# Polymer Conformations in Random Velocity Fields

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A polymer in a random velocity field is investigated in application to turbulent drag reduction. The model employed constrains the links to a constant length. The results differ strongly from the usual linear model and show novel behavior. With no thermal fluctuations included, and with finite stiffness, the steady state of the chain is a straight line. When the stiffness is zero the straight configuration is marginally stable. When thermal fluctuations are included, the amplitude of bending modes has a power-law probability distribution, whose exponent depends continuously upon parameters.

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The study of polymers in a random velocity field has important applications to the problem of drag reduction in turbulent flow. Small amounts of polymer are routinely injected into liquids as this has been found to reduce the amount of dissipation. The reason for this is still not clear. The problem is difficult to understand and is somewhat counterintuitive, as at first sight, one would predict an increase in energy dissipation due to the enhanced low shear viscosity. Theoretical attempts to explain this phenomenon have been hindered by a lack of a good microscopic theory of the polymer's dynamics [1–11] and have been mainly phenomenological. Anisotropy may play an important role and is the subject of much research [12].

In this Letter the microscopic dynamics of a polymer in a random velocity field are investigated. Fully developed turbulence is one example of a random velocity field; however, its statistics are still not well understood, so here certain statistical properties shall be assumed in order to make headway into this problem.

The phenomenon of drag reduction is observed for a large class of polymers. Because of this, one does not want to work with a polymer model containing irrelevant details. The model that is normally studied first in polymer physics is the Rouse model. It approximates the polymer chain as beads connected by linear springs. Unfortunately, and quite surprisingly, it does not work well in the case studied here, because the end-to-end distance $R$ does not behave in a physically sensible manner. It can be shown that $\langle R^n \rangle$ is infinite for sufficiently large $n$ [10]. It is therefore clear that one must add extra nonlinear terms to the model in order to cure this unphysical divergent stretching. This makes analysis more difficult but is necessary in order to have a "zeroth"-order theory of this problem, which is the main aim of this Letter.

The nonlinear model chosen is a rigid link model with stiffness. At first sight it would appear difficult to make much headway in solving a nonlinear, many-body, statistical mechanics problem that is so far from equilibrium; however, as we shall see, the model goes to another fixed point far away from the Gaussian random walk, which can be treated theoretically. The rigid link model has the nonlinear constraint that the distance between monomers is constant; however, the individual links can rotate. A bending energy can also be introduced to give the molecule a finite stiffness. This is done for two reasons. First, resistance to bending is seen in a large variety of polymers, and this Letter makes predictions that may be experimentally observable. Second, the solution to this problem is best understood as a function of the stiffness parameter.

The system is first analyzed with no thermal noise and just the random velocity field alone. It will be shown that for any finite stiffness the exact solution to this problem is simply when the molecule is completely stretched in a straight line. It rotates rigidly and does not bend, that is, this solution is stable. At the point where the stiffness is zero, the behavior is quite different from what is seen in other polymer systems. The straight-line solution is "marginally stable," meaning that the probability of bending decreases as a power of time, $\propto t^{-1/2}$. This is interesting in that this "marginal stability" is occurring in a random sense, rather than deterministically as is normally seen. Another interesting feature of the solution is its behavior at finite temperature. A chain with nonzero stiffness can no longer be completely straight due to the presence of small thermal noise. In equilibrium, this will lead to a Gaussian probability distribution for the amplitude of bending modes. However, in the presence of a random velocity field, one instead finds a power-law probability distribution for bending modes, quite unlike the equilibrium case. The power law that one finds is also quite different from what one finds in equilibrium critical phenomena in that it depends continuously on the chain stiffness and the strength of the random velocity field.

The physics of drag reduction by polymers is greatly simplified by the fact that the end-to-end length of the polymer chain is almost always less than the Kolmogorov dissipation length $l_d$. As an example, take the experiment of Ref. [12]. In this paper $l_d \approx 0.04$ mm, which is more than an order of magnitude larger than the arclength of the chain. In this case the velocity field seen by the chain can be taken to a good approximation to be varying linearly with distance. Therefore the velocity-velocity correlation function to a very good approximation has a quadratic spatial dependence. In a small distance expansion of this correlation function, the next-order quartic term is smaller than the quadratic by the square of the

 

ratio of chain length to $l_d$. Therefore the next-order term should be 2 orders of magnitude smaller than the quadratic term. It is also worthwhile noting the relative strengths of thermal noise and the turbulent velocity field. Again using the experiment of Ref. [12], one must compare the strength of the hydrodynamic force $f_H$ with that due to thermal fluctuations $f_T$. The appropriate measure is $\int\langle f_T(0)f_T(t)\rangle dt/\int\langle f_H(0)f_H(t)\rangle dt$. One estimates $f_H$ as the force on a persistence length of chain $l_p$ which should be approximately $6\pi\eta l_p v$, where $\eta$ is the viscosity and $v$ is the velocity of a segment of chain relative to, say, a chain end. Thus the fluctuation-dissipation theorem gives $\int\langle f_T(0)f_T(t)\rangle dt = 6\pi\eta k_B T l_p$, where $T$ is the temperature. $\int\langle f_H(0)f_H(t)\rangle dt$ can be estimated by replacing the integral by $\tau_H$, the hydrodynamic correlation time at the Kolmogorov dissipation length. Using the Kolmogorov scaling theory of turbulence, it is seen that the above ratio of the two force strengths is about $10^{-2}$. Thus we can conclude that the dominant effect on the chain's dynamics is due to the random velocity field. This is hardly surprising given the experimental finding that polymers often break in highly turbulent flows, and seldom do so in equilibrium.

We now briefly outline the analyzing steps used in the paper and will discuss them further below. Full details of the analysis will be published elsewhere. First, the polymer chain is being advected by the random velocity field. Given the statistics of the velocity in the laboratory frame, one would like to derive the statistics of the velocity field seen in the reference frame of the center of mass of the polymer, that is, the statistics in the Lagrangian frame. For the case of real turbulence this is still an unsolved problem. However, if one takes a model where the statistics are arbitrary in space, but white noise in time, then it is possible to perform a transformation to the Lagrangian frame and calculate the statistics in this frame in terms of the statistics in the laboratory frame. Second, the equation of motion of the rigid link model can be expressed using Lagrange multipliers that physically represent the chain tension. The straight line is then shown to be a solution. Third, a stability analysis is carried out by considering small perturbations about the straight-line solution. One obtains equations for the perturbations that have multiplicative noise. In two dimensions these equations decouple into separate ordinary differential equations. These equations can be analyzed. The behavior of the three-dimensional case is similar to that in two dimensions, but the methods used to treat it will be discussed in detail elsewhere. Finally the analysis is checked by a numerical simulation which confirms the features predicted by the theoretical analysis. These steps will now be discussed in more detail.

Consider a free draining chain in $d>1$ dimensions, with $N$ links and coordinates $\mathbf{r}_{-N/2},\ldots,\mathbf{r}_{N/2}$ in a random velocity field $\mathbf{v}(\mathbf{r},t)$. The equation of motion of the chain is

$$\dot{\mathbf{r}}_i = \mathbf{v}(\mathbf{r}_i,t) + \mathbf{f}_i\{r_k\} . \tag{1}$$

The statistics of the velocity field are white noise in time and are taken to be Gaussian,

$$\langle \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r}',t')\rangle = \Gamma(\mathbf{r}-\mathbf{r}')\delta(t-t') . \tag{2}$$

At this point we have not specified the nature of $f_i$; however, later it will be taken to rigidly constrain the absolute distance between neighboring monomers and to add a stiffness to the chain. We have not included thermal noise in this equation. It is easily added, but not necessary for the present purpose, which is to transform this equation to the Lagrangian frame. Thermal noise does not affect this transformation. As discussed above, for most experimental situations, the arclength of the polymer is much less than the dissipation length scale of the velocity field. Therefore $\Gamma$ need only be expanded out to second order. That is, we are assuming that the velocity field seen by the chain has only a linear variation with distance. The most general form with the correct symmetry properties is [10]

$$\Gamma_{\nu\eta}(\mathbf{r}-\mathbf{r}') = \Gamma_{\nu\mu}(0) - \tfrac{1}{2}\left[A\sum_{\eta}(r_\eta - r'_\eta)^2\delta_{\nu\mu} + B(r_\nu - r'_\nu)(r_\eta - r'_\eta)\right], \tag{3}$$

where the greek subscripts denote the different components of the tensors. By requiring $\nabla\cdot\mathbf{v}=0$, it is easy to show that $A/B=-(d+1)/2$. It should also be pointed out that in the opposite extreme of no external velocity field, and just thermal noise, this formalism correctly yields random walk statistics for the chain.

In order to derive the form of the problem in the Lagrangian frame, it is convenient to use the Einstein-Fokker-Planck equation for the probability distribution of the $\mathbf{r}_i$'s as a function of time, $P(\{\mathbf{r}_i\},t)$. This can be derived from Eq. (1) using the method described by Klyatskin and Tatarskii [13]. In the following the components of the vector $\mathbf{r}_i$ will be denoted by $r_{i\nu}$. Transforming this equation to center-of-mass coordinates yields

$$\dot{r}_{i\nu} = \sum_{\nu} M_{\nu\mu} r_{i\mu} + f_{i\nu}\{\mathbf{r}_k\} , \tag{4}$$

where $r$'s refer to coordinates relative to the center of mass, and $M_{\nu\mu}$ is a random matrix that varies as a function of time with the following Gaussian correlations:

$$\langle M_{\nu\mu}(t)M_{\eta\lambda}(t')\rangle \propto [(d+1)\delta_{\nu\eta}\delta_{\mu\lambda} - \delta_{\nu\mu}\delta_{\eta\lambda} - \delta_{\nu\lambda}\delta_{\mu\eta}]\delta(t-t') . \tag{5}$$

A matrix of this form can be realized by combining two different types of matrices. One is an uncorrelated random matrix and the other is an antisymmetric random matrix.

Now that we have a model for the chain in the center-of-mass reference frame it is possible to analyze its dynamics. We now consider a particular form of $f_{i\nu}\{\mathbf{r}_k\}$, the internal forces between monomers. The chain is modeled as a set of rigid links where the distances between neighboring monomers is constant. Stiffness is included by

adding a potential energy for bending for the $i$th monomer of the form $s_0(\mathbf{r}_{i+1}-\mathbf{r}_i)\cdot(\mathbf{r}_{i-1}-\mathbf{r}_i)$. We now wish to determine the steady-state solution for this model.

We will see that one possible dynamical solution is to have the chain randomly rotate as a straight line. We will examine the stability of such a solution by adding an initial perturbation to the conformation.

With rigid links there must be a tension $t_i$ between the neighboring $i$th and $(i+1)$th monomers. These tensions are nothing more than Lagrange multipliers added to constrain the distance between adjacent links to be constant. The equation of motion of the chain for zero stiffness is then

$$\dot{\mathbf{r}}_i = t_{i+1}\Delta_{i+1} - t_i\Delta_i + \mathbf{M}\mathbf{r}_i\,, \tag{6}$$

where $\Delta_i = \mathbf{r}_{i+1}-\mathbf{r}_i$. We can obtain the tensions as follows. Taking the difference between the equation for $i+1$ and $i$ and taking the derivative of the resulting equation into $\Delta_i$ gives the left-hand side zero, so that

$$0 = \Delta_i\cdot\mathbf{M}\cdot\Delta_i + t_{i+2}\Delta_{i+1}\cdot\Delta_i - 2t_{i+1}\Delta_i\cdot\Delta_i + t_i\Delta_{i-1}\cdot\Delta_i\,. \tag{7}$$

This gives a matrix equation from which one can solve for the tension in terms of the conformation $\Delta_i$'s and the velocity matrix $\mathbf{M}$. If we try a straight-line conformation then $\Delta_i = \Delta$ for all $i$. Solving for the tension yields $t_i^0 = \frac{1}{2}(i^2 - N^2/4)\Delta\cdot M\cdot\Delta$. (Recall $-N/2 \le i \le N/2$.) The equation of motion for $\Delta$ is then

$$\dot{\Delta} = M\cdot\Delta - [\Delta\cdot M\cdot\Delta]\Delta\,. \tag{8}$$

The right-hand side is just the component perpendicular to the rod of the force due to the velocity field. Therefore one sees that the straight line is a solution which will rotate in time according to the above equation.

Now consider adding a small perturbation to $\Delta$, $\Delta_i = \Delta + \epsilon_i$. We are only interested in $\epsilon$ in the direction perpendicular to $\Delta$. Therefore we consider the equation for $\mathbf{a}_i = \Delta\times\epsilon_i$. This gives a multiplicative noise-type equation where all of the $\mathbf{a}_i$ are coupled together. It is therefore convenient to change basis and to look at the $k$th normal mode of such an equation $v_i^k$ that satisfies the eigenvalue equation

$$[(i+2)^2 - N^2/4]v_{i+1}^k - 2[(i+1)^2 - N^2/4]v_i^k + (i^2 - N^2/4)v_{i-1}^k = \lambda_k v_i^k. \tag{9}$$

Then we can write an equation for the amplitude of the $k$th normal mode $\mathbf{a}_i = \mathbf{b}_k v_i^k$ and obtain

$$\dot{\mathbf{b}}_k = \mathbf{C}\cdot\mathbf{b}_k + (\lambda_k+1)\Delta\cdot\mathbf{M}\cdot\Delta\mathbf{b}_k\,. \tag{10}$$

This is just a multiplicative noise equation for $\mathbf{b}_k$. In $d$ equal to two dimensions, the matrix $\mathbf{C}$ is zero, and in three dimensions it is a rather cumbersome expression that is linear in $\mathbf{M}$ and bilinear in $\Delta$. In two dimensions $\mathbf{b}$ has only one component and can be taken to be a scalar. This can then be written as $d\ln b/dt = f(t)$, where $f(t)$ is random and has zero mean. Thus *the logarithm of small-amplitude perturbations performs a random walk in time.* This is quite a novel form of behavior and leads to a kind of marginal stability as is seen from the following argument. Because the chain has a maximum extension it is clear that $b$ is bounded from above. This in turn implies that the random walk $\ln b$ is bounded from above. Although the approximations yielding the multiplicative equation are clearly not valid for large $b$, one only needs to use the fact that when the chain enters the large-$b$ region, say $b > \frac{1}{2}$, it will spend a finite amount of time in this region. However, $\ln b$ is not bounded from below. Hence from the properties of one-dimensional random walks, $\ln b$ will diffuse further and further in the negative $\ln b$ direction. The probability of the walk being near the upper bound decreases as $t^{-1/2}$. In this sense the straight-line solution is marginally stable.

It is easy to see that if finite stiffness is included in this analysis, the random walk will acquire a net drift velocity in the negative direction, and will therefore be exponentially unlikely to be near the upper bound. In this case the straight-line configuration is stable.

The three-dimensional case is complicated by the vector nature of Eq. (10). However, a steady-state solution of this kind of equation is found using the generalized Fokker-Planck equation, and yields similar results to the two-dimensional case. Details of the methods used to analyze such equations will be published elsewhere.

It is straightforward to add thermal noise to the problem as well. When this is done Eq. (10) has an extra additive noise term added on the right-hand side. The steady-state probability distribution for equations of this form can be analyzed. It can be shown that with finite stiffness, the different modes give a power-law decay of the form $P(b_k) \propto b^p$, where $p$ depends continuously on the ratio of the variance of the velocity field to the chain stiffness $s_0$. It has not been possible to find the form of this exponent but weak bounds can be placed on its value. In addition, the exponent $p$ should be independent of the strength of thermal noise. Note that this analysis only includes linear terms so that this approach should only be applicable at low temperatures. Details of this analysis will soon be published.

It is also possible using Eq. (4) to simulate the motion of the polymer chain to check the above analysis. The simulation is very similar to one used previously to investigate electrophoresis [14]. The results are in accord with the above analysis. Without any stiffness, a chain initially in a coiled state will stretch until it appears marginally stable, with the chain straight most of the time and occasionally sojourning, folding like an accordion. The simulation can also be done at finite temperatures. If one chooses the amplitude ratio of velocity fluctuations due to thermal noise to velocity fluctuations of the external random field to be $\frac{1}{10}$, one still obtains highly stretched conformations, as can be seen in Fig. 1. The first four

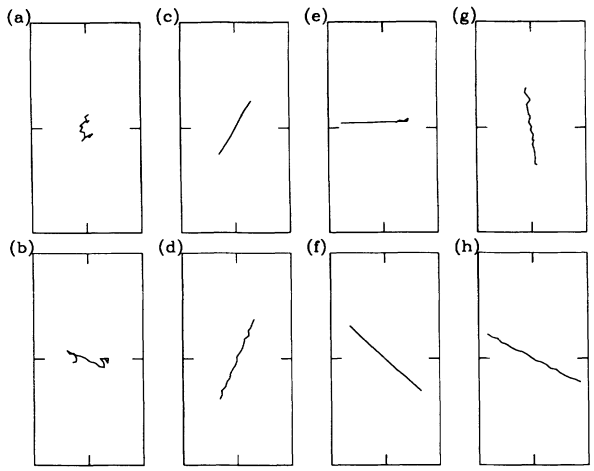


FIG. 1. Snapshots of a chain in random velocity field as a function of time, projected from three dimensions. The strength of thermal velocity is $\frac{1}{10}$ that of the external turbulent field. The times are (in arbitrary units) (a) 1, (b) 2, (c) 3, (d) 4, (e) 31, (f) 32, (g) 33, and (h) 34. At $t=0$, the chain starts out as a random walk and stretches out.

frames, Figs. 1(a)–1(d), show in arbitrary units how a chain of length 20 monomers stretches out from a coiled conformation for $t=1,2,3,4$. Figures 1(e)–1(h) show the chain for $t=31,32,33,34$. This amount of thermal noise should be a typical experimental value.

One could criticize the analysis made here on the grounds that the random velocity field was taken to be white noise in time. This was necessary in the derivation of Eq. (4). However if, instead of deriving this equation, we assume that it is valid with a velocity field that has Gaussian statistics *that need not be white noise,* then the main conclusions should still hold. This is because the stability analysis should be unaffected by finite time correlations.

The most dubious point of this analysis is the assumption that the velocity statistics are Gaussian in the Lagrangian frame. The statistics are certainly not Gaussian in the Eulerian frame. The correct statistics in the Lagrangian reference frame still appear to be unknown, but they are likely to be multifractal. This could substantially alter the above results. The effect should be to greatly increase fluctuations and therefore to destabilize the straight-line solution. As polymer chains experimentally appear to behave differently than rigid rods, this implies that the multifractal nature of turbulence is important in understanding the statistics of polymers in turbulent flows. It may therefore be important in understanding drag reduction.

Therefore an important area for future research is to investigate how multifractal statistics of the velocity field affect the statistics of polymers in turbulent flow. This may be possible to understand in general, without a specific model of Lagrangian statistics, which is at present not available. It may even be possible to use such a theoretical treatment in conjunction with experiments to gain a better understanding of the statistics of fully developed turbulence.

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