Collapse Dynamics of a Polymer Chain: Theory and Simulation

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We present a scaling theory describing the collapse of a homopolymer chain in poor solvent. At time t after the beginning of the collapse, the original Gaussian chain of length N is streamlined to form N/g segments of length R(t), each containing g ∼ t monomers. These segments are statistical quantities representing cylinders of length R ∼ t^{1/2} and diameter d ∼ t^{1/4}, but structured out of stretched arrays of spherical globules. This prescription incorporates the capillary instability. We compare the time-dependent structure factor derived for our theory with that obtained from ultra-large-scale molecular dynamics simulation with explicit solvent. This is the first time such a detailed comparison of theoretical and simulation predictions of collapsing chain structure has been attempted. The favorable agreement between the theoretical and computed structure factors supports the picture of the coarse-graining process during polymer collapse.

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The earliest consistent theoretical picture of the collapse transition stems from de Gennes.[1] In this scenario, when the temperature is shifted by ∆T from θ conditions, a Gaussian coil starts to aggregate, resulting in a uniformly dense sausage-like shape. As time goes on, the minimization of interfacial area drives this sausage-like shape to thicken and shorten until, at the final stage, a globule is formed. More recent work has shown that such uniform sausage-like shapes are highly unstable in solvents due to the capillary instability, which selects for "pearl-necklace" structures over uniform sausages.[5] Attempts made to incorporate the capillary instability in the description of the collapse of a polymer chain,[2][3] however, have so far resulted in no universally accepted theoretical description, particularly in prediction of how the time for collapse scales with chain length. The purpose of this paper is to present a theory based on a new idea for the mechanism of the collapse transition, and to support this theory by comparing directly to results of large-scale molecular dynamics simulations.

Consider a Gaussian coil representing a polymer in θ solvent. We may think of this coil as a Gaussian fractal, created by a hierarchical scheme, demonstrated in the right side of Fig. 1. We subject this system to an instantaneous drop in temperature, which quenches the system rapidly into poor solvent conditions. This effectively introduces monomer-monomer attraction. We assume this quench is so deep that the initial nucleation of the first globules of the collapsed polymer phase appear instantaneously. (Otherwise, addition time scales and regimes would enter the problem.[4][5][6]) The system evolves dynamically according to microscopic equations of motion of chain segments. The segments are straightened arrays of globules, and further straightening streamlines them at larger length scales. This leads to the overall coarse-graining of the chain, on a length scale that is growing with time. This process is the reverse of the hierarchical Gaussian fractal generation.

Because we view the original Gaussian chain made of N monomers of size b_0, we can define a length scale R as the resolution at which the chain appears as a Gaussian chain made of N/g coarse-grained monomers, or segments, of size b = b_0 g^{1/2}, containing g original monomers. Viewing the collapsing chain at a length scale smaller than R reveals straightened segments. However, the overall large scale structure still remains a random walk of segments. This picture is clearly captured in snapshots from simulations, which we discuss below; see Fig. 2.

If we neglect numerical factors associated with detailed shapes of the objects being pulled through the viscous liquid, the hydrodynamic equations of motion for coarse-grained monomers at scale R can be written:

$$ v = f/\eta_o A(R) $$

(1)
where $\eta_0$ is solvent viscosity, $f$ is the chain tension, and $v$ is the drag velocity. The quantity $A(R)$ measures the friction experienced by objects due to the solvent. For Zimm dynamics, $A(R)$ depends on the largest geometric dimension of the object: $A(R) \sim R$. In Rouse dynamics, $A(R) \sim g$ regardless of its geometric size. For now, we assume Zimm dynamics holds, and hence, the velocity scales as $v \sim f/\eta_0 R$.

We account for the chain tension $f$ as follows. By bringing $g_l \sim L$ monomers forming a string of length $L \leq R$ into a globule, one gains free energy $\Delta E/k_B T = g_l \Delta T/\theta$. Thus,

$$f = \frac{\Delta E}{L} = -\frac{k_B T}{b_0} \Delta T/\theta. \quad (2)$$

Note this force $f$ is independent of scale $R$. In this estimation of force, we neglect the surface term correction, $\sim k_B T/b_0 g^{-1/3} (\Delta T/\theta)^{4/3}$, as it decays relatively rapidly with increasing $g$. There are also external forces acting on each segment from the remainder of the chain. But because the segments form a random walk, the vector average of these external forces acting on the ends of any segment is zero. Hence, the initially given Gaussian structure remains through the coarse-graining, as the length of the segments increases.

The velocity $v$ of motion on each scale $R$ is controlled by Eq. (1). After a time $t \sim R/v \sim R^2$, in which all segments move a distance $R$, the configuration on scale $R$ is “relaxed.” We can assume that all monomers of a subchain collapse to a cylindrical configuration, or segment, of length $R(t)$ and diameter $d(t)$. The volume of the cylinder $Rd^2$ should be approximately equal to the total volume of $g$ monomers: $V \approx g^3 R^3$. Since the largest dimension $R$ of the cylindrical object remains the same as for initial Gaussian chain $R \sim g^{1/2}$, we conclude that $g \sim t$, and $d \sim g^{1/4}$. Hence, we arrive at scalings $R \sim t^{1/2}$ and $d \sim t^{1/6}$. (For Rouse dynamics, one obtains $R \sim t^{1/3}$ and $d \sim t^{2/6}$).

It is important to realize that these cylindrical configurations exist only in a statistical sense. Any uniformly dense “cylindrical” configuration would be immediately broken into an array of globules, connected by strings, due to the capillary instability. The relaxation time for the capillary effect $t \sim d^4$, including the coalescence of globules, is short, compared to streamlining time $t \sim R^2$ (or $t \sim d^4$). Thus, the formation of the pearl-necklace structure (within the cylinder) does not require modification of the streamlining description. Our cylinders are arrays of globules characterized by an average diameter of $d$ and inter-globule distance $d$, and overall array length $R$. Mass conservation then requires that each globule consists of $g^{3/4}$ monomers, and the total number of globules is $g^{1/4}$.

Furthermore, there is no energy barrier associated in bringing two separated globules together. This is in contrast to models of other authors, who maintain that globule interaction is the main mechanism of relaxation. Instead of considering the processes of coalescence of globules, and the competition in growth and evaporation in detail, here we adopt the simple viewpoint that the process of streamlining on scale $R$ results in the formation of statistical cylinders of size $R$. The contraction of each segment drags the globules to the larger-scale cylinder. The overall structure is a random walk of such cylinders, which still displays a Gaussian structure on larger scales until the end of coarse-graining stage.

This mechanism allows direct derivation the time-dependent structure factor $S(k, t)$ for a collapsing chain. $S(k, t)$ is a useful function, because it can be both measured experimentally and directly computed from simulations. Below we report the structure factor $S(k)$ of a polymer chain made of cylinders, which in turn are made of linear necklaces of spheres. The structure factor can be

FIG. 2: Simulation snapshots of a collapsing $N = 512$ chain. Time $t$ is measured from the instant at which the solvent quality is changed from “good” to “poor”.

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written as a product of structure factors of its elements:

\[ S(k, t) = S_{\text{gauss}}(R(t))S_{\text{cyl}}(R(t))S_{\text{gib}}(d(t)). \]  \( (3) \)

\( S_{\text{gauss}}(k, t) \) is the structure factor of Gaussian chain consisting of \( N_1(t) = N/g(t) \) unit cylinder elements of average length \( R(t) \). Therefore,

\[ S_{\text{gauss}}(R) = \frac{1}{N_1} \left\{ \frac{2/N_1 [e^{-\alpha(N_1+1)} - e^{-\alpha}] - e^{-2\alpha} + 1}{(1 - e^{-\alpha})^2} \right\} \]  \( (4) \)

where \( \alpha = [kR(t)]^2/3 \). For large \( k \), we note that this expression has a log-log slope of -2, as expected. \( S_{\text{cyl}} \) and \( S_{\text{gib}} \) respectively are the structure factors of cylinder with length \( R(t) \) and a globule of size \( d(t) \):

\[ S_{\text{cyl}}(R, k) = \frac{2}{(kR)^2} \cos(kR + kR Si(kR) - 1) \]  \( (5) \)

\[ S_{\text{gib}}(d, k) = \left[ \frac{3}{(kd)^2} (\sin kd - kd \cos kd) \right]^2 \]  \( (6) \)

\( Si(x) \) is the sine integral of \( x \). The length of cylinders \( R(t) \) and the diameter of globules \( d(t) \) are the parameters which follow the coarse-graining rule suggested above. The large-\( k \) log-log slopes of the relations in Eq. 3 and Eq. 4 are -1 and -4 respectively.

As a test of our theory, we computed the structure factors for a simulated polymer chain undergoing collapse. The collapse of a homopolymer chain in a poor solvent was simulated via molecular dynamics (MD). The prototype system is a single linear freely-jointed polymer chain of length \( N = 512 \) monomers, immersed in a solvent of \( 8 \times 10^4 \) simple particles, contained in a cubic box. The total particle number density, \( \rho \), is 0.85 \( \sigma^{-3} \), giving a box dimension of 45.6 \( \sigma \). All particles interact via standard Lennard-Jones potentials. For “good” solvent conditions, the solvent-solvent, monomer-monomer, and solvent-monomer pair interaction, designated \( U_g(rij) \), is a shifted repulsive Lennard-Jones potential, cut off at \( r = 2^{1/6} \sigma \). For “poor” solvent conditions, the solvent-solvent and monomer-monomer pair interaction is the full Lennard-Jones potential, \( U_{LJ}(rij) \), with a well depth \( \epsilon \) of 1.0 \( k_BT \), cut off at \( r = r_c = 2.5 \sigma \), while the solvent-monomer pair interaction is kept as the repulsive \( U_g \). The shift \( s \) of \( U_{LJ} \) is set such that \( U_{LJ}(r_c) = 0 \). This simple prescription was used previously in smaller-scale homopolymer collapse simulations. \( \} \) Particles connected to each other along the backbone of a chain are constrained via a harmonic potential with an average length of 0.97 \( \sigma \) and a standard deviation of 0.05 \( \sigma \).

The equations of motion are integrated using the velocity-Verlet algorithm, with a time step \( \Delta t \) of 0.001 \( \tau \), where \( \tau = \sqrt{m\sigma^2/k_BT} \). \( m = 1 \). Energy is measured in units of \( k_BT \), which prescribed that the particle diameter, \( d_0 \), be exactly \( \sigma \), for both monomers and solvent particles. Thus the total excluded volume fraction in the system is about 0.45.

The procedure for a single collapse trajectory is as follows. The initial configuration was generated by growing a random walk of length \( N = 512 \) and step length \( l = 0.97 \sigma \), biased such that 1–3 monomers automatically have no overlap. Then the remaining 80,000 solvent particles are added at random locations in the box. Particle overlaps are then removed using a previously detailed warmup technique, \( [16] \) which incrementally increases the excluded volume diameter of the particles from zero to its full value over about 5000 MD time steps in “good” solvent conditions. During this phase, a Langevin-type thermostat with friction \( \Gamma = 5.0\tau^{-1} \) is employed. The amount of time used for this warmup was kept as low as possible in order that the initial configurations remain as Gaussian as possible without significant swelling due to the actual presence good solvent conditions.

Immediately following the warmup, designated for convenience as \( t = 0 \), the quench into poor solvent conditions is performed via instantaneously switching the monomer-monomer and solvent-solvent pair interactions from \( U_g \) to \( U_{LJ} \). The MD integration is run for several thousand \( \tau \), until the chain has fully collapsed into a single globule. During this phase, no thermostat is employed, and the temperature was observed for all runs to fluctuate around 1.0 by less than 0.1\%. The collapse is monitored using the radius of gyration of the chain as a function of time. During this integration, configuration snapshots are stored every ten thousand time steps (10 \( \tau \)) for later analysis. All simulations were run in parallel on 256 processors using domain decomposition. \( [17] \)

A total of 40 independent collapses were simulated, each beginning with a unique chain conformation. The time-dependent structure factor, \( S(k, t) \), was computed at times \( t = 0, 10, 20, 40, 80, \) and 160 \( \tau \), by averaging the static structure factor over all chains at each of those times. We note that the standard deviations were about 20% of the average, which is consistent with large variances in size among the different initial Gaussian chains.

The primary result of this work is a comparison of \( S(k, t) \) predicted by Eq. 3 and \( S(k, t) \) computed from the MD simulations. In order to make this comparison quantitative, we introduced the necessary prefactors in the scaling relations \( R \sim t^{1/2} \) and \( d \sim t^{1/4} \). We then performed a least-squares, conjugate gradient minimization \( [18] \) on the sum of squared errors between the theoretical and computed \( S(k, t) \) for all points for \( k < 1 \) and for all times simultaneously. The resulting comparison is shown in Fig. 3. \( [19] \) Note that the theoretical and computed \( S(k, t) \) agree remarkably well. In particular, both display the three asymptotic slopes of the structure factor components discussed previously. The theory and simulation are linked through the following relations:

\[ R(t) = At^{1/2} \]  \( (7) \)

\[ d(t) = Bt^{1/4} \]  \( (8) \)

with \( A = 1.88(9) \sigma/\tau^{1/2} \) and \( B = 0.78(8) \sigma/\tau^{1/4} \). The poorest agreement appears for the latest time, perhaps signifying the end of the coarse-graining stage of the collapse. Due to the large inherent variability of the simulation data, we do not report goodness-of-fit statistics.

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To complete our picture, we discuss the late-stage collapse dynamics. After the coarse graining stage, a chain becomes a single "cylinder", where the globules are aligned linearly. The terminal globules experience net forces due to the finite size of the chain. The late stage is therefore characterized by "end effects." The typical late stage consists of two globules with connecting string between these two. In this regime, the dynamics are controlled by tension between the two globules and the hydrodynamic friction experienced by the pearls (not by the strings). Both terminal globules move toward the common center of mass by "eating" the string. This procedure is deterministic. Considering the hydrodynamic friction for the sphere with size $R_p \sim 6\pi\eta R_p$ and $R_p \sim N^{1/3}$, the typical distance between the terminal globules should be $N^{1/2}$ (reminiscent of a Gaussian fractal), one can estimate the average characteristic time for the late stage as $\tau \sim R/(\nu) \sim N^{5/6}$ ($\tau \sim N^{3/2}$ for Rouse dynamics). Future work will offer a quantitative comparison of this picture with that observed in ongoing MD simulations.

We have presented a new theory capable of describing the dynamics of polymer collapse in poor solvent. We have proposed that the initially fractal chain recursively straightens on length scales $R(t)$, forming an increasingly coarse-grained random walk of statistical cylinders of length $R \sim t^{1/2}$ and diameter $d \sim t^{1/4}$, in accordance with hydrodynamic equations of motion. These cylinders are statistical objects, whose underlying structure consists of necklace-like configurations of randomly positioned globules connected by strings. This theory successfully incorporates the capillary instability into a hydrodynamic framework. The theoretical time-dependent structure factor is strongly supported by those computed from large-scale MD simulations.

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[18] W. H. Press, in *Numerical recipes in C : the art of scientific computing*, 2nd ed. (Cambridge University Press, Cambridge, UK, 1994), p. 423.