Abstract. We study theoretically the dynamics of living polymers which can add and subtract monomer units at their live chain ends. The classic example is ionic living polymerization. In equilibrium, a delicate balance is maintained in which each initiated chain has a very small negative average growth rate (“velocity”) just sufficient to negate the effect of growth rate fluctuations. This leads to an exponential molecular weight distribution (MWD) with mean \( \bar{N} \). After a small perturbation of relative amplitude \( \epsilon \), e.g. a small temperature jump, this balance is destroyed: the velocity acquires a boost greatly exceeding its tiny equilibrium value. For \( \epsilon > \epsilon_c \approx 1/N^{1/2} \) the response has 3 stages: (1) Coherent chain growth or shrinkage, leaving a highly non-linear hole or peak in the MWD at small chain lengths. During this episode, lasting time \( \tau_{\text{fast}} \sim N^2 \), the MWD’s first moment and monomer concentration \( m \) relax very close to equilibrium. (2) Hole-filling (or peak decay) after \( \tau_{\text{fill}} \sim \epsilon^2 N^2 \). The absence or surfeit of small chains is erased. (3) Global MWD shape relaxation after \( \tau_{\text{slow}} \sim N^2 \). By this time second and higher MWD moments have relaxed. During episodes (2) and (3) the fast variables \( (\bar{N}, m) \) are enslaved to the slowly varying number of free initiators (chains of zero length). Thus fast variables are quasi-statically fine-tuned to equilibrium. The outstanding feature of these dynamics is their ultrasensitivity: despite the perturbation’s linearity, the response is non-linear until the late episode (3). For very small perturbations, \( \epsilon < \epsilon_c \), response remains non-linear but with a less dramatic peak or hole during episode (1). Our predictions are in agreement with viscosity measurements on the most widely studied system, \( \alpha \)-methylstyrene.

PACS. 82.35.-x Polymers: properties; reactions; polymerization. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian Motion. 87.15.Rn Biomolecules: structure and physical properties; Reactions and kinetics; polymerization.

1 Introduction

Living polymers are intriguing examples of soft matter and have major roles in technology and biology. The classic system, of major importance for the synthesis of high-grade polymer materials and the subject of a long history of fundamental experimental and theoretical study, is living anionic polymerization \([12 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25]\). This class of polymerization is widely employed to manufacture polymers with nearly monodisperse MWDs and controlled architectures such as block and star copolymers \([26]\). A recent variant on this theme with immense potential technological impact is living free radical polymerization \([27 28]\). Other examples include worm-like surfactant micelles \([29 30 31 32 33 34 35 36]\) and biological polymers such as actin and tubulin filaments \([37 38 39 40 41 42]\) whose special properties are exploited by living cells for motility and structural integrity.

As polymeric or polymer-like materials, the unique feature of these systems is that the chains are dynamic objects, with constantly fluctuating lengths. When subjected to an external perturbation, they are able to respond dynamically via polymerization and depolymerization reactions allowing a new thermodynamic equilibrium to be attained. These systems are “living” in the sense that a change in their environment leads to a new equilibrium molecular weight distribution (MWD). All of this should be compared to conventional inert polymer materials whose MWDs are frozen.

The subject of this paper is the dynamical response of living polymers. We study the class of living polymers which is exemplified by living ionic polymerization, having the following characteristics: (i) monomers add and subtract from chain ends and (ii) the total number of chains is fixed. In the biological world, actin and microtubule filaments satisfy condition (i), and the dynamics of both filaments and filament caps are frequently described by situation (ii) \([43]\). Worm-like micelles on the other hand in some cases grow from their ends only \([29 30]\) (condition (i)) but do not satisfy condition (ii); the number of micelles is not conserved. Interestingly, this makes their dynamical response very different (see discussion section).
The thermodynamic properties of equilibrium living polymers have been studied in a large number of experiments [2,3,4,5,6,7,8,9,10,11,12,13]. The reason that chain length fluctuations in equilibrium are so large is that even when a state is reached where the monomer concentration reaches a steady state value such that polymer growth rates exactly balance depolymerization, through polymerization and depolymerization reactions monomers continue to be reshuffled among living chains. Thus even if one starts with an essentially monodisperse MWD as shown in fig. 2(a), random addition and subtraction of monomers from chain ends will result in a “diffusive” random walk motion of chain ends in $N$-space (where $N$ is the number of monomer units added to initiator) with a certain characteristic “diffusivity” $D$. Since there is no restoring force to this motion, chain ends will eventually diffuse to distances of the same order as the mean $\bar{N}$, as shown in (b). Note the resulting MWD includes chains of “zero” length (free initiators).

Our main broad conclusion is that, counter-intuitively, the response to a very small perturbation is extremely strong: even though the initial and final MWDs (the latter attained after relaxation is complete) are very close to one another, the MWD at intermediate times is very strongly perturbed from equilibrium, i.e. its shape is very different from either the initial or final equilibrium shapes. In this beyond mean field by accounting for excluded-volume interactions leads to power law modifications [18,19,20,34] to eq. [1]. Moreover, an analogy [14,15,16,17] between a living polymer system and the much studied Ising spin system in the formal limit of spin dimensionality $n$ becoming zero (similar to the well-known analogy in the thermodynamic theory of semidilute polymer solutions [17,18] which can in fact be formulated equivalently to a living polymer system [19]) showed that the polymerization phase transition near the polymerization temperature is second-order with a number of characteristic power-law exponents. The results of a large number of experiments by the group of Greer, measuring both the MWD itself [16] and other thermodynamic properties [21] are apparently consistent with the above theories, favoring somewhat the non mean-field approach.

The most essential feature of living polymers however, namely their ability to respond dynamically to external perturbations, remains largely unexplored. How does an equilibrium living polymer system respond to a small perturbation? A conceptually simple perturbation is the addition of a small amount of extra monomer (an “m-jump”). A similar perturbation, easier to perform in practice, is a “T-jump,” i.e. a small sudden change in temperature. Under such a perturbation, how rapidly and in what manner will the monomer concentration, MWD and mean chain length reach a new equilibrium? In this paper we address these questions theoretically. We will compare our predictions in section 8 with small T-jump viscosity relaxation experiments by Greer et al. [11]. This same group has also monitored monomer and MWD dynamics following much stronger perturbations, finite temperature quenches [12,13] (see fig. 3).

Our main broad conclusion is that, counter-intuitively, the response to a very small perturbation is extremely strong: even though the initial and final MWDs (the latter attained after relaxation is complete) are very close to one another, the MWD at intermediate times is very strongly perturbed from equilibrium, i.e. its shape is very different from either the initial or final equilibrium shapes. In this
sense, there are no small perturbations: a small thermodynamic perturbation well-described by a linear susceptibility (i.e. one inducing a small change in the equilibrium state) has nonetheless a large dynamical effect; intermediate states deviate strongly from equilibrium in the sense that observables are perturbed in a highly non-linear manner. We refer to this as dynamical ultrasensitivity.

A hint of this sensitivity is already apparent in equilibrium, where a very delicate balance is established between growth and shrinkage such that the net polymerization velocity \( v \) is essentially zero, of order \( 1/N_{\infty} \) (due to the small fraction of special non-depolymerizable chains of length \( N = 0 \)). Now the effect of a small \( T \)-jump (say) is to produce a small but finite velocity which overwhelms this tiny velocity value and destroys the delicate balance sustaining equilibrium. Thus if for example \( v \) becomes positive, the MWD will uniformly translate toward larger molecular weights, creating a depletion in the MWD at small chain lengths, as shown schematically in fig 4. This translation process stops only after sufficient monomer has been polymerized such that the monomer concentration drops close to its destination equilibrium value, corresponding to a recovery of the zero net growth rate equilibrium condition. We find that only on a much longer timescale does “diffusion” of chain ends fill up the hole and lead the system to the destination equilibrium MWD, as shown in fig 4.

Why does this hole develop in the MWD? The reason is that chain length scales homogenized by diffusion, \((D\tau)^{1/2}\), are smaller than scales affected by translational motion, \(vt\), for times longer than the timescale \(t^* \approx D/v^2\). Thus if \(t^*\) is shorter than the timescale needed for translation to stop, a depletion hole develops in the MWD. But even when translation is completed earlier than \(t^*\), we find that the perturbation is still nonlinear; even though no hole is formed there is still a large amplitude reduction in the MWD, much larger than the relative magnitude of the initial perturbation, \(\epsilon\).

This work is related to earlier theory of Miyake and Stockmayer [44] who, following a prior treatment by Brown and Szwarc [50], studied analytically and numerically the dynamics in the special case where initially all monomer is unpolymerized (see fig. 5). Their analytical results, applicable in the case of very small depolymerization rates, showed a 2-stage relaxation. During the first, lasting a time \( \sim N_{\infty} \), living chains grow coherently from zero length up to the equilibrium value. In the second stage the shape of the sharply peaked MWD relaxes slowly toward the equilibrium exponential distribution. Although their perturbation analysis broke down during this stage, Miyake and Stockmayer estimated that its duration scales as \( N_{\infty}^2 \). Later theoretical studies addressed the second stage dynamics [51-53] of this special case.

A short announcement of the present work has already appeared [54]. The structure of the paper is as follows. In section 2 we establish the dynamical equations obeyed by living polymers which show the nonlinear coupling between the monomer population and the living chain MWD. For simplicity, we neglect excluded volume interactions and chain length dependent polymerization rates. Starting from the equations of section 2 we then analyze the response to a \( T \)-jump. This response depends on the sign of the velocity induced by the perturbation. The case of positive initial velocity is analyzed in sections 3 and 4, while the negative in section 5. The special case of very small \( T \)-jumps is analyzed in section 6. In section 7 we show that the results of the previous sections directly generalize to small perturbations of arbitrary form. Finally we conclude with a discussion of the results, and the experimental outlook.

2 Living Polymer Dynamics: Monomer-Polymer Coupling

An important aspect of living polymers dynamics is the coupling between the two distinct species present in the solution, free monomers and living chain MWD: on the one hand living chain growth rates depend on the concentration of free monomer and on the other hand, due to mass conservation, monomer concentration if a function of the living chain MWD. Stated differently, living chains grow according to a velocity field which is self-consistently updated depending on the response of the MWD. In this section we develop the equations obeyed by monomer and MWD. The dynamical response to perturbations is discussed in the following sections.

A crucial feature of the living polymer systems we study is that the number of living chains remains fixed. This is what arises in the experiments of Greer et al. [2,4,3], where this number is determined by the amount of initiator initially added in the solution. Denoting \( i_0 \) the concentration of living chains (i.e. chains which have been initiated), mass conservation implies that monomer concentration, \( m_t \), and MWD, \( \phi_t(N) \), \((t \text{ denotes time})\) obey

\[
m_t = m_{\text{tot}} - i_0 \bar{N}_t , \quad \bar{N}_t \equiv \int_0^\infty dN N \phi_t(N) , \quad (2)
\]
where \( m_{\text{tot}} \) is the total monomer concentration (including polymerized monomers), and \( \bar{N}_t \) is mean chain length. Here \( \phi_t \) is normalized to unity and \( N = 0 \) corresponds to free initiator. The coupling between monomer concentration and the MWD is manifest in eq. (2).

Now the dynamical equations obeyed by \( \phi_t \) are

\[
\frac{\partial \phi_t(N)}{\partial t} = -\frac{\partial j_t(N)}{\partial N} , \quad j_t(N) \equiv v_t \phi_t(N) - D_t \frac{\partial \phi_t(N)}{\partial N} , \quad j_t(0) = 0 , \quad (3)
\]

where

\[
v_t \equiv k^+ m_t - v^- , \quad D_t \equiv \frac{k^+ m_t + v^-}{2} / v_i . \quad (4)
\]

Here \( k^+ \) is the propagation rate constant and \( v^- \) is the depolymerization rate. The “diffusion” coefficient \( D_t \) describes fluctuations in the rate of polymerization/depolymerization. Eq. (3) is identical to the diffusion dynamics of a particle in a linear potential with time-dependent slope \(-v_t\) whose time-dependent diffusion coefficient is \( D_t \) (see fig. 3). The novelty here is that due to the coupling between the MWD and monomer, both the slope and diffusivity are functionals of \( \phi_t \) itself.

The reflecting boundary condition in eq. (3) at \( N = 0 \) represents the fact that when a living chain looses all of its monomers and becomes a free initiator molecule (i.e. reaches length \( N = 0 \)) it cannot depolymerize further and must grow again. Now we restate eq. (3) as

\[
\frac{\partial \phi_t}{\partial t} = -v_t \frac{\partial \phi_t}{\partial N} + D_t \frac{\partial^2 \phi_t}{\partial N^2} , \quad \phi_t(0)/\phi_t'(0) = D_t/v_i , \quad (5)
\]

where \( \phi_t' \equiv \phi_t / \partial N \).

Now it might at first seem that despite the coupling of eq. (2), the monomer subsystem would effectively uncouple from the MWD dynamics, since one might naively expect that the monomer dynamics do not depend on the shape of the polymer MWD but only on the number of living chains. This would imply simple first order kinetics for \( m_t \) resulting in exponential relaxation of the monomer concentration, independent of the MWD dynamics. The coupling however arises from the existence of special chains in the MWD of zero length, i.e. free initiator molecules of which there are \( \phi_0(0) \), which unlike all other chains cannot depolymerize. Indeed, the dynamics obeyed by \( m_t \), or equivalently \( v_t \), are

\[
\frac{dv_t}{dt} = -\frac{v_t}{\tau_{\text{fast}}} - \frac{D_t \phi_t(0)}{\tau_{\text{fast}}} \quad \tau_{\text{fast}} \equiv \frac{f}{rv^-} \approx \frac{f}{(1-f)v^-} . \quad (6)
\]

We see clearly that the only aspect of the living MWD which monomers see is \( \phi_t(0) \). Eq. (6) is derived by calculating \( d\bar{N}_t/dt \) by multiplying eq. (3) by \( N \), integrating over all \( N \), using the reflecting boundary condition, and then using eq. (2). The relationship between \( \tau_{\text{fast}} \) and \( \bar{N}_\infty \) follows from eq. (8) below. Here we have introduced the two basic independent dimensionless parameters of the system:

\[
f \equiv \frac{v^-}{k^+ m_{\text{tot}}} , \quad r \equiv \frac{i_0}{m_{\text{tot}}} . \quad (7)
\]

The physical meaning of \( f \) is the following: if the system were a pure solution of unpolymerized monomer (plus solvent and initiator) \( f \) would be the ratio of backward to forward polymerization velocities. The value of \( f \) is temperature dependent, being unity at the polymerization temperature and smaller or larger than unity in the polymer and non-polymer phase, respectively. The parameter \( r \), namely the ratio of living chain to total monomer concentration, is independent of temperature and is always much smaller than unity. Its smallness is related to the mean degree of polymerization being much larger than unity in equilibrium (see eq. (8) below).

Now setting the time derivative in eq. (6) to zero and using eq. (2) it is shown in Appendix A that in equilibrium the Flory-Schultz distribution of eq. (11) is recovered and one has to leading order in \( r \):

\[
\bar{N}_\infty \approx \frac{1}{r} \frac{m_{\infty}}{m_{\text{tot}}} \approx f , \quad v_\infty \approx \frac{v^-}{\bar{N}_\infty} , \quad D_\infty \approx v^- . \quad (8)
\]
where $r \ll 1$ and subscript $\infty$ denotes the $t \to \infty$ equilibrium value for the corresponding variable. We assumed $(1-f)/r^{1/2} \gg 1$, i.e. that the temperature is not extremely close to the polymerization temperature.

An important feature in eq. 8 is that in equilibrium the velocity, i.e. the slope of the “potential” term in eq. (5), settles down to a very small negative value. Were there no diffusion, living chains subject to a negative velocity field would shrink to zero length. However due to the small magnitude of the velocity, diffusion is strong enough to broaden the MWD up to distances of order $N_\infty$, as illustrated in fig. 2. We show in the following section that any apparently small external perturbation has an enormous effect on the velocity which, depending on the direction of the perturbation, may become either very negative or very positive.

### 3 Response to $T$-jump; Positive Velocity Boost

Perhaps the simplest way to perturb an equilibrium living polymer system is by a small temperature change ($T$-jump). Taking as an example $\alpha$-methylstyrene, the data of fig. 4 show equilibrium fraction of polymerized monomer as a function of temperature; evidently, changes in $T$ lead to different values of the equilibrium monomer concentration $m_\infty$ and therefore of $N_\infty$ as well. In this section we consider relaxation dynamics after an equilibrated system is subjected at $t = 0$ to a small temperature change $\delta T$ such that the system will eventually reach new equilibrium values $m_\infty$ and $N_\infty$. That is, we follow the dynamics of the transition from an old equilibrium towards a slightly different new equilibrium state.

The magnitude of the perturbation is measured by the small parameter

$$
\epsilon \equiv \frac{\delta m_0}{m_\infty}, \tag{9}
$$

where we define $\delta m_t \equiv m_t - m_\infty$ and similarly for other quantities. All equilibrium values refer to the destination ($t = \infty$) equilibrium values. Thus $\delta m_0$ is the initial ($t = 0$) deviation from the final equilibrium.

The value of $\epsilon$ is related to the magnitude of the $T$-jump. For example in the case of $\alpha$-methylstyrene, assuming that the system is initially below the polymerization temperature $T_p$ in the region of fig. 7 between 260$^\circ$K and 280$^\circ$K, one has using eq. 9

$$
\epsilon \approx \frac{\delta T}{50^\circ K} \quad (\alpha$-methylstyrene). \tag{10}
$$

Thus for $\alpha$-methylstyrene a temperature increase, $\delta T > 0$, results in a negative $\delta m_0$, i.e. a reduced initial monomer concentration relative to the destination equilibrium value.

Now the $t = 0$ relative perturbation of the MWD is

$$
\frac{\delta \phi_0(N)}{\phi_\infty(N)} \approx \frac{\partial \phi_\infty(N)}{\partial N_\infty} \frac{\delta N_0}{\phi_\infty(N)} = \frac{\epsilon}{\theta} \left(1 - \frac{N}{N_\infty}\right), \quad \theta \equiv 1 - f \tag{11}
$$

This is of order $\epsilon$ and smaller than unity for all $N$ (apart from the unimportant values $N \gg N_\infty$ where the MWD is exponentially small) as shown in fig. 6a).

Because velocity, monomer concentration and mean chain length are all linearly related (see eqs. 2, 5 and 6) changes in these quantities are simply related as

$$
\frac{\delta m_t}{m_\infty} \approx -\theta \frac{\delta N_t}{N_\infty} \approx \frac{\delta D_t}{D_\infty} \approx \frac{\delta v_t}{v_\infty}. \tag{12}
$$

These relations are true for all times. They allow us to follow the dynamics of velocity alone. Once $v_t$ is known, $N_t, m_t, D_t$ are determined.

From eqs. 12 and 9 the initial relative changes in $v, D$ are:

$$
\frac{\delta v_0}{v_\infty} \approx -\epsilon \frac{v_\infty}{N_\infty}, \quad \frac{\delta D_0}{D_\infty} \approx \frac{\epsilon}{2}. \tag{13}
$$

The important point is that since $N_\infty \gg 1$, the relative change in $v$ is much larger than $\epsilon$; the velocity is highly perturbed, as shown in fig. 4. Depending on the sign of $\epsilon$, the velocity may remain negative as in equilibrium, or it
may change sign. Since the relative perturbation in \( D \) is by contrast small, we see that the delicate velocity-diffusion balance which sustained equilibrium is now destroyed.

We will show below that relaxation to equilibrium now occurs in three stages. During the first, dominated by translational motion, the MWD is boosted far from its equilibrium shape. The next stage involves diffusive restoration of the region of the MWD which suffered maximum distortion during the first stage. The third and final episode entails a very slow diffusion-dominated recovery of the global MWD. For the remainder of this section we treat the case of a positive initial velocity boost, where chains initially grow (\( \delta T < 0 \) for \( \alpha \)-methyl styrene). Negative velocity boosts, where chains initially shrink, are considered in section 5.

### 3.1 Coherent Chain Growth: Hole Development

During the first stage of the relaxation process, velocity dominates over diffusion since \( v \) has been so strongly perturbed. Chains thus grow coherently, consuming the excess monomer in a timescale \( \tau_{\text{fast}} \) by which time translation will have halted and a highly non-linear hole will have developed in the MWD (see fig. 9). Here \( \tau_{\text{fast}} \), defined in eq. (10), is the time for the MWD to translate distance \( \delta N_0 \) and reach the destination mean, i.e. \( \tau_{\text{fast}} \approx \delta N_0 / \delta v_0 \) (see eqs. (10), (13) and using eq. (8)).

To see all of this more quantitatively, consider the velocity dynamics eq. (6). Initially, the velocity term on the rhs is much larger in magnitude than the diffusion term. We show in Appendix B that this remains true up until a time \( \tau_{qs} \), defined below. It follows that for these times \( v_t \) relaxes exponentially. The same is true of \( m_t, N_t \) and \( D_t \) which we recall are linearly coupled to \( v_t \) (see eq. (12)). Thus

\[
\delta v_t \approx \epsilon v^*-t/\tau_{\text{fast}} - v_\infty \quad (t \ll \tau_{qs} = \epsilon N_{qs}^3/2g^{-3/2}/v^-) \tag{14}
\]

Note that for \( t \gg \tau_{\text{fast}} \) there are no free initiators (at much longer times these are restored, see below). Thus for these intermediate times all chains are identical as far as on and off monomer kinetics are concerned, and the net rate of monomer-polymer mass exchange can only vanish if \( v_t \) vanishes. For this reason \( v_t \) decays to zero, though much later it will recover its small negative equilibrium value. The \( \phi_t \) dynamics, eq. (5), thus simplify to

\[
\frac{\partial \phi_t}{\partial t} \approx -\epsilon v^* e^{-t/\tau_{\text{fast}}} \frac{\partial \phi_t}{\partial N} + D_\infty \frac{\partial^2 \phi_t}{\partial N^2} \quad (t \ll \tau_{qs}) \tag{15}
\]

where the diffusion coefficient may be approximated by \( D_\infty \) since the contribution of \( D_t \) is negligible (see Appendix B). This linear equation, plus the time-dependent boundary condition of eq. (4), has solution

\[
\phi_t(N) \approx \int_0^\infty dN' G_{t}^{\text{tran}}(N, N') \phi_0(N') \quad (t \ll \tau_{qs}) \tag{16}
\]

which describes a translating and simultaneously broadening MWD, as shown in fig. 9. Here \( G_t^{\text{tran}}(N, N') \) is the propagator of eq. (16) whose properties are calculated in Appendix B.

An important quantity in what follows is \( \phi_t(0) \), i.e. the concentration of free initiators. Using eq. (16) we show in Appendix B that

\[
\frac{\phi_t(0)}{\phi_\infty(0)} \approx \begin{cases} 1 - C (t/t^*)^{1/2} & (t \ll t^*) \\ F (t^*/t)^{3/2} e^{-t^*} t^* \ll t \ll \tau_{\text{fast}} & \end{cases} \tag{17}
\]

where \( C = 4/\pi^{1/2} \) and \( F = \pi^{-1/2} \). Eq. (17) has a clear physical meaning: as the MWD translates, the position of its peak at \( N = 0 \) after time \( t \) has shifted to chain lengths of order \( v_0 t \). Were diffusion absent, this would have created a depletion region in the MWD at small chain lengths.
lengths. However diffusion smooths out inhomogeneities on distances of size \( (D_\infty t)^{1/2} \). Hence for times shorter than the crossover time \( t^* \) for which \( v_0 t^* \approx (D_\infty t^*)^{1/2} \), diffusion has enough time to fill the translationally induced hole and the relative deviation from equilibrium is small. For times longer than \( t^* \), however, the MWD translates a distance away from the origin much larger than what diffusion could have homogenized, a hole develops in the MWD, and the concentration of zero length chains becomes exponentially small.

In eq. \( (17) \) we assumed that the perturbation is large enough such that \( t^* \ll \tau_{fast} \). The special case of extremely small perturbations where this is no longer true is discussed separately in section 5.

### 3.2 Diffusive Length Relaxation: Hole Filling

For times \( t \gg \tau_{fast} \) the fast variables monomer and mean chain length have relaxed very close to their equilibrium values. We have seen that velocity becomes exponentially small. Meanwhile (see below) the number of free initiators \( \phi_t(0) \) is gradually recovering. At a certain moment, therefore, the 2 terms on rhs of eq. \( (6) \) become equal to one another and we show in Appendix B that for all later times the velocity time derivative is much smaller. Hence the velocity dynamics are now fundamentally changed. The new regime is one of quasi-static evolution, enslaved to the dynamics of \( \phi_t(0) \):

\[
\frac{\partial \phi_t}{\partial t} \approx -v - \delta \phi_t(0) \quad (t \gg \tau_{qs}) \quad (18)
\]

Physically, this reflects the fact that the the only aspect of the MWD shape seen by monomers is the amount of special non-depolymerizing zero-length chains. We see that as the MWD slowly rearranges itself, so the fast variables \( v_t, m_t \) and \( N_t \) variables respond quasi-statically.

Notice that the quasi-static regime does not onset after \( \tau_{fast} \) but rather after \( \tau_{qs} \). The reason is that during the initial boost the term \( D_t \phi_t(0) \) in eq. \( (6) \) decays exponentially on a timescale \( t^* \); its magnitude therefore at \( \tau_{fast} \) is much smaller than \( v_t \) which decays on a timescale \( \tau_{fast} \).

(see eqs. \( 14 \) and \( 17 \)). There is thus a cross-over period before the quasi-static balance between the two terms is established.

Now let us examine the MWD dynamics. Since \( v_t \) becomes exponentially small after the MWD stops translating, we have

\[
\frac{\partial \phi_t}{\partial t} \approx D_\infty \frac{\partial^2 \phi_t}{\partial N^2} \quad (\tau_{fast} \ll t \ll \tau_{fill}) \quad (19)
\]

with reflecting boundary conditions at the origin. Here once again the contribution of \( \delta D_t \) is negligible (see eqs. \( 12, 13, \) and \( 21 \)) and the corresponding term has been neglected in eq. \( (19) \). Here

\[
\tau_{fill} \equiv e^2 \theta^{-2} \tau_{slow} \quad , \quad \tau_{slow} \equiv \frac{N_\infty^2}{4D_\infty} \quad (20)
\]

The timescale \( \tau_{slow} \) is the longest relaxation time of the system, the time for the slow global shape characteristics of the MWD to relax. It equals the diffusion time for the MWD width \( N_\infty \). Meanwhile \( \tau_{fill} \) is the diffusion time for the hole width, \( \epsilon N_\infty / \theta \). It is shown in Appendix B that eq. \( (19) \) has solution

\[
\frac{\phi_t(0)}{\phi_\infty(0)} \approx H \left( \frac{t}{\tau_{fill}} \right)^{1/2} e^{-\tau_{fill}/t} \quad (\tau_{fast} \ll t \ll \tau_{fill}) \quad (21)
\]

where \( H = \pi^{-1/2} \). Thus for times shorter than \( \tau_{fill} \) the concentration of zero length chains remains exponentially small while for longer times the hole fills (see fig. \( 11 \)) and \( \phi_t(0) \) recovers its equilibrium value.

### 3.3 Linearized Dynamics at Long Times

For times beyond \( \tau_{fill} \) the hole-filling is complete and the MWD’s non-linear feature has disappeared. Thus, finally, a truly linear regime onsets: relative deviations of all variables from equilibrium are less than unity and perturbation theory can now be applied. This is done in Appendix...
\[
\frac{\delta v_t}{v} \approx -\delta \phi_t(0) \approx \begin{cases} 
J \phi_\infty(0) (\tau_{\text{fill}}/t)^{1/2} & (\tau_{\text{fill}} \ll t \ll \tau_{\text{slow}}) \\
M \epsilon \phi_\infty(0) (t/\tau_{\text{slow}})^{-3/2} e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}}) 
\end{cases}
\]

(22)

where \( J, M \) are positive constants of order unity. Thus \( \delta \phi_t(0) \), and all of the fast variables which remain quasi-statically enslaved to \( \phi_t(0) \), relax exponentially on a time-scale \( \tau_{\text{slow}} \) with a power law prefactor.

4 The Second Moment of the MWD Relaxes More Slowly than the First

A picture has emerged of fast mass-related variables which relax in \( \tau_{\text{fast}} \) and slow MWD shape properties which relax in the much longer time \( \tau_{\text{slow}} \). The MWD's first moment defines the total mass in the polymer system: this is a fast variable and was considered in section 3. The simplest slow shape property is the dispersion \( \Delta_t \),

\[
\Delta_t \equiv \overline{N_t^2} - \bar{N}_t^2, \quad \overline{N_t^2} \equiv \int_0^\infty dN N^2 \phi_t(N),
\]

(23)

which is closely related to the second moment. In this section we consider the very different and slow relaxation in these quantities are much smaller than that of \( \Delta_t \).

Substituting eq. (11) in eq. (23) one finds that following a \( T \)-jump the initial relative perturbation in the dispersion, \( \delta \Delta_0/\Delta_\infty \), is

\[
\frac{\delta \Delta_0}{\Delta_\infty} = -\frac{\epsilon}{\theta}, \quad \Delta_\infty = \overline{N_\infty^2},
\]

(24)

where the equilibrium value, \( \Delta_\infty \), is found using eq. (11). Now the dynamics of the dispersion can be derived by evaluating the time derivatives of \( \overline{N_t^2}, \bar{N}_t \) in eq. (23). These can in turn be calculated by multiplying eq. (15) by \( N^2 \) and \( N \), respectively, integrating over all \( N \) and using the boundary condition of eq. (3).

One has

\[
\frac{1}{\Delta_\infty} \frac{d \Delta_t}{dt} = \frac{1}{2\tau_{\text{slow}}} \frac{D_t}{\Delta_\infty} \left[ 1 - \frac{\bar{N}_t}{\overline{N_\infty^2}} \phi_t(0) \right] \approx -\frac{1}{2\tau_{\text{slow}}} \frac{\delta \phi_t(0)}{\phi_\infty(0)},
\]

(25)

Here we replaced \( D_t \) and \( \bar{N}_t \) with their \( t = \infty \) values. This is correct to leading order since the relative perturbations in these quantities are much smaller than that of \( \phi_t(0) \) which undergoes much larger changes (see section 3).

Now integrating eq. (25) using eqs. (14), (24) and (24) one finds that up to the time \( \tau_{\text{fill}} \) the dispersion has changed very little relative to its value just after the perturbation at \( t = 0 \):

\[
\frac{\Delta_t - \Delta_0}{\Delta_\infty} \approx \begin{cases} 
(C/3)(t/\tau_{\text{slow}})(t/t^*)^{1/2} & (t^* \ll t) \\
t/(2\tau_{\text{slow}}) & (t^* \ll t \ll \tau_{\text{fill}})
\end{cases}
\]

(26)

This is in stark contrast to the first moment which had already relaxed by the much shorter time \( \tau_{\text{fast}} \). The dispersion’s relaxation process does not properly get going until times of order \( \tau_{\text{slow}} \):

\[
\frac{\delta \Delta_t}{\Delta_\infty} \approx \begin{cases} 
\delta \Delta_0/\Delta_\infty + J \epsilon \theta^{-1}(t/\tau_{\text{slow}})^{1/2} & (\tau_{\text{fill}} \ll t \ll \tau_{\text{slow}}) \\
\alpha \epsilon (t/\tau_{\text{slow}})^{-3/2} e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}})
\end{cases}
\]

(27)

where \( \alpha = 8M/39 \). The relative perturbation in the dispersion remains of order \( \epsilon \) for \( t \ll \tau_{\text{slow}} \) and subsequently relaxes exponentially.

5 Response to \( T \)-jump; Negative Velocity Boost

In this section we study the case opposite to section 3, when \( \epsilon < 0 \) and the \( T \)-jump induces a higher equilibrium monomer concentration and a smaller \( \overline{N_\infty} \) (see eq. 9). Such a perturbation in the example of \( \alpha \)-methylstyrene would be produced by an increase in temperature as one may see in fig. 4. In this case the sign of the initial perturbed velocity (eq. 12) is negative (see fig. 7). Thus initially the MWD is not boosted towards larger molecular weights as in section 3, but is instead boosted in the opposite direction, towards smaller \( N \). Therefore, instead of depletion, an excess of small length chains and free initiators is produced, creating instead of a hole, a sharp peak in the MWD near \( N = 0 \) as shown in fig. 11.

Despite the differences between the two cases, many of the results of section 3 remain unchanged. In fact all equations of section 3 up to eq. 10 remain unchanged, the only difference being that \( \epsilon \) is negative. Thus eq. 11 now describes a MWD coherently shrinking and simultaneously broadening with diffuson coefficient \( D_\infty \). But since free initiators cannot depolymerize, excess polymer must build up near \( N = 0 \). Indeed, starting from eq. 10 it is shown in Appendix D that

\[
\frac{\phi_t(0)}{\phi_\infty(0)} \approx \begin{cases} 
1 + C' (t/t^*)^{1/2} & (t^* \ll t) \\
P' (t/t^*) & (t^* \ll t \ll \tau_{\text{fast}})
\end{cases}
\]

(28)
where \( C' = 4/\pi^{1/2} \) and \( F' = 4 \). Eq. (28) has a similar interpretation to eq. (17). For \( t < t^* \) diffusion is fast enough to smooth out the excess polymer accumulated by the negative velocity at the origin and thus \( \phi_0(0) \) remains close to its initial value (see fig. 11(a)). For \( t \approx t^* \) however the flow towards the origin is faster than what diffusion can smear out and a peak forms whose height increases with time, as shown in fig. 11(b). (Once again it is assumed that the perturbation is not so small that \( t^* \ll \tau_{\text{fast}} \); the opposite case is examined in section 5).

After the completion of the first stage at times of order \( \tau_{\text{fast}} \), similarly to section 3, the fast \( m_0, N_0 \) variables have essentially relaxed and start to respond quasi-statically to the slow diffusion-driven shape changes of the MWD. In fact we show in Appendix D that eqs. (14) and (15) still apply, but now with a different crossover timescale, \( \tau_{\text{gs}} = \tau_{\text{fast}} \ln N_\infty \). This difference arises because unlike the positive boost case \( \phi_0(0) \) does not become exponentially small and so needs less time to catch up with the \( v_t \) term in the velocity dynamics, eq. (6).

Similarly to the positive boost, eq. (19) still applies for \( t < \tau_{\text{fill}} \). By this time the accumulation at the origin is able to diffuse to distances of the same size as the region from which it was transferred from during the first stage. Hence \( \phi_0(0) \) becomes of order its initial value, and thereafter perturbation theory is valid. In Appendix D we show that

\[
\phi_t(0)/\phi_\infty(0) \approx \begin{cases} K'(\tau_{\text{fill}}/t)^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{fill}}) \\
1 + J'(\tau_{\text{fill}}/t)^{1/2} & (\tau_{\text{fill}} \ll t \ll \tau_{\text{slow}}) \\
1 + M' (t/\tau_{\text{slow}})^{-3/2} e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}}) \end{cases}
\]

for \( \tau_{\text{fill}} \ll t \ll \tau_{\text{fill}} \). (b) Beyond \( t^* \) diffusion is too slow to counteract coherent chain shrinkage and short chains accumulate at the origin. (c) Coherent shrinkage halts when mean chain length approaches \( N_\infty \).

where \( \phi_0(0) \) is defined by eq. (13). By this time the accumulation at the origin is able to diffuse to distances of the same size as the region from which it was transferred from during the first stage. Hence \( \phi_0(0) \) becomes of order its initial value, and thereafter perturbation theory is valid. In Appendix D we show that

\[
\phi_t(0)/\phi_\infty(0) \approx \begin{cases} K'(\tau_{\text{fill}}/t)^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{fill}}) \\
1 + J'(\tau_{\text{fill}}/t)^{1/2} & (\tau_{\text{fill}} \ll t \ll \tau_{\text{slow}}) \\
1 + M' (t/\tau_{\text{slow}})^{-3/2} e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}}) \end{cases}
\]

where \( K', J', \) and \( M' \) are positive constants of order unity. Note there is apparently no smooth cross-over at \( t = \tau_{\text{fast}} \) between the forms of eqs. (28) and (29). This is because there is in fact an extra episode at times of order \( \tau_{\text{fast}} \) during which the very thin peak spreads from width \( (D_\infty t^*)^{1/2} \) to a width \( (D_\infty \tau_{\text{fast}})^{1/2} \). Note also that the time behavior for \( t \gg \tau_{\text{fill}} \) has been derived using the linearized dynamics of Appendix C.

Finally, to obtain the dispersion dynamics we use eqs. (28) and (29) in eq. (25) to obtain

\[
\delta \Delta t/\Delta_\infty - \delta \Delta_0/\Delta_\infty \approx \begin{cases} -(C'/3)(t/\tau_{\text{slow}})(t/t^*)^{1/2} & (t \ll t^*) \\
-F'/4(t/\tau_{\text{slow}})(t/t^*) & (t^* \ll t \ll \tau_{\text{fast}}) \\
-K' e^\Delta t/(t/\tau_{\text{slow}})^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{fill}}) \\
-J' e^\Delta t/(t/\tau_{\text{slow}})^{1/2} & (\tau_{\text{fill}} \ll t \ll \tau_{\text{slow}}) \\
-\delta \Delta_0/\Delta_\infty - (8M'/39) \epsilon (\tau_{\text{slow}}/t)^{5/2} e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}}) \end{cases}
\]

which is very similar to eqs. (20) and (21) for the positive boost case. Again the dispersion relaxes on a timescale \( \tau_{\text{slow}} \), much longer then the relaxation time of \( N_t \).

6 Very Small \( T^* \)-jumps: \( \epsilon \) less than its critical value \( \epsilon_c \)

Hitherto we implicitly assumed sufficiently strong velocity boosts that the timescale \( t^* \) after which translational motion dominates diffusion and a hole or peak begins to form is shorter than the time for full development of the hole or peak, namely \( \tau_{\text{fast}} \). Now the ratio of these timescales is

\[
\frac{t^*}{\tau_{\text{fast}}} \approx \left( \frac{\epsilon_c}{\epsilon} \right)^2,
\]

\[
\epsilon_c \equiv \frac{\theta^1/2}{N_\infty^1/2},
\]

which defines a critical value of the perturbation parameter, \( \epsilon_c \). Clearly, the system’s response must be different for \( \epsilon \) values below this rather small threshold. We consider
such very small perturbations in this section. Although a full hole or peak does not have time to develop, we will find that the response is still strong and non-linear.

Since such weak perturbations do not involve the creation of a complete hole or a peak in the MWD, one expects that the timescales $t^*$ and $\tau_{\text{fill}}$ associated with their creation and destruction lose their physical meaning as cross-over timescales. This is shown in Appendix E where, using similar arguments to the ones of sections 3 and 5, it is proved that weak perturbations are identical to stronger perturbations except that the regime up to $t^*$ is truncated at $\tau_{\text{fast}}$ and the following regime (which for stronger perturbations lasted till $\tau_{\text{fill}}$) deleted. In Appendix E it is shown that for both positive and negative boosts, one has for the fast variables

$$\frac{\delta v_f}{v} \approx \begin{cases} \epsilon e^{-t/\tau_{\text{fast}}} & (t \ll \tau_{\text{fast}}) \\ -\phi_0(t) & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \end{cases}$$

Note that the timescale $\tau_{\text{qs}}$ does not appear since its magnitude lies between those of $t^*$ and $\tau_{\text{fill}}$.

The evolution of the MWD (see figs. 13 and 14) is similarly shown in Appendix E to lead to the following solution for $\phi_0(t)$ in the case of a positive initial velocity:

$$\frac{\phi_0(t)}{\phi_{\infty}(0)} \approx \begin{cases} 1 - C(t/t^*)^{1/2} & (t \ll \tau_{\text{fast}}) \\ 1 - Q(t/\tau_{\text{fill}})^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \end{cases} (v_0 > 0)$$

while for a negative initial velocity one has instead

$$\frac{\phi_0(t)}{\phi_{\infty}(0)} \approx \begin{cases} 1 + C^*(t/t^*)^{1/2} & (t \ll \tau_{\text{fast}}) \\ 1 + Q^*(t/\tau_{\text{fill}})^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \end{cases} (v_0 < 0)$$

where $Q, Q^*$ are positive constants. Finally, it is straightforward to show that the relaxation for for $t \gg \tau_{\text{slow}}$ is exponential as for the stronger perturbations, eq. (22).

The most important result of this section is that even though the $\epsilon < \epsilon_c$ case is “weak” as compared to sections 3 and 4, the system’s response remains large and nonlinear. One sees from eqs. (33) and (34) that at $\tau_{\text{fast}}$ when the deviation of $\phi_0(t)$ from equilibrium is largest, the relative deviation of $\phi_0(t)$ from equilibrium is much larger than $\epsilon$. Therefore even in the weak case a hole or peak does form in the MWD but of a smaller amplitude as compared to the stronger perturbation case (see figs. 13 and 14).

Now the dispersion dynamics may be similarly evaluated using eqs. (33) and (34) in eq. (24). One finds that $\Delta_t$ relaxes once again on a timescale $\tau_{\text{slow}}$. For the positive initial velocity case one finds

$$\delta \Delta_t/\Delta_{\infty} - \delta \Delta_0/\Delta_{\infty} \approx \begin{cases} (C/3)(t/\tau_{\text{slow}})^{1/2} & (t \ll \tau_{\text{fast}}) \\ Qe^{-1/(t/\tau_{\text{slow}})^{1/2}} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \\ -\delta \Delta_0/\Delta_{\infty} + (8M/39) \epsilon (\tau_{\text{slow}}/t)^{5/2}e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}}) \end{cases}$$

while for a negative initial boost

$$\delta \Delta_t/\Delta_{\infty} - \delta \Delta_0/\Delta_{\infty} \approx \begin{cases} -(C^*/3)(t/\tau_{\text{slow}})^{1/2} & (t \ll \tau_{\text{fast}}) \\ -Q^*e^{-1/(t/\tau_{\text{slow}})^{1/2}} & (\tau_{\text{fill}} \ll t \ll \tau_{\text{slow}}) \\ -\delta \Delta_0/\Delta_{\infty} - (8M^*/39) \epsilon (\tau_{\text{slow}}/t)^{5/2}e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}}) \end{cases}$$

7 General Perturbations

We have so far considered a specific type of perturbation, namely $T$-jumps. In this section we consider general perturbations. We will see that almost all of the phenomenology remains unchanged.

Let us start with another simple type of perturbation: addition of a very small amount of monomer to an equilibrated system. (This would require special care to avoid introducing impurities which in current experimental methods are destroyed by the initiators before polymerization.) Changing the total amount of monomer perturbs both independent system parameters, $r$ and $f$ (see eq. (7)), while a $T$-jump perturbed only $f$. Despite this, the results of the previous sections remain identical. The reason is that since in both cases the initial MWD is an exponential distribution whose mean is different from the new target equilibrium MWD, the only variable parameterizing the perturbation is $\delta N_0$, or equivalently $\delta m_0$. Thus one sees from eq. (14) that monomer addition is simply equivalent to a positive velocity boost induced by a $T$-jump.

Consider now the most general perturbation, i.e. one generating an initial MWD of arbitrary shape as shown in fig. 8(b). (This should be compared to the $T$-jump and $m$-jump which produce initial MWDs of exponential shape with a mean slightly displaced from equilibrium.) Such a general perturbation is small provided

$$\frac{|\delta \phi_0(N)|}{\phi_{\infty}(N)} \lesssim \epsilon$$

(37)
8 Discussion

The peculiarity of living polymers is that different moments of the MWD relax to equilibrium on different timescales. In the present work we have shown that the first moment, i.e. the mean length, $\bar{N}_t$, relaxes on a timescale $\tau_{fast}$. However the shape of the MWD measured by the second moment, or equivalently the dispersion, $\Delta_t$, relaxes after $\tau_{slow}$. Because the two timescales depend on different powers of $N_{\infty}$ their ratio may be extremely large:

$$\tau_{fast} \approx \frac{N_{\infty}}{v^* (1 - f)} , \quad \tau_{slow} \approx \frac{N_{\infty}^2}{4v^*} , \quad (39)$$

where $1/v^*$ is the natural time scale and $f \approx m_{\infty}/m_{tot}$ is approximately the fraction of non-polymerized monomer. Our only assumption has been that $f$ is not extremely close to unity, i.e. the system is not very close to the polymerization temperature.

In addition to the MWD, the other important observable is the free monomer concentration, $m_t$. We emphasize that since the number of chains is fixed by the number of initiators, thus $m_t$ is linearly coupled to $N_t$ by mass conservation for all times. Hence the relaxation of these two quantities is identical and $m_t$ relaxes after $\tau_{fast}$. Note that for certain other living polymers such as end-polymerizing wormlike surfactant micelles, this is not true.\textsuperscript{29, 50, 55} In these systems there is no separate initiator species and a pair of monomers may spontaneously unite to form a living chain. The dynamics are thus very different and $m_t$ and $N_t$ may relax on different timescales. Marques et al.\textsuperscript{29} studied this class of living polymer; after linearizing dynamical equations they found that after a small $T$-jump $m_t$ relaxes much more rapidly than $N_t$ which subsequently relaxes in time $\sim N_{\infty}^2$. In numerical simulations of this same class of system, Milchev et al.\textsuperscript{50} report a $1/t$ decay of mean chain length after a time $\sim N_{\infty}^2$. In the related system of spherical micelle aggregation\textsuperscript{56, 57, 58, 59}, the number of micelles can change and again the kinetics are very different to the present case.

A summary of our findings is shown in fig. 13 for the case emphasized here where a small $T$-jump induces a positive velocity boost to chain growth. The figure shows the very different relaxation times of first and second MWD moments. It also shows the interesting behavior of the number of free initiators, $\phi_t(0)$, which suffers enormous depletion at intermediate times despite ultimately recovering to a level very close to its initial value. We showed that whilst virtually all of the relaxation of the fast variables $N_t, m_t$ occurs on a timescale $\tau_{fast}$, they are actually not completely relaxed by this time. The final very late stages of their relaxation during which their values are fine-tuned (to relative order $1/N_{\infty}$) to the final equilibrium values,
occurs on a timescale $\tau_{\text{slow}}$. During this episode their values evolve quasi-statically, enslaved to $\phi_t(0)$ according to $\delta N/\bar{N}_\infty \approx -\delta m_t/m_\infty \approx \delta \phi_t(0)$. The novel behavior of $\phi_t(0)$, as well as its central role in late relaxation of the fast variables suggests this as an interesting quantity to measure experimentally. This might be achieved spectroscopically and would have the advantage of being a relatively uninvasive probe. We remark that for bifunctional initiators, e.g. those used in studies by the Greer group, the meaning of $\phi_t(0)$ is the concentration of “half-chains,” i.e. those having at least one chain end which is a bare initiator molecule.

We have demonstrated that the type of dynamical response depends on the magnitude and sign of the perturbation. For example, if the temperature change is reversed in sign, then the velocity boost also changes sign. Thus for $\alpha$-methylstyrene a negative $T$-jump produces the positive velocity boost phenomenology of fig. 15 whereas in this case, instead of short chains being annihilated, their number increases dramatically during the relaxation process. As far as perturbation magnitude is concerned, if the relative value $\epsilon$ is less than a critical value $\sim 1/\bar{N}_\infty^{1/2}$ then the response is milder but remains non-linear. For a positive boost, the hole in the MWD is no longer complete, but instead has a relative depth less than unity but still much bigger than $\epsilon$.

How do our predictions compare with experiment? In ref. 11 small $T$-jumps were imposed on $\alpha$-methylstyrene systems in the semi-dilute regime at concentrations high enough to be nearly entangled. Relaxation was monitored by measuring viscosity $\eta$ as a function of time. Now generally we expect viscosity to scale as a polymer-concentration-dependent power of mean chain length, $\eta \sim c_\phi \bar{N}^\gamma$, where the value of $\gamma$ is predicted by standard theories of polymer physics 17. For a general MWD, note the coefficient $c_\phi$ which depends on the shape of the MWD, i.e. it depends on the full function $[\phi(N)]$. (This is because $\eta$ depends not only on the first moment, but in general has a complex dependence on chain length distribution). Thus we predict an initial fast relaxation of $\eta$ lasting time $\tau_{\text{fast}} = \bar{N}/(\theta \epsilon^{- \gamma})$ (corresponding to the relaxation of $N$) followed by a much slower relaxation in $\tau_{\text{slow}}$ (this is the relaxation of the prefactor $c_\phi$). The fast relaxation time is independent of $T$-jump magnitude (i.e. independent of $\epsilon$). Now from eqs. 6 and 7 we can rewrite $\tau_{\text{fast}} = 1/(r k^+ m_\text{tot})$. Using 11 $r = 4.7 \times 10^{-4}$, $m_\text{tot} = 0.29 gm/cm^3$ and a measured value $k^+ \approx 0.2 M^{-1}sec^{-1}$ one estimates $\tau_{\text{fast}} \approx 1000$ secs. (Note that this work involved bifunctional initiators. In ref. 24, we incorrectly estimated $\tau_{\text{fast}}$ to be twice the value calculated here based on a wrong estimate of the number of living chains which was taken to be equal to the number of bifunctional initiators instead of twice this value.) Similarly, with 2 $f \approx 0.5$, $v^- = 0.1 sec^{-1}$ one finds $\tau_{\text{slow}} \approx 1$ month. Hence for these experiments (timescales much less than months) $\eta$ should relax in approximately 1000 secs. In the experiments, jumps $\delta T \approx 1^\circ C$ were imposed at various temperatures in the range $283^\circ K \leq T \leq 290^9 K$. Now the temperature dependence of $\tau_{\text{fast}} \sim 1/k^+$ is determined by $k^+$ which is reported 12 to vary by $\approx 10 \%$ over this temperature range. Thus we expect only a slight variation in the viscosity relaxation time at the different temperatures studied (despite the fact that $\bar{N}_\infty$ changes significantly). These predictions are very close to the experimental findings, where relaxation times at all temperatures were found to be about 2000 seconds, with very little variation from one temperature to another. This is in sharp contrast to the relative changes in $\eta$ itself, which varied by almost an order of magnitude.

We have emphasized small perturbations in this work. In fact, the response to a large perturbation is obtained, qualitatively speaking, by setting $\epsilon = 1$ in our results. This case was addressed by Miyake and Stockmayer 14 who considered an initial condition in which all initiators are free (i.e. $\bar{N}_0 = 0$). They were the first to identify the two timescales of the system, $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$, in the limit of very small depolymerization rates ($f \ll 1$). Their analytical results applied to the $t < \tau_{\text{fast}}$ stage where they found an initially uniformly translating and broadening MWD peak, reaching $\bar{N}_\infty$ after $\tau_{\text{fast}}$ as shown in fig. 4. Seen from the viewpoint of a general perturbation of magnitude $\epsilon$, in this case $\tau_{\text{fill}}$ and $\tau_{\text{slow}}$ coincide because $\epsilon = 1$. That is, the “hole” (in this case the entire region between 0 and $\bar{N}_\infty$) fills up on the same timescale in which the whole MWD relaxes. The linearized dynamics, which for a small perturbation applied for $t > \tau_{\text{fill}}$ due to $\delta \phi_t(0)/\phi_\infty(0)$ becoming small (see section 3.3) cannot be employed. Describing dynamics at times of order $\tau_{\text{slow}}$ in this case is thus a difficult nonlinear problem.

In recent experiments, Greer’s group 12,13 studied such large perturbations using $\alpha$-methylstyrene. After a rapid quench below the polymerization temperature, monomer concentration and MWD were analyzed after a time...
delay. The time dependent relaxation was probed by repeating the procedure for different time delays and samples. They found different relaxation times for the monomer concentration and the MWD width, as predicted by theory. However, $N_t$ and $m_t$ did not have the same relaxation, as mass conservation would seem to dictate. This may be due either to side-reactions during polymerization or living chain ionic association effects which have been studied theoretically. Dynamic light scattering measurements suggest that prior to polymerization the initiators self-assemble into long polymeric structures and it has been suggested that initiators may not all be equally available for polymerization following the $T$-quench. However, lifetimes of aggregate structures would need to be extremely long for these effects to interfere with polymerization dynamics since as we have seen the MWD relaxation times are very large.

In conclusion, our hope is that this work will motivate further experimental study of the dynamical sensitivity of living polymers to small perturbations. The drastic effect on the MWD in the small chain region, in particular the depletion or excess of free initiators, is a natural focus for experimental measurement. One can think of other time-dependent perturbations such as small amplitude thermal cycling which would probe interesting aspects of their ultrasensitive dynamics. Finally, the systems we have analyzed here are model starting points for the considerably more complex biological living polymers, actin filaments and microtubules, which are intimately involved in the locomotion and structural integrity of living cells. This work was supported by the Petroleum Research Fund, grant no. PRF-33944-AC7.

A Derivation of Equilibrium Values $m_\infty$, $\bar{N}_\infty$, $v_\infty$, $D_\infty$.

The equilibrium MWD can be calculated by setting the time derivative in eq. (40) to zero. Its solution is the Flory distribution, eq. (41), where

$$\bar{N}_\infty = -D_\infty/v_\infty .$$

Solving the system of eqs. (40) and (2) for $m_\infty$, $\bar{N}_\infty$ one has

$$m_\infty/m_{tot} = \frac{1}{2} \left( 1 + \frac{r}{2} - \frac{(1-f)^2 + r(1+3f)}{4} \right) \left( 1 - \frac{m_\infty}{m_{tot}} \right).$$

(41)

For $r \ll 1$ and assuming $(1-f)/r^{1/2} \gg 1$, by expanding eq. (41) in powers of $r$ and keeping only the first term of the expansion one recovers eq. (5). The values of $v_\infty$, $D_\infty$ in eq. (5) are obtained by substitution of $m_\infty$, $\bar{N}_\infty$ in eq. (4).

B Self-Consistency of Results of Subsections 3.1 and 3.2

B.1 Coherent Chain Growth

The solution for the $v_t$ dynamics, eq. (13), follows by solving eq. (9) after neglecting the $\phi_t(0)$ term on the rhs. For $t \ll \tau_{eq}$, this is a self-consistent solution since then the $\phi_t(0)$ term is negligible with respect to the remaining terms as can be seen using the solutions for $v_t, \phi_t(0)$ of eqs. (14), (17), and eq. (21).

Eq. (15) is derived by substituting $v_t$ from eq. (14) in eq. (15), replacing $D_t = D_\infty + \delta D_t$, and dropping the $\delta D_t$ term. The fact that this term can be neglected may be seen as follows. Even if $\delta D_t$ did not decrease but remained of order $\delta D_0$ throughout this regime this would lead to replacing $D_\infty$ by $D_\infty(1 + \epsilon)$ in all results obtained in section 3 (see eq. (14)). This upper bound on the effect of $\delta D_t$ can easily be seen to lead to higher order in $\epsilon$ terms (see eq. (17)) and the $\delta D_t$ term can therefore be neglected.

Now let us consider the propagator of the dynamics of eq. (15), which appears in eq. (16). For short times, $t \ll \tau_{fast}$, one may replace $v_t$ in eq. (15) by $v_0$. Eq. (16) then has constant coefficients and its propagator including the boundary condition may be calculated exactly

$$G_t^{\text{trans}}(N, N') = \frac{1}{(4\pi D_\infty t)^{1/2}} \times$$

$$\left\{ e^{-(N-N'-v_0 t)^2/(4D_\infty t)} + e^{-(N'+v_0 t)^2/(4D_\infty t)} \right\} $$

$$- \frac{v_0}{2D_\infty} e^{N_0 t/D_\infty} \text{erfc}\left( \frac{N + N' + v_0 t}{(4D_\infty t)^{1/2}} \right) \quad (t \ll \tau_{fast}) \quad (42)$$

Here $\text{erfc}(x) \equiv 1 - \text{erf}(x)$, where erf is the error function.

The solution for $\phi_t(0)$ is derived by substituting eq. (42) in eq. (16) and setting $N = 0$. One has

$$\frac{\phi_t(0)}{\phi_\infty(0)} \approx \text{erfc}(x) + 2x^2 \text{erf}(x) - 2e^{-1/2}xe^{-x^2},$$

$$x \equiv (t/t^*)^{1/2} \quad (t \ll \tau_{fast}) \quad (43)$$

Here we used the fact that since the values of $N'$ contributing to the integration are much smaller than $\bar{N}_\infty$, one may approximate $\phi_0(N')$ by $\phi_\infty(0)$ in the integrand of eq. (16) (with relative errors of order $1/\bar{N}_\infty$). Eq. (17) of the main text follows from eq. (43) by taking the two corresponding limits. Note that eq. (43) approximates $\phi_t(0)$ for all $t \ll \tau_{fast}$, including times of order $t^*$.

B.2 Hole Filling

Eq. (18) is a self-consistent solution of eq. (6) since for $t \gg \tau_{eq}$, assuming the validity of eqs. (15) and (17) one may verify that eq. (35) is satisfied with the term on the rhs being much smaller in magnitude than both terms on the rhs which balance one another.
Consider now the validity of eq. (14) for $t_\text{fast} \ll t \ll \tau_\text{fill}$. Substituting eq. (21) into eq. (18) one has explicit solutions for $m_t, N_t, v_t, D_t$. One thus sees that in the time regime of consideration the velocity term in eq. (5) is exponentially small and therefore can be deleted in eq. (18) with very small error.

The MWD dynamics are therefore described by eq. (19) whose propagator satisfying reflecting boundary conditions is

$$ G^\text{diff} \left( N, N' \right) = \frac{1}{(4\pi D_\infty t)^{1/2}} \times \left\{ 1 - \left( N-N' \right)^2 / (4D_\infty t) + e^{-\left( N+N' \right)^2 / (4D_\infty t)} \right\} \quad (44) $$

The solution of eq. (18) is thus

$$ \phi_t(N) \approx \int_0^\infty dN' \phi_{t\text{-cross}}(N') G^\text{diff}_{t\text{-cross}}(N, N') \approx \int_{\tau_\text{fill}/\theta}^\infty dN' \phi_0(N' - \epsilon N_\infty / \theta) G^\text{diff}(N, N') \quad (\tau_\text{fast} \ll t \ll \tau_\text{fill}) \quad (45) $$

where $t_{\text{cross}}$ satisfies $\tau_\text{fast} \ll t_{\text{cross}} \ll \tau_\text{gs}$, i.e. it belongs to the time regime described simultaneously by eqs. (18) and (19). In going from the first integral in eq. (45) to the second we used the fact that at $t_{\text{cross}}$ the MWD has approximately the shape of the initial MWD, boosted in the positive direction by $\epsilon N_\infty / \theta$. The effect of diffusion during the initial boost of the MWD may be shown to be small. Notice also that evolution in the last expression in eq. (18) starts at $t = 0$; for $t \gg t_{\text{cross}}$ we may to leading order replace $t - t_{\text{cross}}$ in $G^\text{diff}$ in eq. (45) by $t$.

Substituting eq. (44) in eq. (18) and setting $N = 0$ one obtains

$$ \frac{\delta \phi_t(0)}{\delta \phi_\infty(0)} = \text{erfc} \left[ \left( \frac{\tau_\text{fill}}{t} \right)^{1/2} \right], \quad (\tau_\text{fast} \ll t \ll \tau_\text{fill}) \quad (46) $$

Considering times much shorter than the crossover time $\tau_\text{fill}$, eq. (21) is recovered.

### C Linearized Dynamics, $t \gg \tau_\text{fill}$

Ultrasensitivity is such that the dynamics cannot be linearized until the later stages, $t \gg \tau_\text{fill}$. For these times we may linearize eq. (13) by dropping terms proportional to products of $\delta \phi_t, \delta v_t, \delta D_t$. One has

$$ \frac{\partial \delta \phi_t}{\partial t} \approx -v_\infty \frac{\partial \phi_0}{\partial N} + D_\infty \frac{\partial^2 \phi_0}{\partial N^2} + \mu_t, \quad \mu_t \equiv \frac{\delta v_t}{N_\infty} \cdot \left[ \phi_\infty(N) - \delta(N) \right] \quad (47) $$

with reflecting boundary conditions at the origin. In eq. (47) the $\delta D_t$ term was neglected since its magnitude is smaller by $1/N_\infty$ than the corresponding $\delta v_t$ term. The $\delta$-function in the source term in eq. (47) arises from linearizing the boundary condition in eq. (13). Notice that by definition, $\delta \phi_t(0)$ is normalized to zero and that the source term in eq. (47) preserves this normalization since its integral over all $N$ is zero.

Performing the corresponding linearization in eq. (4) one has

$$ \frac{d}{dt} \delta v_t \approx -\frac{1}{\tau_\text{fast}} \delta v_t - \frac{1}{\tau_\text{fast}} D_\infty \delta \phi_t(0) \quad . \quad (48) $$

Now since eq. (17) is of the same form as eq. (15), its propagator, $G^\text{linear}_{t \rightarrow t'}(N, N')$, is given by eq. (16) with $v_0$ replaced by $v_\infty$. Thus if $\delta \phi_{t_L}(N)$ is known at time $t_L$, then the solution of eq. (17) for subsequent times is

$$ \delta \phi_t(N) \approx \int_0^\infty dN' G^\text{linear}_{t \rightarrow t_L}(N, N') \delta \phi_{t_L}(N') + R_t(N) \quad, \quad (49) $$

where

$$ R_t(N) \equiv \int_0^\infty dN' \int_0^t dt' G^\text{linear}_{t \rightarrow t'}(N, N') \mu_{t'}(N') \approx - \int_{t_L}^t dt' D_\infty \delta \phi_t(0) \left[ \phi_\infty(N) - G^\text{linear}_{t \rightarrow t_L}(N, 0) \right] \quad . \quad (50) $$

Here the last expression for $R_t(N)$ is obtained by performing the $N'$ integration using the expression for $\mu_t$ from eq. (47) and the fact that $\phi_\infty(N)$ remains unchanged when evolved with $G^\text{linear}$. In eq. (50) we also used

$$ \delta v_t \approx -D_\infty \delta \phi_t(0) \quad (51) $$

which is valid throughout the linearized time regime as one may derive using eq. (18). The solution of eqs. (17) and (18) is thus found by setting $N = 0$ in eq. (18), solving for $\delta \phi_t(0)$, and then using the calculated expression in eqs. (49) and (51) to find $\delta \phi_{t_L}(N)$ and $\delta v_t$. Let us now perform this analysis for two time regimes.

(i) $\tau_\text{fill} \ll t \ll \tau_\text{slow}$. In this regime, we will see the source term can in effect be ignored. The top expression on the rhs of eq. (22) is a self-consistent solution of eq. (19) which is proved as follows. As one may see from eqs. (21) and (22) there exists a constant $\beta$ of order unity such that for $t > \beta \tau_\text{fill}$ the relative perturbation in $\phi_\infty(N)$ is much smaller than unity and eq. (17) applies. (More precisely, for any desired relative smallness there exists a different constant $\beta$.) Thus setting $t_L = \beta \tau_\text{fill}$ and $N = 0$ in eq. (49) and using the expression for $\delta \phi_t(0)$ from eq. (22) one finds that with appropriate choice of $J$, eq. (49) is satisfied with $R_t(0)$ being much smaller than the remaining two terms in eq. (49). The integral term in eq. (49) is calculated using the same expression as from eqs. (21), (22), and fig. 10. $\delta \phi_{t_L}(N)$ is of order $\epsilon \phi_\infty(N)$ for $N \ll \epsilon N_\infty$ and of order $\epsilon \phi_\infty(N)$ for larger $N$. We also used

$$ G^\text{linear}_{t \rightarrow t_L}(0, N') \rightarrow \begin{cases} \frac{1}{2} \left( \frac{D_\infty(t - t')} {D_\infty(t - t')} \right)^{1/2} & (N' \ll D_\infty(t - t')) \\ 0 & (N' \gg D_\infty(t - t')) \end{cases} \quad (t, t' \ll \tau_\text{slow}) $$

which may be derived from eq. (12).
(ii) \( t \gg \tau_{\text{slow}} \). Using eq. (52) one finds
\[
G_{t}^{\text{linear}}(0, N') \approx S_{\infty} + (S_{t} - S_{\infty}) \lambda(N') \quad (t \gg \tau_{\text{slow}}),
\]
where
\[
S_{t} \equiv G_{t}^{\text{linear}}(0, 0), \quad S_{\infty} = \phi_{\infty}(0) = 1/\bar{N}_{\infty},
\]
\[
\lambda(N') \equiv \left(1 - \frac{N'}{2N_{\infty}}\right) e^{N'/(2N_{\infty})}.
\]

Now setting \( t_{L} = \tau_{\text{slow}} \) in eq. (49) and using eqs. (50) and (53) one has
\[
\delta \phi_{t}(0) \approx (S_{t} - S_{\infty}) \int_{0}^{\infty} dN' \lambda(N') \delta \phi_{\tau_{\text{slow}}}(N') + \frac{1}{4S_{\infty}\tau_{\text{slow}}} \int_{0}^{\infty} dt' \left(S_{t-t'} - S_{\infty}\right) \delta \phi_{t'}(0)
\]
where we used the fact that \( \delta \phi_{\tau_{\text{slow}}}(N') \) is normalized to zero.

Now the self-consistency of the \( t > \tau_{\text{slow}} \) expression on the rhs of eq. (22) is proved by substituting eq. (22) in eq. (54). Since \( \delta \phi_{\tau_{\text{slow}}}(N') \) is of order \( \epsilon/\bar{N}_{\infty} \), the magnitude of the integral of \( \delta \phi_{\tau_{\text{slow}}}(N') \) in eq. (55) is of order \( \epsilon \). The last integral term in eq. (55) is evaluated using eq. (22) and
\[
S_{t} - S_{\infty} \approx \begin{cases} 
1/(D_{\infty}t)^{1/2} & (t \ll \tau_{\text{slow}}) \\
16S_{\infty} \pi^{-1/2} (\tau_{\text{slow}}/t)^{3/2} e^{-t/(16\tau_{\text{slow}})} & (t \gg \tau_{\text{slow}})
\end{cases}
\]
which may be proved using eqs. (51) and (52). One finds that for \( t \gg \tau_{\text{slow}} \) all terms in eq. (55) have the same time dependence and are of the same order of magnitude. Thus eq. (55) may be satisfied by appropriate choice of the numerical coefficient \( M \) in eq. (22).

D Self-Consistency of the Results of Section 5

D.1 Coherent Chain Shrinking

The validity of eq. (14) is verified using the same arguments as in the first paragraph of Appendix B but now using the expression for \( \phi_{t}(0) \) from eq. (28).

Setting \( N = 0 \) in eq. (14) one obtains eq. (15) with \( x \) now replaced by \(-x\). Considering times much greater and much less than \( t^{*} \) leads to eq. (28).

D.2 Peak Decay

The validity of eq. (18) is proved using exactly the same arguments as the ones in the first paragraph of the corresponding section of Appendix B, but now using the expression for \( \phi_{t}(0) \) from eq. (20). One finds that the crossover time \( \tau_{qs} \approx \tau_{\text{fast}} \ln(\bar{N}_{\infty}) \) is different from the respective crossover time found in Appendix B.

The solution of eq. (19) is now
\[
\phi_{t}(N) \approx \int_{0}^{\infty} dN' \phi_{0}(N' - \epsilon\bar{N}_{\infty}/\theta)G_{t}^{\text{diff}}(N, N') + G_{t}^{\text{diff}}(N, 0) \int_{0}^{\epsilon\bar{N}_{\infty}/\theta} dN' \phi_{0}(N') \quad (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}})
\]
Here the evolved MWD consists of two parts, corresponding to the two terms on the rhs (see fig. 11(c)). The first is the initial MWD, \( \phi_{0} \), shifted by \( \epsilon\bar{N}_{\infty}/\theta \) towards smaller \( N \). The second part is the excess peak accumulated by the negative boost at the origin and whose amount was the polymer initially lying between zero and \( \epsilon\bar{N}_{\infty}/\theta \). Here, as in section 3, the effects of diffusive broadening during \( t < \tau_{\text{fast}} \) have been neglected, and \( \tau_{\text{fast}} \) in eq. (57) has been replaced by zero.

Now substituting eq. (41) in eq. (57) and setting \( N = 0 \) one obtains eq. (20) similarly to the derivation of eq. (21) in Appendix B.

E Self-Consistency of the Results of Section 6

For times \( t \ll \tau_{\text{fast}} \), all results and analysis are identical to those for the strong perturbation (\( \epsilon > \epsilon_{c} \)) case in the regime \( t \ll t^{*} \). Eq. (12) can be shown to be a self-consistent solution using the same arguments as those of Appendices B and D to prove eqs. (14) and (18), respectively. For times longer than \( \tau_{\text{fast}} \) linearization of the dynamics can be performed and the results of Appendix C directly apply.

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Dynamics of Living Polymers

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Abstract. We study theoretically the dynamics of living polymers which can add and subtract monomer units at their live chain ends. The classic example is ionic living polymerization. In equilibrium, a delicate balance is maintained in which each initiated chain has a very small negative average growth rate (“velocity”) just sufficient to negate the effect of growth rate fluctuations. This leads to an exponential molecular weight distribution (MWD) with mean $\bar{N}$. After a small perturbation of relative amplitude $\epsilon$, e.g. a small temperature jump, this balance is destroyed: the velocity acquires a boost greatly exceeding its tiny equilibrium value. For $\epsilon > \epsilon_c \approx 1/\bar{N}^{1/2}$ the response has 3 stages: (1) Coherent chain growth or shrinkage, leaving a highly non-linear hole or peak in the MWD at small chain lengths. During this episode, lasting time $\tau_{\text{fast}} \sim \bar{N}$, the MWD’s first moment and monomer concentration $m$ relax very close to equilibrium. (2) Hole-filling (or peak decay) after $\tau_{\text{fill}} \sim \epsilon^2 \bar{N}^2$. The absence or surfeit of small chains is erased. (3) Global MWD shape relaxation after $\tau_{\text{slow}} \sim \bar{N}^2$. By this time second and higher MWD moments have relaxed. During episodes (2) and (3) the fast variables ($\bar{N}, m$) are enslaved to the slowly varying number of free initiators (chains of zero length). Thus fast variables are quasi-statically fine-tuned to equilibrium.

The outstanding feature of these dynamics is their ultrasensitivity: despite the perturbation’s linearity, the response is non-linear until the late episode (3). For very small perturbations, $\epsilon < \epsilon_c$, response remains non-linear but with a less dramatic peak or hole during episode (1). Our predictions are in agreement with viscosity measurements on the most widely studied system, $\alpha$-methylstyrene.

PACS. 82.35.-x Polymers; properties; reactions; polymerization. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian Motion. 87.15.Rn Biomolecules: structure and physical properties; Reactions and kinetics; polymerization.

1 Introduction

Living polymers are intriguing examples of soft matter and have major roles in technology and biology. The classical system of major importance for the synthesis of high-grade polymer materials and the subject of a long history of fundamental experimental and theoretical study, is living anionic polymerization [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. This class of polymerization is widely employed to manufacture polymers with nearly monodisperse MWDs and controlled architectures such as block and star copolymers [26]. A recent variant on this theme with immense potential technological impact is living free radical polymerization [27, 28]. Other examples include worm-like surfactant micelles [29, 30, 31, 32, 33, 34, 35, 36] and biological polymers such as actin and tubulin filaments [37, 38, 39, 40, 41, 42], whose special properties are exploited by living cells for motility and structural integrity.

As polymeric or polymer-like materials, the unique feature of these systems is that the chains are dynamic objects, with constantly fluctuating lengths. When subjected to an external perturbation, they are able to respond dynamically via polymerization and depolymerization reactions allowing a new thermodynamic equilibrium to be attained. These systems are “living” in the sense that a change in their environment leads to a new equilibrium molecular weight distribution (MWD). All of this should be compared to conventional inert polymer materials whose MWDs are frozen.

The subject of this paper is the dynamical response of living polymers. We study the class of living polymers which is exemplified by living ionic polymerization, having the following characteristics: (i) monomers add and subtract from chain ends and (ii) the total number of chains is fixed. In the biological world, actin and microtubule filaments satisfy condition (i), and the dynamics of both filaments and filament caps are frequently described by situation (ii) [43]. Wormlike micelles on the other hand in some cases grow from their ends only [29, 30] (condition (i)) but do not satisfy condition (ii): the number of micelles is not conserved. Interestingly, this makes their dynamical response very different (see discussion section).
Our presentation will focus on living ionic polymerization, though most of our results are completely general. In these systems, polymers grow reversibly from their ionic ends (see fig. 1). Due to their “living” nature, if fresh monomer is added polymers will grow until the extra monomer has been consumed; further addition of a different monomer species, say, will resume polymer growth. The main achievement of this technique is a distribution of chain lengths with very small Poisson fluctuations around the mean. This monodisperse MWD is not however a true equilibrium distribution. For sufficiently long times slow depolymerization reactions become important and lead to a true equilibrium MWD which is in fact extremely broad. For many applications, for example styrene, the timescale to reach equilibrium is extremely large and depolymerization-induced broadening effects are unimportant [44]. However, in some cases equilibration times are accessible, e.g. an example being methylstyrene whose equilibrium MWD as in (a) and with monomer concentration (grey background) such that polymerization and depolymerization rates balance, random polymerization and depolymerization reactions eventually broaden the distribution up to distances of the same order as the mean \( \bar{N} \), as shown in (b). Note the resulting MWD includes chains of “zero” length (free initiators).

The reason that chain length fluctuations in equilibrium are so large is that even when a state is reached where the monomer concentration reaches a steady state value such that polymer growth rates exactly balance depolymerization, through polymerization and depolymerization reactions monomers continue to be reshuffled among living chains. Thus even if one starts with an essentially monodisperse MWD as shown in fig. 2(a), random addition and subtraction of monomers from chain ends will result in a “diffusive” random walk motion of chain ends in \( N \)-space (where \( N \) is the number of monomer units added to initiator) with a certain characteristic “diffusivity” \( D \). Since there is no restoring force to this motion, chain ends will eventually diffuse to distances of the same order as the mean chain length, resulting in a broad distribution as shown in fig. 2(b). In a simple mean-field picture where monomer-monomer excluded volume interactions are neglected this leads to the Flory-Schultz equilibrium distribution [45, 46, 3]

\[
\phi_\infty(N) = \frac{1}{N_\infty} e^{-N/N_\infty},
\]

where \( N_\infty \) is the equilibrium mean length.

The thermodynamic properties of equilibrium living polymers have been studied in a large number of experimental and theoretical works. According to theory, going beyond mean field by accounting for excluded-volume interactions leads to power law modifications [18, 19, 20, 34] to eq. 1. Moreover, an analogy [14, 15, 16] between a living polymer system and the much studied Ising spin system in the formal limit of spin dimensionality \( n \) becoming zero (similar to the well-known analogy in the thermodynamic theory of semidilute polymer solutions [17, 18]) which can in fact be formulated equivalently to a living polymer system [39] showed that the polymerization phase transition near the polymerization temperature is second-order with a number of characteristic power-law exponents. The results of a large number of experiments by the group of Greer, measuring both the MWD itself [18] and other thermodynamic properties [21] are apparently consistent with the above theories, favoring somewhat the non mean-field approach.

The most essential feature of living polymers however, namely their ability to respond dynamically to external perturbations, remains largely unexplored. How does an equilibrium living polymer system respond to a small perturbation? A conceptually simple perturbation is the addition of a small amount of extra monomer (an “m-jump”). A similar perturbation, easier to perform in practice, is a “T-jump,” i.e. a small sudden change in temperature. Under such a perturbation, how rapidly and in what manner will the monomer concentration, MWD and mean chain length reach a new equilibrium? In this paper we address these questions theoretically. We will compare our predictions in section 8 with small \( T \)-jump viscosity relaxation experiments by Greer et al. [11]. This same group has also monitored monomer and MWD dynamics following much stronger perturbations, finite temperature quenches [12, 13] (see fig. 3).

Our main broad conclusion is that, counter-intuitively, the response to a very small perturbation is extremely strong; even though the initial and final MWDs (the latter attained after relaxation is complete) are very close to one another, the MWD at intermediate times is very strongly perturbed from equilibrium, i.e. its shape is very different from either the initial or final equilibrium shapes. In this

Fig. 1. (a) Schematic of initiation reaction in ionic polymerization. Empty (filled) circle represents initiator (monomer). (b) Polymerization and depolymerization reactions at the ionic chain end of a polymer chain of \( N \) units.

Fig. 2. Fluctuations of living polymer chain length in equilibrium are very large. For clarity, living chains are depicted as if extending from an imaginary substrate. Living ends are shown as filled circles. Even if one starts with a nearly monodisperse MWD as in (a) and with monomer concentration (grey background) such that polymerization and depolymerization rates balance, random polymerization and depolymerization reactions eventually broaden the distribution up to distances of the same order as the mean \( \bar{N} \), as shown in (b). Note the resulting MWD includes chains of “zero” length (free initiators).
This work is related to earlier theory of Miyake and Stockmayer [44] who, following a prior treatment by Brown and Szwarc [50], studied analytically and numerically the dynamics in the special case where initially all monomer is unpolymerized (see fig. 5). Their analytical results, applicable in the case of very small depolymerization rates, showed a 2-stage relaxation. During the first, lasting a time \( \sim N^{-2}_{\infty} \), living chains grow coherently from zero length up to the equilibrium value. In the second stage the shape of the sharply peaked MWD relaxes slowly toward the equilibrium exponential distribution. Although their perturbation analysis broke down during this stage, Miyake and Stockmayer estimated that its duration scales as \( N^{-2}_{\infty} \). Later theoretical studies addressed the second stage dynamics [51,52,53] of this special case.

A short announcement of the present work has already appeared [54]. The structure of the paper is as follows. In section 2 we establish the dynamical equations obeyed by living polymers which show the nonlinear coupling between the monomer population and the living chain MWD. For simplicity, we neglect excluded volume interactions and chain length dependent polymerization rates. Starting from the equations of section 2 we then analyze the response to a \( T \)-jump. This response depends on the sign of the velocity induced by the perturbation. The case of positive initial velocity is analyzed in sections 3 and 4, while the negative in section 5. The special case of very small \( T \)-jumps is analyzed in section 6. In section 7 we show that the results of the previous sections directly generalize to small perturbations of arbitrary form. Finally we conclude with a discussion of the results, and the experimental outlook.

2 Living Polymer Dynamics: Monomer-Polymer Coupling

An important aspect of living polymers dynamics is the coupling between the two distinct species present in the solution, free monomers and living chain MWD: on the one hand living chain growth rates depend on the concentration of free monomer and on the other hand, due to mass conservation, monomer concentration if a function of the living chain MWD. Stated differently, living chains grow according to a velocity field which is self-consistently updated depending on the response of the MWD. In this section we develop the equations obeyed by monomer and MWD. The dynamical response to perturbations is discussed in the following sections.

A crucial feature of the living polymer systems we study is that the number of living chains remains fixed. This is what arises in the experiments of Greer et al. [12,13], where this number is determined by the amount of initiator initially added in the solution. Denoting \( i_0 \) the concentration of living chains (i.e. chains which have been initiated), mass conservation implies that monomer concentration, \( m_t \), and MWD, \( \phi_t(N) \), \((t \text{ denotes time})\) obey

\[
m_t = m_{\text{tot}} - i_0 \bar{N}_t , \quad \bar{N}_t \equiv \int_0^\infty dN \ N \ \phi_t(N) , \quad (2)
\]
where $m_{\text{tot}}$ is the total monomer concentration (including polymerized monomers), and $N_i$ is mean chain length. Here $\phi_t$ is normalized to unity and $N = 0$ corresponds to free initiator. The coupling between monomer concentration and the MWD is manifest in eq. (2).

Now the dynamical equations obeyed by $\phi_t$ are

$$\begin{align*}
\frac{\partial \phi_t(N)}{\partial t} &= -\frac{\partial j_t(N)}{\partial N}, \\
\bar{\phi}(N) &\equiv v_t \phi_t(N) - D_t \frac{\partial \phi_t(N)}{\partial N} , \\
j_t(0) &= 0 ,
\end{align*}$$

where

$$\begin{align*}
v_t &\equiv k^+ m_t - v^- , \\
D_t &\equiv (k^+ m_t + v^-)/2 .
\end{align*}$$

Here $k^+$ is the propagation rate constant and $v^-$ is the depolymerization rate. The “diffusion” coefficient $D_t$, describes fluctuations in the rate of polymerization/depolymerization. Eq. (3) is identical to the diffusion dynamics of a particle in a linear potential with time-dependent slope $-v_t$ whose time-dependent diffusion coefficient is $D_t$ (see fig. 4). The novelty here is that due to the coupling between the MWD and monomer, both the slope and diffusivity are functionals of $\phi_t$ itself.

The reflecting boundary condition in eq. (8) at $N = 0$ represents the fact that when a living chain looses all of its monomers and becomes a free initiator molecule (i.e. reaches length $N = 0$) it cannot depolymerize further and must grow again. Now we restate eq. (3) as

$$\begin{align*}
\frac{\partial \phi_t(N)}{\partial t} &= -v_t \frac{\partial \phi_t(N)}{\partial N} + D_t \frac{\partial^2 \phi_t(N)}{\partial N^2} , \\
\phi_t(0)/\phi_t'(0) &= D_t/v_t ,
\end{align*}$$

where $\phi_t' \equiv \partial \phi_t/\partial N$.

Now it might at first seem that despite the coupling of eq. (2), the monomer subsystem would effectively uncouple from the MWD dynamics, since one might naively expect that the monomer dynamics do not depend on the shape of the polymer MWD but only on the number of living chains. This would imply simple first order kinetics for $m_t$ resulting in exponential relaxation of the monomer concentration, independent of the MWD dynamics. The coupling however arises from the existence of special chains in the MWD of zero length, i.e. free initiator molecules of which there are $\phi_t(0)$, which unlike all other chains cannot depolymerize. Indeed, the dynamics obeyed by $m_t$, or equivalently $v_t$, are

$$\begin{align*}
\frac{dv_t}{dt} &= -v_t \tau_{\text{fast}} - \frac{D_t \phi_t(0)}{\tau_{\text{fast}}} , \\
\tau_{\text{fast}} &\equiv \frac{f}{rv^-} \approx \frac{f N_{\infty}}{(1-f)v^-} .
\end{align*}$$

We see clearly that the only aspect of the living MWD which monomers see is $\phi_t(0)$. Eq. (6) is derived by calculating $dN_i/dt$ by multiplying eq. (3) by $N_i$, integrating over all $N_i$, using the reflecting boundary condition, and then using eq. (2). The relationship between $\tau_{\text{fast}}$ and $N_{\infty}$ follows from eq. (8) below. Here we have introduced the two basic independent dimensionless parameters of the system:

$$\begin{align*}
f &\equiv \frac{v^-}{k^+ m_{\text{tot}}} , \\
r &\equiv \frac{\phi_t(0)}{m_{\text{tot}}} .
\end{align*}$$

The physical meaning of $f$ is the following: if the system were a pure solution of unpolymerized monomer (plus solvent and initiator) $f$ would be the ratio of backward to forward polymerization velocities. The value of $f$ is temperature dependent, being unity at the polymerization temperature and smaller or larger than unity in the polymer and non-polymer phase, respectively. The parameter $r$, namely the ratio of living chain to total monomer concentration, is independent of temperature and is always much smaller than unity. Its smallness is related to the mean degree of polymerization being much larger than unity in equilibrium (see eq. (8) below).

Now setting the time derivative in eq. (5) to zero and using eq. (2) it is shown in Appendix A that in equilibrium the Flory-Schultz distribution of eq. (11) is recovered and one has to leading order in $r$:

$$\begin{align*}
N_{\infty} &\approx \frac{1-f}{r} , \\
m_{\text{tot}} &\approx f , \\
v_{\infty} &\approx -\frac{v^-}{N_{\infty}} , \\
D_{\infty} &\approx v^- .
\end{align*}$$

Fig. 4. There are three stages in the relaxation of living polymers to equilibrium. During the first, living polymers grow coherently as in (a). The translation stops when they have consumed enough monomer such that monomer concentration drops to a value for which polymerization and depolymerization balance (shown in (b)). During the second stage, (c), through “diffusive” random polymerization and depolymerization reactions, the MWD slowly fills the depletion of chains of short lengths. The third and final stage entails global shape relaxation of the MWD on a diffusion timescale corresponding to $N_{\infty}$. 

where \( r \ll 1 \) and subscript \( \infty \) denotes the \( t \to \infty \) equilibrium value for the corresponding variable. We assumed \( (1 - f)/r^{1/2} \gg 1 \), i.e. that the temperature is not extremely close to the polymerization temperature.

An important feature in eq. (8) is that in equilibrium the velocity, i.e. the slope of the “potential” term in eq. (5), settles down to a very small negative value. Were there no diffusion, living chains subject to a negative velocity effect on the velocity which, depending on the direction of the jump becomes either positive (dashed line) or negative (dotted line).

The value of \( \epsilon \) is related to the magnitude of the \( T \)-jump. For example in the case of \( \alpha \)-methylstyrene, assuming that the system is initially below the polymerization temperature \( T_p \) in the region of fig. 7 between 260\(^\circ\)K and 280\(^\circ\)K, one has using eq. (9)

\[
\epsilon \approx -\frac{\delta T}{50^\circ K} \quad (\alpha\text{-methylstyrene}) .
\]

Thus for \( \alpha \)-methylstyrene a temperature increase, \( \delta T > 0 \), results in a negative \( \delta m_0 \), i.e. a reduced initial monomer concentration relative to the destination equilibrium value.

Now the \( t = 0 \) relative perturbation of the MWD is

\[
\frac{\delta \phi_0(N)}{\phi_\infty(N)} \approx \frac{\partial \phi_\infty(N)}{\partial N_\infty} \frac{\delta N_\infty}{\phi_\infty(N)} = \frac{\epsilon}{\theta} \left( 1 - \frac{N}{N_\infty} \right) , \quad \theta \equiv \frac{1 - f}{f} .
\] (11)

This is of order \( \epsilon \) and smaller than unity for all \( N \) (apart from the unimportant values \( N \gg N_\infty \) where the MWD is exponentially small) as shown in fig. 8a).

Because velocity, monomer concentration and mean chain length are all linearly related (see eqs. (2), (5) and (6)) changes in these quantities are simply related as

\[
\frac{\delta m_t}{m_\infty} \approx -\theta \frac{\delta N_t}{N_\infty} \approx \frac{\theta \delta D_t}{D_\infty} \approx \frac{\delta v_t}{v} .
\] (12)

These relations are true for all times. They allow us to follow the dynamics of velocity alone. Once \( v_t \) is known, \( N_t, m_t, D_t \) are determined.

From eqs. (12) and (9) the initial relative changes in \( v, D \) are:

\[
\frac{\delta v_0}{v_\infty} \approx -\epsilon \frac{N_\infty}{v} , \quad \frac{\delta D_0}{D_\infty} \approx \frac{\epsilon}{2} .
\] (13)

The important point is that since \( N_\infty \gg 1 \), the relative change in \( v \) is much larger than \( \epsilon \); the velocity is highly perturbed, as shown in fig. 4. Depending on the sign of \( \epsilon \), the velocity may remain negative as in equilibrium, or it

\[ \]

Fig. 5. Schematic of the MWD dynamics as analyzed by Miyake and Stockmayer [44] and their theoretical predictions regarding the timescales involved. (a) Initially (\( t = 0 \)) all initiators are unpolymerized. (b) For \( t \ll \tau_{fast} \) chains grow coherently with a narrow MWD until its peak reaches the equilibrium mean length \( N_\infty \) at times of order \( \tau_{fast} \). (c) During a third stage lasting up to \( \tau_{slow} \), which was beyond their theoretical analysis, the MWD spreads to the equilibrium MWD.

Fig. 6. Living polymer dynamics are equivalent to diffusion in a potential with slope \(-v_t \). In equilibrium the slope reaches a very small value of order \( 1/N_\infty \) (solid line) resulting in a broad MWD. Under a small \( T \)-jump the slope is strongly perturbed and depending on the direction of the jump becomes either positive (dashed line) or negative (dotted line).

3 Response to \( T \)-jump; Positive Velocity Boost

Perhaps the simplest way to perturb an equilibrium living polymer system is by a small temperature change (\( T \)-jump). Taking as an example \( \alpha \)-methylstyrene, the data of fig. 4 show equilibrium fraction of polymerized monomer as a function of temperature; evidently, changes in \( T \) lead to different values of the equilibrium monomer concentration \( m_\infty \) and therefore of \( N_\infty \) as well. In this section we consider relaxation dynamics after an equilibrated system is subjected at \( t = 0 \) to a small temperature change \( \delta T \) such that the system will eventually reach new equilibrium values \( m_\infty, N_\infty \). That is, we follow the dynamics of the transition from an old equilibrium towards a slightly different new equilibrium state.

The magnitude of the perturbation is measured by the small parameter

\[
\epsilon \equiv \frac{\delta m_0}{m_\infty} ,
\] (9)

where we define \( \delta m_t = m_t - m_\infty \) and similarly for other quantities. All equilibrium values refer to the destination (\( t = \infty \)) equilibrium values. Thus \( \delta m_0 \) is the initial (\( t = 0 \)) deviation from the final equilibrium.
Fig. 7. Fraction of polymerized monomer in equilibrium as a function of temperature for living α-methylstyrene in tetrahydrofuran solvent, initiated by sodium napthalene. Data from ref. [8]. Ratio of mole fraction of total monomer, $m_{\text{t, tot}}$, to initiator is 0.0044. Mole fraction of total monomer is 0.1538. The polymerization temperature $T_p$ is near 295°K.

may change sign. Since the relative perturbation in $D$ is by contrast small, we see that the delicate velocity-diffusion balance which sustained equilibrium is now destroyed.

We will show below that relaxation to equilibrium now occurs in three stages. During the first, dominated by translational motion, the MWD is boosted far from its equilibrium shape. The next stage involves diffusive restoration of the region of the MWD which suffered maximum distortion during the first stage. The third and final episode entails a very slow diffusion-dominated recovery of the equilibrium shape. For the remainder of this section we treat the case of a positive initial velocity boost, where chains initially grow ($\delta T < 0$ for α-methylstyrene). Negative velocity boosts, where chains initially shrink, are considered in section 5.

3.1 Coherent Chain Growth: Hole Development

During the first stage of the relaxation process, velocity dominates over diffusion since $v$ has been so strongly perturbed. Chains thus grow coherently, consuming the excess monomer in a timescale $\tau_{\text{fast}}$ by which time translation will have halted and a highly non-linear hole will have developed in the MWD (see fig. 9). Here $\tau_{\text{fast}}$, defined in eq. (13) and using eq. (8)), is the time for the MWD to translate distance $\delta N_0$ and reach the destination mean, i.e. $\tau_{\text{fast}} \approx \delta N_0/\delta v_0$ (see eqs. (13) and Appendix B).

To see all of this more quantitatively, consider the velocity dynamics eq. (6). Initially, the velocity term on the rhs is much larger in magnitude than the diffusion term. We show in Appendix B that this remains true up until a time $\tau_{\text{res}}$, defined below. It follows that for these times $v_t$ relaxes exponentially. The same is true of $m_{\text{t, N}}$ and $D_t$ which we recall are linearly coupled to $v_t$ (see eq. (12)). Thus

$$\delta v_t \approx \epsilon v^* e^{-t/\tau_{\text{fast}}} - v_{\infty} \quad (t \ll \tau_{\text{res}})$$

Note that for $t \gg \tau_{\text{fast}}$ there are no free initiators (at much longer times these are restored, see below). Thus for these intermediate times all chains are identical as far as on and off monomer kinetics are concerned, and the net rate of monomer-polymer mass exchange can only vanish if $v_t$ vanishes. For this reason $v_t$ decays to zero, though much later it will recover its small negative equilibrium value. The $\phi_t$ dynamics, eq. (6), thus simplify to

$$\frac{\partial \phi_t}{\partial t} \approx -\epsilon v^* e^{-t/\tau_{\text{fast}}} \frac{\partial \phi_t}{\partial N} + D_\infty \frac{\partial^2 \phi_t}{\partial N^2} \quad (t \ll \tau_{\text{res}})$$

where the diffusion coefficient may be approximated by $D_\infty$ since the contribution of $\delta D_t$ is negligible (see Appendix B). This linear equation, plus the time-dependent boundary condition of eq. (6), has solution

$$\phi_t(N) \approx \int_0^\infty dN' G_t^{\text{tran}}(N, N') \phi_0(N') \quad (t \ll \tau_{\text{res}})$$

which describes a translating and simultaneously broadening MWD, as shown in fig. 9. Here $G_t^{\text{tran}}(N, N')$ is the propagator of eq. (16) whose properties are calculated in Appendix B.

An important quantity in what follows is $\phi_t(0)$, i.e. the concentration of free initiators. Using eq. (16) we show in Appendix B that

$$\phi_t(0)/\phi_\infty(0) \approx$$

$$\left\{ \begin{array}{ll} 1 - C (t/t^*)^{1/2} & (t \ll t^*) \\ F (t^*/t)^{1/2} e^{-t^*/t} & (t^* \ll t \ll \tau_{\text{fast}}) \end{array} \right.$$  

$$t^* = \frac{4D_\infty}{v_0^*}$$

where $C = 4/\pi^{1/2}$ and $F = \pi^{-1/2}$. Eq. (17) has a clear physical meaning: as the MWD translates, the position of its peak at $N = 0$ after time $t$ has shifted to chain lengths of order $v_0 t$. Were diffusion absent, this would have created a depletion region in the MWD at small chain
lengths. However diffusion smooths out inhomogeneities on distances of size $\left( D_\infty t \right)^{1/2}$. Hence for times shorter than the crossover time $t^*$ for which $v_0 t^* \approx \left( D_\infty t^* \right)^{1/2}$, diffusion has enough time to fill the translationally induced hole and the relative deviation from equilibrium is small. For times longer than $t^*$ however, the MWD translates a distance away from the origin much larger than what diffusion could have homogenized, a hole develops in the MWD, and the concentration of zero length chains becomes exponentially small.

In eq. (17) we assumed that the perturbation is large enough such that $t^* \ll \tau_{\text{fast}}$. The special case of extremely small perturbations where this is no longer true is discussed separately in section 5.

### 3.2 Diffusive Length Relaxation: Hole Filling

For times $t \gg \tau_{\text{fast}}$ the fast variables monomer and mean chain length have relaxed very close to their equilibrium values. We have seen that velocity becomes exponentially small. Meanwhile (see below) the number of free initiators $\phi_t(0)$ is gradually recovering. At a certain moment, therefore, the 2 terms on rhs of eq. (6) become equal to one another and we show in Appendix B that for all later times the velocity time derivative is much smaller. Hence the velocity dynamics are now fundamentally changed. The new regime is one of quasi-static evolution, enslaved to the dynamics of $\phi_t(0)$:

$$
\delta v_t \approx -v^{-1} \delta \phi_t(0) \quad (t \gg \tau_{qs}) .
$$

Physically, this reflects the fact that the the only aspect of the MWD shape seen by monomers is the amount of special non-depolymerizing zero-length chains. We see that as the MWD slowly rearranges itself, so the fast variables $v_t, m_t$ and $N_t$ variables respond quasi-statically.

Notice that the quasi-static regime does not onset after $\tau_{\text{fast}}$ but rather after $\tau_{qs}$. The reason is that during the initial boost the term $D_t \phi_t(0)$ in eq. (6) decays exponentially on a timescale $t^*$; its magnitude therefore at $\tau_{\text{fast}}$ is much smaller than $v_t$ which decays on a timescale $\tau_{\text{fast}}$ (see eqs. 14 and 17). There is thus a cross-over period before the quasi-static balance between the two terms is established.

Now let us examine the MWD dynamics. Since $v_t$ becomes exponentially small after the MWD stops translating, we have

$$
\frac{\partial \phi_t}{\partial t} \approx D_\infty \frac{\partial^2 \phi_t}{\partial N^2} \quad (\tau_{\text{fast}} \ll t \ll \tau_{\text{fill}}) \quad (19)
$$

with reflecting boundary conditions at the origin. Here once again the contribution of $\delta D_t$ is negligible (see eqs. 12, 13, and 21) and the corresponding term has been neglected in eq. (19). Here

$$
\tau_{\text{fill}} \equiv \epsilon^2 \theta^{-2} \tau_{\text{slow}} \quad , \quad \tau_{\text{slow}} \equiv \frac{N_0^2}{4D_\infty} . \quad (20)
$$

The timescale $\tau_{\text{slow}}$ is the longest relaxation time of the system, the time for the slow global shape characteristics of the MWD to relax. It equals the diffusion time for the MWD width $N_\infty$. Meanwhile $\tau_{\text{fill}}$ is the diffusion time for the hole width, $\epsilon N_\infty / \theta$. It is shown in Appendix B that eq. (19) has solution

$$
\frac{\phi_t(0)}{\phi_\infty(0)} \approx H \left( \frac{t}{\tau_{\text{fill}}} \right)^{1/2} e^{-\tau_{\text{fill}}/t} \quad (\tau_{\text{fast}} \ll t \ll \tau_{\text{fill}}) \quad (21)
$$

where $H = \pi^{-1/2}$. Thus for times shorter than $\tau_{\text{fill}}$ the concentration of zero length chains remains exponentially small while for longer times the hole fills (see fig. 11) and $\phi_t(0)$ recovers its equilibrium value.

### 3.3 Linearized Dynamics at Long Times

For times beyond $\tau_{\text{fill}}$ the hole-filling is complete and the MWD’s non-linear feature has disappeared. Thus, finally, a truly linear regime onsets: relative deviations of all variables from equilibrium are less than unity and perturbation theory can now be applied. This is done in Appendix...
δφ(t) = \frac{\varepsilon}{\tau} \phi(0) \left( 1 + \frac{t}{\tau_{\text{slow}}} \right)^{-1/2} e^{-t/(16\tau_{\text{slow}})}

(27)

where \( \alpha = 8M/39 \). The relative perturbation in the dispersion remains of order \( \varepsilon \) for \( t \ll \tau_{\text{slow}} \) and subsequently relaxes exponentially.

5 Response to \( T \)-jump; Negative Velocity Boost

In this section we study the case opposite to section 3, when \( \varepsilon < 0 \) and the \( T \)-jump induces a higher equilibrium monomer concentration and a smaller \( \bar{N}_\infty \) (see eq. (13)). Such a perturbation in the example of \( \alpha \)-methylstyrene would be produced by an increase in temperature as one may see in Fig. 14. In this case the sign of the initial perturbed velocity (eq. (13)) is negative (see fig. 16). Thus initially the MWD is not boosted towards larger molecular weights as in section 3, but is instead boosted in the opposite direction, towards smaller \( N \). Therefore, instead of depletion, an excess of small length chains and free initiators is produced, creating instead of a hole, a sharp peak in the MWD near \( N = 0 \) as shown in fig. 14.

Despite the differences between the two cases, many of the results of section 3 remain unchanged. In fact all equations of section 3 up to eq. (10) remain unchanged, the only difference being that \( \varepsilon \) is negative. Thus eq. (10) now describes a MWD coherently shrinking and simultaneously broadening with diffusion coefficient \( D_{\infty} \). But since free initiators cannot depolymerize, excess polymer must build up near \( N = 0 \). Indeed, starting from eq. (10) it is shown in Appendix D that

\[ \frac{\phi(t)}{\phi(0)} \approx \begin{cases} 1 + C(t/t^*)^{1/2} & (t \ll t^*) \\ \frac{1}{2} t/\tau_{\text{slow}} & (t^* \ll t \ll \tau_{\text{fill}}) \\ \frac{1}{2} t/\tau_{\text{slow}} & (t > \tau_{\text{fill}}) \end{cases} \]

(28)
where \( C' = 4/\tau^1 \) and \( F' = 4 \). Eq. (28) has a similar interpretation to eq. (17). For \( t < t^* \) diffusion is fast enough to smooth out the excess polymer accumulated by the negative velocity at the origin and thus \( \phi_t(0) \) remains close to its initial value (see fig. 11(a)). For \( t \gg t^* \) however the flow towards the origin is faster than what diffusion can smear out and a peak forms whose height increases with time, as shown in fig. 11(b). (Once again it is assumed that the perturbation is not so small that \( t^* < \tau_{fast} \); the opposite case is examined in section 5).

After the completion of the first stage at times of order \( \tau_{fast} \), similarly to section 3, the fast \( m_t, N_t \) variables have essentially relaxed and start to respond quasi-statically to the slow diffusion-driven shape changes of the MWD. In fact we show in Appendix D that eqs. (14) and (18) still apply, but now with a different crossover timescale, \( \tau_{eq} = \tau_{fast} \ln N_{\infty} \). This difference arises because unlike the positive boost case \( \phi_t(0) \) does not become exponentially small and so needs less time to catch up with the \( v_t \) term in the velocity dynamics, eq. (6).

Similarly to the positive boost, eq. (19) still applies for \( t < \tau_{fill} \). By this time the accumulation at the origin is able to diffuse to distances of the same size as the region from which it was transferred from during the first stage. Hence \( \phi_t(0) \) becomes of order its initial value, and thereafter perturbation theory is valid. In Appendix D we show that

\[
\phi_t(0)/\phi_{\infty}(0) \approx \begin{cases} 
K'(t/\tau_{fill})^{1/2} & (\tau_{fast} < t < \tau_{fill}) \\
1 + J'(t/\tau_{fill})^{1/2} & (\tau_{fill} < t < \tau_{slow}) \\
1 + M' \epsilon (t/\tau_{slow})^{-3/2} e^{-t/(16\tau_{slow})} & (t \gg \tau_{slow}) 
\end{cases}
\]

which is very similar to eqs. (18) and (19) for the positive boost case. Again the dispersion relaxes on a timescale \( \tau_{slow} \), much longer then the relaxation time of \( N_t \).

### 6 Very Small \( T \)-jumps: \( \epsilon < \text{less than its critical value} \) \( \epsilon_c \)

Hitherto we implicitly assumed sufficiently strong velocity boosts that the timescale \( t^* \) after which translational motion dominates diffusion and a hole or peak begins to form is shorter than the time for full development of the hole or peak, namely \( \tau_{fast} \). Now the ratio of these timescales is

\[
\frac{t^*}{\tau_{fast}} \approx \left( \frac{\epsilon_c}{\epsilon} \right)^2, \quad \epsilon_c \equiv \frac{\theta^{1/2}}{N_{\infty}^{1/2}}, \quad (31)
\]

which defines a critical value of the perturbation parameter, \( \epsilon_c \). Clearly, the system’s response must be different for \( \epsilon \) values below this rather small threshold. We consider...
such very small perturbations in this section. Although a full hole or peak does not have time to develop, we will find that the response is still strong and non-linear.

Since such weak perturbations do not involve the creation of a complete hole or a peak in the MWD, one expects that the timescales \( t^* \) and \( \tau_{\text{fill}} \) associated with their creation and destruction lose their physical meaning as cross-over timescales. This is shown in Appendix E where, using similar arguments to the ones of sections 3 and 5, it is proved that weak perturbations are identical to stronger perturbations except that the regime up to \( t^* \) is truncated at \( \tau_{\text{fast}} \) and the following regime (which for stronger perturbations lasted till \( \tau_{\text{fill}} \)) deleted. In Appendix E it is shown that for both positive and negative boosts, one has for the fast variables

\[
\frac{\delta v}{v} \approx \begin{cases} 
\epsilon e^{-t/\tau_{\text{fast}}} & (t \ll \tau_{\text{fast}}) \\
-\delta_\phi(0) & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \end{cases} \tag{32}
\]

Note that the timescale \( \tau_{\phi} \) does not appear since its magnitude lies between those of \( t^* \) and \( \tau_{\text{fill}} \).

The evolution of the MWD (see figs. 13–14) is similarly shown in Appendix E to lead to the following solution for \( \phi_0(0) \) in the case of a positive initial velocity:

\[
\frac{\phi_0(t)}{\phi_0(0)} \approx \begin{cases} 
1 - C(t/t^*)^{1/2} & (t \ll \tau_{\text{fast}}) \\
1 - Q(t/\tau_{\text{fill}})^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \end{cases} \tag{33}
\]

while for a negative initial velocity one has instead

\[
\frac{\phi_0(t)}{\phi_0(0)} \approx \begin{cases} 
1 + C'(t/t^*)^{1/2} & (t \ll \tau_{\text{fast}}) \\
1 + Q'(t/\tau_{\text{fill}})^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \end{cases} \tag{34}
\]

where \( Q, Q' \) are positive constants. Finally, it is straightforward to show that the relaxation for for \( t \gg \tau_{\text{slow}} \) is exponential as for the stronger perturbations, eq. (22).

The most important result of this section is that even though the \( \epsilon < \epsilon_c \) case is “weak” as compared to sections 3 and 4, the system’s response remains large and nonlinear. One sees from eqs. (33) and (34) that at \( \tau_{\text{fast}} \) when the deviation of \( \phi_0(0) \) from equilibrium is largest, the relative deviation of \( \phi_0(0) \) from equilibrium is much larger than \( \epsilon \). Therefore even in the weak case a hole or peak does form in the MWD but of a smaller amplitude as compared to the stronger perturbation case (see figs. 13–14).

Now the dispersion dynamics may be similarly evaluated using eqs. (33) and (34) in eq. (25). One finds that \( \Delta_0 \) relaxes once again on a timescale \( \tau_{\text{slow}} \). For the positive initial velocity case one finds

\[
\delta \Delta_0/\Delta_\infty - \delta \phi_0/\Delta_\infty \approx \begin{cases} 
(C/3)(t/\tau_{\text{slow}})/(t/t^*)^{1/2} & (t \ll \tau_{\text{fast}}) \\
Qe^{-1}(t/\tau_{\text{slow}})^{1/2} & (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}}) \end{cases} \tag{35}
\]

while for a negative initial boost

\[
\delta \Delta_0/\Delta_\infty - \delta \phi_0/\Delta_\infty \approx \begin{cases} 
-(C'/3)(t/\tau_{\text{slow}})/(t/t^*)^{1/2} & (t \ll \tau_{\text{fast}}) \\
Q'e^{-1}(t/\tau_{\text{slow}})^{1/2} & (\tau_{\text{fill}} \ll t \ll \tau_{\text{slow}}) \end{cases} \tag{36}
\]

7 General Perturbations

We have so far considered a specific type of perturbation, namely \( T \)-jumps. In this section we consider general perturbations. We will see that almost all of the phenomenology remains unchanged.

Let us start with another simple type of perturbation: addition of a very small amount of monomer to an equilibrated system. (This would require special care to avoid introducing impurities which in current experimental methods are destroyed by the initiators before polymerization.) Changing the total amount of monomer perturbs both independent system parameters, \( r \) and \( f \) (see eq. (7)), while a \( T \)-jump perturbed only \( f \). Despite this, the results of the previous sections remain identical. The reason is that since in both cases the initial MWD is an exponential distribution whose mean is different from the new target equilibrium MWD, the only variable parameterizing the perturbation is \( \delta \bar{N}_0 \), or equivalently \( \delta m_0 \). Thus one sees from eq. (9) that monomer addition is simply equivalent to a positive velocity boost induced by a \( T \)-jump.

Consider now the most general perturbation, i.e. one generating an initial MWD of arbitrary shape as shown in fig. 8 (b). (This should be compared to the \( T \)-jump and \( m \)-jump which produce initial MWDs of exponential shape with a mean slightly displaced from equilibrium.) Such a general perturbation is small provided

\[
\frac{|\delta \phi_0(N)|}{\phi_\infty(N)} \lesssim \epsilon \tag{37}
\]
The peculiarity of living polymers is that different moments of the MWD relax to equilibrium on different timescales. In the present work we have shown that the first moment, i.e. the mean length, $\bar{N}$, relaxes on a timescale $\tau_{fast}$. However the shape of the MWD measured by the second moment, or equivalently the dispersion, $\Delta$, relaxes after $\tau_{slow}$. Because the two timescales depend on different
occurs on a timescale $\tau_{\text{slow}}$. During this episode their values evolve quasi-statically, enslaved to $\phi_f(0)$ according to $\delta N_\theta/N_\infty \approx -\delta m_l/m_\infty \approx \delta \phi_f(0)$. The novel behavior of $\phi_f(0)$, as well as its central role in late relaxation of the fast variables suggests this as an interesting quantity to measure experimentally. This might be achieved spectroscopically and would have the advantage of being a relatively uninvasive probe. We remark that for bifunctional initiators, e.g. those used in studies by the Greer group, the meaning of $\phi_f(0)$ is the concentration of “half-chains,” i.e. those having at least one chain end which is a bare initiator molecule.

We have demonstrated that the type of dynamical response depends on the magnitude and sign of the perturbation. For example, if the temperature change is reversed in sign, then the velocity boost also changes sign. Thus for $\alpha$-methylstyrene a negative $T$-jump produces the positive velocity boost phenomenology of fig. 15 whereas in this case, instead of short chains being annihilated, their number increases dramatically during the relaxation process. As far as perturbation magnitude is concerned, if the relative value $\epsilon$ is less than a critical value $\sim 1/N_\infty^{1/2}$ then the response is milder but remains non-linear. For a positive boost, the hole in the MWD is no longer complete, but instead has a relative depth less than unity but still much bigger than $\epsilon$.

How do our predictions compare with experiment? In ref. 11 small $T$-jumps were imposed on $\alpha$-methylstyrene systems in the semi-dilute regime at concentrations high enough to be nearly entangled. Relaxation was monitored by measuring viscosity $\eta$ as a function of time. Now generally we expect viscosity to scale as a polymer-concentration-dependent power of mean chain length, $\eta \approx c_\phi N^\gamma$, where the value of $\gamma$ is predicted by standard theories of polymer physics [60,17]. For a general MWD, note the coefficient $c_\phi$, which depends on the shape of the MWD, i.e. it depends on the full function $[\phi(N)]$. (This is because $\eta$ depends not only on the first moment, but in general has a complex dependence on chain length distribution). Thus we predict an initial fast relaxation of $\eta$ lasting time $\tau_{\text{fast}} = N/(\theta \phi^{-})$ (corresponding to the relaxation of $N$) followed by a much slower relaxation in $\tau_{\text{slow}}$ (this is the relaxation of the prefactor $c_\phi$). The fast relaxation time is independent of $T$-jump magnitude (i.e. independent of $\epsilon$). Now from eqs. 6 and 7 we can rewrite $\tau_{\text{fast}} = 1/(k^+ m_\text{tot})$. Using 11 $r = 4.7 \times 10^{-4}$, $m_\text{tot} = 0.29 \text{gm/cm}^3$ and a measured value $12 k^+ \approx 0.2M^{-1}\text{sec}^{-1}$ one estimates $\tau_{\text{fast}} \approx 1000$ secs. (Note that this work involved bifunctional initiators. In ref. 54 we incorrectly estimated $\tau_{\text{fast}}$ to be twice the value calculated here based on a wrong estimate of the number of living chains which was taken to be equal to the number of bifunctional initiators instead of twice this value.) Similarly, with $2 f \approx 0.5$, $\nu^* = 0.1\text{sec}^{-1}$ one finds $\tau_{\text{slow}} \approx 1$ month. Hence for these experiments (timescales much less than months) $\eta$ should relax in approximately 1000 secs. In the experiments, jumps $\delta T \approx 1$ $^\circ$C were imposed at various temperatures in the range $283K \leq T \leq 290K$. Now the temperature dependence of $\tau_{\text{fast}} \sim 1/k^+$ is determined by $k^+$ which is reported 12 to vary by $\approx 10\%$ over this temperature range. Thus we expect only a slight variation in the viscosity relaxation time at the different temperatures studied (despite the fact that $N_\infty$ changes significantly). These predictions are very close to the experimental findings, where relaxation times at all temperatures were found to be about 2000 seconds, with very little variation from one temperature to another. This is in sharp contrast to the relative changes in $\eta$ itself, which varied by almost an order of magnitude.

We have emphasized small perturbations in this work. In fact, the response to a large perturbation is obtained, qualitatively speaking, by setting $\epsilon = 1$ in our results. This case was addressed by Miyake and Stockmayer 14 who considered an initial condition in which all initiators are free (i.e. $N_0 = 0$). They were the first to identify the two timescales of the system, $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$, in the limit of very small depolymerization rates ($f \ll 1$). Their analytical results applied to the $t < \tau_{\text{fast}}$ stage where they found an initially uniformly translating and broadening MWD peak, reaching $N_\infty$ after $\tau_{\text{fast}}$ as shown in fig. 4. Seen from the viewpoint of a general perturbation of magnitude $\epsilon$, in this case $\tau_{\text{fill}}$ and $\tau_{\text{slow}}$ coincide because $\epsilon = 1$. That is, the “hole” (in this case the entire region between 0 and $N_\infty$) fills up on the same timescale in which the whole MWD relaxes. The linearized dynamics, which for a small perturbation applied for $t > \tau_{\text{fill}}$ due to $\delta \phi_f(0)/\phi_{\text{tot}}(0)$ becoming small (see section 3.3) cannot be employed. Describing dynamics at times of order $\tau_{\text{slow}}$ in this case is thus a difficult nonlinear problem 51,52,53.

In recent experiments, Greer’s group 12,13 studied such large perturbations using $\alpha$-methylstyrene. After a rapid quench below the polymerization temperature, monomer concentration and MWD were analyzed after a time
delay. The time dependent relaxation was probed by repeating the procedure for different time delays and samples. They found different relaxation times for the monomer concentration and the MWD width, as predicted by theory \[44\]. However, \(N_t\) and \(m_t\) did not have the same relaxation, as mass conservation would seem to dictate. This may be due either to side-reactions during polymerization or living chain ionic association effects \[61, 62, 63\] which have been studied theoretically \[25\]. Dynamic light scattering measurements \[64\] suggest that prior to polymerization the initiators self-assemble into long polymeric structures and it has been suggested \[13\] that initiators may not all be equally available for polymerization following the \(T\)-quench. However, lifetimes of aggregate structures would need to be extremely long for these effects to interfere with polymerization dynamics since as we have seen the MWD relaxation times are very large.

In conclusion, our hope is that this work will motivate further experimental study of the dynamical sensitivity of living polymers to small perturbations. The drastic effect on the MWD in the small chain region, in particular the depletion or excess of free initiators, is a natural focus for experimental measurement. One can think of other time-dependent perturbations such as small amplitude thermal cycling which would probe interesting aspects of their ultrasensitive dynamics. Finally, the systems we have analyzed here are model starting points for the considerably more complex biological living polymers, actin filaments and microtubules, which are intimately involved in the locomotion and structural integrity of living cells \[39, 40, 41\].

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### A Derivation of Equilibrium Values \(m_\infty, \bar{N}_\infty, v_\infty, D_\infty\).

The equilibrium MWD can be calculated by setting the time derivative in eq. \[19\] to zero. Its solution is the Flory distribution, eq. \[11\], where

\[
\bar{N}_\infty = -D_\infty/v_\infty .
\]

Solving the system of eqs. \[10\] and \[2\] for \(m_\infty, \bar{N}_\infty\), one has

\[
\frac{m_\infty}{m_{\text{tot}}} = \frac{1}{2} \left\{ \frac{1}{2} \left[ 1 + f + \frac{r}{2} - \left( (1 - f)^2 + r(1 + 3f) + \frac{r^2}{4} \right) \right]^{1/2} \right\}
\]

\[
\bar{N}_\infty = \frac{1}{r} \left( \frac{1 - m_\infty}{m_{\text{tot}}} \right) .
\]

For \(r \ll 1\) and assuming \((1 - f)/r^{1/2} \gg 1\), by expanding eq. \[11\] in powers of \(r\) and keeping only the first term of the expansion one recovers eq. \[3\]. The values of \(v_\infty, D_\infty\) in eq. \[5\] are obtained by substitution of \(m_\infty, \bar{N}_\infty\) in eq. \[4\].

### B Self-Consistency of Results of Subsections 3.1 and 3.2

#### B.1 Coherent Chain Growth

The solution for the \(v_t\) dynamics, eq. \[14\], follows by solving eq. \[6\] after neglecting the \(\phi_t(0)\) term on the rhs. For \(t < \tau_{qs}\), this is a self-consistent solution since then the \(\phi_t(0)\) term is negligible with respect to the remaining terms as can be seen using the solutions for \(v_t, \phi_t(0)\) of eqs. \[14\], \[17\], and eq. \[21\].

Eq. \[15\] is derived by substituting \(v_t\) from eq. \[14\] in eq. \[16\], replacing \(D_t = D_\infty + \delta D_t\), and dropping the \(\delta D_t\) term. The fact that this term can be neglected may be seen as follows. Even if \(\delta D_0\) did not have the same

\[
G_t^{\text{trans}}(N, N') = \frac{1}{(4\pi D_\infty t)^{1/2}} \times \left\{ e^{-(N-N' - v_0 t)^2/(4D_\infty t)} + e^{-(N'-N + v_0 t)^2/(4D_\infty t)} \right\} - \frac{v_0}{2D_\infty} e^{N/v_0} \text{erfc} \left( \frac{N + N' + v_0 t}{(4D_\infty t)^{1/2}} \right) \quad (t < \tau_{fast}) \]

Here \(\text{erfc}(x) \equiv 1 - \text{erf}(x)\), where \(\text{erf}\) is the error function.

The solution for \(\phi_t(0)\) is derived by substituting eq. \[16\] in eq. \[15\] and setting \(N = 0\). One has

\[
\frac{\phi_t(0)}{\phi_\infty(0)} \approx \text{erfc}(x) + 2x^2 \text{erfc}(x) - 2\pi^{-1/2} x e^{-x^2}, \quad x \equiv (t/t^*)^{1/2} \quad (t < \tau_{fast})
\]

Here we used the fact that since the values of \(N'\) contributing to the integration are much smaller than \(\bar{N}_\infty\), one may approximate \(\phi_0(N')\) by \(\phi_\infty(0)\) in the integrand of eq. \[16\] (with relative errors of order \(1/\bar{N}_\infty\)). Eq. \[17\] of the main text follows from eq. \[15\] by taking the two corresponding limits. Note that eq. \[18\] approximates \(\phi_t(0)\) for all \(t < \tau_{fast}\), including times of order \(t^*\).

#### B.2 Hole Filling

Eq. \[16\] is a self-consistent solution of eq. \[6\] since for \(t > \tau_{qs}\), assuming the validity of eqs. \[15\] and \[17\] one may verify that eq. \[6\] is satisfied with the term on the lhs being much smaller in magnitude than both terms on the rhs which balance one another.
Consider now the validity of eq. (44) for \( \tau_{\text{fast}} \ll \tau_{\text{fill}} \). Substituting into eq. ([14]) one has explicit solutions for \( m_t, N_t, v_t, D_t \). One thus sees that in the time regime of consideration the velocity term in eq. (5) is exponentially small and therefore can be deleted in eq. (14) with very small error.

The MWD dynamics are therefore described by eq. (14) whose propagator satisfying reflecting boundary conditions is

\[
G^\text{diff}(N, N') = \frac{1}{(4\pi D_\infty t)^{1/2}} \times \left\{ e^{-(N-N')^2/(4D_\infty t)} + e^{-(N+N')^2/(4D_\infty t)} \right\} \quad (44)
\]

The solution of eq. (14) is thus

\[
\phi_t(N) \approx \int_0^\infty dN' \phi_{t-\tau_{\text{cross}}}(N')G^\text{diff}_{t-\tau_{\text{cross}}}(N, N')
\]

\[
\approx \int_{\tau_{\text{fast}}/\theta}^\infty dN' \phi_0(N' - \epsilon N_\infty / \theta)G^\text{diff}(N, N') \quad (\tau_{\text{fast}} \ll t \ll \tau_{\text{fill}}) \quad (45)
\]

where \( \tau_{\text{cross}} \) satisfies \( \tau_{\text{fast}} \ll \tau_{\text{cross}} \ll \tau_{\text{fill}} \), i.e. it belongs to the time regime described simultaneously by eqs. (44) and (19). In going from the first integral in eq. (45) to the second we used the fact that at \( \tau_{\text{cross}} \) the MWD has approximately the shape of the initial MWD, boosted in the positive direction by \( \epsilon N_\infty / \theta \). The effect of diffusion during the initial boost of the MWD may be shown to be small. Notice also that evolution that took place in the last expression in eq. (45) starts at \( t = 0 \); for \( t \gg \tau_{\text{cross}} \) we may leading order replace \( t - \tau_{\text{cross}} \) in \( G^\text{diff} \) in eq. (45) by \( t \).

Substituting eq. (44) in eq. (14) and setting \( N = 0 \) one obtains

\[
\frac{\phi_t(0)}{\phi_{\infty}(0)} \approx \text{erfc} \left[ \left( \frac{\tau_{\text{fill}}}{t} \right)^{1/2} \right], \quad (\tau_{\text{fast}} \ll t \ll \tau_{\text{fill}}) \quad (46)
\]

Considering times much shorter than the crossover time \( \tau_{\text{fill}} \), eq. (21) is recovered.

\section*{C Linearized Dynamics, \( t \gg \tau_{\text{fill}} \)}

Ultrasensitivity is such that the dynamics cannot be linearized until the later stages, \( t \gg \tau_{\text{fill}} \). For these times we may linearize eq. (14) by dropping terms proportional to products of \( \delta \phi_t, \delta v_t, \delta D_t \). One has

\[
\frac{\partial \delta \phi_t}{\partial t} \approx -v_\infty \frac{\partial \phi_t}{\partial N} + D_\infty \frac{\partial^2 \phi_t}{\partial N^2} + \mu_t, \\
\mu_t \equiv \frac{\delta \phi_t}{N_\infty} \left[ \phi_\infty(N) - \delta(N) \right], \quad (47)
\]

with reflecting boundary conditions at the origin. In eq. (47) the \( \delta D_t \) term was neglected since its magnitude is smaller by \( 1/N_\infty \) than the corresponding \( \delta v_t \) term. The \( \delta \)-function in the source term in eq. (47) arises from linearizing the boundary condition in eq. (14). Notice that by definition, \( \delta \phi_t(0) \) is normalized to zero and that the source term in eq. (47) preserves this normalization since its integral over all \( N \) is zero.

Performing the corresponding linearization in eq. (4) one has

\[
\frac{d}{dt} \delta v_t \approx -\frac{1}{\tau_{\text{fast}}} \delta v_t - \frac{1}{\tau_{\text{fast}}} D_\infty \delta \phi_t(0) \quad (48)
\]

Now since eq. (47) is of the same form as eq. (14), its propagator, \( G^\text{linear}_t(N, N') \), is given by eq. (22) with \( v_0 \) replaced by \( v_\infty \). Thus if \( \delta \phi_{t_L}(N) \) is known at time \( t_L \), then the solution of eq. (47) for subsequent times is

\[
\delta \phi_t(N) \approx \int_0^\infty dN' G^\text{linear}_{t-t_L}(N, N') \delta \phi_{t_L}(N') + R_t(N), \quad (49)
\]

where

\[
R_t(N) \equiv \int_0^\infty dN' \int_0^t dt' G^\text{linear}_{t-t'}(N, N') \mu_t(N') \approx - \int_{t_L}^t dt' D_\infty \delta \phi_t(0) \frac{\phi_\infty(N) - G^\text{linear}_{t-t'}(N, 0)}{N_\infty} \quad (50)
\]

Here the last expression for \( R_t(N) \) is obtained by performing the \( N' \) integration using the expression for \( \mu_t \) from eq. (47) and the fact that \( \phi_\infty(N) \) remains unchanged when evolved with \( G^\text{linear} \). In eq. (50) we also used

\[
\delta v_t \approx -D_\infty \delta \phi_t(0) \quad (51)
\]

which is valid throughout the linearized time regime as one may derive using eq. (14). The solution of eqs. (14) and (18) is thus found by setting \( N = 0 \) in eq. (14), solving for \( \delta \phi_t(0) \), and then using the calculated expression in eqs. (49) and (51) to find \( \delta \phi_t(N) \) and \( \delta v_t \). Let us now perform this analysis for two time regimes:

(i) \( \tau_{\text{fill}} \ll t \ll \tau_{\text{slow}} \). In this regime, we will see the source term can in effect be ignored. The top expression on the rhs of eq. (22) is a self-consistent solution of eq. (19) which is proved as follows. As one may see from eqs. (21) and (22) there exists a constant \( \beta \) of order unity such that for \( t > \beta \tau_{\text{fill}} \) the relative perturbation in \( \phi_t(N) \) is much smaller than unity and eq. (47) applies. (More precisely, for any desired relative smallness there exists a different constant \( \beta \).) Thus setting \( t_L = \beta \tau_{\text{fill}} \) and \( N = 0 \) in eq. (49) and using the expression for \( \delta \phi_t(0) \) from eq. (22) one finds that with appropriate choice of \( J \), eq. (49) is satisfied with \( R_t(0) \) being much smaller than the remaining two terms in eq. (49). The integral term in eq. (49) is calculated using the fact that as seen from eqs. (21), (22), and fig. 10 \( \delta \phi_{t_L}(N) \) is of order \( \epsilon \phi_\infty(N) \) for \( N \ll \epsilon N_\infty / \theta \) and of order \( \epsilon \phi_\infty(N) \) for larger \( N \). We also used

\[
G^\text{linear}_{t-t'}(N, N') \rightarrow \begin{cases} 1/\left[D_\infty(t-t')^{1/2} \right] & (N' \ll D_\infty(t-t')) \\
0 & (N' \gg D_\infty(t-t')) \end{cases} \\
(t, t' \ll \tau_{\text{slow}}) \quad (52)
\]

which may be derived from eq. (12).
(ii) \( t > \tau_{\text{slow}} \). Using eq. \( \ref{eq:55} \), one finds

\[
G_t^{\text{linear}}(0,N') \approx S_\infty + (S_t - S_\infty) \lambda(N') \quad (t > \tau_{\text{slow}}),
\]

where

\[
S_t \equiv G_t^{\text{linear}}(0,0), \quad S_\infty = \phi_\infty(0) = 1/\tilde{N}_\infty,
\]

\[
\lambda(N') \equiv \left(1 - \frac{N'}{2\tilde{N}_\infty}\right) e^{N'/2\tilde{N}_\infty}.
\]

Now setting \( t_L = \tau_{\text{slow}} \) in eq. \( \ref{eq:49} \) and using eqs. \( \ref{eq:50} \) and \( \ref{eq:53} \) one has

\[
\delta\phi(0) \approx (S_t - S_\infty) \int_0^\infty dN' \lambda(N') \delta\phi_{\text{slow}}(N') + \frac{1}{4S_\infty \tau_{\text{slow}}} \int_{\tau_{\text{slow}}}^t dt' (S_{t-t'} - S_\infty) \delta\phi(t') (0)
\]

where we used the fact that \( \delta\phi_{\text{slow}}(N') \) is normalized to zero.

Now the self-consistency of the \( t > \tau_{\text{slow}} \) expression on the rhs of eq. \( \ref{eq:22} \) is proved by substituting eq. \( \ref{eq:22} \) in eq. \( \ref{eq:53} \). Since \( \delta\phi_{\text{slow}}(N') \) is of order \( \epsilon/\tilde{N}_\infty \), the magnitude of the integral of \( \delta\phi_{\text{slow}}(N') \) in eq. \( \ref{eq:53} \) is of order \( \epsilon \). The last integral term in eq. \( \ref{eq:53} \) is evaluated using eq. \( \ref{eq:22} \) and

\[
S_t - S_\infty \approx \begin{cases} 
\left(1/(D_{\infty}t)^{1/2} \right) \\
16S_\infty^{-1/2} \tau_{\text{slow}}/t \right)^{3/2} e^{-t/(16\tau_{\text{slow}})} \\ 
\right) \quad (t < \tau_{\text{slow}}) \\
(\tau_{\text{slow}}/t)^{3/2} e^{-t/(16\tau_{\text{slow}})} \\ 
(\tau_{\text{slow}}/t)^{1/2} \quad (t > \tau_{\text{slow}})
\end{cases}
\]

which may be proved using eqs. \( \ref{eq:51} \) and \( \ref{eq:52} \). One finds that for \( t > \tau_{\text{slow}} \) all terms in eq. \( \ref{eq:53} \) have the same time dependence and are of the same order of magnitude. Thus eq. \( \ref{eq:53} \) may be satisfied by appropriate choice of the numerical coefficient \( M \) in eq. \( \ref{eq:22} \).

### D Self-Consistency of the Results of Section 5

#### D.1 Coherent Chain Shrinking

The validity of eq. \( \ref{eq:15} \) is verified using the same arguments as in the first paragraph of Appendix B but now using the expression for \( \phi_\infty(0) \) from eq. \( \ref{eq:28} \).

Setting \( N = 0 \) in eq. \( \ref{eq:15} \) one obtains eq. \( \ref{eq:16} \) with \( x \) now replaced by \(-x\). Considering times much greater and much less than \( t^* \) leads to eq. \( \ref{eq:28} \).

#### D.2 Peak Decay

The validity of eq. \( \ref{eq:18} \) is proved using exactly the same arguments as the ones in the first paragraph of the corresponding section of Appendix B, but now using the expression for \( \phi_\infty(0) \) from eq. \( \ref{eq:29} \). One finds that the crossover time \( \tau_{qs} \approx \tau_{\text{fast}} \ln(\tilde{N}_\infty) \) is different from the respective crossover time found in Appendix B.

The solution of eq. \( \ref{eq:19} \) is now

\[
\phi'(N) \approx \int_0^\infty dN' \phi_\infty(N' - \epsilon\tilde{N}_\infty/\theta)G_t^{\text{diff}}(N,N') +
\]

\[
G_t^{\text{diff}}(N,0) \int_0^{\epsilon\tilde{N}_\infty/\theta} dN' \phi_\infty(N') \quad (\tau_{\text{fast}} \ll t \ll \tau_{\text{slow}})
\]

Here the evolved MWD consists of two parts, corresponding to the two terms on the rhs (see fig. \( \ref{fig:11} \(c\)). The first is the initial MWD, \( \phi_0 \), shifted by \( \epsilon\tilde{N}_\infty/\theta \) towards smaller \( N \). The second part is the excess peak accumulated by the negative boost at the origin and whose amount was the polymer initially lying between zero and \( \epsilon\tilde{N}_\infty/\theta \). Here, as in section 3, the effects of diffusive broadening during \( t < \tau_{\text{fast}} \) have been neglected, and \( \tau_{\text{fast}} \) in eq. \( \ref{eq:57} \) has been replaced by zero.

Now substituting eq. \( \ref{eq:41} \) in eq. \( \ref{eq:57} \) and setting \( N = 0 \) one obtains eq. \( \ref{eq:20} \) similarly to the derivation of eq. \( \ref{eq:21} \) in Appendix B.

### E Self-Consistency of the Results of Section 6

For times \( t \ll \tau_{\text{fast}} \), all results and analysis are identical to those for the strong perturbation (\( \epsilon > \epsilon_c \)) case in the regime \( t \ll t^* \). Eq. \( \ref{eq:32} \) can be shown to be a self-consistent solution using the same arguments as those of Appendices B and D to prove eqs. \( \ref{eq:14} \) and \( \ref{eq:15} \), respectively. For times longer than \( \tau_{\text{fast}} \) linearization of the dynamics can be performed and the results of Appendix C directly apply.

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