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Polymer Chains in Random Layered Flows: A Scaling Approach

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We consider the diffusion of a polymer chain in random layered flows. We use scaling ideas and take the randomness of the flow into account through an Imry-Ma-type argument. For the chain's dynamics both the Zimm approach for screened hydrodynamic interactions and also the Rouse approach are considered. We compute both the internal dynamics of the chain (motion of a segment) and also the center of mass motion; for the Rouse model we recover the exact results obtained by Oshanin and Blumen. The polymer's dynamics at long times turns out to be diffusive or enhanced, depending on the flow's disorder (thread-like or layer-like), and on the hydrodynamic interactions. Furthermore we also evaluate the chain's conformations under these conditions.

1. INTRODUCTION

The study of macromolecules in external flows has attracted recently much attention; in particular the case of random flows is still open.[1] Random flows are especially interesting, since they serve as simple models for turbulent motion. Polymers play here a major role, because when added to turbulent flows they reduce the drag, a fact much discussed in the past. [2–5]

However, the dynamics of polymers immersed in turbulent or random flows is complex, so that only a very few special cases can be solved rigorously. Recently Oshanin and Blumen[1] found an exact solution for a Rouse chain in a random convectional flow. Random flows were introduced by Matheron and de Marsily in their study of underground water layers.[6] In Figure 1. two flow models are sketched. The flows are oriented along the z-axis. The magnitude and direction of the flows are random, but they depend either on the (x, y)-coordinates or on the x-coordinate only. Thus we

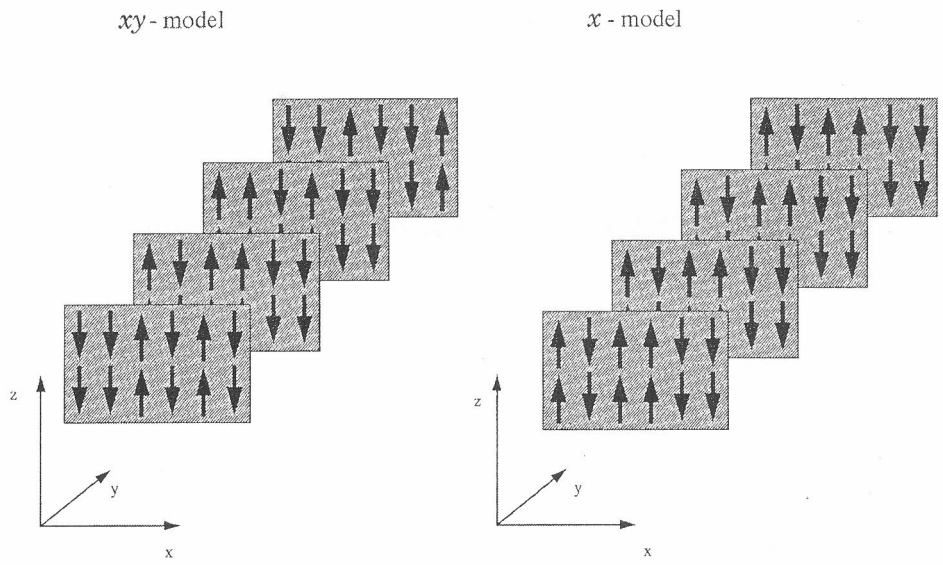

Figure 1. The two random flow models. While in the xy-model the direction of the flow depends both on the x- and on the y-coordinate, in the x-model the direction depends only on x.

call the situations in Figure 1a and Figure 1b the xy-model and the x-model respectively. Notice that in the former case one has flow-threads, in the latter case flow-layers. These models are simplified but, nevertheless, they contain basic features of realistic situations, such as the layered patterns observed in incipient turbulence. The physical consequences of such flow environments are quite impressive: one observes enhanced diffusion, a decrease of the role of hydrodynamic interactions, as well as chain stretching and rupture.

We now analyze the motion of model polymers in such random flows. As for many other problems in polymer physics, scaling arguments can be successfully used to describe complex behaviors from a simple point of view,[7,8] and we apply such scaling arguments to the problem at hand. The essential point here is that for times much longer that the characteristic internal relaxation times, which are either the Zimm-time t_Z or the Rouse-time t_R, the polymers behave like simple Brownian particles subject to an *effective flow*. In the Zimm-model (the polymer coil acts like an impenetrable object) we apply an Imry-Ma type argument to estimate firstly the effective flow, from which, using dynamic scaling, the motion of individual monomers is inferred. For a Rouse chain the individual monomer motion can be calculated directly. Then, using scaling arguments, we obtain the diffusion of the center of mass (CM) and, hence, the effective flow.

The starting point for all these considerations is the motion of a *single Brownian particle* perpendicular to the flow, a problem whose exact solution is well-known. Since there is no flow component in the xy-plane the motion in this plane is unconstrained and hence diffusive. Of main interest is thus the dynamics in the z-direction. As in Ref. 1 we introduce F_0, the mean squared fluctuation of the flow's dragging force. Each flow layer has a certain thickness (correlation length). In order to ease the notation we define all lengths in units of the layer thickness and the time unit as the average time to cross one layer in the (xy)-plane. As a consequence the diffusion constant is unity.

Due to the free random motion in the xy-plane the Brownian particle changes layers (or threads) during the course of its motion. In this way the particle feels at different times different dragging forces in the z-direction. Were these forces completely uncorrelated in *time*, this also would result in an usual Brownian motion in the z-direction, the only difference being that now the corresponding diffusivity in the z-direction is given by F_0 rather than by unity. However, when the particle returns at a certain time t to an already visited layer (or thread), this enhances the motion in the direction of the flow of this layer (or thread). By averaging over the flow disorder one gets for $<z^2(t)>$, the mean squared displacement in the z-direction due to the flow:

$$<z^2(t)> \sim F_0 t^2 / S(t) \tag{1}$$

where $S(t)$ denotes the mean number of distinct visited layers (or threads) during t. In the following we will in general omit the (additive) diffusion effect on $<z^2(t)>$ due to the thermal fluctuations. Furthermore, from the theory of random walks $S(t) \sim \sqrt{t}$ in 1d (*i.e.* for the x-model) and $S(t) \sim t/\ln t$ in 2d (*i.e.* for the xy-model). It follows that:[6,1]

$$<z^2(t)> \sim F_0 t \ln t \sim F_0 t \qquad \text{for the } xy\text{-model} \tag{2}$$

and

$$<z^2(t)> \sim F_0 t^{3/2} \qquad \text{for the } x\text{-model} \ . \tag{3}$$

In the last expression of Eq. (2) we have suppressed logarithmic corrections. This leads to an almost normal diffusion for the xy-model. For the x-model, on the other hand, the diffusion is enhanced, Eq. (3), a fact already noted by Matheron and de Marsily.[6] The diffusion enhancement in Eq. (3) is due to the fact that a random walker returns frequently to already visited layers, in which it experiences the same flow direction. These flow layers carry then the particle much farther away than simple diffusion. Note that Eq. (1) is also valid in the general case of anomalous diffusion[9] in the transverse plane, say when $S(t) \sim t^{\alpha}$, with $\alpha < 1$. Then one has $<z(t)> \sim F_0 t^{2-\alpha}$. One application of this relation is provided by the motion of a single segment of a Rouse chain,[11] see section 3.

Generalizing the results for a single Brownian particle to polymer chains creates two problems. Firstly, different monomers will generally be located in different layers (or threads). This leads to an average over the flow components, resulting in an effective flow. For the Zimm-model we will perform the average within a scaling approach, using an Imry-Ma-type argument.[10] The core of this argument is the law of large numbers, *i.e.* the fact that the fluctuations of n independent random events scale as $\sqrt{n}$. We will outline this procedure in the next section. Secondly, a polymer chain screens the hydrodynamic interaction mediated by the surrounding solvent quite efficiently, see for instance Ref. 11. In fact for low field flows the diffusion coefficients of a polymer in the Zimm-model and of an impenetrable sphere coincide,[11] so that one may well approximate the polymer by such a sphere. However, when the flow disorder is very strong the chain may experience a large stretching, resulting in hydrodynamical »opening«. One expects then the Rouse model to come into play. However, one has to note that for overstretched chains the Gaussian model underlying the Rouse dynamics is violated so that the Rouse model itself may become invalid. In section 4 we discuss a possible Zimm-Rouse cross-over.

Given these facts, for the Zimm model we start by viewing the polymer as an impenetrable object, so that the external flow acts only on the *surface* of the coil created by the chain. The average over the flow directions is taken than over the projection of the coil on the xy-plane. The global motion of the polymer mimicks that of a single Brownian particle subjected to an averaged flow. On the other hand, in the Rouse-model the polymers are permeable (free-draining), so that all monomers are subjected to the flow.

The paper is organized as follows: In the next section we establish the dynamics of a Zimm-chain for long and for short times. Section 3 is devoted to the Rouse-chain; here we study the behavior both in the idealized case of a Gaussian chain and also by taking excluded volume interactions into account. For Gaussian chains we recover the exact results of Ref. 1. In Section 4 we study the conformations of chains under random flow and also discuss possible cross-over phenomena. The paper closes with short conclusions.

2. THE ZIMM-CHAIN IN RANDOM FLOWS

As is well-known, the radius of gyration R of a polymer chain in solution depends on the number of monomers (mass) N and on the microscopic interactions. One has the standard relation:

$$R \sim N^{\nu} , \tag{4}$$

where the exponent ν is approximately 3/5 (Flory – expression) for a good solvent and 1/2 for a Θ-solvent. In the Zimm-model the characteristic time

t_Z for the inner modes of the chain to relax and also for the chain to diffuse over the distance R scales as:[11]

$$t_Z \sim R^3 \ . \tag{5}$$

Measuring lengths in units of R and the time in units of t_Z the diffusion constant in the xy-plane is unity.

Polymers are coiled, and we view them (Zimm-model) as impenetrable but soft objects. We denote their characteristic (hydrodynamic) radius by ρ, and have $\rho \sim R$.

The random flow acts on the projection of the coil on the xy-plane, whose area scales as R^2; integrating the flow over this area gives the effective force experienced by the coil in the z-direction. Now, for uncorrelated flow directions this effective (excess) force averaged over several layers or threads obeys the central limit theorem. In the theory of ferromagnets in random fields this method of averaging is familar from Ref. 10; for this reason it is sometimes called the Imry-Ma method.

In the xy-model there are R^2 independent flow threads, of strength $\sqrt{F_0}$ each, which impinge on the coil. The effective force on the coil is then, according to the central limit theorem, in average given by $\sqrt{F_0}\,\sqrt{R^2} = \sqrt{F_0}R$. In the x-model there are R independent flow layers, each of which contributes to the total force a term $R\sqrt{F_0}$. Given that the flow orientation in the layers is random leads under the central limit theorem to an average force of $\sqrt{F_0}R\sqrt{R}$.

Summarizing the results of this procedure we have for the force:

$$\sqrt{F} \sim \sqrt{F_0}R^{\alpha} \ , \tag{6}$$

with $\alpha = 1$ in the xy-model and $\alpha = 3/2$ in the x-model. For times larger than t_Z the coil may be viewed as a simple Brownian particle subjected to a random flow. Expressing times in units of t_Z, lengths in units of R and using Eq.(2) we get for the xy-model:

$$\langle (z/R)^2 \rangle \sim F(t/t_Z) \ , \tag{7}$$

which, together with Eqs. (4), (5) and (6) yields:

$$\langle z^2 \rangle \sim F_0 R t \sim F_0 N^{\nu} t \ . \tag{8}$$

Note that the effective diffusity in the flow-direction increases with N. This fact is in marked contrast to the motion in the xy-plane, described by the Zimm diffusion coefficient, which goes as R^{-1};[11] hence $\langle x^2 \rangle = \langle y^2 \rangle \sim t/N^{\nu}$.

The same procedure applied to the x-model leads using Eq.(3) to:

$$<(z/R)^2> \sim F(t/t_Z)^{3/2} , \tag{9}$$

and thus we get:

$$<z^2> \sim F_0 R^{1/2} t^{3/2} \sim F_0 N^{\nu/2} t^{3/2} . \tag{10}$$

Note that here, compared to Eq.(8) the effect of the polymer mass is reduced but that the motion is superdiffusive, going as $t^{3/2}$, as in the MdM original model.

So far we have considered only the long time behavior of the chain, *i.e.* $t > t_Z$. To obtain the motion of a single segment of the chain at shorter times $(t < t_Z)$ a simple scaling argument can be invoked: Since t_Z is the only characteristic time scale in the problem, an universal dynamical behavior should be determined by the dimensionless combination $\tau = t/t_Z$.

For the xy-model we write using Eq.(8):

$$<z_s^2> \sim F_0 R t f(t/t_Z) , \tag{11}$$

where $f(\tau)$ is a, yet unknown, scaling function. For large values of τ, *i.e.* for $t >> t_Z$, Eq. (8) has to be recovered, since in this case the single segment motion is constrained by the CM diffusion. From this it follows that $f(\tau) = 1$ for τ large. On the other hand, for $\tau << 1$ the single segment does not know much about the chain's length (it has not yet explored such a large scale). Consequently, in this case the segmental motion should be *independent of* N, and hence independent of R. For a power-law behavior for $f(\tau)$ for small τ, *i.e.* for $f(\tau) \sim \tau^m$ we have to require from Eqs. (11) and (5) that $RR^{-3m} = R^0$; *i.e.* that $m = 1/3$, *independent* of the exponent ν. This leads both for a θ-solvent and for a good solvent to the result:

$$<z_s^2> \sim F_0 t^{4/3} \quad \text{for} \quad t << t_Z . \tag{12}$$

The x-model can be treated in the same way. Using Eqs. (10) and (5) we obtain for the segmental motion that now $m = 1/6$, and thus

$$<z_s^2> \sim F_0 t^{5/3} \quad \text{for} \quad t << t_Z . \tag{13}$$

Both Eqs.(12) and (13) show that the segmental motion is enhanced.

3. THE ROUSE-CHAIN IN RANDOM FLOWS

In the Rouse model each segment of the chain is exposed to the flow. Usually the Rouse model is associated with Gaussian chain statistics and hence neglects excluded volume effects. However, this is formally not necessary: One can account for the excluded volume, while disregarding hydrodynamic effects, see Ref. 11. While this situation is hardly realized in experiments (it exists in computer simulations), we cannot rule it out *a priori* for randomly layered fluids.

We have first to establish t_R, the Rouse-time for general ν. Now t_R gives both the internal relaxation time and also the time necessary for the center of mass of the chain to move over a distance $R \sim N^{\nu}$. The CM diffusion coefficient is then

$$D \sim R^2/t_R \sim N^{2\nu}/t_R \ . \tag{14}$$

On the other hand, since in the Rouse model each segment feels the viscosity of the medium it follows that $D \sim 1/N$ and thus

$$t_R \sim N^{1+2\nu} \ . \tag{15}$$

This reproduces the result of §4.3 in Ref. 11.

To study the dynamics in the Rouse case we start first with the motion of a single segment. At long times, $t >> t_R$, the motion in the xy-plane is diffusive, the segment following the behavior of the CM. Hence for the displacement in the xy-plane we have, say for the x-component:

$$<x_s^2(t)> \sim \frac{t}{N} f(t/t_R) \ . \tag{16}$$

In Eq. (16) we have introduced the scaling function $f(\tau)$, so that $f(\tau) = 1$ for $\tau = t/t_R >> 1$; furthermore, we used $D \sim 1/N$ for the CM motion, as discussed above. Taking now that $f(\tau) \sim \tau^q$ for $\tau << 1$, and noticing, as in the Zimm-case, that for very short times the segmental dynamics is independent of N we obtain $N^{-1}(N^{1+2\nu})^{-q} = N^0$. Hence $q = -1(1 + 2\nu)$ and we thus have for $t << t_R$:

$$<x_s^2(t)> \sim t^{1+q} = t^{2\nu/(1+2\nu)} \ . \tag{17}$$

For $\nu = 1/2$ Eq. (17) reproduces the well-known $\sqrt{t}$ short-time dynamics of the Rouse-segment. Furthermore we can now determine $<z_s^2(t)>$ in the short-time regime, by considering the segment to be rather free and thus to be a simple Brownian particle. Using the extension of Eq. (2) and Eq. (3) to the fractal case, with $\alpha = 2\nu/(1 + 2\nu)$, we find for $t << t_R$

$$\langle z_s^2(t)\rangle \sim F_0 t^{2-\alpha} = F_0 t^{(2+2\nu)/(1+2\nu)} \qquad \text{in the } xy\text{-model} \tag{18}$$

and

$$\langle z_s^2(t)\rangle \sim F_0 t^{2-\alpha/2} = F_0 t^{(2+3\nu)/(1+2\nu)} \qquad \text{in the } x\text{-model} . \tag{19}$$

For $\nu = 1/2$ the last expression reproduces the $t^{7/4}$-result of Ref. 1. For long times such as $t >> t_R$ the Rouse-chain moves as a whole, and hence $\langle z^2\rangle$ is again proportional to t and to $t^{3/2}$ in the xy- and the x-model, respectively. This allows us to determine the dependence of $\langle z^2\rangle$ on N. For $t >> t_R$ we have to match again the short time expressions, Eqs. (18) and (19), to the long-time, single particle dynamics as given by Eq. (2) and Eq. (3). We expect thus a scaling behavior of the form: $\langle z_s^2(t)\rangle = F_0 t^{2-\alpha} g_{xy}(\tau)$ for the xy-model and $\langle z_s^2(t)\rangle = F_0 t^{2-\alpha/2} g_x(\tau)$ for the x-model. For $\tau >> 1$ the scaling functions g must exhibit power law behavior in order to lead to the proper exponents for t in Eq. (2) and Eq. (3). In this way we obtain for $t >> t_R$ (the segmental motion coincides with the CM motion in this limiting case):

$$\langle z^2\rangle \sim F_0 N^1 t \qquad \text{for the } xy\text{-model} \tag{20}$$

and

$$\langle z^2\rangle \sim F_0 N^{1/2} t^{3/2} \qquad \text{for the } x\text{-model} . \tag{21}$$

These results agree with Ref. 1. Interestingly, in this time domain the expressions are independent of ν.

4. CONFORMATIONS OF CHAINS IN RANDOM FLOWS

In this section we discuss briefly the conformations of polymers in random flow fields. In such situations the polymer gets deformed by the flow in the z-direction. Now, the contribution of the flow to the mean squared radius of gyration can be obtained from the dynamical results. We note firstly that in the absence of flows and thermal fluctuations the mechanical equivalent of a Rouse-chain would collapse into a point since the equilibrium distance between connected monomers is zero. Thermal fluctuations lead now to a nonzero radius of gyration R as given by Eq. (4).

Because thermal fluctuations and the randomness of the flows are uncorrelated one has for the mean squared extension Z^2 of the polymer in the direction of the flow $Z^2 = R^2 + \xi^2$, were ξ^2 is the contribution we want to evaluate. We note that R is given by the average fluctuation of the segments around the CM of the chain. Furthermore, the characteristic time for a segment to diffuse over a distance R is given by t_Z in the Zimm-model and by t_R in the Rouse-model. We calculate ξ^2 in the same way, by evaluating for a segment the mean squared displacement due to the flow during the char-

acteristic time t_Z or t_R. This is, at the same time, the »matching condition«, which connects the short to the long time domains. For the Zimm-model these considerations lead to:

$$\xi^2 = \langle z^2(t_Z)\rangle = cF_0N^{4\nu} \quad \text{for the } xy\text{-model} \tag{22}$$

and

$$\xi^2 = \langle z^2(t_Z)\rangle = cF_0N^{5\nu} \quad \text{for the } x\text{-model} . \tag{23}$$

In Eq. (22) and Eq. (23) use was made of Eqs. (8) and (10) and c denotes constant prefactors. As usual in such problems[1,12,13] ξ^2 grows superlinearly with N; this also indicates the limits of validity of the approach for strong external fields, which may overstretch the chain. The condition $\xi^2 << b^2N^2$ with b being the persistence length corresponds to conditions of the form $F_0 << cN^{2-4\nu}$ for the xy-model and $F_0 << cN^{2-5\nu}$ for the x-model.

However, this estimate disregards several effects: First of all, the stretched chain will contract in the direction perpendicular to the flow,[7,14] an effect which will influence the dynamics. Furthermore, as a result of stretching, the hydrodynamic screening is expected to become less important. It is not clear to us now whether this will happen continuously, resulting in a string of hydrodynamic blobs whos sizes depend on F_0, or whether this may happen suddenly, resulting in an overstretched Rouse chain at once. Clearly, here more work is needed.

These features do not affect the Rouse regime for ideal chains. Using the same arguments as before we obtain for ξ^2 in the Rouse-model

$$\xi^2 = \langle z^2(t_R)\rangle = cF_0N^{2+2\nu} \quad \text{for the } xy\text{-model} \tag{24}$$

and

$$\xi^2 = \langle z^2(t_R)\rangle = cF_0N^{2+3\nu} \quad \text{for the } x\text{-model} . \tag{25}$$

In Eqs. (24) and (25) we again denote constant by c and use was made of Eqs. (20) and (21). Eq. (25) reproduces the result of Ref. 1 for $\nu = 1/2$. In the Rouse-model the dependence of ξ^2 on N turns out to be stronger than in the Zimm-case. A rough estimate for the limit of validity of the model in terms of the magnitude of the external flow fields leads to $F_0 << cN^{-2\nu}$ for the xy-model and $F_0 << cN^{-3\nu}$ for the x-model.

5. CONCLUSIONS

In this work we have determined using scaling arguments the motion of a polymer chain subjected to random flows. The polymer was modeled both in the Zimm- and in the Rouse-framework. In several instances the

center of mass as well as single segments of the chain obey anomalous diffusion laws of the form

$$\langle z^2 \rangle \sim t^{\zeta} \tag{26}$$

where $\zeta \neq 1$. Let us now summarize the results for polymers in random flows which differ from those found for simple diffusion:

- Both in the Zimm- and in the Rouse-model we find (see Eqs.(8) and (10) or Eq. (20) and Eq. (21)) that with increasing chain length the displacement in the z-direction increases. This is due to the fact that longer chains diffuse more slowly in the xy-plane and hence change less often the flow patterns to which they are subjected. This feature may possibly be used to separate chains: In a distribution of polymers of different lengths, longer polymers travel larger distances along the z-axis.
- Both in the Zimm- and in the Rouse-model the exponent ζ for the segmental motion turns out to be larger in the short-time domain, compare Eqs. (8), (10), (12), (13) and (18–21). This is in marked contrast to the usual situation (in the absence of external flow fields), where ζ for short times is smaller than for long times.
- In addition to dynamical effects, the polymer chain becomes stretched in the direction of the flow. This may abolish the hydrodynamic screening, resulting in a Zimm-Rouse cross-over.

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SAŽETAK

Polimerni lanci u strujama sa slučajnim slojevima: Skalirajući pristup

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Razmotrena je difuzija polimernih lanaca u strujama sa slučajnim slojevima. Korištene su ideje skaliranja, a slučajnost struje uzeta je u obzir korištenjem argumenta tipa Imry-Ma. Za opis dinamike lanaca korišten je kako Zimmov pristup sa zasjenjenim hidrodinamičkim međudjelovanjima tako i Rouseov pristup. Izračunana je unutarnja dinamika lanca (gibanje segmenata) kao i gibanje težišta. U slučaju Rouseova modela reproducirani su točni rezultati Oshanina i Blumena. Dinamika polimera nakon dugog vremena ili je difuzijskog tipa ili je pojačana, ovisno o neuređenosti struje i hidrodinamičkim međudjelovanjima. Konačno, za gornje uvjete izračunana je i konfiguracija lanaca.