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# From Semi-Flexible Polymers to Membranes: Anomalous Diffusion and Reptation

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**Abstract.** — The dynamics of semi-flexible polymers and membranes is discussed. The effect of thermal undulations on both the transversal and longitudinal Mean Square Displacement (MSD) of a tagged “monomer” is studied in free polymers and membranes. The two MSDs are found to be proportional to one another, and behave as  $\sim t^{3/4}$  for polymers and  $\sim t^{2/3}$  for membranes on the short time scale. The longitudinal motion is shown to be linked to the dynamics of fluctuations of the projected length (area) of the polymer (membrane). We demonstrate how, at long times, these fluctuations lead to reptation motion of the polymer (membrane) in the longitudinal direction. We generalize this approach to investigate the motion of a membrane between two plates and a polymer in a tube. The latter problem is used as a model for polymer motion in semi-dilute solutions in which the persistence length is longer than the entanglement length. Such systems are not suitable for the classical reptation model of de-Gennes and of Doi and Edwards, which was designed for chains that are flexible on the entanglement distance. The reptation diffusion coefficient and relaxation times that we obtain have the same scaling with chain length  $L$  as in the classical reptation model, but differ greatly in factors that are dependent on the ratio of persistence length to entanglement length. We also discuss the diffusion of a tagged “monomer” under imposed tension and liquid crystalline order.

## 1. Introduction

The dynamics of flexible polymer chains in entangled networks is well described by the reptation model (henceforth referred to as classical reptation) developed some years ago by de Gennes [1] and by Doi and Edwards [2] and discussed by many others [3]. In such networks, which appear both in melts and in semi-dilute or concentrated solutions, the chain segments between two consecutive entanglement points (along a tagged chain) are flexible. The classical reptation model thus assumes that  $L_e \gg L_p$ , where  $L_e$  is the (real space) distance between two such entanglement points, and  $L_p$  is the persistence (Kuhn) length. The reptation is viewed as resulting from the motion of loop-like defects along the tube contour (the so-called “primitive path”). This motion is described by the “bead and spring” Rouse model, because the chain is rather flexible between its nearest entanglement points.

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There are, however, semi-flexible polymer networks in which the persistence length is so long that  $L_p \gtrsim L_e$ . One well known example, of particular biological importance, is the actin-filament network, which is part of the cytoskeleton of plasma membranes [4-8]. Here  $L_p \sim 4 - 17 \mu\text{m}$  (depending on the method of estimation), whereas  $L_e \sim 1 \mu\text{m}$ . Other examples emerge in the field of giant cylindrical micelles. For instance, the CPCI/Sal system at 5% micelle volume fraction is a solution of equilibrium, worm-like, micelles in which  $L_p \simeq L_e \simeq 150 \text{ \AA}$  [9]. At higher volume fractions ( $\lesssim 30\%$ ) the system remains isotropic and  $L_e < L_p$ . Here, knowledge of the chain diffusion coefficient and relaxation times is extremely important for understanding the viscoelastic properties. We believe that the dynamics of these networks cannot be described by the classical reptation model, even though others have attempted to explain experimental data using it [5]. Nevertheless, reptation in an actin-filament network has been directly observed using fluorescence video microscopy [5]. Viscoelastic measurements in the worm-like micellar systems [9] also indicate the existence of reptation. Clearly, some other mechanism that leads to reptation motion is present, allowing for the polymer to diffuse and for stress to relax, and we describe such a mechanism here. Another description of reptation in such networks has been presented by Semenov [10], and we compare the two approaches.

Membrane bilayers are the 2-Dimensional (2-D) analog of the semi-flexible polymers [11]. These are semi-flexible surfaces that are also characterized by a persistence length  $L_p$  (usually denoted as  $\xi_\kappa$ ), which was first recognized by de Gennes and Taupin [11, 12]. On length scales shorter than  $L_p$  the membrane undulates with an elastic bending energy penalty. On length scales much longer than  $L_p$ , however, the membrane is effectively flexible and its shape can fluctuate with no energy cost. These characteristics are similar to those of semi-flexible polymers. The persistence length is related to the bending modulus  $\kappa$ . In membranes, where  $\kappa$  has dimensions of energy, the persistence length was found to be exponential in the bending modulus [11, 12]

$$L_p \simeq a \exp \left[ \frac{4\pi}{3} \frac{\kappa}{k_B T} \right] \quad (1)$$

where  $a$  is a molecular length (basically the bilayer thickness); the numerical factor  $\frac{4\pi}{3}$  is somewhat sensitive to the form of calculation [11]. In semi-flexible polymers,  $\kappa$  has a dimension of energy $\times$ length and the persistence length is linear in  $\kappa$  [13-15]

$$L_p \simeq \frac{\kappa}{k_B T}. \quad (2)$$

The situation  $a \ll L_p$  is thus common in membrane systems and less common in polymer systems (with  $a$  taken to be the cross-section diameter). Nevertheless, as described above, a large number of polymers (or polymer-like objects) have a persistence length large enough to enable studying undulations of wavelengths  $\lambda$  in the regime  $a \ll \lambda \ll L_p$ . We will show that these undulations are extremely important for the reptation motion discussed earlier.

To understand how these concepts are connected, consider first a membrane sheet of a size smaller than  $L_p$ . A surfactant molecule belonging to the membrane, or a particle attached to it (*e.g.*, a protein molecule), can move in the transversal (normal) direction only by means of collective membrane motion, the so-called thermal undulations. This motion should therefore be slower than that of a free particle. Indeed, it has been recently shown that such a particle will perform *anomalous subdiffusion* in which its Mean Square Displacement (MSD) increases as  $\sim t^{2/3}$  [16]. This motion becomes slower as the rigidity of the membrane increases. This anomalous diffusion leaves its fingerprint in the dynamic structure factor [16] as a stretched exponential decay  $S(q, t) \sim e^{-(\Gamma_q t)^{2/3}}$  (where  $\mathbf{q}$  is the scattering wave vector and  $q = |\mathbf{q}|$ ), which

has been experimentally detected [17]. Similar behavior, a transversal MSD increasing as  $\sim t^{3/4}$ , and a stretched exponentially decaying dynamic structure factor  $S(q, t) \sim e^{-(\Gamma_q t)^{3/4}}$ , have been experimentally observed [6, 7] and theoretically predicted [18] for semi-flexible polymers.

Thermal undulations of the membrane also imply that the projected area, *i.e.* the projection of the true membrane area onto the base planar surface, is smaller than the true area. The mean value of the projected area, or that of the excess area, has been a useful concept for understanding the physics of membranes [11]. It is equivalent to the (mean) end-to-end distance in the physics of semi-flexible polymers, which we shall refer to here as the projected length. An interesting question, which has not been considered thus far, concerns the static and dynamic effects of undulations on the *fluctuations* of the projected length (area) of the polymer (membrane) around its mean value. Such fluctuations are not necessarily small (relative to the mean) since these objects are not macroscopic. We show here how the dynamics of these fluctuations is related to the dynamics of thermal undulations. For example, a point on the polymer (membrane) performs anomalous diffusion in a direction parallel to the polymer (membrane) mean axis (plane), as well as in a transversal direction. At long times, these excess length (area) fluctuations cause a *reptation* motion of the polymer (membrane) in the longitudinal (parallel) direction. Although this contribution to the longitudinal translation diffusion coefficient is at best marginal for free polymers, it becomes dominant when the coherent translation is inhibited, as with polymers in entangled networks. For membranes, such a possibility is less obvious, however, membrane reptation is a very new concept and contributes to the (parallel) translational diffusion coefficient. A closely related problem is the transport of vesicles through pores or channels whose radius is smaller than the mean radius of the vesicles. Such transport can occur only by means of membrane thermal undulations. Our later discussion of a planar membrane sandwiched between two parallel walls can provide greater insight into this problem.

Direct visualization of microscopic motion in membrane and polymer systems has recently been made possible by using enhanced video-microscopy techniques [5, 7, 19, 20]. Thus the mean-square displacement of a molecule (particle) attached to a membrane (polymer) can be detected. For example, the reptation of actin filaments (in a network) was directly observed using fluorescence microscopy, and the so-called curvilinear diffusion coefficient of a polymer along its tube contour was directly measured [5]. Moreover, it is now possible to manipulate such objects using various tools such as micropipettes [21, 22], optical tweezers [19] or magnetic tweezers [7]. It would be interesting to explore the diffusion of polymers and membranes with additional conditions and constraints. Two such constraints are considered here. The first is the effect of imposing tension on the membrane (polymer). The second is the excluded volume constraints exerted on a membrane in the liquid crystalline lamellar phase. Interesting new behaviors and crossovers emerge.

This paper is organized as follows. We start (Sect. 2) by introducing previous work on the dynamics of (free) membranes and semiflexible polymers, with particular attention to the effect of thermal undulations on the transversal diffusion of a tagged particle. In Section 3 we show how these thermal undulations affect the projected length (area) fluctuations. This concept is first used then to describe the reptation of free polymers and membranes. Later we generalize the approach to describe the reptation of semi-flexible polymers in strongly entangled networks. In Section 4 we consider the effects of tension and liquid crystalline-excluded volume constraints on the diffusion of a tagged monomer. Our conclusions are summarized in Section 5.

## 2. Free Polymers and Membranes in Equilibrium

2.1. MEMBRANES. — We consider a free fluid membrane of linear size  $L \lesssim L_p$  that is floating (in equilibrium) in the solvent. For simplicity we have assumed that the membrane terminates with edges. For self-assembled membranes this is usually energetically unfavorable and either macroscopic sheets or finite vesicles emerge instead. In this section we will focus, however, on the short time behavior that is sensitive only to the short wavelength undulations and not to the large scale shape. Thus it does not matter if we consider a membrane with edges, a vesicle, a membrane in a lamellar ( $L_\alpha$ ) phase, or a piece of membrane in the sponge ( $L_3$ ) phase.

The undulations of a membrane piece can be described by the Helfrich bending free-energy [23], evaluated for small deformations  $\nabla h \ll 1$ ,

$$H = \frac{1}{2} \kappa \int d^2 \rho (\nabla^2 h(\rho))^2 = \frac{1}{2L^2} \sum_{\mathbf{k}} \kappa k^4 h_{\mathbf{k}} h_{-\mathbf{k}}, \quad (3)$$

where  $\rho$  is a 2-D vector on the base (planar) surface,  $\kappa$  is the bending modulus, and  $h_{\mathbf{k}} = \int d^2 \rho e^{i\mathbf{k} \cdot \rho} h(\rho)$  is the 2-D Fourier transform of the local displacement field  $h(\rho)$ . The term  $\nabla^2 h(\rho)$  is the mean curvature written for small deformations. Using the equipartition theorem we can obtain from equation (3) the equilibrium spectrum of undulations

$$\langle h_{\mathbf{k}} h_{-\mathbf{k}} \rangle = \frac{k_B T L^2}{\kappa k^4} \quad (4)$$

Thus undulation amplitudes increase rapidly with increasing wavelengths (decreasing wavenumbers  $k$ ), since such wavelengths are less expensive in bending energy.

As usual for linear response, the time-dependent correlation function of  $h_{\mathbf{k}}(t)$  decays exponentially from its equilibrium value

$$\langle h_{\mathbf{k}}(t) h_{-\mathbf{k}}(0) \rangle = \frac{k_B T L^2}{\kappa k^4} e^{-\omega(k)t} \quad (5)$$

To find the relaxation frequency  $\omega(k)$ , the hydrodynamics of the solvent surrounding the membrane and its coupling to the membrane motion have to be considered. These have been calculated using the Navier-Stokes equations with inertia being neglected [24, 25], because of the short (mesoscopic) length scales involved. A simple alternative approach to this is made possible using the Oseen hydrodynamic interaction tensor [2]. This tensor, also derived from the Navier-Stokes equations, linearly relates the velocity vector of a point particle in position  $\mathbf{r}$  in the solvent to a force acting on another point particle in position  $\mathbf{r}'$ , with boundary conditions taken at infinity. These boundary conditions are proper for studying the linear dynamics of membrane undulations. Although the membrane is not flat, and this does alter the hydrodynamic interaction between two distant points on the membrane, this modification only leads to a non-linear contribution to the dynamics. Thus the hydrodynamic interaction between two such distant points on the membrane is almost the same as if the membrane connecting them were absent. Because the elastic force and motion are primarily transversal for small undulations, only the diagonal part of the Oseen tensor is relevant. This is given by [26]

$$\Lambda(\rho) = \frac{1}{8\pi\eta\rho}, \quad (6)$$

where  $\eta$  is the viscosity. The Langevin equation of motion for  $h(\rho, t)$  becomes

$$\frac{\partial h(\rho, t)}{\partial t} = - \int d^2 \rho' \Lambda(|\rho - \rho'|) \kappa \nabla_{\rho'}^4 h(\rho', t) + \zeta(\rho, t), \quad (7)$$

where  $\zeta(\boldsymbol{\rho}, t)$  is white noise. Fourier transforming equation (7) leads to

$$\frac{\partial h_{\mathbf{k}}(t)}{\partial t} = -\omega(k)h_{\mathbf{k}}(t) + \zeta_{\mathbf{k}}(t), \quad (8)$$

where the relaxation frequency  $\omega(k)$  is given by [24, 25]

$$\omega(k) = \frac{\kappa k^3}{4\eta} \quad (9)$$

$\omega(k)$  is thus simply a product of the energy spectrum  $\kappa k^4$  and the 2-D Fourier transform  $\Lambda(k) = 1/4\eta k$  of the hydrodynamic interaction  $\Lambda(\boldsymbol{\rho})$ . The spectrum of the white noise Fourier component  $\zeta_{\mathbf{k}}(t)$  follows from the fluctuation-dissipation theorem

$$\langle \zeta_{\mathbf{k}}(t)\zeta_{-\mathbf{k}}(t') \rangle = 2k_{\text{B}}T\Lambda(k)\delta(t-t'). \quad (10)$$

Equation (8) is easily solved to give equation (5).

Using the Langevin equation (8), the transversal MSD, is expressed as [16] (Appendix A)

$$\langle (\Delta h(t))^2 \rangle \equiv \langle (h(t) - h(0))^2 \rangle = \frac{1}{2\pi^2} \frac{k_{\text{B}}T}{\kappa} \int \frac{d^2k}{k^4} (1 - e^{-\omega(k)t}). \quad (11)$$

The lower and upper limits of these integrals are  $k = \pi/L$  and  $k = \pi/a$ , respectively. (The circular boundary conditions used here imply that all tagged points within the membrane are equivalent, resulting with no dependence on the lateral coordinate  $\boldsymbol{\rho}$  [27].) For times  $\frac{\eta a^3}{\kappa} \ll t \ll \frac{\eta L^3}{\kappa}$  the integration limits can be set to zero and infinity respectively, and the integral is evaluated to give [16]

$$\langle (\Delta h(t))^2 \rangle \simeq 0.17 \left[ \left( \frac{k_{\text{B}}T}{\kappa} \right)^{\frac{1}{2}} \frac{k_{\text{B}}T}{\eta} t \right]^{\frac{2}{3}} \quad (12)$$

From equation (11) we can see that the MSD saturates at the equilibrium value (which is denoted by omitting the argument  $t$ )

$$\langle (\Delta h)^2 \rangle = 2 \langle h^2 \rangle \simeq \frac{1}{2\pi^3} \frac{k_{\text{B}}T}{\kappa} L^2 \quad (13)$$

as required from ergodicity. The saturation occurs effectively with times  $t \gtrsim \tau_s$ , where  $\tau_s$  is obtained as  $1/\omega$  ( $q = \pi/L$ ) *i.e.*

$$\tau_s \simeq \frac{4}{\pi^3} \frac{\eta L^3}{\kappa} \quad (14)$$

Note, however, that if the membrane is entirely free to move in the solvent, the absolute transversal MSD, in contrast to the one measured relative to the base surface (and discussed previously), will not saturate, but rather will crossover at  $t \sim \tau_s$  to a linear time dependence that is controlled by the diffusion of the center of mass.

An interesting implication, resulting from this analysis, concerns the dynamic structure factor  $S(q, t)$  (where  $q$  is the scattering wavenumber), which was discussed in references [16, 28]. The  $t^{2/3}$  increase of the MSD (Eq. (12)) was found to lead to a stretched exponential decay,  $S(q, t) \sim e^{-(\Gamma_q t)^{2/3}}$ . This relaxation has been observed in sponge and powder lamellar phases with large wavenumbers  $q$  that are sensitive to single membrane dynamics [29]. The good quantitative agreement between theory and experiment provides a sound basis for the whole approach.

2.2. SEMI-FLEXIBLE POLYMERS. — Next we consider a semi-flexible polymer of length  $L \lesssim L_p$ , which is the 1-D membrane analog. Two well known examples, of particular biological importance, are actin filaments, where  $L_p \simeq 4 - 17 \mu\text{m}$  [5,30], and microtubules, where  $L_p \simeq 6 \text{ mm}$  [22]. The bending energy here can be described in a similar way to equation (3), with a 1-D integral replacing the 2-D integral. The scalar membrane displacement is replaced by a 2-D vector  $\mathbf{h}(x) = (h^{(y)}(x), h^{(z)}(x))$  (perpendicular to  $x$ ) describing the displacement in the two (assumed equivalent) transverse directions [31]. Thus

$$H = \frac{1}{2} \kappa \int dx \left( \frac{\partial^2 \mathbf{h}}{\partial x^2} \right)^2 = \frac{1}{2L} \sum_k \kappa k^4 \mathbf{h}_k \cdot \mathbf{h}_{-k}, \quad (15)$$

where  $\mathbf{h}_k = \int dx e^{ikx} \mathbf{h}(x)$ . Here the bending modulus  $\kappa$  has dimensions of energy $\times$ length. The undulation correlation functions for the two transverse directions are similar to equation (5)

$$\langle h_k^{(\alpha)}(t) h_{-k}^{(\beta)}(0) \rangle = \delta_{\alpha\beta} \frac{k_B T L}{\kappa k^4} e^{-\omega(k)t}, \quad (16)$$

but the relaxation frequency  $\omega(k)$  is different. The 1-D Fourier transform of the Oseen interaction (Eq. (6)) is

$$\Lambda(k) = \int_a^L \frac{\cos(kx)}{4\pi\eta x} dx, \quad (17)$$

(where  $a$  is basically the cross-section diameter playing the role of a short wavelength cutoff), which is roughly independent of  $k$ . This is in contrast with the  $1/k$  divergence for the 2-D, membrane, case. More accurately,  $\Lambda(k)$  diverges logarithmically as  $ka \rightarrow 0$  and  $\omega(k)$  is asymptotically [18]

$$\omega(k) \simeq \frac{\kappa k^4}{4\pi\eta} \ln[1/ka]. \quad (18)$$

The long-range hydrodynamic interaction thus has only a *marginal* effect on the relaxation frequency because of the one-dimensional nature of the problem. The transversal MSD is the sum of contributions from the two equivalent (but independent) directions  $y$  and  $z$  and becomes

$$\langle (\Delta \mathbf{h}(t))^2 \rangle = \frac{4k_B T}{\pi\kappa} \int_{\pi/L}^{\pi/a} \frac{dk}{k^4} (1 - e^{-\omega(k)t}). \quad (19)$$

In evaluating the integral in equation (19), the logarithmic dependence of  $\omega(k)$  is incorporated to the leading order. The asymptotic behavior for times  $\frac{\eta a^4}{\kappa} \ll t \ll \frac{\eta L^4}{\kappa}$  is evaluated to give [18,32]

$$\langle (\Delta \mathbf{h}(t))^2 \rangle \simeq 0.082 \left\{ \ln \left[ \frac{\kappa \ln \left( \frac{L}{\pi a} \right) t}{4\pi\eta a^4} \right] \left( \frac{k_B T}{\kappa} \right)^{\frac{1}{3}} \frac{k_B T}{\eta} t \right\}^{\frac{3}{4}} \quad (20)$$

As for membranes, the MSD saturates, as it should, at the equilibrium amplitude mean square difference

$$\langle (\Delta \mathbf{h})^2 \rangle = 2 \langle \mathbf{h}^2 \rangle = \frac{2}{45} \frac{k_B T}{\kappa} L^3. \quad (21)$$

In equation (21) the numerical prefactor has been evaluated by exact summation over Fourier modes (using  $k = p\pi/L$  - where  $p$  is a natural number - and  $\sum_{p=1,2,\dots} p^{-4} = \pi^4/90$ ), rather than

the integral approximation in equation (19). The saturation occurs effectively on times  $t \gtrsim \tau_s$ , where

$$\tau_s = \frac{4}{\pi^3} \frac{\eta L^4}{\kappa \ln[L/\pi a]}. \quad (22)$$

The subdiffusion described by equation (20) has been found [18] to lead to a stretched exponential relaxation of the dynamic structure factor  $S(q, t) \sim e^{-(\Gamma_q t)^{3/4}}$  with a relaxation rate  $\Gamma_q \sim \left(\frac{k_B T}{\kappa}\right)^{1/3} \frac{k_B T}{\eta} q^{8/3}$ . This was first observed in a dynamic light scattering experiment [6]. More recently, this evolution has been observed in real space by optical videomicroscopy [7, 20].

So far we have dealt with the transverse motion in either polymers or membranes, summarizing previously obtained results. Next we will use these results and consider the evolution of longitudinal fluctuations that are coupled to the transverse motion and cause a reptation (creeping) motion of both polymers and membranes.

### 3. Projected Length (Area) Fluctuations and Reptation Motion of Semi-Flexible Polymers (Membranes)

**3.1. REPTATION OF FREE POLYMERS.** — We will begin with a discussion of semi-flexible polymers, since the concept of reptation is probably more relevant to them. When a polymer undulates, its arc length is conserved, and therefore the projected length, *i.e.* the end-to-end distance, is smaller than its actual length. Since undulations are random, the projected length also fluctuates around its mean value. We will show that these fluctuations allow the polymer to reptate along its baseline axis. If the polymer is free to move in the solvent, this mechanism will simply add to the conventional translational diffusion of a stiff rod. The reptation we discuss becomes more important in semi-dilute solutions, in the “large” concentration regime where the entanglement length is *shorter* than (or equal to) the persistence length. Here the translational diffusion of a persistence segment is inhibited. Nevertheless, the whole polymer can still diffuse by moving excess length, somewhat similarly to the well known reptation process of flexible polymers, where the persistence length is however much shorter than the entanglement length. The classical reptation model is sometimes used for interpreting results even when the opposite limit holds [5], which is obviously not adequate. The following calculation for the projected length fluctuations will provide a method of determining the correct curvilinear diffusion coefficient that should replace the Rouse diffusion coefficient used in the classical reptation model. Once the curvilinear diffusion coefficient is found, we can proceed to calculate other observables, such as the long time diffusion coefficient, as was done for the classical reptation model.

**3.1.1. Projected Length Fluctuations.** — We first have to calculate the dynamics of projected length (end-to-end distance) fluctuations. We shall start with the usual Monge gauge relation between the true length  $L$  and the projected length  $L_o(t)$ . The latter is a stochastic time-dependent variable, as a result of the undulations. Thus

$$L = \int_0^{L_o(t)} dx \sqrt{1 + \left(\frac{\partial \mathbf{h}(x, t)}{\partial x}\right)^2} \simeq L_o(t) \left(1 + \frac{1}{2} \overline{\left(\frac{\partial \mathbf{h}(x, t)}{\partial x}\right)^2}\right), \quad (23)$$

where we have defined, for convenience, the spatial (not to be confused with the ensemble) average

$$\overline{\left(\frac{\partial \mathbf{h}(x, t)}{\partial x}\right)^2} = \frac{1}{L_o(t)} \int_0^{L_o(t)} dx \left(\frac{\partial \mathbf{h}(x, t)}{\partial x}\right)^2 \quad (24)$$



Both  $\overline{(\partial\mathbf{h}(t)/\partial x)^2}$  and  $L_o(t)$  are stationary stochastic variables that are related by the above constraint (with  $L$  kept constant). Performing an ensemble average in equation (23) (exactly summing over Fourier modes, using  $\sum_{p=1,2,\dots} 1/p^2 = \pi^2/6$ ), and inverting the result to the same order in  $k_B T/\kappa$ , we obtain a known expression [13,14] for the mean projected length  $\bar{L}_o \equiv \langle L_o \rangle$

$$\bar{L}_o \simeq L \left( 1 - \frac{1}{6} \frac{k_B T}{\kappa} L \right). \quad (25)$$

The fluctuations in the projected length are calculated from equation (23) by solving for  $L_o(t)$  to first order in  $(\partial\mathbf{h}/\partial x)^2$ . The time-dependent mean square (MS) difference of the projected length is obtained as

$$\langle (\Delta L_o(t))^2 \rangle \equiv \langle (L_o(t) - L_o(0))^2 \rangle = \frac{L^2}{4} \left\langle \left[ \overline{\left( \frac{\partial\mathbf{h}(x,0)}{\partial x} \right)^2} - \overline{\left( \frac{\partial\mathbf{h}(x,t)}{\partial x} \right)^2} \right]^2 \right\rangle. \quad (26)$$

The ensemble average in equation (26) is calculated in Appendix B. We find that it can be *exactly* related to the transverse MSD calculated in Section 2, and we obtain

$$\langle (\Delta L_o(t))^2 \rangle = \frac{k_B T}{2\kappa} L \langle (\Delta\mathbf{h}(2t))^2 \rangle, \quad (27)$$

where  $\langle (\Delta\mathbf{h}(t))^2 \rangle$  is given by equations (19) or (20). (Note however, that the argument on the right hand side is  $2t$ .) This implies, for example, that at short times,  $\langle (\Delta L_o(t))^2 \rangle$  is roughly

$$\langle (\Delta L_o(t))^2 \rangle \simeq \text{const } L \left( \frac{k_B T}{\kappa} \right)^{5/4} \left( \frac{k_B T}{\eta} t \right)^{3/4} \quad (28)$$

The latter is valid for  $t \ll \tau_s$  where  $\tau_s$  is given by equation (22). As  $t \rightarrow \infty$  ( $t \gtrsim \tau_s/2$  effectively), the projected length MS difference saturates, as it should, at the equilibrium value

$$\langle (\Delta L_o)^2 \rangle = 2 \langle (\delta L_o)^2 \rangle = \frac{1}{45} \left( \frac{k_B T}{\kappa} \right)^2 L^4 \quad (29)$$

where we have defined  $\langle (\delta L_o)^2 \rangle \equiv \langle (L_o - \bar{L}_o)^2 \rangle$ . Note that we express the right hand side of equations (27-29) using  $L$  rather than  $\bar{L}_o$ , since the difference between the two is no longer important (to the given order of the calculation) [33].

**3.1.2. Reptation.** — The fact that the projected length fluctuates implies that both ends of the polymer move at random, with equal probability to jump to either side, left or right. As a first approximation, the two ends of the polymer can be assumed to move independently. It takes some time, of order  $\tau_s$ , for one end to know about a hop of the other end, during which the first end can explore its phase space. These dynamic fluctuations can thus cause a longitudinal *reptation* (or creeping) motion of the polymer (along its baseline axis), since excess length can be transmitted by these fluctuations from one end of the polymer to the other. When, for example, the left end makes a jump to the right, this creates a local excess length “defect” [1] on the left end which, when transmitted to the right end after the time  $\tau_s$ , causes the whole polymer to move to the right [34].

In a linear mode analysis of polymer conformations (*e.g.*, as in the Rouse model of flexible chains [2]) the lowest,  $q = 0$  mode, which corresponds to the translation of the center of mass, only gives the usual Stokes translational diffusion coefficient of the object as if it was rigid (*i.e.*, coherent translation). A complete treatment of the reptation motion therefore requires a non-linear theory that couples between different modes. Nevertheless, we shall estimate the diffusion coefficient associated with this reptation motion on time scales  $t \gg \tau_s$ , without requiring such a description. A more refined calculation, which still involves a linear-type description but is made self-consistent with our calculation of the projected length fluctuations, is described in Appendix C. Here we shall use only our intuition, which does correctly yield all scaling properties, but cannot give the precise numerical prefactors; these will be taken from Appendix C.

From the physical picture described above, clearly, the basic hopping length of the random walk that the polymer makes at long times is basically  $\sim \langle (\Delta L_o)^2 \rangle^{1/2}$ , which is calculated above. The time interval during which these hoppings occur is the saturation time  $\tau_s$ . Thus the reptation diffusion coefficient of a free semi-flexible, rod-like polymer, can be simply estimated as  $D_{\text{rep}} \simeq \langle (\Delta L_o)^2 \rangle / \tau_s$  [35]. In the more refined estimate (Appendix C) we confirm this result and obtain a more accurate numerical prefactor. The reptation diffusion coefficient is then

$$D_{\text{rep}} = \frac{\ln[L/\pi a]}{15\pi} \frac{(k_B T)^2}{\eta \kappa} = \frac{k_B T \ln[L/\pi a]}{15\pi \eta L_p} \quad (30)$$

(where  $L_p$  is the persistence length, Eq. (2)).

Interestingly,  $D_{\text{rep}}$  is effectively independent of  $L$  (to within a logarithm). This is a counter-intuitive result, and is due to the fact that both the grid spacing  $\langle (\Delta L_o)^2 \rangle^{1/2}$  and the hopping time  $\tau_s$ , scale as  $L^4$ , which cancels out this dependence. Note, however, that the overall longitudinal diffusion coefficient is the *sum* of  $D_{\text{rep}}$  found above, and the conventional rod translation diffusion coefficient [2]  $D_{\parallel} \simeq k_B T \ln(L/a) / 2\pi \eta L$  which is associated with a coherent translation (only the latter is obtained from the  $q = 0$  mode in a linear theory). Therefore, since the scope of our discussion is  $L \lesssim L_p$ , the contribution of reptation motion to the overall diffusion is at best marginal (when  $L \simeq L_p$ ) and negligible when  $L \ll L_p$ .

**3.2. REPTATION OF SEMI-FLEXIBLE POLYMERS IN ENTANGLED NETWORKS.** — We now consider a network of polymers (*i.e.* a semi-dilute solution) with the following properties: first, the persistence length  $L_p$  is much longer than the monomer scale  $a$ ,  $L_p \gg a$ , as always assumed; second, we now consider (contrary to the previous discussion) polymers that are much longer than their persistence length,  $L \gg L_p$ ; third, and most important,  $L_p$  is longer than, or of the order of, the entanglement length  $L_e$ , which means that there is at least one entanglement per persistence (Kuhn) segment. To summarize, we assume that  $a \ll L_e \lesssim L_p \ll L$ .

We *define* the entanglement length  $L_e$  as the mean distance on which a monomer is free to move without collisions with monomers of neighboring chains [36]. (This definition has been used also for the regime  $L_e \gg L_p$  [2].) We are not concerned here with the precise dependence of  $L_e$  on the monomer volume fraction  $\phi$ . However, knowledge of this parameter is needed to make our results useful. A way to circumvent this difficulty has been offered by Käs *et al.* [5], who, by using video microscopy to view the single actin polymer motion in the network, were able to estimate the length  $L_e$ . They determined that  $L_e \sim \phi^{-0.5 \pm 0.15}$ . Comparing their data for  $L_e$  to data for the network mesh size  $\xi_m$  [5] (*i.e.* the mean distance between adjoining polymers) obtained from permeation measurements, we find, within experimental error, that  $L_e \simeq \xi_m$ . Several theoretical predictions for the concentration dependence of  $L_e$  (which, unfortunately do not agree with one another) appear in the literature [2, 37–39].

A low bound for  $L_e$  presumably should be the mesh size  $\xi_m$  (which contradicts, however, the result of Semenov [37],  $L_e \sim \xi_m^{6/5}/L_p^{1/6}$ ). In the limit  $L_p \gg \xi_m$ , for which, on the local scale, the system appears like a system of stiff rods,  $\xi_m$  has been found [40] to scale with the polymer volume fraction  $\phi$  as  $\xi_m \sim \phi^{-1/2}$ . The latter scaling behavior has been confirmed in actin by fluorescence photobleaching measurements of monomer diffusion [6].

Because of the entanglement constraints, a persistence length segment cannot move as a whole. Nevertheless, excess length is able to diffuse from one persistence unit to another, and so through the whole polymer, resulting again in a reptation motion of the whole polymer. This is somewhat similar to the classical reptation model [1,2]. The latter, however, *cannot be applied* straight forwardly here since it holds only in the limit  $L_p \ll L_e$ . To use the concepts of the reptation model, we first must replace the Rouse dynamics, which are used to describe the curvilinear diffusion of a flexible chain, by a new calculation. Our results will be conveniently expressed in terms of the persistence length  $L_p = \kappa/k_B T$  (instead of  $\kappa$ ) since this quantity is more natural for describing polymers with  $L \gg L_p$ .

Our approach is very much different from that of Semenov [10,41], who used the Rouse diffusion coefficient,  $D_c = k_B T/\zeta N$ , as an input for curvilinear diffusion, where  $N = L/L_p$  is the effective polymer index, and  $\zeta$  is a “monomeric” (*i.e.* persistence unit) friction coefficient. The latter is estimated as  $2\pi\eta L_p/\ln(L_p/a)$  [2,10]. Hence Semenov’s approach appears to ignore the problem of how persistence units move around “corners” imposed by the entanglement matrix.

**3.2.1. A Polymer in a Tube.** — We first modify the above calculation for  $D_{rep}$  to deal with a polymer *in a tube* whose diameter is set (self-consistently) to the entanglement length  $L_e$ . The polymer collides with the tube walls at different points with a *mean* distance  $\xi_1$  between consecutive collisions (the “deflection length”) [42], which is the 1-D analog of the so-called Helfrich-Servuss “patch size” [11,43] for a membrane held between two plates. It is related to  $L_e$  by

$$\xi_1 = (45)^{1/3} L_p^{1/3} L_e^{2/3}, \quad (31)$$

where the numerical constant  $(45)^{1/3}$  depends somewhat on the method of calculation. To be consistent with the rest of the calculations,  $\xi_1$  has been found by equating  $\langle(\Delta h)^2\rangle = 2\langle h^2\rangle$  (where, say,  $h \equiv h^{(y)}$ ) with  $L_e^2$  for a polymer of length  $\xi_1$ . This yields equation (31) with the given numerical prefactor.

The fluctuations of the projected length are cutoff by  $\xi_1$  (rather than by  $L$ ). The size of a collision segment (*i.e.* the piece of polymer between two consecutive collision points) can *fluctuate* around its mean value  $\xi_1$ . Using  $L = \xi_1$  either in equation (27) with  $\langle(\Delta \mathbf{h})^2\rangle = 2L_e^2$ , or in equation (29), we find the variance of these fluctuations (using also Eq. (31))

$$\langle(\Delta \xi_1)^2\rangle = \frac{\xi_1 L_e^2}{L_p} = (45)^{1/3} \frac{L_e^{8/3}}{L_p^{2/3}}. \quad (32)$$

The time  $\tau_e$  for these fluctuations to explore their phase space, which we shall call the entanglement time, is found from equation (22) with  $L = \xi_1$  to be

$$\tau_e \simeq \frac{180(45)^{1/3}}{\pi^3 \ln[\xi_1/\pi a]} \frac{\eta L_p^{1/3} L_e^{8/3}}{k_B T} \quad (33)$$

The variance of the tube contour length is easily obtained by simply taking  $\langle(\Delta\mathbf{h})^2\rangle = 2L_e^2$  in equation (29). Thus

$$\langle(\Delta L_o)^2\rangle = \frac{\bar{L}_o L_e^2}{L_p} \quad (34)$$

Using an alternative viewpoint, which is very useful in connection with the dynamics,  $\Delta L_o$  is regarded as the sum of the fluctuations in the size of different collision segments,  $\Delta L_o = \sum_{j=1}^n \Delta\xi_1^{(j)}$ . The number of segments in this sum is  $n = \bar{L}_o/\xi_1$ . This sum has the form of a random position of a random walker in 1-D. We may thus use the Gaussian random walk result

$$\langle(\Delta L_o)^2\rangle = \frac{\bar{L}_o}{\xi_1} \langle(\Delta\xi_1)^2\rangle. \quad (35)$$

Using equation (32) in equation (35) leads *exactly* to equation (34).

Next we consider the dynamics of these fluctuations in  $L_o$ . This process is cooperative, since a dynamic fluctuation in the position of a given collision point changes the length of the two neighboring collision segments to which this point connects. To describe this process, we use the *analogy* to the "bead and spring" (Rouse) model of Gaussian flexible polymers. Let us denote the curvilinear position of a collision point along the tube contour by  $s_j$ . The length of a collision segment  $j$  is then given by  $\xi_1^{(j)} = s_{j+1} - s_j$ . We may construct a fictitious Hamiltonian for a chain of beads connected by springs,  $H = K_s/2 \sum_j (s_{j+1} - s_j - \xi_1)^2$ . The spring constant  $K_s$  is chosen in such a way that the equipartition theorem is obeyed, *i.e.*  $K_s = k_B T / \langle(\Delta\xi_1)^2\rangle$ . The Langevin equations of motion for the positions  $s_j$  are derived in a way similar to the flexible polymer case (Rouse model) and solved using normal coordinates [2]. The result is that the longest relaxation time  $\tau_R$  is proportional to  $n^2$ , so that

$$\tau_R \simeq \left(\frac{\bar{L}_o}{\xi_1}\right)^2 \tau_e. \quad (36)$$

(Numerical factors were omitted on purpose in Eq. (36) but the final result for the diffusion constant will be more precise.) An equivalent route is to calculate the time it takes for a perturbation to diffuse from one end of the polymer to the other, taking its diffusion coefficient to be  $\xi_1^2/\tau_e$ . The latter also leads to equation (36), which allows us to express the curvilinear diffusion coefficient as  $D_c \simeq \frac{\langle(\Delta L_o)^2\rangle}{\tau_R}$ . Using equations (31), (34) and (36) leads to (using the numerical prefactors from Appendix C)

$$D_c \simeq \frac{(45)^{1/3} \ln[\xi_1/\pi a]}{15\pi} \left(\frac{L_e}{L_p}\right)^{2/3} \frac{k_B T}{\eta L}. \quad (37)$$

If we use this curvilinear diffusion coefficient in the theory of reptation, we immediately obtain the time it takes for the chain to disengage from its original tube  $\tau_{\text{rep}} = L^2/\pi^2 D_c$ , *i.e.*

$$\tau_{\text{rep}} = \frac{15}{\pi(45)^{1/3} \ln[\xi_1/\pi a]} \left(\frac{L_p}{L_e}\right)^{2/3} \frac{\eta L^3}{k_B T}. \quad (38)$$

The long time ( $t \gg \tau_{\text{rep}}$ ) chain diffusion coefficient is estimated as  $D_{\text{rep}} \simeq R_g^2/\tau_{\text{rep}}$ , where  $R_g$  is the radius of gyration,  $R_g \simeq (L_p L)^{1/2}$ . Thus we obtain (using a more accurate numerical prefactor [2])

$$D_{\text{rep}} = \frac{1}{3} D_c \frac{L_p}{L} = \frac{\ln[\xi_1/\pi a]}{(45)^{2/3} \pi} \frac{k_B T L_p^{1/3} L_e^{2/3}}{\eta L^2} \quad (39)$$

Note the scaling behaviors  $D_c \sim L^{-1}$ ,  $\tau_{\text{rep}} \sim L^3$ , and  $D_{\text{rep}} \sim L^{-2}$ . These scaling properties are *identical* to those of the classical reptation model for flexible polymers. The prefactors, however, are different and can lead to a significant quantitative difference. To appreciate this, consider the limit  $L_p \gg L_e$ . From equation (37) we see that, for a given  $L$ ,  $D_c$  is smaller here, by a factor of  $(L_e/L_p)^{2/3}$ , than that of classical reptation  $D_c \sim k_B T / \eta L$ . As a result,  $\tau_{\text{rep}}$  (Eq. (38)) is larger by a factor of  $(L_p/L_e)^{2/3}$ . These results are quite intuitive, since a flexible chain has much more excess length (relative to the tube contour length) available to it, to be used in the reptation, than the semi-flexible chain. However, the reptation diffusion coefficient  $D_{\text{rep}}$  in our semi-flexible network is  $\sim (L_p/L_e)^{1/3}$  times *larger* (for a given  $L$ ) than that of a flexible network. This counter-intuitive result may be explained by noting that in a flexible network the radius of gyration is much smaller (for a given  $L$ ) than that of a semi-flexible polymer, leading to this unexpected result. If we redefine, however, the polymer index as  $N = L/L_p$  (rather than  $N = L/a$ ), and compare the two expressions at a given  $N$  (rather than a given  $L$ ),  $D_{\text{rep}}$  of the semi-flexible network now appears much smaller than that of a flexible network.

**3.2.2. Curvilinear MSD of a Monomer.** — Let us now focus on an arbitrary monomer  $j$  and evaluate its MSD,  $\langle (\Delta s_j(t))^2 \rangle$ , *along the tube contour*. (In this part we shall concentrate only on the main scaling behaviors.) This quantity can sometimes be directly measured, *e.g.*, in fluorescence video microscopy [5], but it is also needed for the calculation of the real space MSD described next. It is characterized by three regimes.

The first regime,  $t < \tau_e$ , corresponds to the free diffusion (discussed in Sect. 3.1) of a semi-flexible polymer having an effective length  $\xi_1$ . Here the curvilinear MSD  $\langle (\Delta s_j(t))^2 \rangle$  is shown in Appendix C to be proportional to the projected length fluctuations. This is intuitively clear at least for the two end monomers of a collision segment. Assuming that these move independently of each other on a timescale much shorter than  $\tau_e$  implies that  $\langle (\Delta \xi_1(t))^2 \rangle \simeq 2 \langle (\Delta s_j(t))^2 \rangle$ .

The second regime,  $\tau_e < t < \tau_R$ , corresponds to the short time behavior of the Rouse-like motion previously discussed, in which the monomer is diffusing among different tube collision segments, but the saturation (equilibrium) limit of  $\langle (\Delta L_o(t))^2 \rangle$  (Eq. (34)) has not yet been reached. Following Doi and Edwards [2] this is simply

$$\langle (\Delta s_j(t))^2 \rangle \simeq \frac{L}{\xi_1} \langle (\Delta \xi_1)^2 \rangle \left( \frac{t}{\tau_R} \right)^{1/2} \simeq \langle (\Delta \xi_1)^2 \rangle \left( \frac{t}{\tau_e} \right)^{1/2} \quad (40)$$

The third regime,  $t > \tau_R$ , corresponds to regular curvilinear diffusion with the diffusion coefficient  $D_c$ . To summarize, we find that

$$\langle (\Delta s_j(t))^2 \rangle \simeq \begin{cases} \left[ \frac{L_e^{8/9}}{L_p^{11/9}} \frac{k_B T}{\eta} t \right]^{3/4} & \text{for } t \ll \tau_e; \\ \left[ \frac{L_e^{8/3}}{L_p^{5/3}} \frac{k_B T}{\eta} t \right]^{1/2} & \text{for } \tau_e \ll t \ll \tau_R; \\ \left( \frac{L_e}{L_p} \right)^{2/3} \frac{k_B T}{\eta L} t & \text{for } t \gg \tau_R. \end{cases} \quad (41)$$

3.2.3. *Real Space MSD of a Monomer.* — We may now proceed to calculate the real space MSD of a tagged monomer (following the calculations for the classical reptation model [2,44]). Since this is usually measured by collecting signals from many different atoms along a single chain and on different chains (*e.g.*, as in NMR or fluorescence photobleaching measurements [6]), we should average the motion over all polymer configurations. The MSD then becomes isotropic. For  $t < \tau_e$ , both longitudinal and transversal motions contribute in general to give

$$\langle (\Delta r_j(t))^2 \rangle \simeq \left[ 1 + \text{const} \left( \frac{L_e}{L_p} \right)^{2/3} \right] \left[ \frac{k_B T}{\eta L_p^{1/3}} t \right]^{3/4}, \quad (42)$$

where  $\text{const} \sim 1$ . Note that for  $L_e \sim L_p$ , both the first and second term in equation (42) (first square brackets) contribute similarly. If  $L_e \ll L_p$ , the second term, resulting from the longitudinal motion, is negligible.

When  $t > \tau_e$ , the transversal motion is constrained to the tube cross-section and only the longitudinal motion can proceed. (Analogous to classical reptation [2], the regime  $\tau_e < t < \tau_R$  may be called the “breathing” regime.) Let us first focus on the subregime  $\tau_e \ll t \ll \tau_{\text{per}}$ , where

$$\tau_{\text{per}} \simeq \frac{\eta}{k_B T} \frac{L_p^{17/3}}{L_e^{8/3}} = \left( \frac{L_p}{L_e} \right)^{16/3} \tau_e \quad (43)$$

is the diffusion time over a single persistence length. Here configurational averaging amounts only to averaging over the random orientations that the different persistence units take. We now separate the discussion into two situations: (i)  $L \gg L_p^3/L_e^2$  for which  $\tau_R \gg \tau_{\text{per}}$ , and (ii)  $L \ll L_p^3/L_e^2$  for which  $\tau_R \ll \tau_{\text{per}}$ .

Consider first case (i),  $L \gg L_p^3/L_e^2$ . In the regime  $\tau_e \ll t \ll \tau_{\text{per}}$  this gives

$$\langle (\Delta r_j(t))^2 \rangle \simeq L_e^2 + \text{const} \left[ \frac{L_e^{8/3} k_B T}{L_p^{5/3} \eta} t \right]^{1/2} \quad (44)$$

The second term in equation (44) is negligible up to times  $t \sim \tau_c$  where

$$\tau_c \simeq \frac{\eta L_p^{5/3} L_e^{4/3}}{k_B T} = \left( \frac{L_p}{L_e} \right)^{4/3} \tau_e \quad (45)$$

corresponds to the longitudinal diffusion time over one entanglement length. For  $t \gg \tau_c$  the second term is dominant. For later times, where  $\tau_{\text{per}} \ll t \ll \tau_{\text{rep}}$ , the segment diffuses on length scales much larger than  $L_p$  along the (assumed Gaussian) tube; however, the chain has not yet disengaged from its original tube. This suggests that  $\langle (\Delta r_j(t))^2 \rangle \simeq L_p \langle (\Delta s_j(t))^2 \rangle^{1/2}$ . Finally, when  $t \gg \tau_{\text{rep}}$  the diffusion of a polymer segment is identical to the diffusion of the center of mass, with a diffusion coefficient  $D_{\text{rep}}$  given previously. These results, taking now (for simplicity)  $L_e \ll L_p$ , are summarized below.

Case (i):  $L \gg L_p^3/L_e^2$

$$\langle (\Delta r_j(t))^2 \rangle \simeq \begin{cases} \left[ \frac{k_B T}{\eta L_p^{1/3}} t \right]^{3/4} & \text{for } t \ll \tau_e; \\ L_e^2 & \text{for } \tau_e \ll t \ll \tau_c; \\ \left[ \frac{L_e^{8/3}}{L_p^{5/3}} \frac{k_B T}{\eta} t \right]^{1/2} & \text{for } \tau_c \ll t \ll \tau_{\text{per}}; \\ \left( L_p^{7/3} L_e^{8/3} \frac{k_B T}{\eta} t \right)^{1/4} & \text{for } \tau_{\text{per}} \ll t \ll \tau_R; \\ \left( \frac{k_B T L_p^{4/3} L_e^{2/3}}{\eta L} t \right)^{1/2} & \text{for } \tau_R \ll t \ll \tau_{\text{rep}}; \\ \frac{k_B T L_p^{1/3} L_e^{2/3}}{\eta L^2} t & \text{for } \tau_{\text{rep}} \ll t. \end{cases} \quad (46)$$

Case (ii):  $L \ll L_p^3/L_e^2$ . Here we find that

$$\langle (\Delta r_j(t))^2 \rangle \simeq \begin{cases} \left[ \frac{k_B T}{\eta L_p^{1/3}} t \right]^{3/4} & \text{for } t \ll \tau_e; \\ L_e^2 & \text{for } \tau_e \ll t \ll \tau_c; \\ \left[ \frac{L_e^{8/3}}{L_p^{5/3}} \frac{k_B T}{\eta} t \right]^{1/2} & \text{for } \tau_c \ll t \ll \tau_R; \\ \left( \frac{L_e}{L_p} \right)^{2/3} \frac{k_B T}{\eta L} t & \text{for } \tau_R \ll t \ll \tau_{\text{per}}; \\ \left( \frac{k_B T L_p^{4/3} L_e^{2/3}}{\eta L} t \right)^{1/2} & \text{for } \tau_{\text{per}} \ll t \ll \tau_{\text{rep}}; \\ \frac{k_B T L_p^{1/3} L_e^{2/3}}{\eta L^2} t & \text{for } \tau_{\text{rep}} \ll t. \end{cases} \quad (47)$$

Note that cases (i) and (ii) differ only in the intermediate time regime  $\min[\tau_{\text{per}}, \tau_R] \ll t \ll \max[\tau_{\text{per}}, \tau_R]$ .

**3.3. REPTATION OF MEMBRANES.** — In membranes the projected area can also fluctuate, and this can cause reptation motion of the membrane. It will modify the longitudinal diffusion coefficient, and is a very interesting concept in itself. There is, of course, no membrane analog (in 3-D) to the entangled polymer network where this motion is dominant. However, if the membrane is sandwiched between two plates that do not allow slippage upon contact, the only mechanism of transport is again reptation.

**3.3.1. Free Membrane.** — We approach this process by considering now the fluctuations of the excess area. The short time behavior can be related, similarly to equation (27), to the transversal MSD

$$\langle (\Delta S_o(t))^2 \rangle = \frac{k_B T}{2\kappa} S \langle (\Delta h(2t))^2 \rangle, \quad (48)$$

with  $S = L^2$ ,  $L$  being the linear dimension. Equation (48) saturates at the equilibrium limit

$$\langle (\Delta S_o)^2 \rangle \simeq \frac{1}{4\pi^3} \left( \frac{k_B T}{\kappa} \right)^2 S^2. \quad (49)$$

The saturation time is  $\sim \tau_s$ , equation (14).

To consider the longitudinal reptation motion of a free membrane, we first find the fluctuations of projected length in an arbitrary direction. The projected area is written as

$S_o(t) = L_x(t)L_y(t)$ , where  $L_x$  and  $L_y$  are projected lengths along the  $x$  and  $y$  axes. They are assumed to be *independent* (but, by symmetry, equivalent) stochastic variables (with mean  $\bar{L}_o$ ). This is not entirely correct but is sufficient for our approximate description. Accordingly we find

$$\langle (\Delta S_o(t))^2 \rangle = 2 \left( \langle L_x^2 \rangle \langle L_y^2 \rangle - \langle L_x(0)L_x(t) \rangle \langle L_y(0)L_y(t) \rangle \right). \quad (50)$$

Noting that the two axes are equivalent, we obtain the following relation between the MS difference of the projected length in an arbitrary direction (dropping the axis subscript) and the MS difference of the projected area,

$$\langle (\Delta L_o(t))^2 \rangle \simeq 2L^2 \left[ 1 - \left( 1 - \frac{\langle (\Delta S_o(t))^2 \rangle}{2L^4} \right)^{1/2} \right]. \quad (51)$$

Using equation (48) in equation (51) with  $\kappa \gtrsim k_B T$  leads to

$$\langle (\Delta L_o(t))^2 \rangle \simeq \frac{k_B T}{4\kappa} \langle (\Delta h(2t))^2 \rangle. \quad (52)$$

The short time fluctuations of the *projected length* are thus *independent* of the membrane size, which strongly differs from the 1-D case, equation (27). To discuss reptation, we require for the equilibrium variance

$$\langle (\Delta L_o)^2 \rangle \simeq \frac{1}{8\pi^3} \left( \frac{k_B T}{\kappa} \right)^2 L^2. \quad (53)$$

The long time reptation diffusion coefficient of a free-membrane is then

$$D_{\text{rep}} \simeq \frac{\langle (\Delta L_o)^2 \rangle}{\tau_s} \simeq \frac{1}{32} \left( \frac{k_B T}{\kappa} \right) \frac{k_B T}{\eta L} \quad (54)$$

(The numerical prefactor is only roughly estimated here because we did not perform a more accurate calculation, as was done in Appendix C for 1-D.) Thus, apart from numerical prefactors,  $D_{\text{rep}}$  is basically  $k_B T/\kappa$  times the Stokes-Einstein (coherent) translation diffusion coefficient,  $D \sim k_B T/\eta L$ . The overall diffusion coefficient is again simply the sum of the two coefficients. For  $\kappa \gg k_B T$ , reptation is therefore negligible, and becomes marginally important when  $\kappa \sim k_B T$ .

**3.3.2. A Membrane Sandwiched between Two Plates.** — Next we consider the reptation of a membrane sheet held between two plates with gap  $d$ . The collision length (or the Helfrich-Servuss “patch size”) is now [11, 43]

$$\xi_2 \simeq (2\pi^3)^{1/2} (\kappa/k_B T)^{1/2} d. \quad (55)$$

The overall fluctuations in the projected area are obtained from equation (48) by replacing  $\langle (\Delta h)^2 \rangle$  by  $d^2$ , leading to

$$\langle (\Delta S_o)^2 \rangle = \frac{k_B T}{2\kappa} S d^2. \quad (56)$$

Then, using equation (51), the fluctuations in the linear dimension along an arbitrary axis obey

$$\langle (\Delta L_o)^2 \rangle \simeq \frac{k_B T}{4\kappa} d^2, \quad (57)$$

which is *independent* of  $L$ .



The Rouse-like time  $\tau_R$  of these fluctuations is given by equation (36) (with a prefactor of 1/2 because of the 2-D nature of the problem) with

$$\tau_e = \frac{2}{\pi^3} \frac{\eta \xi_2^3}{\kappa} \quad (58)$$

Using  $D_{\text{rep}} = \langle (\Delta L_o)^2 \rangle / \tau_R$  we obtain

$$D_{\text{rep}} \simeq \frac{\pi^{3/2}}{16\sqrt{2}} \left( \frac{k_B T}{\kappa} \right)^{1/2} \frac{k_B T d}{\eta L^2}. \quad (59)$$

This result crosses over to equation (54) when  $L \simeq \xi_2$ . Note that  $D_{\text{rep}} \sim L^{-2}$ , which is very different from the scaling behavior of the (curvilinear) reptation diffusion coefficient of semi-flexible polymers in a tube,  $D_c \sim L^{-1}$  (but spuriously identical to the scaling of the long time reptation diffusion coefficient in a network). Reptation of a membrane between two plates, as in a lamellar phase, is thus very slow. If there are slip boundary conditions on the plates, and they do not curve in space, the usual (coherent) translation diffusion coefficient will dominate. However, if the two plates slowly curve in space (but remain parallel), or if the membrane cannot slip at the contact points, coherent translation diffusion will be inhibited, and the reptation mechanism will take over.

#### 4. Polymers and Membranes under Tension

4.1. MEMBRANES. — Here we shall consider the effect of tension  $\sigma$  (units of force per unit length) on the transversal mean-square displacement of a tagged (fixed) point on a membrane. Tension can be imposed externally (*e.g.*, using micropipettes [21] or laser tweezers [19]) on a membrane sheet that has been initially in equilibrium. In addition, when vesicles are prepared by non-equilibrium processes the membrane is often under tension. This is because the volume-to-surface ratio does not have time to relax to the minimum energy (due to the small permeability of the membrane).

The equilibrium spectrum of undulations is again derived from the Helfrich bending free-energy, equation (3), now with the addition of surface tension (evaluated again for small deformations)

$$H = \frac{1}{2} \int d^2\rho \left[ \sigma (\nabla h(\rho))^2 + \kappa (\nabla^2 h(\rho))^2 \right] = \frac{1}{2} \sum_{\mathbf{k}} [\sigma k^2 + \kappa k^4] h_{\mathbf{k}} h_{-\mathbf{k}}. \quad (60)$$

The transversal MSD now becomes

$$\langle (\Delta h(t))^2 \rangle = \frac{k_B T}{2\pi^2} \int \frac{d^2 k}{\sigma k^2 + \kappa k^4} (1 - e^{-\omega(k)t}) \quad (61)$$

with the relaxation frequency  $\omega(k)$  given by

$$\omega(k) = \frac{\sigma k + \kappa k^3}{4\eta} \quad (62)$$

This expression shows a crossover behavior in time that is controlled by the natural inverse length scale  $k^* = \sqrt{\sigma/\kappa}$ . Short time behavior is influenced by large wavenumbers  $k \gg k^*$ , and is thus equivalent to that of a tenseless membrane. The long time behavior is controlled by the

long wavelength undulations that are strongly suppressed by the tension. The crossover time  $t^*$  obeys

$$t^* = \frac{4\eta\kappa^{1/2}}{\sigma^{3/2}} \quad (63)$$

The asymptotic behaviors of equation (61) are then

$$\langle(\Delta h(t))^2\rangle \simeq \begin{cases} 0.17 \left[ \left( \frac{k_B T}{\kappa} \right)^{\frac{1}{2}} \frac{k_B T}{\eta} t \right]^{\frac{2}{3}} & \text{for } \frac{\eta\alpha^3}{\kappa} \ll t \ll t^*; \\ \frac{k_B T}{\pi\sigma} \left[ \ln \left( \frac{t}{t^*} \right) + 0.58 \right] & \text{for } t^* \ll t \ll \frac{\eta L}{\sigma} \end{cases} \quad (64)$$

The MSD saturates at times  $t \gtrsim \frac{4\eta L}{\pi\sigma}$  at the equilibrium value  $\langle(\Delta h)^2\rangle = \frac{k_B T}{\pi\sigma} \ln \left( \frac{L}{\pi} \sqrt{\frac{\sigma}{\kappa}} \right)$  as required from ergodicity. In practice, logarithmic dependences are usually hard to detect. Thus, the slow, logarithmic increase of the MSD at the long time regime suggests that it may appear to saturate (at times  $t \sim t^*$ ) at the value  $\sim k_B T/\sigma$ , which could be several times smaller than the equilibrium value.

We can see that the two asymptotes in equation (64) match to within a numerical constant when extrapolated to  $t = t^*$ , yielding  $\langle(\Delta h(t^*))^2\rangle \simeq k_B T/\sigma$ . It is therefore interesting to check whether the full evolution can, at least to a good approximation, be described by a single scaling function  $f(t/t^*)$ , *i.e.*

$$\langle(\Delta h(t))^2\rangle = \frac{k_B T}{\sigma} f(t/t^*), \quad (65)$$

where, for consistency with equation (64),  $f(x)$  must have the following asymptotes

$$f(x) \sim \begin{cases} x^{2/3} & \text{for } x \ll 1; \\ \ln(x) + \text{const} & \text{for } x \gg 1. \end{cases} \quad (66)$$

The validity of this scaling ansatz in the crossover regime  $x \sim 1$ , which is not verified in the above asymptotic analysis, is checked numerically in Figure 1. We can see that, with the appropriate rescaling of variables, the data for three different values of  $\sigma$  collapse with very high precision onto a single curve.

An interesting implication resulting from this analysis concerns the dynamic structure factor  $S(q, t)$ . As discussed previously, the  $t^{2/3}$  increase of the MSD was shown [16] to lead to a stretched exponential decay,  $S(q, t) \sim e^{-(\Gamma_q t)^{2/3}}$ . Using the approach described in reference [16], we can conclude that for scattering geometries in which the scattering vector  $\mathbf{q}$  lies roughly perpendicular to the membrane plaquettes, or when the angular distribution of plaquettes is isotropic,  $S(q, t)$  will decay algebraically at the long time regime  $t \gg t^*$ ,  $S(q, t) \sim t^{-\alpha}$ , where  $\alpha \simeq q^2 k_B T/\sigma$ . This should be detectable for  $q < q^*$  ( $q^* = k^*$  above). For large scattering wavenumbers,  $q \gg q^*$ , this decay is much less relevant since the structure factor has already relaxed (up to times  $t \sim t^*$ ) to a vanishingly small value that is difficult to measure in practice.

4.2. SEMI-FLEXIBLE POLYMERS. — For semi-flexible polymers under tension, the mean-square displacement becomes, instead of equation (19),

$$\langle(\Delta \mathbf{h}(t))^2\rangle = \frac{4k_B T}{\pi} \int_{\pi/L}^{\pi/a} \frac{dk}{\sigma k^2 + \kappa k^4} \left( 1 - e^{-\omega(k)t} \right), \quad (67)$$

with  $\omega(k)$  given by (for  $ka \ll 1$ )

$$\omega(k) \simeq \frac{\sigma k^2 + \kappa k^4}{4\pi\eta} \ln[1/ka]. \quad (68)$$

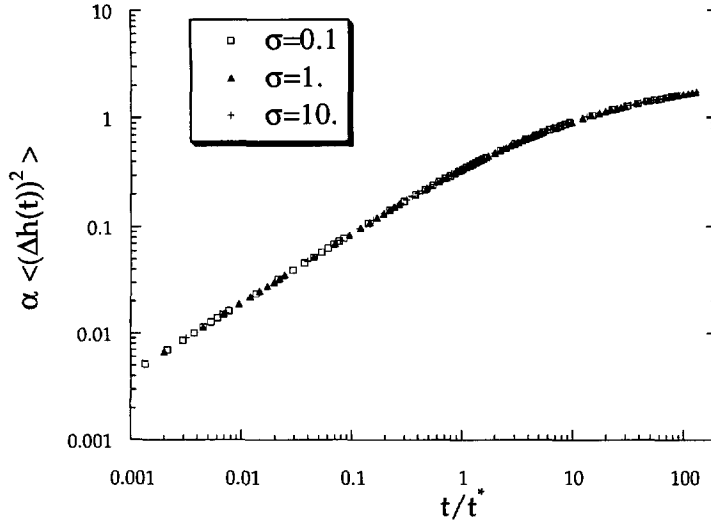


Fig. 1. — Transversal MSD  $\langle (\Delta \mathbf{h}(t))^2 \rangle$  of a tagged membrane molecule, against reduced time  $t/t^*$  (with  $t^*$  given by Eq. (63)), for three different values of surface tension  $\sigma$  (arbitrary units);  $\alpha = \sigma/2$ ;  $\kappa = k_B T = 1$  used in all cases. Note the clear data collapse, and the crossover from power-law to logarithmic behavior at  $t/t^* \simeq 1$ .

The logarithmic dependence in  $\omega(k)$  is again considered only to the leading order. High order effects are ignored by replacing  $k$  with  $k^* = \sqrt{\sigma/\kappa}$ . As in the case of membranes, we find a crossover behavior to a tension-dominated (anomalous) diffusion that is set by the characteristic length scale  $1/k^* = \sqrt{\kappa/\sigma}$ . The crossover time here is

$$t^* = \frac{4\pi\eta\kappa}{\sigma^2} \quad (69)$$

The asymptotic behavior becomes

$$\langle (\Delta \mathbf{h}(t))^2 \rangle \simeq \begin{cases} 0.082 \left\{ \ln \left[ \frac{\kappa \ln \left( \frac{\kappa}{\sigma a^2} \right) t}{8\pi\eta a^4} \right] \left( \frac{k_B T}{\kappa} \right)^{\frac{1}{3}} \frac{k_B T}{\eta} t \right\}^{\frac{3}{4}} & \text{for } \frac{\eta a^4}{\kappa} \ll t \ll t^*; \\ 0.45 \left\{ \ln \left[ \frac{\sigma \ln \left( \frac{\kappa}{\sigma a^2} \right) t}{8\pi\eta a^2} \right] \frac{(k_B T)^2}{\sigma\eta} t \right\}^{\frac{1}{2}} & \text{for } t^* \ll t \ll \frac{\eta L^2}{\sigma} \end{cases} \quad (70)$$

The MSD saturates, as it should, at the ensemble average value  $\langle (\Delta \mathbf{h})^2 \rangle \simeq \frac{k_B T}{\sigma} L$  for times  $t \gtrsim \frac{\eta L^2}{\sigma}$ .

The two asymptotic laws match (to within a numerical constant) at  $t = t^*$ , which means that again the MSD may be expressed by a single scaling function  $g(t/t^*)$ , *i.e.*

$$\langle (\Delta \mathbf{h}(t))^2 \rangle = \frac{k_B T \kappa^{1/2}}{\sigma^{3/2}} g(t/t^*). \quad (71)$$

The additional asymptotic logarithmic dependencies described in equation (70) slightly break this scaling hypothesis. If these are ignored,  $g(x)$  must have the following asymptotes

$$g(x) \sim \begin{cases} x^{3/4} & \text{for } x \ll 1; \\ x^{1/2} & \text{for } x \gg 1. \end{cases} \quad (72)$$

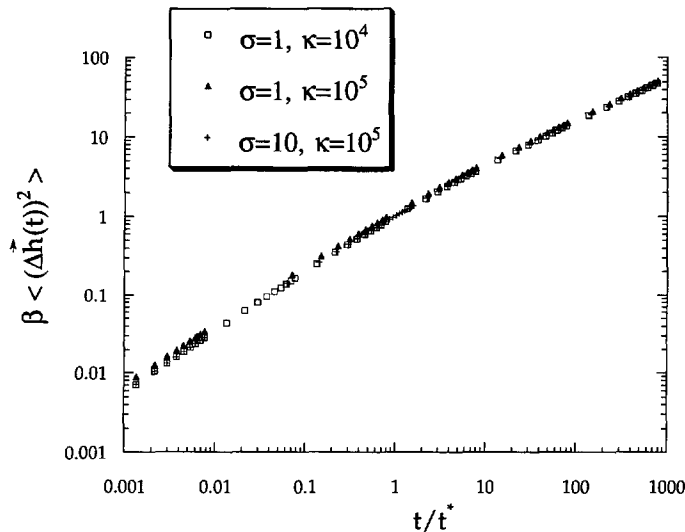


Fig. 2. — Transversal MSD  $\langle (\Delta \mathbf{h}(t))^2 \rangle$  of a tagged monomer belonging to a semi-flexible polymer, against the reduced time  $t/t^*$  (with  $t^*$  given by Eq. (69)), for three different combinations of the surface tension  $\sigma$  and the bending modulus  $\kappa$  (arbitrary units);  $\beta = \sigma^{3/2}/(4\kappa^{1/2})$ ;  $k_B T = 1$  used in all cases.

This scaling ansatz is checked numerically in Figure 2. To obtain these numerical results, the hydrodynamic interaction corrections to  $\omega(q)$  were calculated to a high order ( $o(q^8)$ ) beyond the logarithmic term. We see that the scaling is less good than in the 2-D membrane case, presumably because of the additional logarithmic dependences.

**4.3. FLEXIBLE POLYMERS.** — It is interesting to compare these results to the transversal MSD of *flexible* polymers under strong tension. A simple static picture, designed for polymers under good solvent conditions, has been provided by Pincus [1, 45], and we would like to generalize his heuristic approach for the dynamics [46]. In this approach, a flexible polymer under tension may be viewed as being separated into blobs of size  $\xi_\sigma = k_B T / \sigma$ . Within each blob the chain does not feel the tension and is swollen in the usual way, *i.e.* the number of monomers in each blob is given by  $g_\sigma = (\xi_\sigma/a)^{5/3}$ , where  $a$  is the monomer size. The blobs make a sequential array in a direction parallel to the force, with no backward steps. In the vertical direction to the force the blobs make a Gaussian random walk. The extension of the chain is then easily calculated using  $L \simeq (N/g_\sigma)\xi_\sigma$ , where  $N$  is the polymer index. This gives  $L \simeq Na(\sigma a/k_B T)^{2/3}$ . The radius of gyration in the vertical direction is  $\langle r_\perp^2 \rangle \simeq L\xi_\sigma$ , which gives  $\langle r_\perp^2 \rangle \simeq Na^2(k_B T/\sigma a)^{1/3}$ . Thus  $r_\perp/L \sim (g_\sigma/N)^{1/2} \ll 1$  in this strong tension regime.

Since in each blob the chain does not feel the tension, the dynamics at short times must be identical to that of a free chain in good solvent. The latter is well described by the Zimm model. This implies that a tagged monomer will perform an anomalous diffusion  $\langle (\Delta r_\perp(t))^2 \rangle \simeq (k_B T t / \eta)^{2/3}$ . This behavior will in fact occur in all directions. When the root MSD reaches the blob size  $\xi_\sigma$ , the monomer will move in the vertical direction to the force by collective diffusion of blobs. The hydrodynamic interaction between these moving blobs can be neglected (to “zero” order) since the array they form is 1-D (since  $r_\perp \ll L$ ) and the interaction is therefore weak (logarithmic). The diffusion of blobs can be then described by the Rouse model. In fact, since  $r_\perp \ll L$  the Rouse model becomes identical to the model of a string under tension,

namely, the MSD will be the same as in equation (70). Indeed, the Rouse model predicts  $\langle(\Delta r_{\perp}(t))^2\rangle \simeq (k_B T \xi_{\sigma} t / \eta)^{1/2}$ , which is similar to equation (70) if we use  $\xi_{\sigma} = k_B T / \sigma$  [47]. To summarize, therefore

$$\langle(\Delta r_{\perp}(t))^2\rangle \simeq \begin{cases} \left(\frac{k_B T}{\eta} t\right)^{\frac{2}{3}} & \text{for } \eta a^3 / k_B T \ll t \ll \tau_{\sigma}; \\ \left(\frac{(k_B T)^2}{\eta \sigma} t\right)^{1/2} & \text{for } \tau_{\sigma} \ll t \ll \eta \xi_{\sigma} L^2 / k_B T, \end{cases} \quad (73)$$

where  $\tau_{\sigma}$  is the Zimm time of a single blob

$$\tau_{\sigma} = \frac{\eta \xi_{\sigma}^3}{k_B T} = \frac{\eta (k_B T)^2}{\sigma^3} \quad (74)$$

Note that although the long time evolution in equations (73) and (70) is similar, the relevant tensions can be quite different in the two cases. For flexible polymers we require  $\sigma \gg k_B T / R_g$  for the tension dominated evolution to exist (MSD  $\sim t^{1/2}$ ), whereas for semi-flexible polymers we need to have  $\sigma \gg k_B T L_p / L^2$ .

## 5. Transversal Motion in Lamellar Phases

Membrane bilayers often form dilute lamellar phases that are stabilized by the Helfrich steric undulation forces. For simplicity we have assumed that the bilayers are uncharged so that the only long range interaction between the bilayers is due to steric undulation forces. Thus on length scales shorter than the Helfrich-Servuss "patch size"  $\xi_2 \sim (\kappa / k_B T)^{1/2} d$ , the membrane behaves like a free membrane. On longer length scales the inter-membrane collisions become important. The short time transversal motion of a tagged membrane particle should therefore be identical to that of a free membrane. However, when the MSD reaches the interlayer spacing, collective membrane motion should begin to play a role.

In order to describe this collective membrane motion, we shall use the common description of the elasticity of smectics. The elastic free-energy, which is applicable to wavelengths  $\lambda \gg \xi_2$ , is written as [48]

$$F = \int d^3x \left[ \frac{1}{2} K (\nabla_{\perp}^2 u)^2 + \frac{1}{2} \bar{B} \left( \frac{\partial u}{\partial z} \right)^2 \right]. \quad (75)$$

Here,  $u(\mathbf{r})$  describes the displacements of all layers in the system;  $K$  is the smectic bending modulus and is related to the single layer modulus  $\kappa$  by  $K = \kappa / d$ ;  $\bar{B}$  is the effective compression modulus, which for the undulation-controlled Helfrich type interlayer repulsions, is given by [11]  $\bar{B} = \frac{9\pi^2}{64} \frac{(k_B T)^2}{\kappa d^3}$ .

Before we turn to the dynamics, we will first review some known results for the equilibrium fluctuations. From equation (75), the equilibrium spectrum of  $u_{\mathbf{q}}$  is given by

$$\langle u_{\mathbf{q}} u_{-\mathbf{q}} \rangle = \frac{k_B T}{K q_{\perp}^4 + \bar{B} q_z^2}, \quad (76)$$

where  $q_z$  and  $\mathbf{q}_{\perp}$  are the two components of the wave vector in the transversal ( $z$ ) and longitudinal directions, respectively. (Note that  $\mathbf{q}_{\perp} \equiv \mathbf{k}$  was denoted in the previous sections without

the subscript  $\perp$ .) The mean square amplitude is calculated [48] using equation (76)

$$\langle u^2 \rangle = \frac{k_B T}{4\pi\sqrt{KB}} \ln\left(\frac{L}{\xi_2}\right), \quad (77)$$

where  $L$  is again the lateral system linear size. The logarithmic divergence in equation (77) is well known as the Landau-Peierls effect, which indicates that the layers are wandering a lot in space and true long-range order is absent.

If we would like to focus on the displacement profile  $h(\boldsymbol{\rho})$  of a single layer located at, for example,  $z = 0$ , it can be obtained from the 3-D field  $u(\mathbf{r}) = u(\boldsymbol{\rho}, z)$  by putting  $z = 0$ . This leads to the following relation between the correlation functions of the planar and spatial displacements

$$\langle h_{\mathbf{q}_\perp} h_{-\mathbf{q}_\perp} \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} dq_z \langle u_{\mathbf{q}} u_{-\mathbf{q}} \rangle. \quad (78)$$

Using equation (76) in equation (78) we obtain

$$\langle h_{\mathbf{q}_\perp} h_{-\mathbf{q}_\perp} \rangle = \frac{k_B T}{2\sqrt{KB}} \frac{1}{q_\perp^2} = \frac{4}{3\pi} \frac{d^2}{q_\perp^2}, \quad (79)$$

where the second equality holds only for undulation force stabilized smectics. Interestingly, the scaling behavior  $\langle |h_{\mathbf{q}_\perp}| \rangle \sim q_\perp^{-2}$  is identical to that of a *single* membrane under tension. If we now calculate  $\langle h^2 \rangle$  using equation (79) we get of course the result equation (77).

We now turn to discuss the transversal MSD of a tagged particle attached to one of the layers. The result equation (77) implies that the MSD will continue to increase with time even after it has reached  $\sim d^2$ , since the long time limit  $\langle u^2 \rangle$  is larger than  $d^2$  by a factor of  $\ln(L/\xi_2)$ . To consider this evolution we need to know the relaxation frequency of a certain Fourier component of the displacement field. It is in principle dependent on the two components of the wave vector,  $q_z$  and  $\mathbf{q}_\perp$ . An approximate expression for a general oblique  $\mathbf{q}$  has been obtained in reference [17]

$$\omega(\mathbf{q}) = \frac{K q_\perp^4 + \bar{B} q_z^2}{\eta q^4 + \frac{12\eta}{d^2} q_z^2} q_\perp^2. \quad (80)$$

In the limit  $\sqrt{\frac{K}{B}} q_\perp^2 \ll q_z$ , equation (80) reduces to the dispersion relation of the baroclinic mode [49]

$$\omega(\mathbf{q}) = \frac{d^2}{12\eta} \bar{B} q_\perp^2. \quad (81)$$

This mode corresponds to a modulation of the interlayer spacing. The relaxation is limited by the Poiseuille flow within the layers, since the membranes are assumed to be impermeable. In the opposite limit,  $\sqrt{\frac{K}{B}} q_\perp^2 \gg q_z$  (assuming that  $\sqrt{\frac{K}{B}} \sim d$ , i.e.  $\kappa \sim k_B T$ ), the pure undulation mode dispersion relation

$$\omega(\mathbf{q}) = \frac{K}{\eta} q_\perp^2 \quad (82)$$

is obtained. This corresponds to coherent sinusoidal bending of the layers keeping the local interlayer spacing intact.

Given  $\omega(\mathbf{q})$ , we may proceed to calculate the MSD using the 3-D analog of equation (11)

$$\langle (\Delta u(t))^2 \rangle = \frac{k_B T}{4\pi^3} \int \frac{d^3 q}{K q_\perp^4 + \bar{B} q_z^2} (1 - e^{-\omega(\mathbf{q})t}). \quad (83)$$

Since this is a complicated integral, we approximate it by separating the integration over  $q_z$  into the two regimes,  $|q_z| < \sqrt{\frac{K}{B}} q_\perp^2$  and  $|q_z| > \sqrt{\frac{K}{B}} q_\perp^2$ , and approximating  $\omega(\mathbf{q})$  in each regime by equations (82) and (81), respectively [50]. Thus

$$\begin{aligned} \langle (\Delta u(t))^2 \rangle &\simeq \frac{k_B T}{2\pi^3} \times \left[ \int d^2 q_\perp \left( 1 - e^{-\frac{K}{\eta} q_\perp^2 t} \right) \int_0^{\sqrt{\frac{K}{B}} q_\perp^2} \frac{dq_z}{K q_\perp^4 + B q_z^2} \right. \\ &\quad \left. + \int d^2 q_\perp \left( 1 - e^{-\frac{d^2}{12\eta} B q_\perp^2 t} \right) \int_{\sqrt{\frac{K}{B}} q_\perp^2}^\infty \frac{dq_z}{K q_\perp^4 + B q_z^2} \right]. \end{aligned} \quad (84)$$

The upper limit of  $q_\perp$  is again set to  $\pi/\xi_2$ . Performing the integrations we obtain

$$\langle (\Delta u(t))^2 \rangle \simeq \frac{k_B T}{4\pi\sqrt{KB}} \ln \left[ \frac{\pi^2}{\sqrt{12}} \frac{\sqrt{KB}d}{\xi_2^2 \eta} t \right] \simeq \frac{2}{3\pi^2} d^2 \ln \left[ C \frac{(k_B T)^2}{\eta \kappa d^3} t \right], \quad (85)$$

where  $C$  is a numerical constant,  $C = 3/(16\sqrt{12})$ . The second equality in equation (85) holds for smectics stabilized by undulation forces. A similar logarithmic increase is obtained even when only the undulation modes are present, *e.g.*, when  $\bar{B}$  is large due to coulombic interactions, for example, so that the baroclinic modes are fastly decaying and do not influence the long time evolution of the MSD. The effect of constraining the membrane in a lamellar phase is thus quite similar to the effect of imposing tension (compare to Eq. (64)).

To summarize these results, the MSD in a lamellar phase behaves roughly as

$$\langle (\Delta u(t))^2 \rangle \sim d^2 \begin{cases} \left( \frac{\kappa}{k_B T} \right)^{1/3} \left( \frac{t}{t^*} \right)^{2/3} & \text{for } t \ll t^*; \\ \ln \left( \frac{t}{t^*} \right) & \text{for } t^* \ll t \ll \frac{L}{d} t^*, \end{cases} \quad (86)$$

where  $t^* \simeq \eta d^3 \kappa / (k_B T)^2$ .

## 6. Conclusions

We have examined here the transversal and longitudinal motion of 1-D (polymer) and 2-D (membrane) semi-flexible objects subject to various constraints such as confinement and tension. Particular attention was given to the reptation of semi-flexible polymers confined in an entangled network. This generalizes the classical model of de Gennes and of Doi and Edwards for flexible polymer networks. With the polymer being relatively stiff between two consecutive entanglement points along the chain, reptation becomes significantly slower than in the flexible polymer case, but still exists. We have shown that the concept of reptation also applies to membranes, for which this concept is new. Although for membranes this phenomenon is usually expected to be less relevant to real experimental situations than in polymer systems, it may be extremely important for understanding the transport of membranes (*e.g.*, vesicles) through porous material.

Probing local motion in membranes and semi-flexible polymers can be a very powerful tool for measuring the bending constant of these objects and, when applicable, the tension they endure. The latter situation is mostly relevant for systems far from equilibrium. The rich variety of power-laws characterizing the anomalous diffusion of tensed and untensed objects can be used to distinguish between them and as a tool to determine the value of the tension. The mean-square displacement was also shown to be sensitive to excluded volume constraints in the liquid crystalline order. Experimental applications to entangled microtubule systems have been recently put forward [20].

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**Appendix A**

Here we derive equation (11) for the mean-square displacement. The stochastic field  $h(\rho, t)$  is expressed through its Fourier transform

$$h(\rho, t) = \frac{1}{L^2} \sum_{\mathbf{k}} h_{\mathbf{k}}(t) e^{i\mathbf{k}\cdot\rho} \tag{A.1}$$

This leads to

$$\langle [h(\rho, t) - h(\rho, 0)]^2 \rangle = \frac{1}{L^4} \sum_{\mathbf{k}} \langle h_{\mathbf{k}}(t) h_{-\mathbf{k}}(t) \rangle + \langle h_{\mathbf{k}}(0) h_{-\mathbf{k}}(0) \rangle - 2 \langle h_{\mathbf{k}}(t) h_{-\mathbf{k}}(0) \rangle, \tag{A.2}$$

where we have used  $\langle h_{\mathbf{k}}(t) h_{\mathbf{q}}(t') \rangle \propto \delta_{\mathbf{k}, -\mathbf{q}}$ . Consistent with the Langevin equation (8), and as ergodicity also requires, the equal time correlation functions  $\langle h_{\mathbf{k}}(t) h_{-\mathbf{k}}(t) \rangle$  are independent of time (*i.e.*  $h_{\mathbf{k}}(t)$  is a stationary stochastic process) and are equal to  $L^2 k_B T / \kappa k^4$ . Using also equation (5) for  $\langle h_{\mathbf{k}}(t) h_{-\mathbf{k}}(0) \rangle$  and transforming the sum on  $\mathbf{k}$  to an integral, we immediately obtain equation (11).

**Appendix B**

Here we derive the relation (27) between the projected length MS difference and the MSD of a monomer in the transversal direction. Since the statistics of undulations in the two transversal directions is identical, we may calculate the average in equation (26) for one direction (say “ $y$ ”) and multiply the right hand side by 2. Opening the square brackets in equation (26) and denoting  $h \equiv h^{(y)}$  we obtain

$$\langle (\Delta L_o(t))^2 \rangle = L^2 \left[ \left\langle \left( \left( \frac{\partial h}{\partial x} \right)^2 \right)^2 \right\rangle - \left\langle \left( \frac{\partial h(x, t)}{\partial x} \right)^2 \left( \frac{\partial h(x, 0)}{\partial x} \right)^2 \right\rangle \right]. \tag{B.1}$$

Next, using Fourier expansion we may easily find the relations

$$\left\langle \left( \frac{\partial h(x, t)}{\partial x} \right)^2 \left( \frac{\partial h(x, 0)}{\partial x} \right)^2 \right\rangle = \left\langle \left( \frac{\partial h}{\partial x} \right)^2 \right\rangle^2 + \frac{2}{L^4} \sum_{\mathbf{k}} k^4 \langle h_{\mathbf{k}}(t) h_{-\mathbf{k}}(0) \rangle^2 \tag{B.2}$$

and

$$\left\langle \left( \left( \frac{\partial h}{\partial x} \right)^2 \right)^2 \right\rangle = \left\langle \left( \frac{\partial h}{\partial x} \right)^2 \right\rangle^2 + \frac{2}{L^4} \sum_{\mathbf{k}} k^4 \langle h_{\mathbf{k}} h_{-\mathbf{k}} \rangle^2 \tag{B.3}$$

Inserting equations (B.2) and (B.3) into equation (B.1) and using equation (16) we arrive at

$$\langle (\Delta L_o(t))^2 \rangle = 2 \left( \frac{k_B T}{\kappa} \right)^2 \sum_{\mathbf{k}} \frac{1}{k^4} \left( 1 - e^{-2\omega(\mathbf{k})t} \right). \tag{B.4}$$

Comparing the latter equation to equation (19) leads to equation (27).



### Appendix C

Here we propose a more complete treatment of the reptation motion of a free semi-flexible polymer. The approach described here is inspired by a similar calculation in the classical reptation model for the contour length fluctuations [2]. It can easily be generalized to describe the reptation of membranes, and we shall therefore avoid doing it explicitly. In contrast to the Monge gauge ( $h(x)$  representation) used throughout the text, we shall use here the function  $x(s)$  where  $s$  is the curvilinear position of a monomer from one of the ends (the origin) and  $x(s)$  is its position in base coordinates. The two representations are related by

$$\frac{ds}{dx} = \left[ 1 + \left( \frac{\partial h}{\partial x} \right)^2 \right]^{1/2} \simeq 1 + \frac{1}{2} \left( \frac{\partial h}{\partial x} \right)^2 \quad (\text{C.1})$$

According to our definitions

$$\langle x(L) - x(0) \rangle = \bar{L}_o. \quad (\text{C.2})$$

We shall express  $x(s)$  in a Fourier series [2]

$$x(s, t) = X_o(t) + 2 \sum_{p=1,2,\dots} X_p(t) \cos(p\pi s/L) + s \frac{\bar{L}_o}{L} \quad (\text{C.3})$$

(We have used, for convenience, a real Fourier transform.) The third term, which is linear in  $s$ , insures that (i) the constraint given by equation (C.2) is obeyed, (ii)  $dx/ds|_0 = dx/ds|_L$ , which is forced because the two ends are equivalent, and (iii) that  $\langle d^2x/ds^2 \rangle = 0$ , which follows because, in the absence of spontaneous curvature, the polymer is, on the average, uncurved (straight). Note that although our approximate approach is a linear one (*i.e.* the modes in equation (C.3) do not interact), the exact description should involve non-linear free-energy terms that will couple different modes.

The power spectrum of fluctuations  $\langle X_p^2 \rangle$ , and the spectrum of relaxation times  $\tau_p$ , will be determined self-consistently by using equation (C.3) to calculate  $\langle (\Delta L_o(t))^2 \rangle$  in both the short and the long time limits, and equating it with equations (28) and (29). This will require certain assumptions regarding the  $p$ -dependence of  $\langle X_p^2 \rangle$  and  $\tau_p$ .

From equation (C.3) we obtain

$$\begin{aligned} L_o(t) &= x(L, t) - x(0, t) \\ &= \bar{L}_o + 2 \sum_{p>0} X_p(t) (\cos(p\pi) - 1) \\ &= \bar{L}_o - 4 \sum_{p=1,3,5 \dots} X_p(t). \end{aligned} \quad (\text{C.4})$$

The projected length mean square fluctuation becomes

$$\langle (\Delta L_o(t))^2 \rangle = 32 \sum_{p=1,3,5 \dots} (\langle X_p^2 \rangle - \langle X_p(t) X_p(0) \rangle). \quad (\text{C.5})$$

Assuming now

$$\langle X_p(t) X_p(0) \rangle = \langle X_p^2 \rangle e^{-t/\tau_p} \quad (\text{C.6})$$

we obtain

$$\langle (\Delta L_o(t))^2 \rangle = 32 \sum_{p=1,3,5 \dots} \langle X_p^2 \rangle (1 - e^{-t/\tau_p}). \quad (\text{C.7})$$

Now let us introduce the Ansatz  $\langle X_p^2 \rangle = C_1 p^{-\mu}$  and  $\tau_p^{-1} = C_2 p^{-\mu} \ln\left(\frac{L}{p\pi a}\right)$ , where  $C_1$ ,  $C_2$  and  $\mu$  are yet unknown constants, to be determined by comparing equation (C.7) to equation (27) at different time regimes. Let us first consider short times. For  $t \ll \tau_1$  equation (C.7) may be approximated by transforming the sum to an integral to give  $\langle (\Delta L_o(t))^2 \rangle \sim t^{1-\frac{1}{\mu}}$ . We compare this to equation (28), which uniquely specifies the value  $\mu = 4$ . By comparing the  $t \rightarrow \infty$  limit of equation (C.7) to equation (29), *i.e.* by looking at the equilibrium fluctuations, we obtain (using  $\sum_{p=1,3,5,\dots} p^{-4} = \pi^4/96$ ) the coefficient  $C_1$ , which leads to

$$\langle X_p^2 \rangle = \frac{1}{15\pi^4} \left( \frac{k_B T}{\kappa} \right)^2 L^4 p^{-4} \quad (\text{C.8})$$

$C_2$  can be obtained, either from equating the short time evolution, or the saturation time for the projected length fluctuations  $\tau_s/2 = \tau_1$  (Eq. (22)). These two options do not give exactly the same numerical prefactors (in the expression for  $C_2$ ), but the difference is very small (less than 10%). Using the second choice leads to

$$\tau_p^{-1} = \frac{\pi^3 \kappa \ln\left(\frac{L}{p\pi a}\right)}{2 \eta L^4} p^4. \quad (\text{C.9})$$

Note that  $\langle X_p^2 \rangle \propto (k_B T/\kappa)^2$ , which again demonstrates that the hidden description behind this linear self-consistent approach is in fact non-linear.

It is useful to construct the Langevin equation describing the dynamics of  $X_p$ . This must have the form

$$\frac{\partial X_p}{\partial t} = -\frac{X_p}{\tau_p} + \zeta_p(t). \quad (\text{C.10})$$

The random force  $\zeta_p(t)$  obeys

$$\begin{aligned} \langle \zeta_p(t) \zeta_p(t') \rangle &= 2(1 + \delta_{p0}) \frac{\langle X_p^2 \rangle}{\tau_p} \delta(t - t') \\ &= \frac{(1 + \delta_{p0}) (k_B T)^2 \ln\left(\frac{L}{p\pi a}\right)}{15\pi \eta \kappa} \delta(t - t'). \end{aligned} \quad (\text{C.11})$$

Here, the expressions for  $\langle X_p^2 \rangle$  and  $\tau_p^{-1}$ , which were determined for positive  $p$ , are *assumed* to hold also in the limit  $p \rightarrow 0$ . Equation (C.10) is well behaved in this limit (in which  $\tau_p^{-1} = 0$ ) except for the logarithm in the power spectrum of  $\zeta_p$ . We can eliminate this problem by using  $p = 1$  in the logarithm instead of  $p = 0$ , without further justification.

We are now able to calculate the MSD of an arbitrary monomer  $s$  in the longitudinal direction. Using equations (C.3, C.8-C.11) we find

$$\langle (\Delta x(s, t))^2 \rangle = 2D_{\text{rep}} t + 8 \sum_{p=1,2,\dots} \langle X_p^2 \rangle \cos^2(p\pi s/L) \left(1 - e^{-t/\tau_p}\right) \quad (\text{C.12})$$

where

$$D_{\text{rep}} = \frac{1}{15\pi} \frac{(k_B T)^2 \ln\left(\frac{L}{\pi a}\right)}{\eta \kappa} \quad (\text{C.13})$$

Thus for long times where  $t \gg \tau_1 (= \tau_s/2)$  we obtain

$$\langle (\Delta x(s, t))^2 \rangle \simeq 2D_{\text{rep}}t, \quad (\text{C.14})$$

which shows that the polymer center of mass is performing regular diffusion that is controlled by the reptation mechanism. On short timescales,  $t \ll \tau_1$ , the first, regular diffusion term in equation (C.12) is negligible, and the sum can be approximately transformed into an integral. For the two end monomers  $s = 0$  and  $s = L$ , comparing this result with equation (C.7) (using  $\sum_{p=1,3,\dots} \simeq \frac{1}{2} \int_0^\infty dp$ ), we obtain the relation

$$\langle (\Delta x(0, t))^2 \rangle = \langle (\Delta x(L, t))^2 \rangle \simeq \frac{\langle (\Delta L_o(t))^2 \rangle}{2} \quad (\text{C.15})$$

This indicates that the motion of the two ends is not correlated on the short timescale where  $t \ll \tau_s$ . This is physically reasonable since we do expect that a perturbation at one end will travel to the other end on a time scale of the order of  $\tau_s$ . For monomers that are closer to the middle point of the polymer,  $\cos^2(p\pi s/L)$  in the sum is oscillating fast with increasing  $p$ , and we may (approximately) replace it by its average 1/2, to obtain (transforming again to an integral)

$$\langle (\Delta x(L/2, t))^2 \rangle \simeq \frac{\langle (\Delta L_o(t))^2 \rangle}{4} \quad (\text{C.16})$$

These relations are used in equation (41) to obtain the short time regime  $t \ll \tau_e$ .

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