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Irreversible polymer collapse in 2 and 3 dimensions

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We describe scaling arguments and simulations of the kinetics of irreversible polymer collapse. Scaling predicts and simulations confirm that irreversible collapse is dominated by diffusion of the polymer ends which accrete monomers and small aggregates. Exponents found by simulations agree closely with scaling relations. In three dimensions the collapse time is predicted to scale only linearly with polymer length. Our results are contrasted with deGennes' mean field theory of collapse in the reversible regime of small departures from θ -solvent conditions.

Homopolymer collapse - the flexible coil to globule transition - has long been considered an important problem in the kinetics of long polymers. Some authors have considered it as a simplest first model for the initial stages of protein folding.¹ Most of the research in this area has been dedicated to the thermodynamics rather than the kinetics of collapse. In considering the kinetics, deGennes has described a mean field argument for the kinetics of polymer collapse during slight departures from θ -solvent conditions.² Under these conditions he suggested the polymer initially collapses into a sausage shape. Then diffusion thickens the sausage uniformly as the ends contract. Grosberg et al³ refined this picture by considering the effects of topological constraints relevant to later stages of collapse.

We have investigated the polymer collapse problem in the limit of large departures from good solvent conditions so that monomers that encounter each other stick irreversibly.⁴ This irreversible sticking is the driving force of the collapse. We also restrict our study to diffusive monomer

motion and short range interactions. In order to investigate polymer collapse in this regime we have developed scaling arguments and performed simulations. Our analysis suggests that in direct contrast to the mean field scenario discussed by deGennes irreversible polymer collapse is dominated by the motion of the ends of the polymer that diffuse along the polymer contour accreting monomers and smaller aggregates.

To develop a scaling argument for irreversible collapse we assume that both (a) uniform collapse along the contour and (b) ends which diffuse and accrete monomers, play a role in collapse. We assume that rings do not play a role. Let $M(t)$ be the average mass of an aggregate along the polymer. Let $M_0(t)$ be the mass of the aggregate at either end of the polymer. At every time step the end aggregate has a probability proportional to its diffusion constant of collecting mass by accreting its immediate neighbor aggregate separated by a distance d_0 with a mass $M(t)$. Since d_0 is the aggregate separation, it is not affected by aggregate size. Thus $M_0(t)$ satisfies

$$\frac{dM_0(t)}{dt} = M(t)D_0(t)/d_0^2 \quad (1)$$

Where $D_0(t) = 1/M_0(t)^{1/d}$ is the diffusion constant of the end at time t . Assuming scaling:

$$M_0(t) \sim t^{s_0} ; M(t) \sim t^s \quad (2)$$

We obtain:

$$s_0 = (s+1)d/(d+1) \quad (3)$$

The two exponents are equal and uniform collapse occurs only for $s=s_0=d$. For $s<d$, $s_0>s$ and the growth of the ends is faster than the growth of the width of the chain and end collapse dominates for long enough polymers.

We have generalized the scaling relation for $D_0(t) = 1/M_0(t)^x$ where x is allowed to vary from the Stokes' law value. While Stokes' law for aggregate diffusion describes the primary effect of hydrodynamics, it is possible that local properties of the polymer influence the effective diffusion constant during collapse. In this case the scaling relation (3) is changed to:

$$s_0 = (s+1)/(x+1) \quad (3')$$

The size of s may be estimated by considering a polymer with fixed ends at their equilibrium separation (removing the dynamics of the end motion from the problem). The collapse of such a polymer would result in a rod of aggregates of average mass $M=N/R$ where N is the number of original monomers and $R\sim N^\nu$ is the average end-to-end distance. The time over which this collapse occurs may be approximated roughly by the Rouse time $\tau\sim N^{2\nu+1}$ (consistent with deGennes argument). The fixed-end polymer collapse now serves as a model for the collapse of the original polymer along the contour away from the ends. The average mass at time t is determined by the maximal segment length $N(t)\sim t^{1/(2\nu+1)}$ that relaxes by time t :

$$M(t)\sim N(t)/R(t) \quad (4)$$

or

$$s=(1-\nu)/(2\nu+1) \quad (5)$$

This value of s (see Table I) is small and implies that $s_0\gg s$. A larger but still small value of s is obtained by assuming Zimm relaxation $\tau\sim N^{3\nu}$ or $s=(1-\nu)/3\nu$, which with (without) excluded volume gives $s=0.22$ ($1/3$) in 3-d. Thus scaling predicts an end dominated collapse where the mass of the ends increases more rapidly and eventually dominates aggregation along the contour.

The two results Eqs. 3 and 5 were tested by comparison with Monte-Carlo simulations. Our simulations are based on a lattice Monte-Carlo algorithm recently developed for simulating high-molecular-weight polymers.⁵ This novel two-space algorithm, in its original form, has been shown to be significantly faster than previous state-of-the-art techniques.⁶ Odd monomers and even monomers of a polymer are distinct and may most easily be described as residing in two separate spaces. Each monomer occupies one cell of a square lattice. Both connectivity of the polymer and excluded volume are imposed by requiring that, in the opposite space, only the nearest neighbors along the contour reside in the 3×3 neighborhood of cells around each monomer. Motion of monomers is performed by Monte-Carlo steps that satisfy the polymer constraints. Since adjacent monomers (and only adjacent monomers) may lie on-top of each other the local motion of the

polymer is flexible. Despite the unusual local polymer properties the behavior of long polymers is found to agree with conventional scaling results.

The simulation of polymer collapse starts from a set of equilibrium polymer configurations generated by Monte-Carlo simulations of two kinds with no theoretical or measured difference in properties. The first is the two-space dynamics that satisfies dynamic scaling. The second is a non-local 'reptation' Monte-Carlo that randomly moves monomers from one end to the other and is faster than the local Monte-Carlo but for equilibrium geometries provides equivalent results.

Polymer collapse is simulated by eliminating the excluded volume constraint. While excluded volume is relevant to the initial polymer conformation in good solvent, and to the final collapsed size, it does not enter in the scaling relation Eq. 3 given above. Therefore we do not expect it to affect the overall behavior of irreversible polymer collapse, though the precise value of s , s_0 could be affected. Similarly, the growth of the surface area of the aggregates was not included. We have performed simulations of polymer collapse that include both excluded volume and surface area growth and have obtained results similar to those reported here.⁷

Once the excluded volume constraint is eliminated, local Monte-Carlo (diffusive) dynamics are performed. Monomers are no longer stopped from entering the neighborhood of another monomer, however, they continue to be required not to leave any neighbors behind. This enables monomers of the same type (odd or even) to aggregate by moving on top of each other. The mass of an aggregate is set to the total number of monomers which reside on the same site. Aggregates are moved as a unit but are assigned a diffusion constant which scales by $D \sim 1/M^x$ where Stokes' law for spherical bodies in d -dimensions corresponds to $x=1/d$. The polymer dynamics are then simulated by selecting an aggregate (monomers are included as aggregates of mass 1) and moving the aggregate in one of four compass directions with a probability given by the diffusion constant and only if connectivity constraints allow -- the aggregate does not leave any neighbors behind. One time interval consists of performing a number of aggregate moves equal to the number of remaining aggregates -- taken to be the number at the end of the time interval. Simulations were performed in both 2 and 3 dimensions.

Figs. 1 and 2 show the results of our simulations. Fig. 1 shows the results for Stokes' law diffusion for two different polymer lengths, while Fig. 2 shows the results for different values of x . The time evolution of the average mass of the polymer ends, and the average mass of aggregates not including the ends are both shown. Longer polymers follow the collapse of the shorter polymers but extend it to longer times. This is consistent with the end dominated collapse where the length of the polymer only enters through the time at which the ends meet. The scaling behavior follows the exponents shown in Table I. Values are compared with the scaling relation result and are in close agreement with a small but possibly non-zero deviation. The agreement with the scaling relationship Eq. 3 is striking since there are corrections which may be expected due to the neglect of changes in curvature and compression of the polymer. In 2-d the value of s deviates from the rough argument of Eq. 5. However, the smallness of this exponent is correctly described. In 3-d the estimate given for Zimm relaxation without excluded volume $s=1/3$ is in coincidence with the simulations though it is hard to justify this result. Finally, the small values of s may indicate that s results from a logarithmic correction rather than a power law. Efforts to fit the curves to logarithmic scaling are not conclusive. Consistent with the rapidly diminishing probability of long rings⁸ we find they have a negligible significance in collapse.

When the diffusion constant scaling x is varied (Fig. 2) the end dominated collapse persists. The scaling relation is satisfied and the size of s is nearly constant over the range investigated. A reasonable value for s_0 may be obtained from a single value for s in each dimension and use of the scaling relation Eq. (3'). For larger values of x , s decreases gradually.

The collapse time in end-dominated collapse scales as $\tau \sim N^{1/s_0}$. We find $1/s_0 = 1.293 \pm 0.001$ in 2-d and 1.018 ± 0.005 in 3-d (errors are statistical) for Stokes' law diffusion. Thus the collapse time is predicted to scale linearly with polymer length in 3-d. The maximum values allowed by the scaling relations are $3/2$ in 2-d and $4/3$ in 3-d. This result also addresses the question: Are the polymers simulated long enough to show the asymptotic collapse mechanism? The scaling of the collapse time is significantly lower than other collapse mechanisms. The sausage collapse scaling

of deGennes is 2 or 2.2 (without hydrodynamic interactions) in 3-d. Thus it is unlikely that a faster process than end-dominated collapse will take over for longer polymers.

Finally, we ask how far does the end-dominated collapse extend into the reversible regime. First we note that according to the argument of deGennes,² the parameter

$$z=N^{1/2}\Delta T \quad (6)$$

controls the departure from the θ -point. ΔT is the difference between the theta temperature θ and the collapse temperature. Thus the irreversible regime is obtained for long enough polymers as well as for large ΔT . In what follows we show by a rough scaling argument that for small $\Delta T/\theta$ the transition from the mean field regime to irreversible collapse is controlled by z . We estimate the crossover point as the temperature at which the time for end-dominated collapse is lower than the mean field estimate for uniform collapse. For end-dominated collapse it is assumed that all processes occur in the reversible regime as in the irreversible regime but slowed by the reverse reactions leading to a time renormalization factor of:

$$(1 - e^{-\Delta T/\theta}) \approx \Delta T/\theta \quad (7)$$

for $\Delta T \ll \theta$. We then write Eq. 2 as:

$$M_0(t) = (v t \Delta T/\theta)^{s_0} \quad (2')$$

where v is an elementary attempt frequency. For $s_0=1$, $v\Delta T/\theta$ is the velocity of the end aggregate. Setting $M_0(t)=N$ gives the time τ_e of the end-dominated collapse:

$$\tau_e = v^{-1}(\theta/\Delta T) N^{1/s_0} \quad (8)$$

deGennes' mean field result gives the characteristic collapse time τ_c as:

$$\tau_c = (\eta a^3/k\theta) N^2 (\Delta T/\theta) \quad (9)$$

where a is the monomer size, η is the solvent viscosity and k is Boltzman's constant. Comparing Eqs. 8 and 9, the crossover temperature is given by:

$$(N^{1-1/2s_0} \Delta T)/\theta = (v\eta a^3/k\theta)^{-1/2} \quad (10)$$

Eq. 10 gives the temperature relative to θ -point below which the collapse becomes end-dominated rather than mean-field. According to our simulations for the case of homopolymer collapse in three

dimensions s_0 is unity and Eq. 10 becomes $z/\theta = \text{const}$. Thus z controls the crossover from mean field to end-dominated collapse. The constant right hand side in Eq. 10 is of order one for a low viscosity solvent and for a frequency of $\nu = 10^{12}/\text{sec}$. This frequency must be replaced by the rate of monomer encounters. For example, if $\nu = 10^{10}$ and $N = 10^4$ crossover occurs for $\Delta T/\theta$ of order 0.1.

In conclusion, we have found that polymer collapse in both 2- and 3- dimensions appears to reduce to 1-dimensional collapse by driven diffusion of the polymer ends. The only modification is the change in the diffusion constant due to the accretion of mass onto the ends. End-dominated collapse is reminiscent of nucleation in the kinetics of first-order phase transitions. Dominance of end motion arises from the greater mobility of the ends as compared to an aggregate along the contour. Without curvature in the chain an aggregate along the contour is unable to move to coalesce with either neighbor because it is bonded to the neighbor on the other side. Aggregation along the contour is fastest in regions of high curvature and increases with increasing dimension. It is not clear if there is a finite crossover dimension to the mean-field infinite-dimension behavior of uniform-polymer-collapse where all points along the contour have equal aggregation probability.

End-dominated collapse is a significant departure from the usual expectation that linear and ring polymer dynamics are similar, the primary prior exception being reptation in polymer melts. Our results indicate ring collapse is much slower than linear polymer collapse. This prediction may be the easiest for experimental verification.

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Table I: Power law exponents for the scaling of end mass (s_0) and mass along the contour (s) during polymer collapse, as defined in the text. The first column gives estimated scaling values for s (Eq. 5). The second and third columns are fitted to the simulation results between the dashed lines in Fig. 1. Fits were chosen to minimize standard errors. Errors given are only statistical. Results are compared to the scaling relation given by Eq. 3. Results in 1-d are exact.

	s [Eq. 5]	s	s_0	$s_0(s)$ [Eq. 3]	$s_0-s_0(s)$
1-d	0	0	0.5	0.5	0
2-d	0.10	0.154 ± 0.001	0.7734 ± 0.0006	0.7695 ± 0.0006	0.004 ± 0.001 (0.5%)
3-d	0.18	0.337 ± 0.002	0.982 ± 0.005	1.003 ± 0.002	-0.021 ± 0.005 (2%)

Figure Captions:

Fig. 1. Plot of the time evolution during polymer collapse of the average total mass of the polymer ends $M_0(t)$ and of the average mass $M(t)$ of aggregates not including the ends. (a) Shows collapse in 2-d of polymers of length $N=1000$ (500 samples), and $N=500$ (1000 samples). (b) Shows collapse in 3-d of polymers of length $N=500$ (500 samples), and $N=250$ (1000 samples). Scaling exponents fitted to the longer polymer collapse for times between the vertical dashed lines are given in Table I and discussed in the text.

Fig. 2. Exploration of the variation of polymer collapse with x where the diffusion constant scales as $D \sim 1/M^x$. In the top panels of (a) and (b) are plots of the time evolution during polymer collapse of the average total mass of the polymer ends $M_0(t)$ and of the average mass $M(t)$ of aggregates not including the ends. (a) Shows collapse in 2-d of polymers of length $N=500$ (500 samples) for $x=\{0.4,0.5,0.6,0.75,0.9,1.0\}$. (b) Shows collapse in 3-d of polymers of length $N=250$ (500 samples) for $x=\{1/3,0.5,0.75,1\}$. In the bottom panels the scaling exponents s_0 and s fitted to the plots of M_0 and M are plotted as a function of x . For 3-d $N=250$ except at $x=1/3$ where $N=500$. The value of $s_0(s)$ obtained from the scaling relation Eq. (3') is also plotted.

Fig. 1.

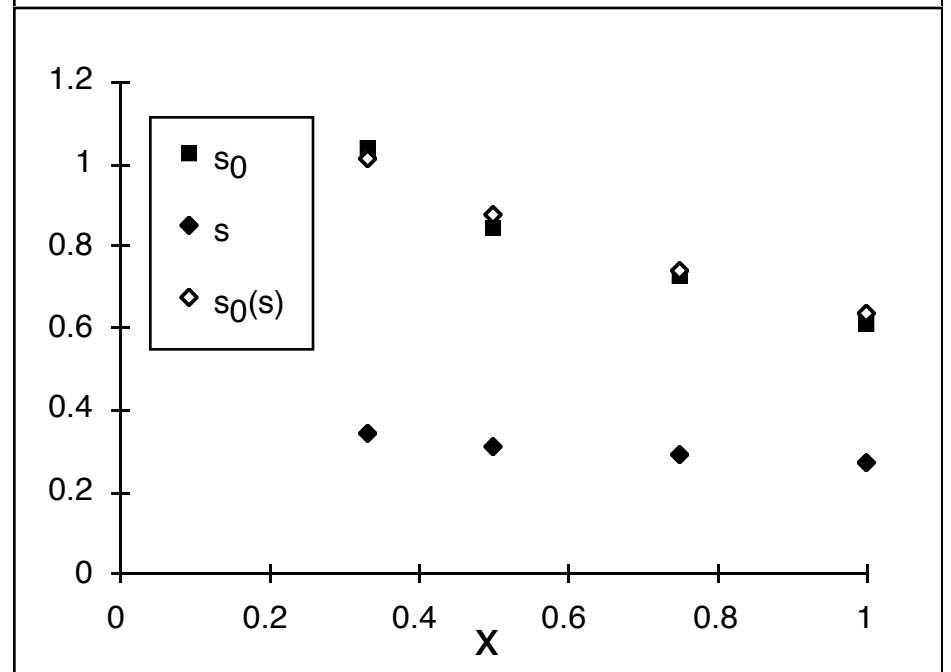
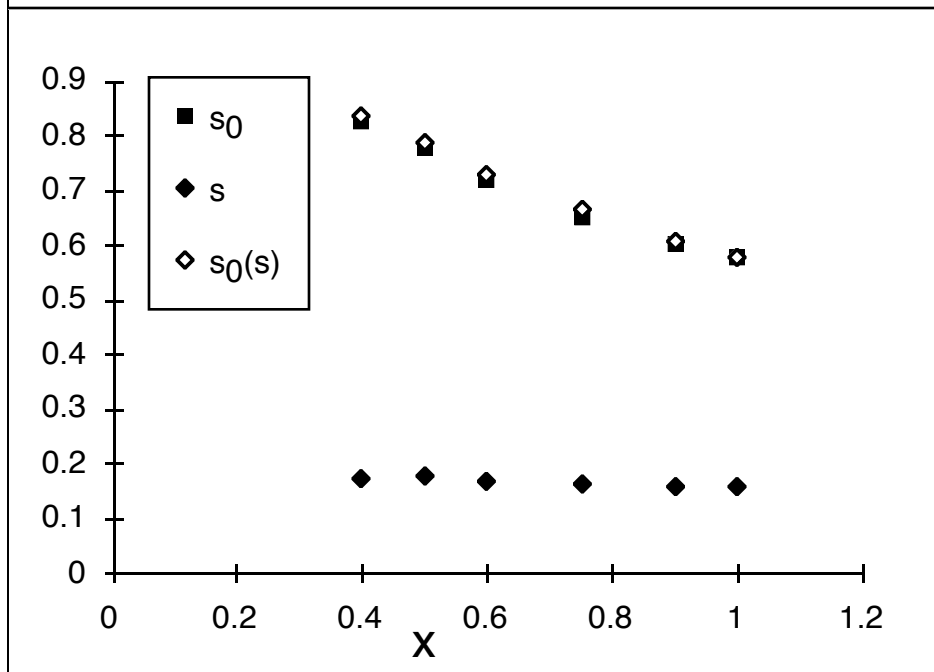
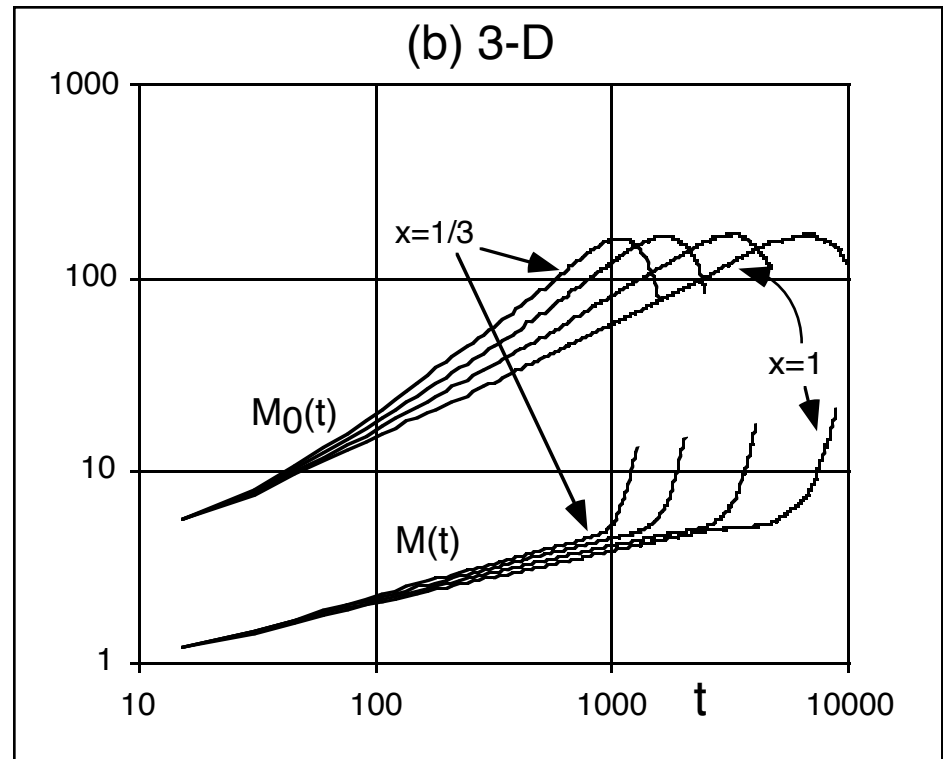
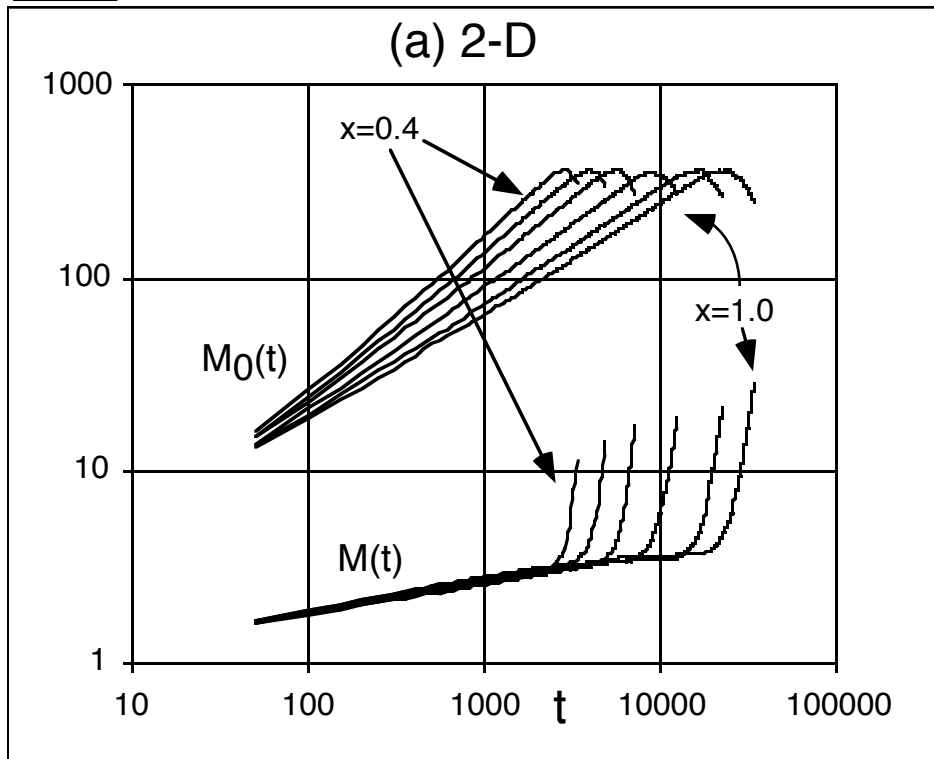


Fig. 2

