Anomalous polymer dynamics is non-Markovian: memory effects and the generalized Langevin equation formulation

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Abstract. Any first course on polymer physics teaches that the dynamics of a tagged monomer of a polymer is anomalously subdiffusive, i.e., the mean-square displacement of a tagged monomer increases as $t^\alpha$ for some $\alpha < 1$ until the terminal relaxation time $\tau$ of the polymer. Beyond time $\tau$ the motion of the tagged monomer becomes diffusive. Classical examples of anomalous dynamics in polymer physics are single polymeric systems, such as phantom Rouse, self-avoiding Rouse, self-avoiding Zimm, reptation, translocation through a narrow pore in a membrane, and many-polymeric systems such as polymer melts. In this pedagogical paper I report that all these instances of anomalous dynamics in polymeric systems are robustly characterized by power-law memory kernels within a unified generalized Langevin equation (GLE) scheme, and therefore are non-Markovian. The exponents of the power-law memory kernels are related to the relaxation response of the polymers to local strains, and are derived from the equilibrium statistical physics of polymers. The anomalous dynamics of a tagged monomer of a polymer in these systems is then reproduced from the power-law memory kernels of the GLE via the fluctuation-dissipation theorem (FDT). Using this GLE formulation I further show that the characteristics of the drifts caused by a (weak) applied field on these polymeric systems are also obtained from the corresponding memory kernels.
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1. Introduction

One of the most common phrases of wisdom in polymer physics is that a polymer, in its
terminal relaxation time $\tau$, displaces itself by its own size in physical space [1,2]. Being
constructed from monomers connected in series, a polymer has a wide range of length
scale dependent relaxation times. The longest one of them is the terminal relaxation
time $\tau$, manifested in the decay of the polymer’s end-to-end vector correlation function.
(E.g., for a phantom Rouse polymer of length $N$, the relaxation time corresponding to
length scale $N/p$ scales $\sim (N/p)^2$ with $p$ a positive integer, implying that $\tau \sim N^2$ for a
phantom Rouse polymer [2]). The terminal relaxation time $\tau$ of a polymer scales with
its length as a power-law $\tau \sim N^\kappa$ for some exponent $\kappa$, while its own size in space
scales as $N^\nu$ for some exponent $\nu$. If the polymer is to displace itself by its own size
in time $\tau$, in the simplest of cases the mean-square displacement of a tagged monomer
of a polymer must behave $\sim t^{2\nu/\kappa}$, and since the quantity $2\nu/\kappa$ is not necessarily unity,
the dynamics of a tagged monomer in a polymer must be anomalous till the terminal
relaxation time. If asked to provide canonical examples of such anomalous behavior, a
polymer physicist would almost certainly cite single polymer dynamics, such as phantom
Rouse ($\nu = 1/2, \kappa = 2$), self-avoiding Rouse ($\nu \approx 0.588$ in three dimensions (3D), $\nu = 3/4$
in two dimensions (2D) and $\kappa = 1 + 2\nu$) and self-avoiding Zimm ($\nu \approx 0.588$ in 3D,
$= 3/4$ in 2D and $\kappa = 3\nu$) polymers. (The correct single polymer dynamics in a fluid
was first presented by Zimm [3]. In this paper I refer to such polymers, for which the
monomers interact with each other via hydrodynamic interactions, as Zimm polymers. A
few years earlier than Zimm, Rouse [4] put forward a model for single polymer dynamics
that neglects the hydrodynamic interactions between the monomers. Although incorrect,
the corresponding (Rouse) polymer dynamics, for polymers that are self-avoiding, as well
as the phantom ones, i.e., polymers that can intersect themselves, resides at the heart
of polymer physics [2]—and widely used till today—largely due to its simplicity.) Given
such an abundance of anomalous dynamics in polymeric systems, a natural question is
whether it is possible to provide a generic stochastic foundation for it.

In a recent letter [5], hereafter referred to as Ref. I, I reported that the anomalous
dynamical behavior for phantom Rouse, self-avoiding Rouse and Zimm polymers, and
that of polymer translocation through a narrow pore in a membrane can be theoretically
formulated via the following generalized Langevin equation (GLE), wherein the velocity
$\vec{v}(t)$ of a tagged monomer and the force $\vec{\phi}(t)$ it experiences, are related to each other via

$$\vec{\phi}(t) = - \int_0^t dt' \mu(t-t') \vec{v}(t') + \vec{g}(t). \quad (1)$$

In equation (1) $\mu(t)$ is the memory kernel, and the stochastic noise term $\vec{g}(t)$ satisfies the
condition that $\langle \vec{g}(t) \rangle_0 = 0$, while the fluctuation-dissipation theorem (FDT) $\langle \vec{g}(t) \cdot \vec{g}(t') \rangle_0 \equiv \langle \vec{\phi}(t) \cdot \vec{\phi}(t') \rangle_{t'=0} = 3k_B T \mu(t-t')$ in 3D. Here $k_B$ is the Boltzmann constant, $T$ is the
temperature, and $\langle \cdots \rangle_0$ denotes an average over the stochastic noise realizations, including
an average over equilibrium configurations of the polymers at $t = 0$. Equation (1) can be
inverted to write

$$\vec{v}(t) = - \int_0^t dt' a(t-t') \vec{\phi}(t') + \vec{h}(t), \quad (2)$$

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where \( \tilde{\mu}(s)\tilde{a}(s) = 1 \) in the Laplace space, \( \langle \vec{h}(t) \cdot \vec{h}(t') \rangle_0 = 0 \), with the corresponding FDT \( \langle \vec{h}(t) \cdot \vec{h}(t') \rangle_0 \equiv \langle \vec{v}(t) \cdot \vec{v}(t') \rangle_{\vec{\varphi}=0} = 3k_B T a(t-t') \). In Ref. I, I argued that on the one hand \( \mu(t) \) is the mean relaxation response of the polymers to local strains, and can be derived from the equilibrium statistical physics of polymers; and on the other, \( a(t) \) characterizes the anomalous dynamics via the FDT: as the mean-square displacement of a tagged monomer is obtained by integrating \( \langle \vec{v}(t) \cdot \vec{v}(t') \rangle_{\vec{\varphi}=0} \) twice in time. An important property of the anomalous dynamics that transpires through this exercise is that if \( \mu(t) \sim t^{-\alpha} \) for some \( \alpha \), then the anomalous dynamics is also \( \alpha \). In other words, according to Ref. I, the anomalous dynamics for phantom Rouse, self-avoiding Rouse and Zimm polymers, and that of polymer translocation through a narrow pore in a membrane are connected to the mean relaxation response of the polymers to local strains.

The purpose of this paper is to provide a pedagogical account of the unified GLE foundation (1) and (2) for the classical examples of anomalous polymer dynamics, including the ones considered in Ref. I. The precise issues covered in this paper are the following.

(i) I provide an elaborate derivation of equations (1) and (2) for phantom Rouse polymers, which is the only fully analytically tractable polymer dynamical system.

(ii) I substantially supplement the scaling results of Ref. I with simulation data, and extend the GLE formulation to the cases of a single reptating polymer, and polymer melts.

(iii) Given the GLE formulation I show that the characteristics of the drifts caused by a (weak) applied field on these polymeric systems, too, are obtained from the corresponding memory kernels: if \( \mu(t) \sim t^{-\alpha} \) for some \( \alpha \), then the anomalous dynamics is also \( \alpha \). This could be thought of as the analog of the Nernst–Einstein relation [6].

(iv) Since the GLE is a description of the trajectories in phase space, this paper explicitly brings to light the non-Markovian character of the anomalous dynamics for polymeric systems. A natural question that then arises is ‘Is it possible to provide a probabilistic description of these trajectories in phase space?’ While in this paper I leave this question for further research, I note that in a limited context—for the anomalous dynamics of polymer translocation through a narrow pore in a membrane—the fractional Fokker–Planck equation (fFPE) has been put forward in recent times [7]. In this equation, an extension of the standard Fokker–Planck equation, anomalous dynamics is a consequence of introducing power-law waiting times before each jump of the concerned particle, as the jump length and the waiting times for any jump is obtained from fixed probability distributions, independently of their values at previous jumps. It is worth emphasizing (as it emerges from the GLE formulation elaborated in this paper) that there is no power-law waiting time for the movements of the concerned monomer; instead if it makes a move at any time, there is an enhanced chance to undo this move in subsequent times; this is where anomalous dynamics in polymeric systems stem from. This establishes that the fFPE is unsuitable to describe the anomalous polymer dynamics (polymer translocation included) that are considered in this paper.

The paper is organized in five sections. Section 2 is devoted to single polymeric systems. Therein I provide (a) an elaborate derivation of equations (1) and (2) for
phantom Rouse polymers, (b) the characterization of $\mu(t)$ as the mean relaxation response of the polymers to local strains, and (c) the GLE formulation for self-avoiding Rouse, self-avoiding Zimm, polymer reptation, and polymer translocation through a narrow pore in a membrane. In section 3 I provide the GLE formulation for the anomalous dynamics of a polymer melt, a many-polymeric system. In section 4 I show that the characteristics of the drifts caused by a (weak) applied field on these polymeric systems are obtained from the corresponding memory kernels. This could be thought of as an analog of the Nernst–Einstein relation. Section 5 is devoted to a critique of recent attempts to model by the fFPE the anomalous dynamics of polymer translocation through a narrow pore in a membrane. The paper is finally concluded in section 6.

But before I begin, in table 1 I provide a summary list of the polymeric systems with anomalous dynamics and the corresponding memory kernel $\mu(t)$ for which the GLE formulation is argued in this paper.

2. The GLE formulation for anomalous dynamics in single polymeric systems

2.1. The GLE formulation for phantom Rouse polymers

2.1.1. Derivation of equation (1) from the Rouse equation. Consider a phantom Rouse polymer of length $N$. It is described by the Rouse equation; in the continuum representation it reads

$$\gamma \frac{\partial \vec{r}_n(t)}{\partial t} = k \frac{\partial^2 \vec{r}_n(t)}{\partial n^2} + f_n(t),$$

(3)

where $\vec{r}_n(t)$ is the location of the $n$th monomer at time $t$, $\gamma$ is the damping coefficient of the surrounding fluid, and $k$ is the spring constant for the springs connecting the consecutive monomers. The stochastic force $f_n(t)$ satisfies the conditions $\langle f_n(t) \rangle = 0$ and the FDT $\langle f_m(t) f_n(t') \rangle = 2\gamma k_B T \delta(m-n) \delta_{\sigma \lambda} \delta(t-t')$, for $\sigma, \lambda = (x, y, z)$. Equation (3) is supplemented by the ‘open’ boundary conditions that the chain tension of the polymer at the free ends must vanish; i.e., $\langle \partial \vec{r}_n/\partial n \rangle|_{n=0} = (\partial \vec{r}_n/\partial n)|_{n=N} = 0$.

Since the Rouse equation is linear in $\vec{r}_n(t)$, it can be solved to obtain all correlation functions using the mode expansion technique [2]. Two noteworthy results borne out of this exercise are: (a) the terminal relaxation time $\tau = \gamma N^2/(\pi^2 k)$, and (b) the MSD of the middle monomer increases as $t^{1/2}$ until time $\tau$, and only after that time does the motion of the middle monomer become diffusive, with the diffusion coefficient scaling $\sim 1/N$. It is this subdiffusive motion of the middle monomer that I obtain from the GLE (1) and (2), which in turn I derive exactly from equation (3). For this problem $\vec{\phi}(t)$ is given by the net force it experiences (forces exerted on the middle monomer by the ones it is connected to, or equivalently, the chain tensions at the middle monomer), i.e.,

$$\vec{\phi}(t) = k \left[ \left. \frac{\partial \vec{r}_n(t)}{\partial n} \right|_{n=(N/2)+} - \left. \frac{\partial \vec{r}_n(t)}{\partial n} \right|_{n=(N/2)-} \right].$$

(4)

Note that using equation (4) the Rouse equation for the middle monomer can be written as

$$\gamma \vec{v}(t) = \vec{\phi}(t) + \vec{f}_{N/2}(t).$$

(5)

Given equations (1)–(5), an issue that may come to mind is the following. While the GLE formulation (1) and (2) has a distinct memory kernel—I have shown in Ref. I...
Table 1. Summary list of the polymeric systems (polymers of length $N$) with anomalous dynamics, and the corresponding memory kernel $\mu(t)$, for which the GLE formulation is reported in this paper.

| Polymeric system                  | Scaling of $\tau$ | Mean-square displacement | $\mu(t)$                                           |
|-----------------------------------|-------------------|---------------------------|----------------------------------------------------|
| Phantom Rouse                     | $\sim N^2$        | $\sim t^{1/2}$ till $\tau$ and $\sim t$ thereafter | $\sim t^{-1/2} \exp(-t/\tau)$                    |
| Self-avoiding Rouse               | $\sim N^{1+2\nu}$ | $\sim (2\nu/(1+2\nu))$ till $\tau$ and $\sim t$ thereafter | $\sim t^{-2\nu/(1+2\nu)} \times \exp(-t/\tau)$ |
| Self-avoiding Zimm                | $\sim N^{3\nu}$   | $\sim t^{2/3}$ till $\tau$ and $\sim t$ thereafter | $\sim t^{-2/3} \exp(-t/\tau)$                    |
| Phantom Rouse polymer translocation | $\sim N^2$        | (translocation time)      | $\sim t^{-1} \exp(-t/\tau)$ translocation time $\sim N^2$ |
|                                    |                   |                           |                                                    |
| Self-avoiding Rouse polymer translocation | $\sim N^{1+2\nu}$ | (translocation time)      | $\sim t^{-1/(1+2\nu)} \times \exp(-t/\tau)$ translocation time $\sim N^{2+\nu}$ |
|                                    |                   |                           |                                                    |
| Self-avoiding Zimm polymer translocation | $\sim N^{3\nu}$   | (translocation time)      | $\sim t^{-1/(3\nu)} \times \exp(-t/\tau)$ translocation time $\sim N^{2+\nu}$ |
|                                    |                   |                           |                                                    |
| Reptation; repton model (curvilinear coordinate) | $\sim N^2$        | $\sim t^{1/2}$ till $\tau$ and $\sim t$ thereafter | $\sim t^{-1/2} \exp(-t/\tau)$                    |
|                                    |                   |                           |                                                    |
| Melt (reptation theory)            | $\sim N^3$        | $\sim t^{1/4}$ between $\tau_e$ and $\sim N^2$ and $\sim t$ and $\sim t$ thereafter | $\sim t^{-1/4}$ between $\tau_e$ and $\sim N^2$ (as much as data can resolve) |

$^a \tau_e$ is the so-called entanglement time for polymer melts in the reptation theory [2]. Note that if $\mu(t) \sim t^{-\alpha}$, then the anomalous dynamics exponent is also $\alpha$.

that $\mu(t) \sim t^{-1/2} \exp(-t/\tau)$, and similarly $a(t) \sim t^{-3/2} \exp(-t/\tau)$ for phantom Rouse polymers—equations (3)–(5) do not: e.g., in equation (5) the velocity of the middle monomer at any time is simply proportional to the forces at the same time exerted by the monomers it is connected to (plus a $\delta$-correlated random noise). From this it may appear that the GLE formulation (1) and (2) is in contradiction with equations (3)–(5). In truth however, there is no contradiction among equations (1)–(5). First of all, the fact that there is no explicit memory kernel in the Rouse equation does not mean that a phantom polymer does not have memory. As noted in the very first paragraph of the introduction, the relaxation time corresponding to a length scale $N/p$ scales $\sim (N/p)^{2}$.
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with \( p \) an integer [2] shows that a phantom polymer does have memory; in fact, below I will show that the memory kernel \( \mu(t) \) is indeed built from the long relaxation times for fluctuations at long length scales of the polymer. (In this context, it is worth recalling the work by Zwanzig [8], wherein the memory of the concerned particle arises due to its coupling to a thermal bath of harmonic oscillators, effected via a Hamiltonian. For the present case, the fluctuation modes effectively play the role of a thermal bath that is coupled to the motion of a monomer due to chain connectivity, giving rise to the memory kernel \( \mu(t) \).) Secondly, while equations (1) and (2), being the inverse Laplace transforms of each other, describe exactly one relation between \( \vec{v}(t) \) and \( \vec{\phi}(t) \), equation (5) provides the second relation between the two quantities, so that out of equations (1) and (2) and (5) one can form closed equations for both \( \vec{v}(t) \) and \( \vec{\phi}(t) \). Indeed, in section 2.1.2 I use the closed form equation for \( \vec{\phi}(t) \) to obtain the velocity autocorrelation function (of course, it is the same velocity autocorrelation function as obtained in Ref. I, and as summarized in the introduction of this paper).

Without further ado, below I derive the GLE (1) for phantom polymers from the Rouse equation (3).

Three ingredients are necessary to derive equation (1). The first one of them is the dynamics for both halves of the polymer when the middle monomer is held fixed at, say, \( \vec{R} \). Being a phantom polymer, when the middle monomer held fixed, the two halves of the polymer evolve independently of each other. With \( \vec{r}_n(t) = \vec{r}_n(t) - \vec{R} \), the corresponding equations for each half of the phantom polymer satisfy the (Rouse) equation

\[
\gamma \frac{\partial \vec{r}_n'}{\partial t} = k \frac{\partial^2 \vec{r}_n'(t)}{\partial n^2} + f_n(t),
\]

for \( n \neq 0 \). Equation (6) is supplemented by the ‘open’ boundary conditions that the chain tension of the phantom polymer at the free ends must vanish; i.e., \( (\partial \vec{r}_n/\partial n)|_{n=0} = (\partial \vec{r}_n'/\partial n)|_{n=N} = 0 \) (additionally \( \vec{r}_0' = 0 \) by definition). In order to analyze the motion of the two halves of the phantom polymer I define

\[
\vec{Y}_p^{(r)}(t) = \frac{1}{N} \int_0^{N/2} \sin \frac{\pi(2p+1)n}{N} \vec{r}_{n+N/2}'(t),
\]

and

\[
\vec{Y}_p^{(l)}(t) = -\frac{1}{N} \int_{-N/2}^0 \sin \frac{\pi(2p+1)n}{N} \vec{r}_{n+N/2}'(t)
\]

for \( p = 0, 1, \ldots \), for the right and the left half, such that

\[
\vec{r}_{n+N/2}'(t) = 4 \sum_p \vec{Y}_p^{(r)}(t) \sin \frac{\pi(2p+1)n}{N} \Theta(n) - 4 \sum_p \vec{Y}_p^{(l)}(t) \sin \frac{\pi(2p+1)n}{N} \Theta(-n).
\]

Note that equation (9) is consistent with the open boundary conditions, as well as the fact that the middle monomer remains fixed. The independent evolution of each half satisfies the Langevin equation (LE)

\[
\gamma_p \frac{\partial \vec{Y}_p}{\partial t} = -k_p \vec{Y}_p(t) + \vec{f}_p(t),
\]

for \( \vec{Y}_p = [\vec{Y}_p^{(l)}, \vec{Y}_p^{(r)}] \), \( \gamma_p = 2N \gamma \), \( k_p = 2\pi^2 k(2p+1)^2/N \), \( \langle \vec{f}_p(t) \rangle = 0 \) and \( \langle f_{p\sigma}(t) f_{q\lambda}(t') \rangle = \gamma_p k_B T \delta(t - t') \delta_{pq} \delta_{\sigma \lambda} \).

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The second ingredient is the equilibrium averages of $Y_p$ and $Y_p^2$. First, $\langle Y_p^{(r)}(t) \rangle = \langle Y_p^{(l)}(t) \rangle \equiv 0$ by isotropy. Secondly, by left–right symmetry $\langle [Y_p^{(r)}(t)]^2 \rangle = \langle [Y_p^{(l)}(t)]^2 \rangle$; and they are obtained from the LE (10) as

$$\langle [Y_p^{(r)}(t)]^2 \rangle = \langle [Y_p^{(l)}(t)]^2 \rangle = 3Nk_B T/[4\pi^2 k(2p + 1)^2]. \quad (11)$$

The third ingredient is that in terms of the mode amplitudes $\vec{Y}_p^{(l)}(t)$ and $\vec{Y}_p^{(r)}(t)$ with the middle monomer fixed at $\vec{R}$, the force $\vec{\phi}(t)$ on the middle monomer in equation (4) is given by

$$\vec{\phi}(t) = 4k \sum_p \frac{\pi(2p + 1)}{N} [\vec{Y}_p^{(r)}(t) + \vec{Y}_p^{(l)}(t)]. \quad (12)$$

With these ingredients, I consider an ensemble of phantom polymers (let us label it as ensemble $\mathcal{X}$ for future reference) in equilibrium at time 0, such that for each of the polymers in this ensemble the velocity history of the middle monomer up to time $t > t_m$ is given by

$$\vec{v}(t > t_m) = \sum_{i=0}^m \vec{\delta}_i \delta(t - t_i) \quad (13)$$

for some $m$ and a sequence $\{\vec{\delta}_i\}$, with $t_0 = 0$. (One does not need not be alarmed that in equation (13) the velocity is represented by a sum over $\delta$-functions in time: such a representation only simplifies the following analysis.) Note here, using equations (7), (8) and (13,) that

$$\vec{Y}_p(t_i^+) = \vec{Y}_p(t_i^-) - \frac{2}{N} \sum_{i=0}^m \vec{\delta}_i \quad \text{for } i = 0, \ldots, m. \quad (14)$$

Let us now determine the evolution of the forces the middle monomer of a phantom polymer, belonging to the ensemble $\mathcal{X}$, experiences as a function of time. With the velocity history as in equation (13), using equation (10), the mode amplitudes for a member polymer of the ensemble evolve as

$$\vec{Y}_p(t > t_m) = e^{-k_p(t-t_m)/\gamma_p} \vec{Y}_p(t_m^+) + \frac{1}{\gamma_p} \int_{t_m}^t dt' e^{-k_p(t-t')/\gamma_p} f_p(t') \quad (15)$$

for $\vec{Y}_p = [\vec{Y}_p^{(l)}, \vec{Y}_p^{(r)}]$. Thereafter, using equations (12)–(15)

$$\vec{\phi}(t > t_m) = -\frac{8}{N} \vec{\delta}_m \sum_p e^{-k_p(t-t_m)/\gamma_p} + 4 \sum_p \frac{\pi(2p + 1)}{N} \vec{g}_p^{(m)}(t), \quad \text{with}$$

$$\vec{g}_p^{(m)}(t) = e^{-k_p(t-t_m)/\gamma_p} [\vec{Y}_p^{(r)}(t_m^-) + \vec{Y}_p^{(l)}(t_m^-)] + \frac{1}{\gamma_p} \int_{t_m}^t dt' e^{-k_p(t-t')/\gamma_p} [f_p^{(r)}(t') + f_p^{(l)}(t')]. \quad (16)$$

Further, as I extend equations (14) and (15) further back in time to write

$$[\vec{Y}_p^{(r)}(t_m^-) + \vec{Y}_p^{(l)}(t_m^-)] = -\frac{2}{N} \vec{\delta}_{m-1} e^{-k_p(t_m-t_{m-1})/\gamma_p} + e^{-k_p(t_m-t_{m-1})/\gamma_p} [\vec{Y}_p^{(r)}(t_{m-1}^-) + \vec{Y}_p^{(l)}(t_{m-1}^-)] + \frac{1}{\gamma_p} \int_{t_{m-1}}^{t_m} dt' e^{-k_p(t_m-t')/\gamma_p} [f_p^{(r)}(t') + f_p^{(l)}(t')], \quad (17)$$

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equation (16) becomes
\[
\phi(t > t_m) \frac{k}{N} = -\frac{8}{N} \delta r_m \sum_p e^{-k_p(t-t_m)/\gamma_p} - \frac{8}{N} \delta r_{m-1} \sum_p e^{-k_p(t-t_{m-1})/\gamma_p} + 4 \sum_p \frac{\pi(2p + 1)}{N} g^{(m-1)}_p(t), \quad \text{with}
\]
\[
g^{(m-1)}_p(t) = e^{-k_p(t-t_{m-1})/\gamma_p} \left[ Y_p^{(r)}(t_{m-1}) + Y_p^{(l)}(t_{m-1}) \right] + \frac{1}{\gamma_p} \int_{t_{m-1}}^t dt' e^{-k_p(t-t')/\gamma_p} \left[ f_p^{(r)}(t') + f_p^{(l)}(t') \right].
\]

At this point, a comparison between equations (16) and (18) shows that the force \(\phi(t > t_m)\) on the middle monomer of a polymer, belonging to ensemble \(X\), can be extended all the way to time \(0^-\), to write
\[
\frac{\phi(t > t_m)}{k} = \sum_{i=0}^{m} \left[ -\frac{8}{N} \delta r_i \sum_p e^{-k_p(t-t_i)/\gamma_p} + 4 \sum_p \frac{\pi(2p + 1)}{N} g^{(0)}_p(t) \right], \quad \text{with}
\]
\[
g^{(0)}_p(t) = e^{-k_p t/\gamma_p} \left[ Y_p^{(r)}(0^-) + Y_p^{(l)}(0^-) \right] + \frac{1}{\gamma_p} \int_0^t dt' e^{-k_p(t-t')/\gamma_p} \left[ f_p^{(r)}(t') + f_p^{(l)}(t') \right].
\]

It is now seen, by converting the sum to an integral, that
\[
\bar{q}_i(t) = -\frac{8k}{N} \delta r_i \sum_p e^{-k_p(t-t_i)/\gamma_p} = -2\delta r_i \sqrt{\frac{\pi \gamma k}{t - t_i}} e^{-(t-t_i)/\tau}.
\]

It is also seen, using equation (11), that \(\langle g(t) \rangle_0 = 0\), with the FDT
\[
\langle g(t) \cdot \bar{g}(t') \rangle_0 = \frac{24k_B T}{N} \sum_p e^{-k_p t/\gamma_p} = 6k_B T \sqrt{\frac{\pi \gamma k}{t - t'}} e^{-(t-t')/\tau}
\]
assuming \(t > t'\). Here \(\langle \cdot \cdot \cdot \rangle_0\) denotes an average over the noise realizations, including an average over the configurations of the polymers of the ensemble \(X\) at \(t = 0^-.\)

The equilibrium condition for ensemble \(X\) at \(t = 0^-\) is necessary in equations (20) and (21) to have \(\langle Y_p^{(r)}(t) \rangle_{0^-} = \langle Y_p^{(l)}(t) \rangle_{0^-} \equiv 0\) by isotropy, and also to provide us with \(\langle \{Y_p^{(r)}(t)\}^2 \rangle_{0^-} = \langle \{Y_p^{(l)}(t)\}^2 \rangle_{0^-} = 3Nk_B T / [4\pi^2 k(2p + 1)^2] \) (these are the results of equation (11)). In other words, by means of equations (19)–(21), I have derived the
GLE (1) for the motion of the middle monomer of a phantom Rouse polymer, with
\[ \mu(t) = 2\sqrt{\frac{\pi\gamma k}{t}} \exp(-t/\tau). \quad (22) \]

As claimed earlier, note that a comparison of equation (22) with equation (20) shows that \( \mu(t) \) is indeed built from the polymer’s memory, i.e., from the long relaxation times for fluctuations at long length scales. In this context, it is worth recalling the work by Zwanzig [8], wherein the memory of the concerned particle arises due to its coupling to a thermal bath of harmonic oscillators, effected via a Hamiltonian. For the present case, the memory kernel \( \mu(t) \) arises due to the physical connectivity of the monomers; nevertheless, the fluctuation modes of the polymer effectively play the role of a thermal bath coupled to the motion of a monomer.

Henceforth I drop the subscript ‘0’ from the angular brackets; when applicable, an average over an equilibrium ensemble of polymers at \( t = 0 \) will be understood.

2.1.2. Anomalous dynamics for phantom polymers, and the derivation of equation (2) for phantom polymers. Having derived equation (1) for phantom polymers in section 2.1.1, I now proceed to characterize the anomalous dynamics for the middle monomer of a phantom polymer using equation (5). Together, equations (1) and (5) yield
\[ \gamma \ddot{v}(t) = -\int_0^t \mathrm{d}t' \mu(t-t') \ddot{v}(t') + \left[ \ddot{g}(t) + \dot{f}_{N/2}(t) \right]. \quad (23) \]
I then use the Laplace transform to express
\[ \ddot{v}(t) = \int_0^t \mathrm{d}t' \beta(t-t') \left[ \ddot{g}(t') + \dot{f}_{N/2}(t') \right], \quad (24) \]
where in the Laplace space \( \tilde{\beta}(s)[\gamma + \tilde{\mu}(s)] = 1 \). Note that the noise term \( \tilde{\rho}(t) \) in equation (23) also satisfies the FDT, as it should: the \( \int_{-t/2}^{t/2} \dot{f}(t) \) part accounts for the viscous work involving \( \gamma \) (this follows from the Rouse equation (3)), while the \( \ddot{g}(t) \) accounts for \( \mu(t) \), as in equation (22).

Before proceeding further I make the observation that equations (23) and (24) are closed w.r.t. the velocity \( \ddot{v}(t) \) of the middle monomer. In fact, equations (23) and (24) provide the trajectory description in the \( (\vec{r},\vec{v}) \) phase space, and clearly demonstrates that the stochastic process underlying the anomalous dynamics for phantom polymers is non-Markovian. I will return to this issue in section 4.

The calculation for \( \langle \ddot{v}(t) \cdot \ddot{v}(t') \rangle \) based on equation (24) can be found in the appendix. I quote the result below, assuming \( t > t' \):
\[ \langle \ddot{v}(t) \cdot \ddot{v}(t') \rangle = 3k_B T \beta(t-t'), \quad (25) \]
where \( \beta(t) \) can be obtained by Laplace inverting the relation \( \tilde{\beta}(s)[\gamma + \tilde{\mu}(s)] = 1 \). Since from equation (22), \( \tilde{\mu}(s) = 2\sqrt{\pi\gamma k} (s + \tau^{-1})^{-1/2} \), and therefore \( \tilde{\beta}(s) = [\gamma + 2\sqrt{\pi\gamma k} (s + \tau^{-1})^{-1/2}] \). Consequently, at long times, i.e., for times \( (t-t') \gg \gamma/k \) but \( (t-t') \ll \tau \) (this is possible in the limit of large \( N \): recall that \( \tau = \gamma N^2/(\pi^2 k) \)), the relation
Anomalous polymer dynamics is non-Markovian

\[ \hat{\beta}(s)[\gamma + \hat{\mu}(s)] = 1 \] in the Laplace space can be inverted to obtain

\[ \langle \vec{v}(t) \cdot \vec{v}(t') \rangle \sim (t - t')^{-3/2}e^{-t'(t-t')/\tau}. \]  \( \text{(26)} \)

Subsequently, the result that the mean-square displacement (MSD) of the middle monomer increases \( \sim t^{1/2} \) till time \( \tau \) and \( \sim t \) thereafter is obtained by integrating of \( \langle \vec{v}(t) \cdot \vec{v}(t') \rangle \) twice in time.

It is important to note here that the following result transpires through the above exercise: if \( \mu(t) \sim t^{-\alpha} \) for some \( \alpha \), then the MSD of the middle monomer will increase as \( t^{\alpha} \).

Interestingly, instead of going through the equations (23)–(25), one can choose an alternative route to arrive at equation (26) from that I took in Ref. I. Given the GLE (1), one arrives at equation (2), namely, at

\[ \vec{v}(t) = -\int_0^t dt' a(t-t')\vec{v}(t') + \vec{h}(t), \]  \( \text{(27)} \)

with \( \hat{\mu}(s)\hat{a}(s) = 1 \) in the Laplace space, and the corresponding FDT \( \langle \vec{h}(t) \cdot \vec{h}(t') \rangle_0 \equiv \langle \vec{v}(t) \cdot \vec{v}(t') \rangle \mid_{\phi=0} = 3k_BT a(t-t') \). Thereafter, in order to obtain the velocity autocorrelation function (26) from equation (27), one proceeds along the following manner. From the Rouse equation (3) or (4), one needs to appreciate that \( \gamma/k \) is proportional to the middle monomer’s reaction time to balance out the chain tensions \( \langle \partial R_n(t)/\partial n \rangle \mid_{n=(N/2)+}^{} \) and \( \langle \partial R_n(t)/\partial n \rangle \mid_{n=(N/2)}^{} \). Thus, for \( (t-t') \gg \gamma/k \) one is always at a limit \( \phi \approx 0 \), implying that

\[ \langle \vec{v}(t) \cdot \vec{v}(t') \rangle \approx \langle \vec{v}(t) \cdot \vec{v}(t') \rangle \mid_{\phi=0} = 3k_BT a(t-t'), \]  \( \text{(28)} \)

i.e., I arrive back at equation (26), which I have elaborated via equations (3)–(25).

To summarize section 2 so far: (i) up to equation (26) I have provided an elaborate derivation for the GLE formulation for the anomalous dynamics of phantom polymers, explicitly demonstrating that the stochastic process underlying the anomalous dynamics of the middle monomer is non-Markovian. (ii) Given that the GLE formulation (1) and (2) dictates that if \( \mu(t) \sim t^{-\alpha} \), then the anomalous dynamics exponent is also \( \alpha \), characterization of \( \mu(t) \) is sufficient to lead one to the anomalous dynamical behavior of phantom polymers.

In the following subsections 2.2–2.4 and in section 3 I will consider the anomalous dynamics for self-avoiding Rouse and Zimm polymers, polymer translocation through a narrow pore in a membrane, polymer reptation and polymer melts. These systems are not analytically tractable like phantom polymers have been. Nevertheless, as I have demonstrated above for phantom polymers, and summarized in Ref. I, characterizing \( \mu(t) \) will turn out to be powerful enough to arrive at the anomalous dynamical behavior for all these polymeric systems via the GLE description (1) and (2). To this end, one needs to identify the generic properties involving \( \mu(t) \) and FDT; these are carried out in section 2.1.3 below.

\(^1\) Note that \( \hat{\mu}(s)\hat{a}(s) = 1 \) yields \( \hat{a}(s) \sim (s + \tau^{-1})^{1/2} \), the inverse Laplace transform of which, strictly speaking, does not exist. This can be traced back to equation (16), where I have ignored the minimum distance between the consecutive monomers providing the ultraviolet cutoff for \( p \) for the summation. In reality, the \( t^{-1/2} \) behavior does not extend all the way to \( t = 0 \), implying that the inverse Laplace transform of \( \hat{a}(s) \) is indeed given by \( t^{-3/2} \).
2.1.3. Three generic issues for polymeric systems: (a) \( \mu(t) \) as the polymer’s mean relaxation response to local strain, (b) fluctuation-dissipation theorem, and (c) equation (23) for polymeric systems in general. I begin by having observed the following from equation (1): \( \mu(t) \) is the mean response of the polymer to a local strain. (For phantom polymers, the strain is due to the alteration in the chain tensions \( k(\partial \vec{r}_n(t)/\partial n)|_{n=(N/2)+} \) and \( k(\partial \vec{r}_n(t)/\partial n)|_{n=(N/2)-} \), caused by moving the middle monomer by a distance \( \delta \vec{r} \) at time \( t_0 \) and fixing it at its new position \( \forall \). Then on average, the local strain then relaxes in time \( (t-t_0)^{-1/2} \), i.e., \( \langle \vec{\phi}(t) \cdot \vec{\phi}(t_0) \rangle_{\vec{v}=0} \sim (t-t_0)^{-1/2} \). Based on this observation, I now discuss three generic issues that would be instrumental for arriving at the anomalous dynamics for polymeric systems, as these systems are not analytically tractable like phantom polymers have been.

(i) While the mean response of a polymer to a local strain depends on how the strain is created, the identification of \( \mu(t) \) as the polymer’s mean local strain relaxation response alone allows one to write down the GLE, as I argue below. First, given the identification of \( \mu(t) \) as the polymer’s mean local strain relaxation response one can always write the stochastic equation (1) with \( \langle \vec{g}(t) \rangle = 0 \), which holds by definition. Next, to obtain the FDT, consider equation (1) for an ensemble of polymers with \( \vec{v}(t) = 0 \forall t \) and \( \vec{\phi}(t_0) = \vec{g}_0 \), a specific value. For such an ensemble \( \vec{g}(t) \equiv \vec{\phi}(t) \), and since \( \mu(t) \) is the polymer’s mean local strain relaxation response, \( \langle \vec{\phi}(t) \cdot \vec{\phi}(t_0) \rangle = g_0^2 \mu(t-t_0) \) for \( t > t_0 \). Extending this to the dynamics of a polymer in an equilibrium ensemble (where \( \vec{g}_0 \) is also chosen from the equilibrium ensemble), one has \( \langle \vec{g}(t) \cdot \vec{g}(t_0) \rangle \equiv \langle \vec{\phi}(t) \cdot \vec{\phi}(t_0) \rangle_{\vec{v}=0} = \langle \phi^2(t) \rangle_{\vec{v}=0} \mu(t-t_0) \).

(ii) Conversely—i.e., turning the argument of (a) around—the existence of the FDT \( \langle \vec{g}(t) \cdot \vec{g}(t_0) \rangle = C \mu(t-t_0) \) for some constant \( C \), along with \( \langle \vec{g}(t) \rangle = 0 \) also implies that the polymer’s mean relaxation response to local strains—created at time \( t_0 \)—is \( \propto \mu(t-t_0) \). Let us assume that the polymer’s mean relaxation response to local strains, created at time \( t_0 \), is given by \( \eta(t-t_0) \) for some function \( \eta \). Using (a) above, one deduces that the corresponding FDT will have to take the form \( \langle \vec{g}(t) \cdot \vec{g}(t_0) \rangle = \langle \phi^2(t_0) \rangle \eta(t-t_0) \), which, by construction equals \( C \mu(t-t_0) \); i.e., \( \eta(t) \propto \mu(t) \).

(iii) In addition, for a tagged monomer in a polymeric system, one anticipates equation (5) to generically hold true, with \( \gamma \) being an effective damping coefficient of the surrounding medium (that includes the interactions with other monomers!). Together, they then yield equation (23), which is a closed form equation for \( \vec{v}(t) \). It is equation (23) that tells us that if the monomer makes a move at any time, there is an enhanced chance to undo this move at subsequent times; this is where anomalous dynamics in polymeric systems stem from.

In sections 2.2–2.4 and 3, in order to arrive at the GLE formulation (1) and (2) for the anomalous dynamics for self-avoiding Rouse and Zimm polymers, polymer translocation through a narrow pore in a membrane, polymer reptation and polymer melts, I will use (ii)–(iii) above, since these systems are not analytically tractable like phantom polymers have been. In some cases I will obtain \( \mu(t) \) directly, and in others I will calculate \( \langle \vec{\phi}(t) \cdot \vec{\phi}(t') \rangle_{\vec{v}=0} \). Wherever possible, I will do both.

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2.2. The GLE formulation (1) and (2) for the anomalous dynamics of self-avoiding Rouse and Zimm polymers

The monomers of a self-avoiding polymer interact over a long-range, which prohibits one from writing down an exact equation for the velocities of the monomers in terms of the forces they experience. However, some properties of self-avoiding polymers are well known; two of them I need here for a polymer of length $N$ are: (i) the terminal time $\tau$ scales as $\sim N^{1+2\nu}$ for a Rouse polymer, and as $\sim N^{3\nu}$ for a Zimm polymer [2]; and (ii) the entropic spring constant of a polymer scales as $N^{-2\nu}$ [1]. Here $\nu$ is the Flory exponent, in 3D $\nu \approx 0.588$, and in 2D $\nu = 3/4$. With these properties I now characterize $\mu(t)$ as the polymers’ mean local strain relaxation response, as described in section 2.1.3.

Imagine that one moves the middle monomer of a self-avoiding polymer by a small distance $\delta r$ at $t=0$ and holds it at its new position $\delta r(t)$. Following the terminal time scaling for self-avoiding polymers (i), at time $t$, counting away from the middle monomer, all the monomers within a backbone distance $n_t \sim t^{1/(1+2\nu)}$ for a Rouse, and $\sim t^{1/(3\nu)}$ for a Zimm polymer equilibrate to the new position of the middle monomer. However, since the remaining $(N-n_t)$ monomers are not equilibrated to the new position of the middle monomer at time $t$, these $n_t$ monomers are stretched by a distance $\delta r$. With the entropic spring constant of these $n_t$ equilibrated monomers scaling as $\sim n_t^{-2\nu}$ (following property (ii)), the mean force the middle monomer will experience at its new position is given by $\delta f(t) \sim n_t^{-2\nu}(\delta r) \sim t^{-2\nu/(1+2\nu)}(\delta r)$ for a Rouse, and $\delta f(t) \sim n_t^{-2\nu}(\delta r) \sim t^{-2/3}(\delta r)$ for a Zimm polymer (force = (spring constant) $\times$ (stretching distance)). This power-law behavior lasts only till the terminal time $\tau$. (For a phantom polymer, the time behavior of equation (22) is recovered from this argument upon simply replacing $\nu$ by $1/2$.) In the light of point (a) in section 2.1.3, the above leads one to the GLE formulation (1) for self-avoiding Rouse and Zimm polymers, with the corresponding FDT.

Further, having anticipated, as in point (c) in section 2.1.3, that an effective equation (23) does hold true, I demonstrate the FDT directly for self-avoiding Rouse polymers in the following manner. Imagine that I hold fixed the middle monomer of a self-avoiding Rouse polymer, and keep taking snapshots of the polymer configuration at fixed intervals of time, i.e., at $t = t_0, (t_0 + \Delta t), (t_0 + 2\Delta t), \ldots$. Afterward, I take the snapshot at time $t$ and evolve it $K$ number of times over a short time interval $\delta t$ and note down the average displacement $\bar{\delta x}$ over these $K$ evolutions. A look at equation (23) then tells us that this averaging process kills the $f_{N/2}$ term, and since $\delta f(t) \equiv 0$ by construction, the result is a quantity $\bar{\delta x}$, which, in the limit of $(K \to \infty, \delta t \to 0)$, is simply proportional to the average of $\bar{\delta f}(t)$. These $\bar{\delta x}$ values for $t = t_0, (t_0 + \Delta t), (t_0 + 2\Delta t), \ldots$ can then be used to calculate $\mu(t-t') \equiv \langle \bar{\delta f}(t) \cdot \bar{\delta f}(t') \rangle_{t'=0}$, proxied by $\langle \bar{\delta x}(t) \cdot \bar{\delta x}(t') \rangle$. Such an exercise was indeed performed in [9]: using a Monte Carlo lattice polymer model with $N = 400$, $\Delta t = 50$, $K = 10^6$ and $\delta t = 1$ (see [9] for model details). The corresponding result, confirming the $t^{-2\nu/(1+2\nu)}$ power-law behavior of $\mu(t)$ is shown in figure 1.

Given that if $\mu(t) \sim t^{-\alpha}$ then the anomalous dynamics exponent is also $\alpha$, the well-known scaling of the MSD $\sim t^{(2\nu)/(1+2\nu)}$ for self-avoiding Rouse and $\sim t^{2/3}$ for self-avoiding Zimm polymers up to time $\tau$ and $\sim t$ thereafter is trivially reproduced from the GLE formulation (1) and (2) [9, 10].
Figure 1. Simulation data for $\mu(t)$ for a self-avoiding Rouse polymer in a Monte Carlo lattice polymer model for $N = 400$, obtained from equation (23) and the FDT (see text for details). With $2\nu/(1 + 2\nu) \approx 0.54$ in 3D the solid (black) curve corresponds to $\mu(t) = 0.275t^{-0.54}\exp(-t/\tau)$, where $\tau$ was measured to be $\approx 223801$. Figure reproduced from [9] with permission from American Institute of Physics.

2.3. The GLE formulation (1) and (2) for the anomalous dynamics of unbiased polymer translocation through a narrow pore in a membrane

Polymer translocation is a process where a polymer passes through a narrow pore in a membrane. Of interest here is the so-called unbiased (i.e., in the absence of any force or field) translocation: the polymer passes through the pore purely due to thermal fluctuations, and the dynamics is anomalous [11]. For this system, below I now characterize $\mu(t)$ as the polymers’ mean local strain relaxation response, as described in point (a) of section 2.1.3, in the following manner.

A translocating polymer consists of two sub-polymers—one on each side of the membrane—exchanging monomers through the pore. When a monomer translocates, the polymer locally stretches on the side the monomer translocates from, and locally compresses on the other. Consequently, the polymer’s chain tensions at the pore changes: it increases on the side of the membrane which the monomer translocates from, and decreases on the other. The relevant mean polymeric response therefore, is to a (local) strain due to the injection of extra monomers at the tether point of a polymer tethered on a membrane.

Consider the case where $n$ extra monomers are injected at $t = 0$ into a polymer tethered on a membrane, at the tether point. First, it has been shown in [12] that for phantom Rouse polymers the mean response to such a strain is given by $\mu(t) \sim t^{-1}e^{-t/\tau}$, with $\tau \sim N^2$. For self-avoiding polymers $\mu(t)$ is obtained as follows. Given that the terminal time $\tau$ for a tethered polymer of length $N$ scales as $\sim N^{1+2\nu}$ for a Rouse and $\sim N^{3\nu}$ for a Zimm polymer, at time $t$, counting away from the tether point, all the monomers within a backbone distance $n_t \sim t^{1/(1+2\nu)}$ for a Rouse, and $\sim t^{1/(3\nu)}$ for a Zimm polymer, equilibrate to the injected monomers. The real space extent of $n_t$ monomers is...
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Figure 2. The mean relaxation response \( \sim t^{-(1+\nu)/(1+2\nu)} \) to local strain \( \mu(t) \), created by injecting \( n \) monomers at \( t = 0 \) into a self-avoiding Rouse polymer tethered on a membrane, at the tether point. The data are obtained using a Monte Carlo lattice polymer model. (a) In 2D: for \( N = 250, n = 5 \). In 2D \( (1 + \nu)/(1 + 2\nu) \approx 0.7 \); the solid line corresponds to a power-law \( t^{0.7} \). (b) In 3D: for \( n = 10 \) and \( N = 50 \) (red), 100 (green) and 150 (blue). In 3D \( (1 + \nu)/(1 + 2\nu) \approx 0.73 \); the solid line corresponds to a power-law \( t^{0.73} \). The choice of the scaling variable also confirms the terminal exponential decay of \( \mu(t) \) behaving as \( \sim \exp(-t/\tau) \), with \( \tau \sim N^{1+2\nu} \) for self-avoiding Rouse polymers. The figures are taken from [13] and [14], where the details of the polymer model and simulation details can be found, with permissions from IOP Publishing Ltd, UK (original articles published on 25 January 2008 and 8 October 2007 respectively).

2.4. The GLE formulation (1) and (2) for a reptating polymer

The notion of polymer reptation was originally introduced by De Gennes in the context of gel electrophoresis [17]. Gel electrophoresis is a method to isolate DNA fragments. In a
Figure 3. A two-dimensional lattice representation of the repton model. The pores are represented by cells formed by a square lattice, while the polymer is represented by points ('reptons') connected by bonds. The rules governing this model are described in the text.

typical experiment, agarose powder is dissolved in water, and upon waiting for a sufficient time the agarose forms the cross-links of a gel. The sizes of the pores within the gel are controlled by the concentration of agarose. When DNA molecules are injected into this gel, they collect their charge from the solution, and with the application of an electric field—typically of strengths of a few volts per cm—the DNA molecules are driven through the pores in the gel. For a given pore size of the gel, the mobility of the DNA molecules caused by the electric field crucially depends on their lengths, leading to length dependent segregation, which in turn allows one to separate the DNA strands by their lengths. The DNA persistent length under a typical gel electrophoresis experimental condition is in the range 400–800 Å, which is typically the size of the pores in the gel itself. In other words, the gel prevents the polymer from moving transverse to its configuration, and only the longitudinal, or curvilinear, motion of the DNA contributes to its motion under the applied electric field—this is the central idea of polymer reptation.

I consider here the three-dimensional repton model, one of the simplest models with explicit reptation (longitudinal/curvilinear) moves. The model was originally conceived by Rubinstein [18] to describe the motion of entangled polymers, and was later co-opted by Duke [19] to describe the mobility of DNA polymers in gel electrophoresis. A two-dimensional lattice representation of this model is shown in figure 3: the network of the agarose gel is represented by the crossing points of the grid lines of the lattice, whereas the cells of the lattice correspond to the gel pores. The DNA polymer, represented by points connected by bonds, resides in the gel. The points are called ‘reptons’: along the backbone of the polymer two consecutive reptons are one persistent length apart. This allows more than one repton to occupy the same cell, but simultaneously two neighboring reptons cannot be more than one cell apart. The movements of the reptons are given by the following dynamical rules. A repton in the interior of the polymer can move to one
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of its adjacent cells, provided one of its neighbor reptons is already in that cell, and the other neighbor repton is in the cell it leaves. The two end reptons can move into any of the neighboring cells, so long as the bond between the end repton and its neighbor is separated by not more than one cell.

The dynamical rules of the repton model ensure that while the transverse motion for a repton in the interior of the polymer remains blocked, it can only move towards (and away from) its neighbors: this encodes explicitly the longitudinal or curvilinear motion of the polymer in the repton model. Further, in any spatial dimension, the curvilinear conformation of a reptating polymer can be described by a string of 0s and 1s, corresponding to whether two consecutive monomers reside within the same cell or not—this forms the ‘curvilinear coordinate’ description of the polymer. (E.g., the curvilinear coordinate description of the two-dimensional polymer in figure 3, from the left end to the right, is given by the sequence 0111110111111101111111011101.) The 0s in the curvilinear coordinate description of the repton model are also known as the ‘stored lengths’, as they correspond to local compression of the polymer: the number of stored lengths within any given lattice site is clearly one less than the number of monomers occupying that site. The dynamics of the repton model is then summarized by the two following simple rules: within the polymer motion takes place only by exchanging a 0 with a 1, while at the ends of the polymer, a 0 can become a 1, or vice versa. The equilibrium density of stored lengths is a parameter in the repton model; for the simulation results reported in this paper, this parameter was chosen to be $1/3$.

The dynamics of reptation is anomalous [2]; i.e., for a polymer of $N$ reptons the MSD of the middle repton increases as $\sim t^{1/4}$ up to time $\sim N^2$; thereafter, the MSD for the middle monomer increases as $\sim t^{1/2}$ till time $\sim N^3$, after which the motion becomes diffusive. I confirm this anomalous dynamical behavior of the middle repton in figure 4. By the time the MSD behavior becomes diffusive, the middle monomer displaces itself by the size of the polymer, and since by construction the repton model describes a phantom polymer (i.e., in equilibrium the size of a reptating polymer of $N$ reptons scales as $\sim N^{1/2}$), the diffusion coefficient of the polymer scales as $1/N^2$ [20, 21]. In fact, given that the polymer’s motion is only curvilinear, and the polymer’s contour itself performs a random walk in space, one realizes that if this anomalous dynamics of the middle monomer is translated back into curvilinear coordinates, then the MSD of the middle repton increases as $\sim t^{1/2}$ up to time $\sim N^2$, and becomes diffusive thereafter. It is this anomalous dynamics of the middle monomer in curvilinear coordinates that I show to stem from the GLE (1) and (2). In particular, I demonstrate that the forces on the middle monomer in the curvilinear coordinate, at zero middle repton velocity, satisfy the FDT, leading one to

$$\mu(t) \sim t^{-1/2} \exp(-t/\tau)$$

with $\tau \sim N^2$. As described in point (b) of section 2.1.3, this establishes the GLE formulation (1) and (2) for the repton model.

The above implies that the anomalous dynamics for polymer reptation is described by the GLE, resulting in the scaling of the MSD in the curvilinear coordinate as $\sim t^{1/2}$ till time $\tau$ and diffusive thereafter, as confirmed in figure 4. In the curvilinear coordinate, the polymeric motion is described by the motion of the stored lengths or the 1s, which undergo the so-called tagged-particle diffusion [21, 22]. At zero velocity of the middle repton, the force it experiences is proportional to the curvilinear gradient of stored lengths at its location. In order to obtain the correlation in the forces on the middle repton at zero velocity, I number the reptons $1, 2, \ldots, N$, hold the middle repton (tagged by $N/2$) fixed,
Figure 4. The MSD $\langle \Delta r^2(t) \rangle$ of the middle repton for polymers with $N$ reptons: $N = 201$ (circles), 501 (pluses) and 1001 (crosses). Data averaged over 1024 independent polymer realizations. Up to time $\approx 0.25N^2$ the MSD behaves as $t^{1/4}$, after which it crosses over to $\sim t^{1/2}$ behavior. The onset of the diffusive behavior at time $\sim N^3$ is not shown, although increased slopes at late times for shorter polymers can be seen clearly.

Figure 5. The $\sim t^{-1/2} \exp(-t/\tau)$ behavior of $\mu(t)$, obtained via the FDT in the curvilinear coordinate for the anomalous dynamics of the middle repton for three different values of $N$: $N = 201$ (circles), 501 (pluses) and 1001 (crosses). Data averaged over 1024 independent polymer realizations. The solid line corresponds to the power-law $t^{-1/2}$. The choice of the scaling variable also confirms the terminal exponential decay of $\mu(t)$ behaving as $\sim \exp(-t/\tau)$, with $\tau \sim N^2$.

and monitor the difference $g(t) = \rho_{N/2,5}(t) - \rho_{N/2,-5}(t)$, where $\rho_{m,n}(t)$ is the number of stored lengths between reptons $m$ and $m + n$. The correlation in the force on the middle repton at zero velocity is then proxied by $\langle g(t)g(t') \rangle$. The expected behavior of $\mu(t-t') \propto \langle g(t)g(t') \rangle \sim t^{-1/2} \exp(-t/\tau)$ is shown in figure 5, with $\tau \sim N^2$.  

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3. The GLE formulation (1) and (2) for the anomalous dynamics of polymer melts

3.1. Polymer melts and reptation theory

Mobility of individual polymers in systems containing long polymers decreases with increasing density, causing their dynamics to slow down. A notable manifestation of slow dynamics in dense polymeric systems such as polymer melts is that their viscosity scales with their molecular weight as a power-law, with the viscosity exponent $m_\eta$; experimentally measured to be $3.4 \pm 0.2$ over an impressive range of molecular weights and chemical compositions [23]. The fact that the slow dynamics of dense polymeric systems can actually be attributed to the polymers becoming entangled, especially if the polymers are long, was the seminal idea of De Gennes [1]. He argued that entanglement restricts the polymers to only sliding past each other—thereby reducing their mobility—as it is impossible for them to slide across each other. Indeed, the dynamics of a melt can be quantitatively understood by taking the entanglement idea to analyze the motion of a single polymer in a melt [1,2]—referred to as the tagged polymer henceforth.

To approach the scaling of $m_\eta$ by obtaining that of $D$, De Gennes considered the melt to only represent a rigid static network for the tagged polymer, with the tagged polymer reptating through this network. Such a formulation reduces the many-polymer problem of a melt to an effective single (tagged) polymer problem, wherein the movements of the tagged polymer are restricted only to reptation, i.e., stored length transportation due to (longitudinal) fluctuations along its contour. By using the longest available timescale $\tau_r \sim N^2$ for the stored length distribution within the tagged polymer’s contour in this reduced problem, he obtained $D \sim N^{-2}$, i.e., $m_\eta = 3$ [1,2,17]. (The discrepancy between the predictions of reptation theory and the experimental value for $m_\eta$ remains to this day, and is beyond the scope of this paper.)

The prediction of reptation theory for the anomalous dynamics of the middle monomer of the tagged polymer in a melt, beyond the so-called entanglement time $\tau_e$, is the same as that for the repton model discussed in section 2.4: at times $\gg \tau_e$, the MSD of the middle monomer increases as $\sim t^{1/4}$ up to time $\sim N^2$; thereafter, it increases as $\sim t^{1/2}$ till time $\sim N^3$, after which the motion becomes diffusive. Such a picture is consistent with the fact that by the time the dynamics becomes diffusive, the middle monomer displaces itself by the size of the polymer, which scales as $\sim N^{1/2}$ in a melt [1], yielding the result $D \sim N^{-2}$. For the GLE description of the anomalous dynamics for a many-body problem like a polymer melt, I make use of computer simulations to demonstrate the FDT for the force experienced by the middle monomer of the tagged polymer, as described below.

3.2. Simulation details

The simulations have been performed with the lattice polymer model described in [24]. This model combines a very high computational efficiency with realistic polymer dynamics. All the simulations are three-dimensional, with the lattice polymers residing on a face-centered-cubic lattice. Polymer contours are self- and mutually-avoiding. Monomers adjacent in the string are located either in the same, or in neighboring lattice sites. Multiple occupation of lattice sites is not allowed, except for a string of adjacent monomers belonging to the same polymer. A two-dimensional version of the model is illustrated in figure 6.
Figure 6. Illustration of the two-dimensional version of the lattice polymer model. Polymers are shown by darker colors and their contours in lighter colors. In the upper polymer, interior monomers 2, 4, 6, 9, 10 and 11 can either move along the contour, or move sideways; monomer 7 can join either 6 or 8; the end monomers 1 and 12 can move to any empty nearest-neighbor site. In the lower polymer, interior monomers 3, 5, 6, 10 and 11 can either move along the contour, or move sideways; monomer 1 can move to any empty nearest-neighbor site, and monomer 12 can join its neighbor 11. In this configuration, because of the self- and mutually-avoiding property of the polymers, all other monomers cannot make a move. Statistically once per unit of time, each monomer attempts to move up and down along the contour, as well as sideways.

The simulations are performed for a system of size $60^3$ with an overall monomer density unity per lattice site. The polymers move through a sequence of random single-monomer hops to neighboring lattice sites. These hops can be along the contour of the polymer, thus explicitly providing reptation dynamics. They can also change the contour ‘sideways’, providing Rouse dynamics (figure 6). Each monomer attempts to move along the contour, as well as sideways stretching or reducing the backbone, statistically once per unit of time. Due to the possibility that adjacent monomers belonging to the same polymer can occupy the same site, overall approximately 40% of the sites typically remain empty. The number of stored lengths within any given lattice site is one less than the number of monomers occupying that site.

Initial thermalizations were performed as follows: completely crumpled up polymers are placed in lattice sites at random. The system is then brought to equilibrium by letting it evolve for $\tau_{eq}(N)$ units of time, with a combination of intermediate redistribution of stored lengths within a polymer$^2$; for the polymer lengths concerned here $\tau_{eq}(N) > 10^9$. The entanglement time for this model is $\approx 10^5$.

$^2$ This was done in conformation with detailed balance.

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Figure 7. $\mu(t)$ for the middle monomer of a tagged polymer in a polymer melt: $N = 750$ (circles), 1500 (pluses). Data averaged over 512 independent polymer melt realizations. The solid line corresponds to the power-law $t^{-1/4}$. Beyond the entanglement time $\tau_e$, the data are consistent with an initial power-law behavior $\mu(t) \sim t^{-1/4}$.

3.3. The FDT for the forces on the middle monomer of the tagged polymer in a polymer melt

First, I anticipate, as in point (c) in section 2.1.3, that an effective equation (23) does hold true for the middle monomer of the tagged polymer in a polymer melt. Then I follow the same procedure as I did for demonstrating the FDT for the case of self-avoiding Rouse polymers; namely, I hold the middle monomer fixed and keep taking snapshots of the polymer configuration at fixed intervals of time, i.e., at $t = t_0, (t_0 + \Delta t), (t_0 + 2\Delta t), \ldots$. Afterward, I take the snapshot at time $t$ and evolve it $K$ number of times over a short time interval $\delta t$ and note down the average displacement $\vec{\delta x}$ over these $K$ evolutions. Once again, a look at equation (23) tells us that this averaging process kills the $\vec{f}_N/2$ term, and since $\vec{v}(t) \equiv 0$ by construction, the result is a quantity $\vec{\delta x}$, which, in the limit of $(K \to \infty, \delta t \to 0)$, is proportional to the average of $\vec{g}(t)$. These $\vec{\delta x}$ values for $t = t_0, (t_0 + \Delta t), (t_0 + 2\Delta t), \ldots$ can then be used to calculate $\mu(t - t') \equiv \langle \vec{g}(t) \cdot \vec{g}(t') \rangle_{\vec{v}=0}$, proxied by $\langle \vec{\delta x}(t) \cdot \vec{\delta x}(t') \rangle$.

The corresponding result for $N = 750$ and 1500 for $\Delta t = 10 000$ and 50 000 respectively, with $K = 100 000$ and $\delta t = 1$ is shown in figure 7. Beyond the entanglement time $\tau_e$, the data are consistent with an initial power-law behavior $\mu(t) \sim t^{-1/4}$ (but are not sufficient to conclude what follows afterward). Nevertheless, this exercise provides a clear indication that the anomalous dynamics of the middle monomer of the tagged polymer is described by the GLE between the entanglement time $\tau_e$ and $\sim N^2$.

4. Drifts in polymeric systems driven by weak forces: analog of the Nernst–Einstein relation

Until now, I have considered classical polymeric systems with anomalous dynamics in the absence of external driving forces, and demonstrated that their anomalous dynamics are...
Anomalous polymer dynamics is non-Markovian described by a unified GLE scheme (1) and (2) with power-law memory kernels. I now demonstrate that their GLE formulation is robust: it also adequately describes drifts in polymeric systems driven by weak forces, as it should.

The expected drift results—when the polymeric system starts to evolve at $t = 0$ under the application of external forces—are shown in table 2. Note in table 2 that if $\mu(t) \sim t^{-\alpha}$, then the drift exponent is also $\alpha$: I elaborate on this below. Note also that not all results in table 2 are demonstrated in sections 4.1 and 4.2 using computer simulations; these are clearly marked.

### 4.1. The standard extension of the GLE formulation to driven polymeric systems

The external constant force $\vec{F}$ is switched on a specified monomer over an equilibrated polymer ensemble at $t = 0$, and is assumed to be weak enough that it does not distort the memory kernel (or the FDT for $\vec{g}(t)$). With these assumptions—if the system’s dynamics is not rate-limited by some other process—equations (1) and (2) retain their forms, however, equation (5) needs to be modified to include the external force, so that it becomes

$$\gamma \vec{v}(t) = \vec{\phi}(t) + \vec{F} + \vec{f}(t),$$

from where I have dropped the subscript $N/2$ from $\vec{f}(t)$. Together with equations (1) and (2), equation (29) provides us with

$$\vec{v}(t) = \int_0^t dt' \beta(t - t') [\vec{g}(t') + \vec{F} + \vec{f}(t')],$$

where $\beta(t)$ is defined in equation (24).

An ensemble average of equation (30) implies that

$$\langle \vec{v}(t) \rangle = \int_0^t dt' \beta(t - t') \vec{F}.$$  

(31)

With $\mu(t) \sim t^{-\alpha}\exp(-t/\tau)$ for some $\alpha$, at long times (times still $\ll \tau$), equation (31) yields

$$\langle \vec{v}(t) \rangle \sim t^{\alpha-1} \vec{F}; \quad \text{i.e.,} \quad \langle [\vec{x}(t) - \vec{x}(0)] \rangle \sim \vec{F}t^\alpha,$$

(32)

which lasts till time $\tau$, after which $\langle \vec{x}(t) \rangle$ increases as $t\vec{F}$. Such behavior can be thought of as the analog of the Nernst–Einstein relation [6].

I now demonstrate equation (32) for a self-avoiding Rouse polymer, and the repton model in the curvilinear coordinate.

#### 4.1.1. A self-avoiding Rouse polymer under a weak force on an end monomer

Using the Monte Carlo lattice polymer model that was used to generate figure 1 (details of the model can be found in [9]), a force $\vec{F} = F\hat{z}$ was applied at $t = 0$ onwards on one of the end monomers of a set of equilibrated self-avoiding Rouse polymer realizations at $t = 0$, and the average displacement $\langle \Delta z(t) \rangle$ of this monomer was tracked as a function of time. The result, presented in figure 8, confirms equation (32). Note the labeling of the axes in figure 8: they confirm that in the steady state ($t > \tau$) the drift scales as $1/N$ as it should.
Table 2. The expected drift results, from the analysis in sections 4.1 and 4.2— when the systems start evolving at \( t = 0 \) under the application of weak forces— following the results of table 1. The top table relates to section 4.1 and the bottom two tables relate to section 4.2. Note in table 2 that if \( \mu(t) \sim t^{-\alpha} \), then the drift exponent is \( \alpha \). Note also that not all results are explicitly demonstrated in sections 4.1 and 4.2 using computer simulations; these are clearly marked.

| Polymeric system                      | \( \mu(t) \)                                                                                                                                                                                                 | \( \langle \vec{v}(t) \rangle \)                                                                 |
|---------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Self-avoiding Rouse                  | \( t^{-2\nu/(1+2\nu)} \exp(-t/\tau) \)                                                                                                                                                               | \( t^{-1/(1+2\nu)} \vec{F} \) till \( \tau \) and \( \sim \vec{F} \) thereafter \( \langle \vec{x}(t) - \vec{x}(0) \rangle \sim t^{2\nu/(1+2\nu)} \vec{F} \) till \( \tau \), and \( \sim t \vec{F} \) thereafter |
| Self-avoiding Zimm                    | \( t^{-2/3} \exp(-t/\tau) \)                                                                                                                                                                          | \( t^{-1/2} \vec{F} \) till \( \tau \) and \( \sim \vec{F} \) thereafter \( \langle \vec{x}(t) - \vec{x}(0) \rangle \sim t^{2/3} \vec{F} \) till \( \tau \) and \( \sim t \vec{F} \) thereafter (not shown here) |
| Reptation; repton model (curvilinear coordinate) | \( t^{-1/2} \exp(-t/\tau) \)                                                                                                                                                                          | \( t^{-1/2} \vec{F} \) till \( \tau \) and \( t \sim \vec{F} \) thereafter \( \langle \vec{x}(t) - \vec{x}(0) \rangle \sim t^{1/2} \vec{F} \) till \( \tau \) and \( t \sim \vec{F} \) thereafter |
| Melt (reptation theory)               | \( t^{-1/4} \) between \( \tau_e \) and \( \sim N^2 \) \((\text{as much as data can resolve})\)                                                                                                    | \( t^{-3/4} \) between \( \tau_e \) and \( \sim N^2 \) \((\text{not shown here})\)                                        |

| Polymeric system                      | \( \mu(t) \)                                                                                                                                                                                                 | Number of translocated monomers in time \( t \)                                                                 |
|---------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Phantom Rouse field-driven polymer translocation (3D) | \( t^{-1} \exp(-t/\tau) \) \((\text{\( \tau \) not translocation time})\)                                                                                                                               | \( t \) translocation time \( \sim N \) \((\text{not shown here})\) |
| Self-avoiding Rouse field-driven polymer translocation (3D) | \( t^{-1+(1+\nu)/(1+2\nu)} \) \times \exp(-t/\tau) \((\text{\( \tau \) not translocation time})\)                                                                 | \( t^{1+(1+\nu)/(1+2\nu)} \) translocation time \( \sim N^{(1+2\nu)/(1+\nu)} \) |
| Self-avoiding Zimm field-driven polymer translocation | \( t^{-1+(1+\nu)/(3\nu)} \exp(-t/\tau) \) \((\text{\( \tau \) not translocation time})\)                                                                 | \( t^{1+(1+\nu)/(3\nu)} \) translocation time \( \sim N^{3\nu/(1+\nu)} \) \((\text{not shown here})\) |
| Self-avoiding Zimm pulled polymer translocation | \( t^{-1/2} \exp(-t/\tau) \) \( \tau \sim N^2 \) \((\text{\( \tau \) not translocation time})\)                                                                 | \( t^{1/2} \) translocation time \( \sim N^2 \)                                              |

4.1.2. The repton model with a weak curvilinear force on the middle repton. Similarly, for the repton model a curvilinear force \( \vec{F} \) was applied from \( t = 0 \) onwards on the middle repton of a set of equilibrated polymer realizations to \( t = 0 \), and the average curvilinear displacement \( \langle \Delta s(t) \rangle \) of this monomer was tracked as a function of time. The result, presented in figure 9, again confirms equation (32). Note the labeling of the axes in figure 9: they confirm that in the steady state \( (t > \tau) \) the drift scales as \( 1/N \) as it should.
Table 2. (Continued.)

| Polymeric system | $\mu(t)$ | Number of monomers adsorbed in time $t$ |
|------------------|-----------|----------------------------------------|
| Phantom Rouse    | $\sim t^{-1} \exp(-t/\tau)$ | $\sim t$ (adsorption time $\sim \mathcal{N}$ (not shown here)) |
| (3D)             |           |                                        |
| Self-avoiding Rouse | $\sim t^{-(1+\nu)/(1+2\nu)} \exp(-t/\tau)$ | $\sim t^{(1+\nu)/(1+2\nu)}$ (adsorption time $\sim \mathcal{N}^{(1+2\nu)/(1+\nu)}$) |
| (3D)             |           |                                        |
| Self-avoiding Zimm | $\sim t^{-(1+\nu)/(3\nu)} \exp(-t/\tau)$ | $\sim t^{(1+\nu)/(3\nu)}$ (adsorption time $\sim \mathcal{N}^{3\nu/(1+\nu)}$ (not shown here)) |
| (3D)             |           |                                        |

$^a$ $\tau_e$ is the entanglement time for polymer melts within the reptation theory [2].

4.2. A different extension of the GLE description to driven polymeric systems

If the external force is not acting on a specified monomer (or the system’s dynamics is rate-limited by some other process), then a different generalization of the GLE (1) and (2) is required to obtain the drifts. This holds for dynamics of field-driven translocation in 3D [25], polymer adsorption on a solid surface in 3D [26], and polymer translocation by means of a pulling force $F$ [28]. For the first two cases, the force does not act on a specific monomer; instead, it acts respectively on the monomer that is in the pore, and on the monomer that is just in contact with the adsorbing surface. However, for polymer translocation by means of a pulling force, the force does act on an end monomer, but the translocation dynamics is rate-limited by polymer dynamics at the pore. For these problems, a description based on equation (1) alone is sufficient, with $\vec{\phi}(0) \neq 0$, provided, once again, that the force $\vec{F}$ is small enough that it does not distort the memory kernel or the FDT for $\vec{g}(t)$. In that case, equation (1) reads

$$\vec{\phi}(t) = \vec{\phi}(0) - \int_0^t dt' \mu(t-t') \vec{v}(t') + \vec{g}(t),$$

leading one to

$$\langle \vec{v}(t) \rangle = \int_0^t dt' a(t-t') \langle [\vec{\phi}(0) - \vec{\phi}(t')] \rangle,$$

which is essentially an extension of equation (2). If $\langle \vec{\phi}(t) \rangle$ becomes a constant fairly soon after the force starts acting on the polymer, then from equation (34) one has

$$\langle \vec{x}(t) - \vec{x}(0) \rangle \sim t^\alpha$$

up to time $\tau$, and $\sim t$ thereafter.

I now demonstrate the time scaling of equation (35) for field-driven translocation of a Rouse polymer, adsorption of a Rouse polymer on a solid surface, and translocation of a Rouse polymer by means of a pulling force.

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4.2. Field-driven polymer translocation and polymer adsorption on a solid surface. With the memory kernel \( \mu(t) \) for a translocating polymer shown in figure 2, I proceed directly to the simulation data to demonstrate equation (35) for field-driven translocation (translocation driven by a field \( E \) that only acts on the monomer in the pore) and polymer adsorption on a solid surface (with energy of adsorption \( \varepsilon \) per monomer), both in 3D. These results were originally reported, using a Monte Carlo lattice polymer code, in [25] and [26], where the reader can find the details on the simulations. The force felt by the monomer in the pore for translocation, and by the monomer in contact with the adsorbing surface, respectively, are directed perpendicular to the membrane and the adsorbing surface. Consequently, their dynamics is described simply by using the (scalar) components of the velocities and forces on the monomers perpendicular to the membrane and the adsorbing surface.

For field-driven translocation in 3D, a polymer of length \( N \) was threaded fixed halfway through the pore and was thermalized with the field \( E \) switched on, acting only on the monomer in the pore perpendicular to the membrane (this makes \( \phi(0) \neq 0 \)). Then translocation was started at \( t = 0 \). It was shown in [25] that \( \langle \phi(t) \rangle \) approaches a constant fairly quickly.

Similarly, for polymer adsorption on a solid surface in 3D, a polymer of length \( N \) was thermalized with one end held tethered on the surface. For this case, entropy-related stretching of a polymer close to a surface makes \( \phi(0) \neq 0 \). Adsorption was started at \( t = 0 \) (see [26] for further details).

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Figure 8. Confirmation of equation (32) for an end monomer of a self-avoiding Rouse polymer: data collapse for the displacement \( \langle \Delta z(t) \rangle \) in the \( \hat{z} \)-direction, under the application of a force \( \vec{F} = F \hat{z} \) from \( t = 0 \) onwards. Data are obtained using the same Monte Carlo lattice polymer model that was used to generate figure 1: \( N = 300, F\lambda/(k_B T) = 0.075 \) (circles) and \( N = 400, F\lambda/(k_B T) = 0.1 \) (pluses), where \( \lambda \) is the lattice constant. Data averaged over 8 192 equilibrated polymer realizations at \( t = 0 \). Following equation (32), \( \langle \Delta z(t) \rangle \) is expected to behave as \( t^{2\nu/(1+2\nu)} \approx t^{0.54} F \) till the terminal relaxation time \( \tau \sim N^{1+2\nu} \), after which it should behave as \( t F \). Note the labeling of the axes: they confirm that in the steady state \((t > \tau)\) the drift scales as \( 1/N \) as it should.

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Figure 9. Confirmation of equation (32) for the middle repton of the repton model. Data collapse for the curvilinear displacement \( \langle \Delta s(t) \rangle \), under the application of a curvilinear force \( F \) from \( t = 0 \) onwards: \( N = 201, F\lambda/(k_B T) = 0.1 \) (circles), \( N = 501, F\lambda/(k_B T) = 0.25 \) (pluses) and \( N = 1001, F\lambda/(k_B T) = 0.5 \) (crosses), where \( \lambda \) is the lattice constant. Data averaged over 16 384 independent polymer realizations at equilibrium at \( t = 0 \). Following equation (32) \( \langle \Delta s(t) \rangle \) is expected to behave as \( t^{1/2}F \) till the terminal relaxation time \( \tau \sim N^2 \), after which it should behave as \( tF \). Note the labeling of the axes: they confirm that in the steady state \( (t > \tau) \) the drift scales as \( 1/N \) as it should.

The data for field-driven polymer translocation and polymer adsorption in 3D, are reproduced from [25] and [26] in figures 10 and 11 respectively; both confirm equation (35). It however needs to be mentioned here that for field-driven polymer translocation and polymer adsorption to a solid surface in 2D, the memory kernel is overruled by conservation of energy: for these problems, the number of monomers translocated and the number of monomers adsorbed respectively scale as \( \sim t^{1/(2\nu)} \), i.e., the translocation and the adsorption timescales as \( N^{2\nu} \). The reader can find more details on this in [13].

4.2.2. Polymer translocation by a pulling force. The setup for polymer translocation by a pulling force is as follows. A polymer is threaded through a narrow pore in a membrane, and a latex bead is attached to one of the end monomers. An optical tweezer captures the bead, and pulls the polymer perpendicularly away from the membrane, facilitating translocation of the polymer through the pore [27]. Here I consider translocation of a self-avoiding Rouse polymer, with the membrane placed on the \( yz \)-plane, while the bead is pulled with a constant force \( F \) along the +x direction, causing the polymer to translocate from left to right. As mentioned earlier, the translocation is rate-limited by the events at the pore, so the action of the force \( F \) alone does not determine the translocation dynamics.

It is clear from this setup that the polymer on the right of the membrane would be stretched due to the action of the force, but not on the left of the membrane. Therefore, although for this setup the power-law part of the memory kernel for the polymer on the left of the membrane is still given by \( \sim t^{-(1+\nu)/(1+2\nu)} \), one needs to establish the memory

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Figure 10. Demonstration of the time scaling of equation (35) for polymer translocation driven by a field $E$ in 3D. Reproduced from [25] with permission from IOP Publishing Ltd, UK (original article published on 15 February 2008).

A note about the choice of variables: in order to avoid saturation effects [25] the average time $\langle t \rangle$, required to have $s$ monomers translocated for the first time, is plotted (instead of plotting the average number of translocated monomers $\langle s(t) \rangle$) as a function of $t$ for $N = 400$ (average over 16 000 polymer realizations for each field), $N = 800$ (average over 16 000 polymer realizations for each field), and $N = 1200$ (5000 polymer realizations for $E\lambda/(k_B T) = 0.05$, and 7500 polymer realizations each for $E\lambda/(k_B T) = 0.15$ and 0.25). Here $\lambda$ is the lattice constant.

The data for $N = 800$ correspond to real time values, while the data for $N = 400$ and $N = 1200$ have been shifted by $\pm 500$ units along the $x$-axis for clarity. The solid line has been added as a guide to the eye.

kernel for the stretched part of the polymer on the right of the membrane. Indeed, as I show below, the power-law part of the memory kernel for the stretched part of the polymer on the right of the membrane is given by $t^{-1/2}$: it is once again obtained from the mean relaxation of a (local) strain in the polymer at the pore, when the strain is caused by monomer insertion into a stretched polymer tethered on a membrane at the tether point. In order to do so, one does need two ingredients: (i) the terminal decay time $\tau$ of a stretched polymer of length $N$ tethered on a membrane scales as $\sim N^2$ [28], (ii) the shape of the stretched polymer is that of a cylinder, where the radius of the cylinder is given by that of the Pincus blob $\xi$. The magnitude of the pulling force $F$ determines the value of $\xi$, in terms of which the spring constant of a stretched polymer of length $N$ is given by $\sim k_B T/(N\xi)$ [1].

Consider the case when $n$ extra monomers are injected at $t = 0$, at the tether point of a self-avoiding Rouse polymer, which is tethered on a membrane at one end, and is stretched by a force applied at the open end. Given (i)–(ii) above, at time $t$, counting away from the tether point, all the monomers within a backbone distance $n_t \sim t^{1/2}$ will equilibrate to the new situation. However, since the polymer is stretched, its shape is that of a cylinder, and the real space extent of $n_t$ monomers is $r(n_t) \sim n_t$, but since the remaining $(N - n_t)$ monomers are not equilibrated to the injected monomers at time $t$, there are $(n_t + n)$ monomers squeezed into a space that extends only to $r(n_t)$. The
corresponding compressive force (force = (spring constant) × (stretching distance)) from these \((n_t + n)\) monomers, felt at the tether point, and hence \(\mu(t)\), is then given by \(\sim[\delta r(n_t)]/(n_t \xi) \sim n[\partial r(n_t)/\partial n_t]/(n_t \xi) = n/(n_t \xi)\), which scales as \(\sim t^{-1/2}\) [28]. (Once again, this behavior lasts only till the terminal time \(\tau\).) The explicitly evaluated \(t^{-1/2}\) power-law behavior of the mean relaxation response of a stretched self-avoiding Rouse polymer, tethered on a membrane, to a local strain caused by monomer injection at the tether point is shown in figure 12. The data in figure 12, obtained by using a Monte Carlo lattice polymer model, are reproduced from [28], from where the reader can find the details of the model.

Having put all the above together, one finds that for translocation of a self-avoiding Rouse polymer with a pulling force, there are two different (power-law) memory kernels for the polymer on the two sides of the membrane: on the left it is \(t^{-(1+\nu)/(1+2\nu)}\) and on the right it is \(t^{-1/2}\). The system’s dynamics is determined by the slower of the two: i.e., by \(t^{-1/2}\). Thus, when the polymer is threaded fixed halfway through the pore and thermalized...
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Figure 12. Mean relaxation response of a stretched self-avoiding Rouse polymer, tethered on a membrane, to a local strain caused by monomer injection at the tether point at $t = 0$. The data are obtained for $N = 100$ and $F\lambda/(k_BT) = 1$, using a Monte Carlo lattice polymer model. Here $\lambda$ is the lattice constant. The solid line corresponds to the power-law $\sim t^{-1/2}$. Figure reproduced from [28] with permission from Elsevier Inc.

with the force on one of the end monomers, $\phi(0) \neq 0$, and one expects equation (35) to hold true, with $\alpha = 1/2$. This is verified, using a Monte Carlo lattice polymer model in figure 13. The data are reproduced from [28].

5. A critique on the use of fractional Fokker–Planck equation to describe anomalous dynamics for polymer translocation

In this short section, I return to the issue of the non-Markovian property of the anomalous dynamics in polymeric systems.

The fact that in polymeric systems, the motion of a tagged monomer is non-Markovian is as such not surprising: in 3D, a polymer with $N$ monomers resides in a phase space of $6N$ dimensions (in many-polymeric systems such as polymer melts, the dimension of the phase space is six times the entire number of monomers in the systems), while the dimension of the phase space associated with a tagged monomer is only six. Thus, if one is to follow the dynamics of a tagged monomer, one is essentially taking a projection of the entire system’s dynamics on to a few degrees of freedom. While the dynamics of the entire system is no doubt Markovian, a projection on to a few selected degrees of freedom can indeed render the dynamics non-Markovian—this is the very foundation of the GLE [29, 30].

As I have shown in this paper, the dynamics of a tagged monomer in a wide range of single polymeric (phantom Rouse, self-avoiding Rouse, self-avoiding Zimm, reptation, translocation through a narrow pore in a membrane), as well as many-polymeric (polymer melts) systems is robustly formulated by the GLE (1) and (2). It is also worth emphasizing
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Figure 13. Mean time required, for $F \lambda/(k_B T) = 1$, to translocate $s$ monomers for the first time, for $s = 5, 10, 15, \ldots, N$: from left to right $N = 200, 400, 600$. The time axis corresponding to $N = 400$ is the true time, for the $N = 200$ and $N = 600$ cases the time axis is divided and multiplied by a factor 2 respectively. The angular brackets denote an average over 48,000 polymer realizations. A note about the choice of variables: in order to avoid saturation effects [28] the average time $\langle t \rangle$ required to have $s$ monomers translocated for the first time is plotted (instead of plotting the average number of translocated monomers $\langle s(t) \rangle$ as a function of $t$). The solid line corresponds to an exponent $1/2$. Figure reproduced from [28] with permission from Elsevier Inc.

that—as apparent from equation (23)—in this GLE formulation if the concerned monomer makes a move at any time, there is an enhanced chance to undo this move in subsequent times; this is where anomalous dynamics in polymeric systems stem from. Anyhow, the GLE describes trajectories in the phase space. Given this, a question that naturally arises is: ‘how does one formulate a probabilistic description of the trajectories in phase space for anomalous polymer dynamics?’ What I am appealing to is that the Fokker–Planck equation is a probabilistic formulation of the trajectories described by the Langevin equation; so what would be an appropriate probabilistic description of the trajectories described by equations (1) and (2), or for that matter equation (23)?

While for now I will leave this question for future research, here, this section will not be complete without mentioning that in a limited context—to describe the anomalous dynamics of polymer translocation—the fractional Fokker–Planck equation (fFPE) has been postulated [7]. In this equation, an extension of the standard Fokker–Planck equation, anomalous dynamics is a consequence of introducing power-law waiting times before each jump of the concerned particle, as the jump length and the waiting times for any jump are obtained from fixed probability distributions, independently of their values at previous jumps. Given that there is no power-law waiting time for the movements of the concerned monomer (instead if it makes a move at any time, there is an enhanced chance to undo this move at subsequent times; this is where anomalous dynamics in polymeric systems stem from), not only is the application of fFPE to describe polymer
translocation not correct, but also it remains a far cry from describing the examples of anomalous dynamics in the polymeric systems that are considered in this paper.

6. Conclusion

Extending the work of a recent letter [5], in this pedagogical paper I extensively elaborated on the fact that the anomalous dynamics of a tagged monomer in a wide range of single polymeric (phantom Rouse, self-avoiding Rouse, self-avoiding Zimm, reptation, translocation through a narrow pore in a membrane), as well as many-polymeric (polymer melts) systems is robustly formulated by the GLE. In this GLE formulation the velocity $\vec{v}(t)$ of a tagged monomer and the force $\vec{\phi}(t)$ it experiences, are related to each other via

$$\vec{\phi}(t) = -\int_0^t dt' \mu(t-t')\vec{v}(t') + \vec{g}(t).$$

In equation (36) $\mu(t)$ is the memory kernel, and the stochastic noise term $\vec{g}(t)$ satisfies the condition that $\langle \vec{g}(t) \rangle_0 = 0$, while the fluctuation-dissipation theorem (FDT) $\langle \vec{g}(t) \cdot \vec{g}(t') \rangle_0 = \langle \vec{\phi}(t) \cdot \vec{\phi}(t') \rangle_{\vec{\phi}=0} = 3k_BT\mu(t-t')$ in 3D. Here $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\langle \cdots \rangle_0$ denotes an average over the stochastic noise realizations, including an average over equilibrium configurations of the polymers at $t=0$. Equation (36) can be inverted to write

$$\vec{v}(t) = -\int_0^t dt' a(t-t')\vec{\phi}(t') + \vec{h}(t),$$

with $\tilde{\mu}(s)\tilde{a}(s) = 1$ in the Laplace space, $\langle \vec{h}(t) \rangle_0 = 0$, and the corresponding FDT $\langle \vec{h}(t) \cdot \vec{h}(t') \rangle_0 \equiv \langle \vec{v}(t) \cdot \vec{v}(t') \rangle|_{\vec{\phi}=0} = 3k_BTa(t-t')$. On the one hand $\mu(t)$ is the mean relaxation response of the polymers to local strains, and can be derived from the equilibrium statistical physics of polymers; and on the other, $a(t)$ characterizes the anomalous dynamics via the FDT: as the mean-square displacement of a tagged monomer is obtained by integrating $\langle \vec{v}(t) \cdot \vec{v}(t') \rangle|_{\vec{\phi}=0}$ twice in time. An important property of the anomalous dynamics that transpires through this exercise is that if $\mu(t) \sim t^{-\alpha}$ for some $\alpha$, then the anomalous dynamics is also $\alpha$. In other words, the anomalous dynamics for polymeric systems are connected to the mean relaxation response of the polymers to local strains. The anomalous dynamics and the mean relaxation response of the polymers to local strains, as shown in equation (23), works in the following way: if the concerned monomer makes a move at any time, there is an enhanced chance to undo this move in subsequent times; this is where anomalous dynamics in polymeric systems stem from.

Further, the characteristics of the drifts caused by a (weak) applied field on polymeric systems, too, are obtained from the corresponding memory kernels: if $\mu(t) \sim t^{-\alpha}$ for some $\alpha$, then the drift exponent is also $\alpha$. This could be thought of as the analog of the Nernst–Einstein relation.

Given that the GLE provides the trajectory description in the phase space, I bring to light the non-Markovian character of the anomalous dynamics for polymeric systems. The fact that the motion of a tagged monomer is non-Markovian is as such not surprising: in 3D, a polymer with $N$ monomers resides in a phase space that has $6N$ dimensions (in many-polymeric systems such as polymer melts, the dimension of the phase space
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is 6 times the entire number of monomers in the systems), while the dimension of the
phase space associated with a tagged monomer is only six. Thus, if one is to follow
the dynamics of a tagged monomer, one is essentially taking a projection of the entire
system’s dynamics on to a few degrees of freedom. While the dynamics of the entire system
is no doubt Markovian, such a projection on to a few degrees of freedom can indeed
render the dynamics non-Markovian—this is the very foundation of the GLE [29,30].

Given this, a question that naturally arises is: “how does one formulate a probabilistic
description of the trajectories in phase space for anomalous polymer dynamics?” While
for now I leave this question for future research, I note that anomalous dynamics in
polymeric systems cannot be captured by, e.g., the fractional Fokker–Planck equation
(fFPE) which has been recently postulated [7] to describe the anomalous dynamics of
polymer translocation through a narrow pore in a membrane. In this equation, an
extension of the standard Fokker–Planck equation, anomalous dynamics is a consequence
of introducing power-law waiting times before each jump of the concerned particle, as
the jump length and the waiting times for any jump are obtained from fixed probability
distributions, independently of their values at previous jumps. Given that there is no
power-law waiting time for the movements of the concerned monomer (instead if it makes
a move at any time, there is an enhanced chance to undo this move at subsequent times;
this is where anomalous dynamics in polymeric systems stem from), not only is the
application of fFPE to describe polymer translocation not correct, but also it remains
a far cry from describing the examples of anomalous dynamics in the polymeric systems
that are considered in this paper.

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Appendix. Derivation of $\langle \vec{v}(t) \cdot \vec{v}(t') \rangle$ for phantom polymers (i.e., equation (25))

I start with the velocity autocorrelation function as in equation (25)

$$V(t, t') = \langle \vec{v}(t) \cdot \vec{v}(t') \rangle = \int_0^t dt_1 \beta(t - t_1) \int_0^{t'} dt_2 \beta(t' - t_2)$$

$$\times \left[ \langle \vec{g}(t_1) \cdot \vec{g}(t_2) \rangle + \langle \vec{f}_{N/2}(t_1) \cdot \vec{f}_{N/2}(t_2) \rangle \right].$$

(A.1)

I am interested in the behavior of $\langle \vec{v}(t) \cdot \vec{v}(t') \rangle$ in the limit of large $(t, t')$ with finite $(t - t')$. In this limit I expect $V(t, t') \rightarrow V(t - t')$. Nevertheless, I take a dual Laplace transform of $V(t, t')$: one with Laplace variable $s$ for $t$, and the other with Laplace variable $s'$ for $t'$.

$$\hat{V}(s, s') = \int_0^\infty dt e^{-st} \int_0^\infty dt' e^{-s't'} V(t, t')$$

$$= \int_0^\infty dt e^{-st} \int_0^\infty dt' e^{-s't'} \int_0^t dt_1 \beta(t - t_1) \int_0^{t'} dt_2 \beta(t' - t_2)$$

$$\times \left[ G(t_1, t_2) + \Delta(t_1, t_2) \right].$$

(A.2)

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Upon having interchanged integration variables, I rewrite {\tilde{V}(s, s')} as
\[
{\tilde{V}(s, s')} = \int_0^\infty dt e^{-st} \int_0^\infty dt' e^{-s't'} \int_0^t dt_1 \beta(t - t_1) \int_{t_1}^{t'} dt_2 \beta(t' - t_2) \left[ G(t_1, t_2) + \Delta(t_1, t_2) \right]
\[
= \int_0^\infty dt_1 e^{-st_1} \int_0^\infty dt_2 e^{-s't_2} \left[ G(t_1, t_2) + \Delta(t_1, t_2) \right] \int_{t_1}^{t_2} dt' e^{-s(t-t_1)} \beta(t - t_1)
\[
\times \int_{t_2}^{t'} dt' e^{-s'(t-t_2)} \beta(t' - t_2) = \tilde{\beta}(s) \tilde{\beta}(s') \int_0^\infty dt_1 e^{-st_1}
\[
\times \int_{t_1}^{t_2} dt_2 e^{-s't_2} \left[ G(t_1, t_2) + \Delta(t_1, t_2) \right].
\]
(A.3)

With \( G(t_1, t_2) = 3k_B T \mu(\|t_1 - t_2\|) \) and \( \Delta(t_1, t_2) = 6\gamma k_B T \delta(t_1 - t_2) \), I choose to represent \( \Delta(t - t') \) as
\[
\Delta(t - t') = 6\gamma k_B T \left\{ \begin{array}{ll}
\lim_{\Delta \to 0} \frac{1}{\Delta} & \text{if } |t - t'| \leq \Delta/2 \\
0 & \text{otherwise}.
\end{array} \right.
\]
(A.4)

Thereafter, having recalled that \( \tilde{\beta}(s) = [\gamma + \tilde{\mu}(s)]^{-1} \), I obtain
\[
{\tilde{V}(s, s')} = 3k_B T \tilde{\beta}(s) \tilde{\beta}(s') \left[ \frac{\tilde{\beta}^{-1}(s)}{s - s'} + \frac{\tilde{\beta}^{-1}(s')}{s - s'} \right] = 3k_B T \left[ \frac{\tilde{\beta}(s')}{s' - s} + \frac{\tilde{\beta}(s)}{s - s'} \right],
\]
(A.5)

which implies, assuming \( t > t' \), that
\[
\langle \vec{v}(t) \cdot \vec{v}(t') \rangle = 3k_B T \tilde{\beta}(t - t').
\]
(A.6)

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