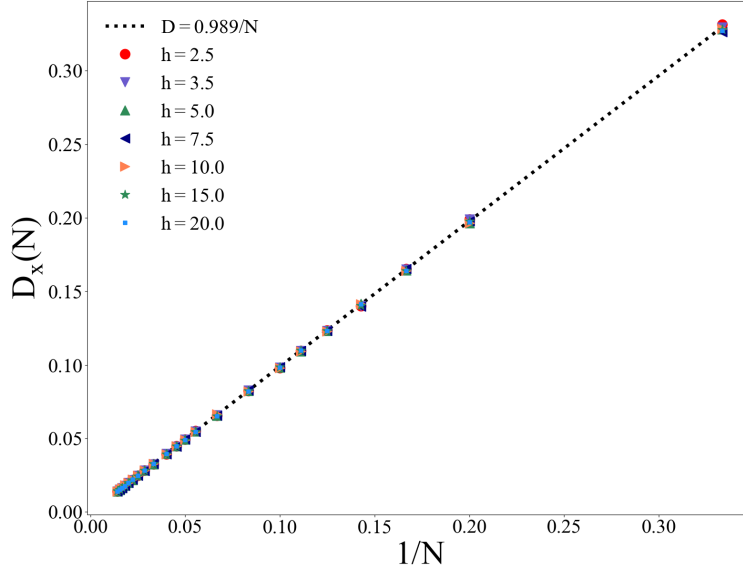


Figure A.3: Polymer chain axial diffusion coefficient D_x vs the inverse of the polymer size $1/N$. The dotted line is the fitting function: $D_x = 0.989(1)/M$.

as $D(N) \sim 1/N$ in tubes. Figure A.3 shows our simulation results for the axial diffusion coefficient $D_x(N, h)$. We first notice that D_x is not a function of the tube width h , as expected. The slope confirms that the diffusion coefficient is indeed proportional to $1/N$, with the same coefficient we found in free solution shown in Fig. 2 in Chapter 4.

According to polymer physics, a long chain confined to a narrow tube with a diameter $h \ll R_g^\circ(N)$ forms a series of $M(N, h) = N/g$ non-overlapping and undisturbed (i.e., self-avoiding walks) blobs of size $\simeq h$ (see Fig. 1.4) containing $g(h)$ monomers each, with $R_g^\circ(g) \simeq h$. The resulting axial radius of gyration of this string of blobs is:

$$R_{gx} \simeq Mh = \frac{N}{g} h \quad (\text{A.6})$$

Since $R_g^\circ(g) \sim N^\nu$, this blob construction predicts the following scaling laws

$$g \sim h^{1/\nu} ; \quad R_{gx} \sim N h^{1-1/\nu} . \quad (\text{A.7})$$

A.2. LINEAR POLYMER CHAINS IN TUBES

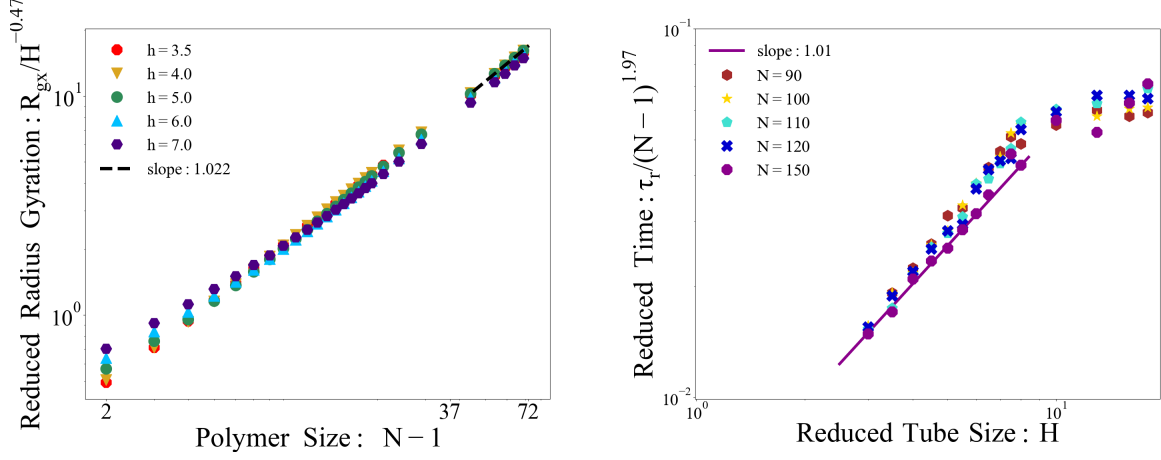


Figure A.4: Left panel: Rescaled axial radius of gyration R_{gx} of linear polymer chains in tubes *vs* number of segments, $N - 1$. The data points for different tube widths $h = H + 2$ collapse for long chains. Right panel: Rescaled relaxation time τ_r of linear polymer chains in tubes *vs* effective tube width $H = h - 2$. The fitted slope 1.01(5) was obtained using the $N = 150$ data set.

If the blobs are large enough (which means that $g \gg 1$), the Flory exponent $\nu = \frac{3}{5}$ is expected to be valid, and this then predicts

$$g \sim h^{5/3} ; \quad R_{gx} \sim N h^{-2/3} . \quad (\text{A.8})$$

The relaxation time of a confined Rouse chain of $M = N/g$ blobs is [1]

$$\tau_R \simeq M^2 \tau_g = \left(\frac{N}{g} \right)^2 \tau_g, \quad (\text{A.9})$$

where τ_g is the blob relaxation time. Equation A.2 indicates that the latter scales as

$$\tau_g \sim g^{1+2\nu} . \quad (\text{A.10})$$

Finally, we obtain

$$\tau_R \sim N^2 g^{2\nu-1} \sim N^2 h^{2-1/\nu} . \quad (\text{A.11})$$

A.2. LINEAR POLYMER CHAINS IN TUBES

If the blobs are large enough so that $\nu = \frac{3}{5}$, we obtain

$$\tau_R \sim N^2 h^{1/3} . \quad (\text{A.12})$$

As our blobs generally contain $8 \leq g \leq 20$ monomers, we must use Eq. A.5 to make predictions here (in other words, we must use $\nu \simeq 0.699$ instead of the asymptotic value $\nu = 3/5$). We also use the effective diameter $H \equiv h - 2$ instead of h since the bead size is not negligible. This leads to the approximate scaling laws from the equations above:

$$g \sim H^{1/0.699(3)} \sim H^{1.431(6)}$$

$$R_{gx} \simeq MH = (N/g) H \sim NH^{-0.431(6)}, \quad (\text{A.13})$$

$$\tau_g \sim g^{2.62(4)} .$$

In addition, according to Eq. A.9, we now have:

$$\tau_R \sim N^2 g^{0.62(4)} \sim N^2 H^{0.89(6)} \quad (\text{A.14})$$

Our simulation results are consistent with these predictions; as shown in Fig. A.4, the fits give:

$$\begin{aligned} R_{gx}(N, H) &= 0.22(1) \quad (N-1)^{1.02(2)} \quad H^{-0.47(3)} , \\ \tau_R(N, H) &= 0.0051(3) \quad (N-1)^{1.97(2)} \quad H^{+1.01(5)} . \end{aligned} \quad (\text{A.15})$$

A long polymer chain inside a tube resembles a rod composed of interconnected blobs of size h . The length of this 'rod' relates to the span of the polymer chain, as we discussed in Chapter 2. Using Eq. A.15 and the polymer span discussion in Chapter 2 (below Eq. 25), the number of monomers in a blob can be estimated to be

$$g(H) \approx 1.3 H^{3/2}. \quad (\text{A.16})$$

Equation A.16 is crucial in our work as it gives the minimum number of monomers needed to form a blob for a given tube diameter h . Indeed, many of our projects have shown that the size of the blob is critical for phase changes in system behaviour.

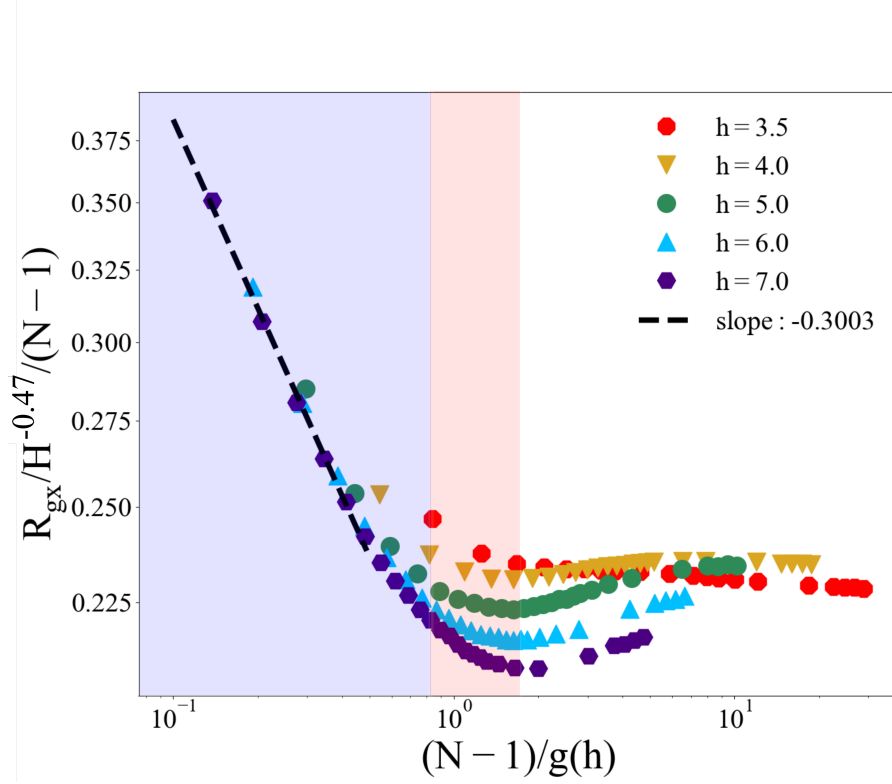


Figure A.5: Rescaled version of the left panel of Fig. A.4. The blue background indicates that the polymer chain is not yet long enough to form a blob in the tube, while the red area indicates that we have approximately, 1-2 blobs.

In order to demonstrate the importance of the blob size, Figure A.5 presents a rescaled plot of the left panel of Fig. A.4. When the polymer chains are too short to form a blob in a given tube, the case is essentially indistinguishable from free chains (or $H \rightarrow \infty$). This implies that polymer chains with fewer than $g(H)$ monomers are not fully constrained in a tube of width H , which is the blue area in Fig. A.5. The dashed line fit in the figure is consistent with the fact that $R_g \sim (N-1)^{0.699}$ for short chains (see Eq. A.5). However, for polymer chains that *can* form $\gtrsim 2$ blobs, we observe that the data quickly converges toward a plateau – see the white zone in Fig. A.5. The transition zone is in red.

A.3 RING POLYMER CHAINS IN TUBES

In Section 5.1, we investigated the physics of collisions between charged ring polyelectrolytes and neutral linear polymer chains. The only difference between these two types of polyelectrolytes is their topological shape. This short section examines the conformations of ring polymers in tubes.

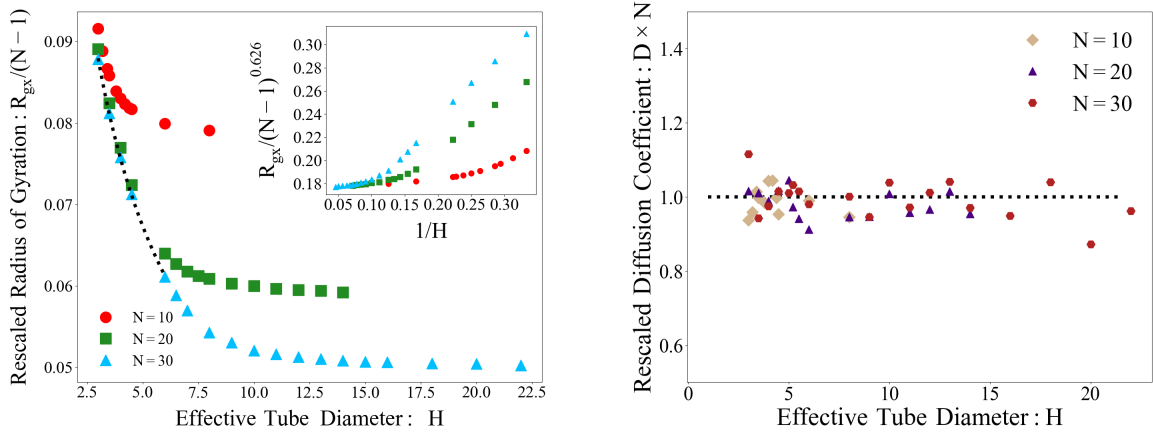


Figure A.6: Left: Rescaled radius of gyration of three different ring polymers *vs* the effective tube diameter $H = h - 2$. The dotted line shows the fitted scaling law $H^{-0.522}$, which is valid for $H \leq 5.5$. Right: Scaled diffusion coefficient for ring polymers *vs* the effective tube diameter H . The horizontal dotted line shows the theoretical prediction for Rouse chains.

The left panel of Fig. A.6 shows how the axial radius of gyration R_{gx} of the three different rings varies with the effective tube width $H = h - 2$ under confinement. In the blob regime (narrow tubes), the data can be fitted using the following form:

$$R_{gx}(N, H) = 0.156(1) (N - 1)^{1.0(1)} H^{-0.522(3)} \quad H \leq 7.5. \quad (\text{A.17})$$

These scaling laws are very similar to what we found for linear chains – see Eq. A.15.

As the right panel of Fig. A.6 shows, the diffusion coefficient of the ring polymer chains also satisfies the predictions of the Rouse model, i.e. $D = 1/N$ in our units.

In the large tube diameter limit, we can treat the chain as being in a free solution situation. The inset of Fig. A.6 shows that in the large H limit, the data converges

A.3. RING POLYMER CHAINS IN TUBES

towards the scaling law

$$R_g(N) \simeq 0.165(3)(N - 1)^{0.626} \quad H \gg R_g. \quad (\text{A.18})$$

The pre-factor is close to half of what we found for linear chains in Eq. A.5. The scaling exponent 0.626 is directly obtained from Eq. A.4 (ring and linear polymer chains share the same Flory exponent).

B

SUPPLEMENTARY DATA FOR CHAPTER 3

This Appendix contains the plots that we defined as "data not shown" in Chapter 3.

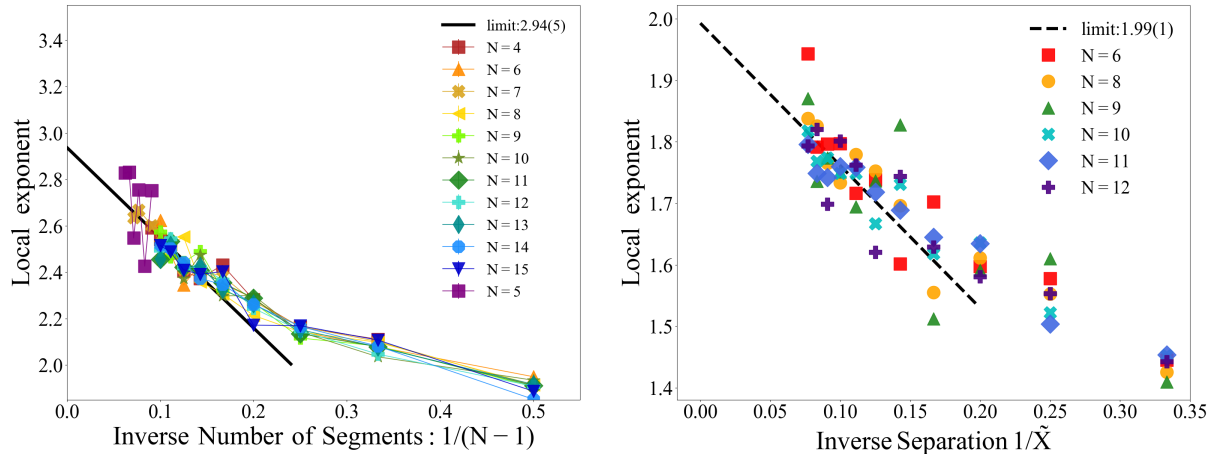


Figure B.1: Asymptotic scaling limits for $N \rightarrow \infty$ and $\tilde{X} \rightarrow \infty$, for monodisperse systems. The related discussion is on page 69, below Eq. 3 in Chapter 3.

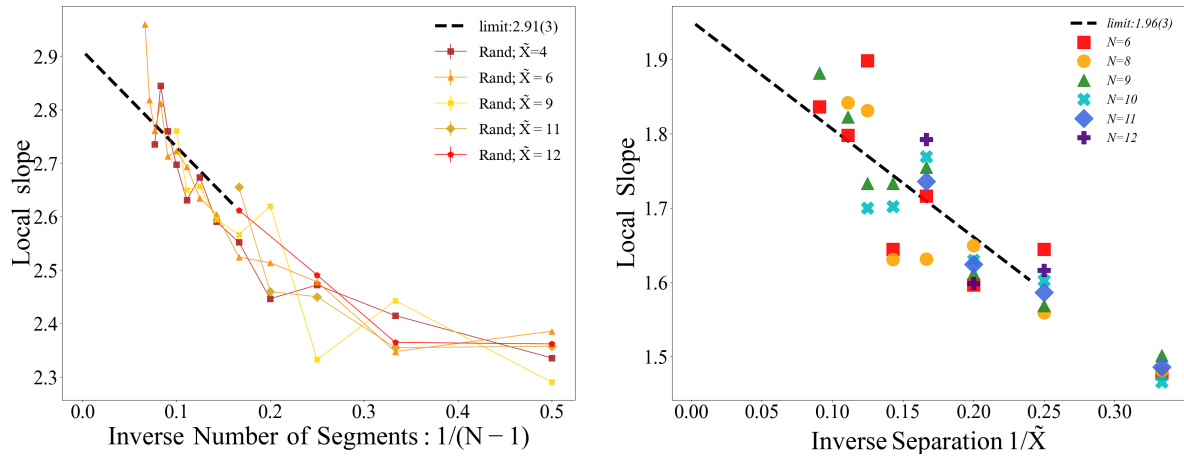


Figure B.2: Asymptotic scaling limits for $N \rightarrow \infty$ and $\tilde{X} \rightarrow \infty$, for random systems. The related discussion is on page 73, above Eq. 14 in Chapter 3.

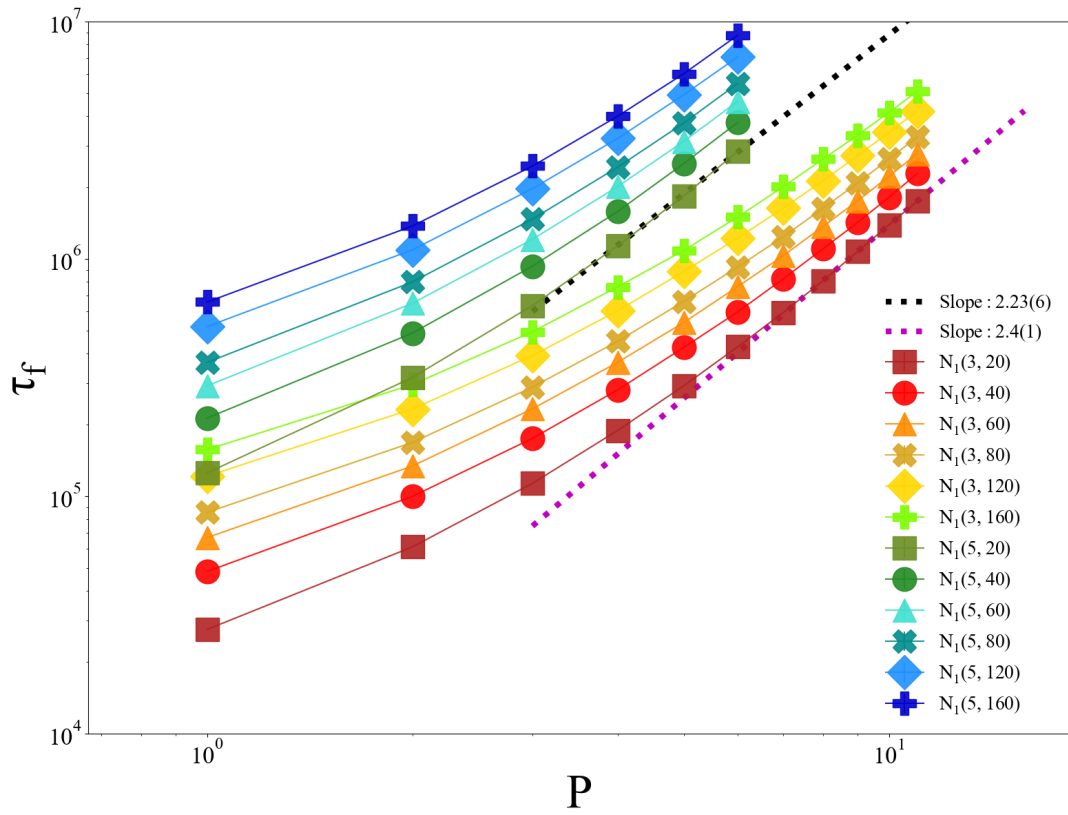


Figure B.3: Separation time τ_f vs parameter P for multiple systems. The two dashed lines are fits for $P \gg 1$. The related discussion is on page 72, a few lines below Fig. 4, in Chapter 3.

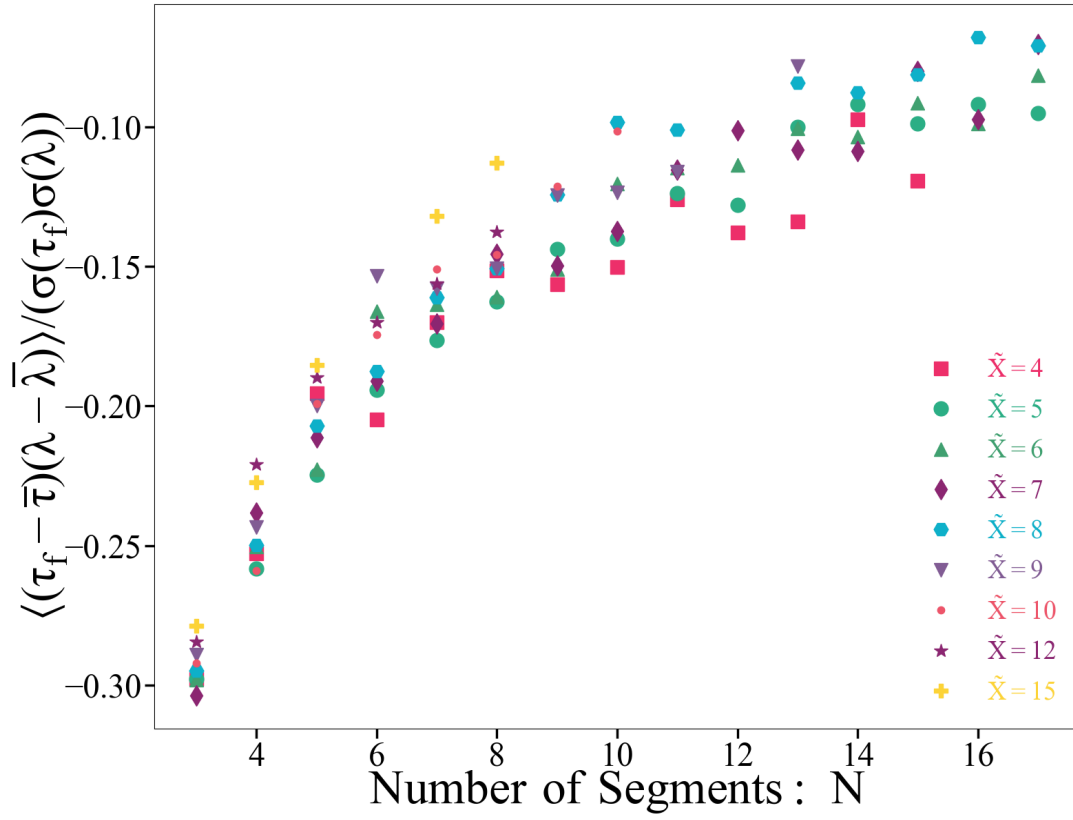


Figure B.4: Cross-correlation function between τ_f and λ vs N . The related discussion is on page 74, at the middle of the page.

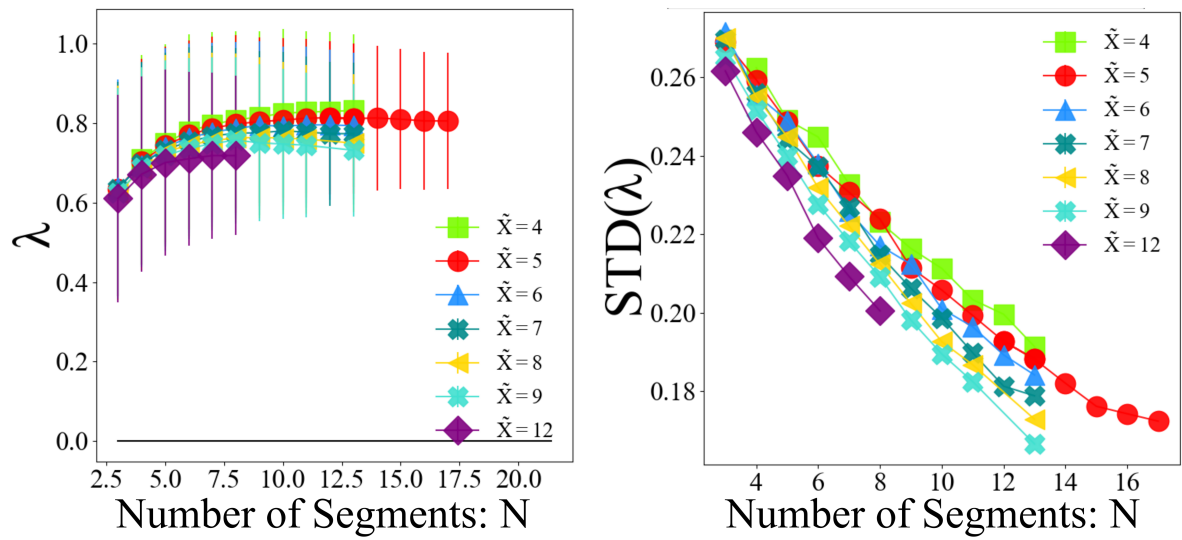


Figure B.5: Left: The data points give the mean value of λ , while the vertical error-bars represent the corresponding standard deviation. Right: the standard deviation of the distribution of λ values. The related discussion is on page 74, above Eq. 17, in Chapter 3.