Local Strain Relaxation Dictates Polymer Melt Viscosity

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Abstract

A remarkable manifestation of slow dynamics in dense polymeric systems is that their viscosity scales with their molecular weight as a power-law, with the “viscosity exponent” $m_\eta$, experimentally measured to be $3.4 \pm 0.2$. Following De Gennes’ work in 1971, current understanding of this slow dynamics is based upon an effective single-polymer theory that pictures every polymer in such systems moving within a rigid static network formed by the surrounding ones, yielding $m_\eta = 3$. We change this picture fundamentally. We report collective many-polymer effects, wherein for each polymer, the surrounding ones generate a dynamical restoring force, characterized by a power-law in time: $\sim t^{-\alpha}$. With $\alpha = 0.78 \pm 0.03$. Further analysis provides $m_\eta = 2 + 1/\alpha = 3.28 \pm 0.05$. This new understanding reconciles four decades of theory-experiment discrepancy for $m_\eta$, a major unsolved problem in polymer physics.

1 Introduction

Mobility of individual polymers in systems containing long polymers decreases with increasing density, causing their dynamics to slow down. A notable manifestation of slow dynamics in dense polymeric systems is that their viscosity scales with their molecular weight as a power-law, with the viscosity exponent $m_\eta$; experimentally measured to be $3.4 \pm 0.2$ over an impressive range of molecular weights and chemical compositions [1]. The fact that the slow dynamics of dense polymeric systems can actually be attributed to the polymers becoming entangled, especially if the polymers are long, was the seminal idea of De Gennes [2]. He argued that entanglement restricts the polymers to only sliding past each other — thereby reducing their mobility — as it is impossible for them to slide across each other. This physics holds for all dense polymeric systems — for polymer melts as well as for entangled solutions — hence for the sake of brevity, throughout this paper (including the title), we collectively refer to dense polymeric systems as “melt” or “polymer melt”, unless specifically mentioned otherwise. Indeed, the dynamics of a melt can be quantitatively understood by taking the entanglement idea to analyze the motion of a single polymer in a melt [2,3] — referred to as the tagged polymer henceforth. In the absence of external forces, the tagged polymer is set in motion by thermal fluctuations. Of these, the transversal ones, i.e., the fluctuations perpendicular to the contour of the tagged polymer, do not contribute to its bulk transport, since the bulk transport of the polymer in the transversal directions is blocked by the presence of the surrounding ones. Longitudinal fluctuations, on the other hand, cause transport of stored lengths within its contour, as well as enable its ends to extend or retract its contour. The ends of the tagged polymer, thus, explore new areas via longitudinal fluctuations, eventually resulting in bulk transport over long distances.

As long as the tagged polymer has not moved over a distance comparable to its size, it remembers part of its shape. Both the viscosity and the relaxation time, i.e., the typical time $\tau$ required by the tagged polymer to rid itself of this memory, scale with its length $N$ as
Since polymers in a melt obey random-walk statistics, the diffusion coefficient $D$ obeys the relation $D \tau \sim N$, implying that $D \sim N^{1-m_\eta}$. In other words, $m_\eta$ can be obtained from the proper characterization of $D$.

To approach the scaling of $m_\eta$ by obtaining that of $D$, De Gennes considered the melt to only represent a rigid static network for the tagged polymer, and formulated his celebrated reptation theory, which provides the basis for all dynamical aspects of dense polymeric systems to this day. Such a formulation reduces the many-polymer problem of a melt to an effective single (tagged) polymer problem, wherein the movements of the tagged polymer is restricted only to reptation, i.e., “stored length” transportation due to (longitudinal) fluctuations along its contour. By using the longest available time-scale $\tau_r \sim N^2$ for the stored length distribution within the tagged polymer’s contour in this reduced problem, he obtained $D \sim N^{-2}$, i.e., $m_\eta = 3 \ [2, 3, 5]$. Over the years, many explanations have been put forward to resolve the (reptation) theory-experiment discrepancy for $m_\eta$ — i.e., 3 vs. 3.4. Two of the prominent ones are contour length fluctuations (CLF) [6–8] and constraint release (CR) [9] — both effective single-polymer theories in the same spirit as reptation theory — arguing that experimental results are plagued by finite-length effects. CLF theory takes into account the fact that the contour length of the tagged polymer fluctuates with a magnitude $\propto \sqrt{N}$ (left out by reptation theory), which causes finite-length corrections in the viscosity exponent in the form $m_\eta \sim N^{1/3 - a/\sqrt{N}}$ for some $a > 0$. CR theory states that due to the finite length of the surrounding polymers, the tagged polymer has the occasional opportunity for transversal motion. According to CR theory such occasional opportunity would come along less frequently for longer polymers, hence the surrounding polymers would increasingly represent a rigid static network for the tagged polymer, i.e., asymptotically $m_\eta$ would approach 3 from above. While the existence of the CLF and CR phenomena are beyond doubt, whether the finite-length corrections they individually, or in combination [10], produce are strong enough to explain recent experimental evidence and re-analysis of older experiments with large-molecular-weight polymers is a matter of intense debate till today [1, 11–15].

In all fairness, it is therefore appropriate to say that De Gennes’ conclusion “the exponent $m_\eta$ represents one of the major unsolved problems in polymer physics” [16] — made in 1985 after the development of CLF theory — still holds today.

Buoyed by our recent success of explaining the exponents for single polymer translocation through narrow pores by means of restoring forces that stem from polymer dynamics [17–19], here we shed new light on the slow dynamics of dense polymeric systems, in terms of collective many-polymer effects. We report that the dynamical involvement of the surrounding polymers generates a restoring force on the tagged polymer, suppressing its longitudinal fluctuations — a collective many-polymer effect termed as the dynamic response of the melt hereafter. Somewhat rephrased, effective single polymer theories, as discussed above, are incomplete. Via a theoretical framework that combines the dynamic response of the melt with the transportation of stored lengths along the tagged polymer’s contour, we provide the route towards a satisfactory theory-experiment reconciliation for $D$ and $m_\eta$. This dynamic response originates from the localized strain relaxations in the polymers, and is characterized by a power-law $\sim t^{-\alpha}$ in time. Although the dynamic response at any given time is fairly weak, we show that it persists until a time $t_s \sim N^{2/\alpha}$. With $\alpha = 0.78 \pm 0.03$, $t_s \sim N^{2.56 \pm 0.10}$ far outlasts $\tau_r$ of reptation theory, and yields $D \sim N^{-(1+1/\alpha)} = N^{-2.28 \pm 0.05}$ and $m_\eta = 2 + 1/\alpha = 3.28 \pm 0.05$. In other words, the experimentalists have been right after all — and that is the central message of this paper.

Before we delve into the physics of the dynamic response, we make a few remarks to put our work in proper perspective (all the remarks are elaborated in due course of this paper). (a) All our (lattice-based) Monte Carlo simulations for self- and mutually-avoiding polymers in three dimensions [20] are performed with an overall density of one monomer per lattice site. Due to the possibility that adjacent monomers belonging to the same polymer can occupy the same site, overall approximately 40% of the sites typically remain empty. Our systems are thus dense enough for entanglement, but not tightly packed. (Details of the model and the polymers’ dynamics, definition of stored lengths, equilibration times we have used etc. can be found in the Appendix and Fig. 4.) (b) The physics we report here holds for dense systems like polymer melts in particular, and for entangled solutions, which exhibit $m_\eta \approx 3.4$ as well [21]. (c) The physics reported here is conceptually different from earlier works on many-polymer effects by Deutsch, Semenov and Rubinstein [22–24]: while the latter find an unrealistic exponential increase of the viscosity due
to “activated dynamics”, we report a slowing-down of the dynamics in power-law fashion, due to subtle memory effects in the surrounding polymers. (d) Although we cannot provide a direct comparison with CR theory, for the polymer lengths we consider, CLF theory can only provide an eventually inadequate correction of less than 0.1 for \( m_\eta \) over its reptation theory prediction (i.e., \( m_\eta = 3 \)); moreover, the dynamic response of the melt reported here is a collective many-polymer effect which simply cannot be explained by CLF or CR theory.

## 2 Physics of the dynamic response

Using targeted simulations, first we illustrate that the longitudinal fluctuations of the tagged polymer are indeed suppressed by the dynamic response of the melt, a feature that is absent in all effective single-polymer theories. In a snapshot of the melt, thermalized for a long time, we randomly tag a polymer, and attempt to manually slide it in a random direction, without changing the polymer’s configuration within its contour; at \( t = 0 \) [Fig. I(a) to I(b)]. The attempted move is accepted if excluded-volume constraints are not violated. Note that this constitutes a move that satisfies detailed balance; hence the configurations before and after the manual sliding move are sampled from the Boltzmann distribution. Looking only at the configurations after successful moves, we subsequently observe the tagged polymer sliding back, as the dynamics of the melt is restarted with the tagged polymer at its new position. To quantify this back-sliding effect, we measure \( y(t) \), the displacement \( \vec{x}_i(t) - \vec{x}_i(0) \) projected on the direction of the contour \( \vec{x}_{i+1}(0) - \vec{x}_{i-1}(0) \), summed over all monomers \( i \) [Fig. II(c)]. Our reason to leave the polymer’s configuration unchanged within its contour during the manual sliding at \( t = 0 \) is to demonstrate that the sliding-back phenomenon is simply beyond all effective single-polymer theories. These theories only take into account the transportation of stored lengths within the tagged polymer’s contour; according to them the manual sliding of the contour without changing the stored length distribution within it would not excite any internal fluctuation mode of the tagged polymer, and thus would not produce the subsequent back-sliding of the tagged polymer. Note that, albeit characteristically entirely different from ours, Deutsch, Semenov and Rubinstein also observed a similar sliding-back phenomenon [22–24], whose physics we address in the following section.

It may seem from the above simulations that the (most obvious) contributor to the sliding back phenomenon is the enhancement and depletion of the local density

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**Figure 1:** (a,b) Two-dimensional illustration of dynamic response of the melt suppressing the mobility of the tagged polymer. At time \( t = 0 \), we randomly tag a polymer (red) and slide it in a random direction, without changing the polymer’s configuration within its contour. Panels (a) and (b) show the situation before and after the red polymer has undergone this process. Surrounding polymers are shown in blue. (c) As a response to the new situation after an accepted sliding move, the melt exerts a back-sliding force on the tagged polymer, towards its configuration before the manual sliding. The quantity \( y(t) \) (see text for definition), averaged over one and two million manual-sliding operations, for \( N = 25 \) and \( 50 \) respectively, is plotted. The error bars are of the order of the symbol sizes. For times beyond the red dots, \( y(t) \) shows only fluctuations: crucially, note from Fig. 1(c) that the back-sliding lasts longer for longer polymers. We have also checked that \( y(t) \) vanishes in the absence of the manual sliding of the tagged polymer, as it should.
around the extending or retracting end of the tagged polymer. However, only restoring the average local monomeric density does not suffice to take away the restoring force on the tagged polymer; density fluctuations like these — at the scale of single monomers — decay sufficiently fast, by times of order of single monomeric equilibration time [since our monomers have a jump-rate of unity by definition, local density fluctuations caused by the extending or the retracting end of the tagged polymer cannot live longer than times of $O(1)$], so their role can simply be ignored. In fact, originating from the dynamics of the surrounding polymers, the dynamic response of the melt decays as $t^{-\alpha}$ with $\alpha < 1$, lasting up to $\tau_s \sim N^{2/\alpha}$ (follows in the next section). Consequently, the time-integral of this restoring force is very large for long polymers, even if its magnitude at any given time is small.

The real physics of the dynamic response of the melt suppressing the mobility of the tagged polymer, is, as follows. The mobility of the tagged polymer is effected by the extension (resp. retraction) of its contour; so, if one end of the tagged polymer extends (resp. retracts itself along the contour), it locally distorts the contour shapes of the surrounding polymers, thereby creating localized strains in them. Before the tagged polymer’s contour can settle in its new position, the surrounding polymers must relax this strain, a process that requires a finite time $\tau_s$. Until then, the persistence of the localized strains in the surrounding polymers provides the tagged polymer’s end with a drive to reverse its movement; i.e., effectively suppresses its mobility.

Before we characterize the dynamic response, we return to point (b) at the end of the introduction, and remark that this physics also holds for entangled solutions. In entangled solutions the solvent molecules can be easily pushed away by an extending contour of the tagged polymer, but the finite time required for the surrounding polymers to relax their localized strains would still provide the drive to reverse the longitudinal movements of the tagged polymer.

3 Characterizing the dynamic response

To answer the question “up to what time $\tau_s$ does this restoring force persist?”, let us consider a polymer (labeled A) near the tagged polymer on which monomer $n^*$, by the direct action of the tagged polymer’s contour extension, is pushed away to a slightly different physical location, say at time $t = 0$. Since polymer A no longer satisfies random-walk statistics from the new position of $n^*$, its (entropic) chain tension is locally perturbed at $n^*$, which shows up as perturbation of stored length density by an amount $\delta \rho_0$ at $n^*$, i.e., $\delta \rho_0 \propto \delta_{n,n^*}$. This perturbation will give rise to a local strain of magnitude $\epsilon_0 \propto \delta_{n,n^*}$ at $t = 0$, and will excite all fluctuation modes of polymer A. The amplitude $a_m$ of the $m$-th mode $\psi_m$ can be obtained from the equation $\epsilon_0 = \sum_m a_m(0) \psi_m$, $m = 1, 2, \ldots, N$. Typically, in polymer physics, the $m$-th fluctuation mode of a polymer has an associated relaxation time $\tau_m \sim (N/m)^{3\beta}$ for some $\beta$, where $\tau_s \sim N^{3\beta}$ is the longest relaxation time, corresponding to the slowest mode $m = 1$ of the polymer. The subsequent evolution of this strain will then be given by $\epsilon(t) = \sum_m a_m(0) \psi_m \exp(-t/\tau_m)$. The local contribution of these summed over a large number of exponentials at $n^*$ will yield a power-law, implying that $\epsilon_n(t) \sim t^{-\alpha}$ for some $\alpha$, apart from the overall terminal exponential decay $\sim \exp(-t/\tau_s)$. Such power-laws are often referred to as “memory effects”.

We approach the time-evolution of a localized perturbation in stored length density like the above by solving a different problem, wherein we inject $p \sim O(1)$ extra monomers in polymer A at $n^*$ [i.e., $\delta \rho_0 = p \delta_{n,n^*}$ at $t = 0$] and ask ourselves how this excess monomer density at $n^*$ evolves in time. Given that the longest time-scale in the polymer $\tau_s \sim N^{3\beta}$, at long times, all the monomers of polymer A within a backbone distance $n_t \sim t^{1/\beta}$ from $n^*$ can be considered equilibrated to the new situation. However, since this internally equilibrated part of polymer A stretches in physical space only to $r(n_t) \sim \sqrt{n_t}$, and not to the equilibrated distance $r(n_i) \sim \sqrt{n_i} + \bar{p}$, at time $t$, the free energy of polymer A is increased by an amount $\delta F \sim k_B T \delta r^2(n_t)/r^2(n_i)$. These $p$ monomers thus encounter a “chemical potential” $\mu = 1/p \frac{\partial F}{\partial n_t} = 1/p \frac{\partial F}{\partial r(n_i)} \frac{\partial r(n_i)}{\partial n_t} \sim t^{-2/\beta}$, which leads us to the expectation that $\delta \rho_n(t)$, the local stored length density at $n^*$ for the monomer injection problem $\sim t^{-2/\beta} \exp(-t/\tau_s)$. The relation between the local strain relaxation and local density of stored lengths as explained above then implies $\alpha = 2/\beta$. In other words, one can obtain $\beta$ from $\alpha$, and vice versa.

Before we measure $\alpha$, we return to point (c) of the introduction. Deutsch, Semenov and Rubinstein [22–24] discussed an “experiment” similar to ours in Fig. [1] a tagged polymer slides along its contour, and experiences
an opposing force. However, while they concentrated on
the magnitude of the force as a function of sliding dis-
tance, we focus on its magnitude as a function of time.
In other words, they considered a static problem, which
provided them with a time-invariant magnitude of the
opposing force, yielding an unrealistic exponential scal-
ing behavior of melt relaxation time $\tau$ with $N$. In con-
trast, we approach the dynamic problem, which provides
us with the power-law behavior of the restoring force.

We measure $\alpha$ by further targeted simulations, us-
ing a tiny probe in the melt. Our probe consists of
five monomers, which we completely crumple within
the same lattice site at $t = 0$. The probe is con-
structed in the following manner. In a snapshot of the
melt at $t = 0$, which is properly thermalized, we man-
ually remove five units of stored lengths from one poly-
mer and crumple them at one end [Fig. 1(a) to 2(a)].
We subsequently restart the dynamics of the melt and
let these five monomers unfold, while holding the rest
$(N - 5)$ monomers of this polymer frozen at their new
positions (to prevent the stored lengths in the unfolding
monomers from disappearing through the backbone of
the parent polymer). In these targeted simulations, note
that the tiny probe — the five unfolding monomers —
mimic the (longitudinal) contour extension phenomeno-

Figure 2: (a) Crumpling five units of stored lengths in the red polymer of Fig. 1(a) at one of its ends. For the subsequent
time evolution the frozen $(N - 5)$ monomers are shown in yellow, and the unfolding monomers in red. Note that if there
were more than five units of stored lengths, any five of them can be chosen to be crumpled at one end. (b) The unfolding
monomers (in red) giving rise to localized strain in the surrounding polymers (only one affected polymer shown for clarity),
the frozen monomers are shown in yellow. The subsequent relaxation of strain in the surrounding polymers requires their spatial
redistribution (schematically, from the dashed line to the solid line configuration). The spatial extent up to which the strain
in the affected surrounding polymer has relaxed after time $t$ is shown by the blue circle. (c) Behaviour of $dZ_5(t)/dt$ for polymer
lengths $N = 50$, 100 and 200. The power-law behaviour of $dZ_5(t)/dt$ at long times with exponent $(1 + \alpha)$ shows that $Z_5(t)$,
i.e., the restoring force of the surrounding polymers against the contour extension of the tagged polymer, converges to some
$N$-dependent offset $Z^*$ at $t \to \infty$ as a power-law with exponent $\alpha$. For clarity, the $dZ_5(t)/dt$-values for $N = 50$, 100 and 200
are multiplied by 1, 10 and 100 respectively.
the slowest “Rouse mode within a tube”, as often assumed in the field of entangled polymeric systems [3] (Rouse modes have \( \beta = 2 \) and would consequently yield \( \alpha = 1 \)). Instead, the physics of the modes dictating the slow dynamics of entangled systems arises from collective many-polymer effects, as clearly evidenced here.

4 Scaling of \( D \): Direct verification

To test the scaling of \( \tau_s \) with \( N \), we measure the mean squared displacement \( \langle \Delta r^2(t) \rangle \) for the middle monomer of the tagged polymer as a function of time. Following existing literature [3], for the physics reported in this paper, we expect four regimes for \( \langle \Delta r^2(t) \rangle \): (a) \( \sim t^{1/2} \) for \( t < \tau_e \), with the entanglement time \( \tau_e \) independent of \( N \) (note that this \( t^{1/2} \) behaviour indeed can be obtained by summing over the Rouse modes [3]; since regime (a) is a non-entangled regime, the Rouse mode description does not contradict the existence of much slower collective many-polymer mode in the entangled regime as we report here), (b) \( \sim t^{1/4} \) for \( \tau_e < t < \tau_s \), corresponding to stored length transportation along the contour, (c) \( \sim t^{1/2} \) for \( \tau_s < t < \tau \), and (d) \( \sim t \) for \( t > \tau \). The notoriously-difficult-to-observe regime (a) to (b) crossover [25] is shown in Fig. 3. In principle, the crossover from one regime to the next should show up as peaks in the curvature \( c(t) = \frac{\partial^2 \log[\langle \Delta r^2(t) \rangle]}{\partial \log(t)^2} \), but in view of the difficulty to identify the crossover from regime (a) to (b), only the (b) to (c) regime crossover can be captured [inset, Fig. 3], wherein the collapse of the \( x \)-location of the peak in \( c(t) \) confirms the prediction \( \tau_s \sim N^{2.56 \pm 0.10} \).

Finally, having put all the ingredients together, we obtain \( D \sim N^{-(1 + 1/\alpha)} = N^{-2.28 \pm 0.05} \), as opposed to \( N^{-2} \) (at least asymptotically) predicted by all effective single polymer theories; yielding \( m_\eta = 2 + 1/\alpha = 3.28 \pm 0.05 \), in decent agreement with the experimentally-observed value.

Returning briefly to point (d) at the end of the introduction, we note that the effect of contour length fluctuations for our model can be estimated as follows. If we tag a single polymer in our model, block its transversal motion, and remove all other polymers, the result is well-approximated by the repton model [26]. For this model, the diffusion coefficient is given by \( D = \frac{1}{3N^2} \left( 1 + \frac{2a}{\sqrt{N}} \right) \), in which the finite-length correction is attributed to CLF. The effective exponent for the diffusion is obtained as \( \frac{\partial \log(D)}{\partial \log(N)} = -2 - a/\sqrt{N} \). Accurate numerical results yield \( a \approx 1 \) [27]. For polymer lengths \( N = 135, \ldots, 500 \) as used in the inset of Fig. 3 CLF affects this effective exponent, as well as the related viscosity exponent, thus by less than 0.1. This is confirmed by the lack of any systematic trend in the collapse in this inset.

5 Conclusion

In summary, our work reported in this paper sheds new light on the slow dynamics in dense (entangled) poly-
meric systems, wherein we have shown that collective many-polymer effects, in the form of (dynamical) restoring forces, suppress the longitudinal fluctuations of each polymer — the only mode of fluctuations that keeps polymers mobile in dense systems. We have demonstrated that the collective many-polymer effects produce slower modes than the modes arising out of “single (Rouse) polymer dynamics within a tube”, which, to date, has been the main paradigm in theoretical literature on dense systems. Using this new physics, we have explained the experimentally observed scalings of the viscosity and the relaxation time $\tau$, considered to be a major unsolved problem in polymer physics. By altering the paradigm of the effective single-polymer theories that has been in place for four decades, our work opens exciting and intriguing perspectives on how similar restoring forces may play a role in dynamical phenomena in dense environments, such as cells, inter- and intra-cellular transport, and self-organization properties, or systems like polymer gels. Additionally, how to microscopically characterize the slow fluctuation modes that arise out of collective many-polymer effects, as reported here, remains a challenging problem.

Acknowledgments

Ample computer time from the Dutch national supercomputer facility SARA is gratefully acknowledged. We thank Robin C. Ball and Hans van Leeuwen for useful discussions.

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Appendix: Technical notes

Our simulations have been performed with the lattice polymer model described in Ref. [20]. This model combines a very high computational efficiency with realistic polymer dynamics. All our simulations are three-dimensional, with the lattice polymers residing on a face-centered-cubic lattice. Polymer contours are self- and mutually-avoiding. Polymers consist of a string of monomers. Monomers adjacent in the string are located either in the same, or in neighboring lattice sites. Multiple occupation of lattice sites is not allowed, except for a string of adjacent monomers belonging to the same polymer. A two-dimensional version of our model is illustrated in Fig. 4.

Our simulations are performed with an overall monomer density unity per lattice site. The polymers move through a sequence of random single-monomer hops to neighboring lattice sites. These hops can be along the contour of the polymer, thus explicitly providing reptation dynamics. They can also change the contour “sideways”, providing Rouse dynamics (see Fig. 4). Each monomer attempts to move along the contour, as well as sideways stretching or reducing the backbone, statistically once per unit of time. Due to the possibility that adjacent monomers belonging to the same polymer can occupy the same site, overall approximately 40% of the sites typically remain empty. The number of stored lengths within any given lattice site is one less than the number of monomers occupying that site.

Initial thermalizations were performed as follows: completely crumpled up polymers are placed in lattice sites at random. The system is then brought to equilibrium by letting it evolve for $\tau_{\text{eq}}(N)$ units of time; typically, for $N \leq 50$, $\tau_{\text{eq}}(N) = 10^5$; for $75 \leq N \leq 180$, $\tau_{\text{eq}}(N) = 10^6$; for $N \geq 200$, $\tau_{\text{eq}}(N) = 10^7$.

The simulation results in Fig. 2(c) are obtained by averaging over 7.5 million unfolding experiments, performed in statistically independent systems with size $40^3$. Mainly due to long equilibration times, these simulations required around 250,000 processor hours.

The simulation results in Fig. 3 were obtained from simulations with a system size of $60^3$ sites, over a total time of $t_{\text{tot}} = 100N^{2.5}$ for the shorter polymers, and $t_{\text{tot}} = 50N^{2.5}$ and $25N^{2.5}$ for lengths $N = 300$ and 500. Combined, these simulations took around 4000 processor hours.

Figure 4: Illustration of the two-dimensional version of the lattice polymer model. Polymers are shown by darker colors and their contours in lighter colors. In the upper polymer, interior monomers 2, 4, 6, 9, 10 and 11 can either move along the contour, or move sideways; monomer 7 can join either 6 or 8; the end monomers 1 and 12 can move to any empty nearest-neighbor site. In the lower polymer, interior monomers 3, 5, 10 and 11 can either move along the contour, or move sideways; monomer 1 can move to any empty nearest-neighbor site, and monomer 12 can join its neighbor 11. In this configuration, because of the self- and mutually-avoiding property of the polymers, all other monomers cannot make a move. Statistically once per unit of time, each monomer attempts to move up and down along the contour, as well as sideways.