Swelling Dynamics of Collapsed Polymers

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ABSTRACT: We study different regimes in the dynamics of swelling of a long polymer chain from a compact globule. Depending on the age or degree of self-entanglement inside of the globule, we consider the limiting cases of "freshly formed" globule and "old" globule. Considering the density of polymer in a globule, which influences the mobility of solvent inside of the globule, we also distinguish "wet" and "dry" initial configurations. For each of these regimes, we discuss the leading dissipation mechanism governing the dynamics of swelling. Our theoretical predictions are nicely corroborated by large-scale molecular dynamics simulations.

I. Introduction

Historically, the process of polymer collapse has attracted more attention than the process of swelling.[1−11] A major motivation of the collapse studies is the analogy with protein folding. On the theoretical side many models were proposed based on de Gennes' seminal "*expanding sausage*" model.[1] Nowadays it is possible to set up large-scale simulations with explicit solvent particles that can discriminate between theories. For example, Abrams et al.[12] proposed that collapse is dominated by a streamlining process where larger and larger chain sections with a pearl-necklace structure align, while the overall end-to-end distance remains constant, until, in a last step, the resulting dumbbell collapses. This theory is supported by large-scale simulations.[12]

Relatively fewer theoretical efforts have been invested in the reverse problem of homopolymer globule swelling.[7,8,13,14] Swelling of homopolymer globules bears some similarity with protein denaturation. This analogy is in many cases less deep than that between homopolymer collapse and protein folding, as early stages of swelling are more sensitive to the details of the interactions and hence less universal. Most available theories describe the swelling of a homopolymer globule in terms similar to those depicting collapse.[7,8,13] This implies at least two major simplifications: (1) The overall shape of expanding polymer is assumed to remain homogeneous upon swelling, and (2) a phantom chain model is used. We will make clear that both these assumptions may fail. The importance of topological constraints was recognized by Rabin, Grosberg, and Tanaka, who first proposed a description of a knotted swollen globule.[14] We have suggested very recently that there exists an arrested, intermediate state during swelling of a highly entangled globule. This conjecture was confirmed by computer simulation. In a short note, we focused on the distinct monomer−monomer and entanglement−entanglement correlations that develop in the arrested state.[15] Eventually, the globule swells back to the coil state. This is corroborated by light scattering experiments (both static and dynamic) performed on very long poly-NIPAM chains in the group of Wu.[16,17] These experiments are not time-resolved but allow measurement of the "compactness" of the polymer, through the ratio of the hydrodynamic radius to the radius of gyration, in the initial and final states. In this paper, we discuss in some detail the intricacies of homopolymer globule swelling.

Only very naively might the swelling from a compact globule to an extended conformation be thought as the time reversal of collapse. These two processes are different both in their geometrical appearance and in their scaling regimes. For example, during collapse, parts of a polymer are brought together by contracting the polymer chain, and as a result the transient configurations are axially symmetric. On the other hand, during swelling, the dynamics is often controlled by the rate of penetration of solvent into the globule, and the resulting configurations are spherically symmetric. The initial statistical fluctuations, like fluctuations of the end-to-end vector, do not play any role in the swelling process whereas they do in collapse.[12] Another difference between the two processes is that, for collapse, the initial coil configuration is rather well characterized and universal (though strongly fluctuating), while the globular state, which is the initial configuration for swelling, requires additional characterization, which we now discuss.

Characterization of a Globule. Depending upon the method of preparation of the initial configuration (i.e., the history of the globule) and upon its compactness, we consider two major parameters related to the structure of a globule and to its density: (i) its "age"[18] and (ii) its solvent content. These span a phase diagram depicted in Figure 1. We consider the age to range from "fresh" for newly collapsed globules to "old" for fully equilibrated globules. Swelling of a "fresh" globule is quite different from swelling of an "old" globule. Right after a polymer chain is collapsed into the spherical compact globule, the segment of a chain between monomers *i*, *k* is compactly folded and is ready to

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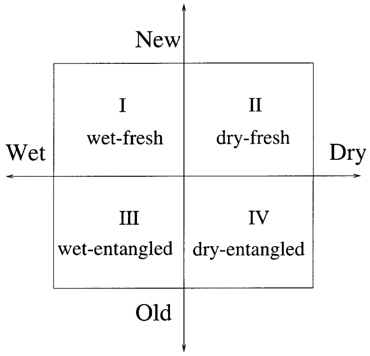

Figure 1. Diagram of states for a collapsed globule.

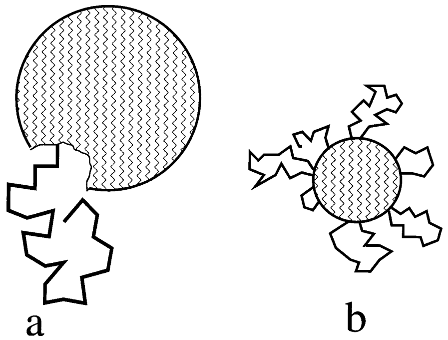

Figure 2. Swelling of a dry-fresh globule: monomer solvation and peeling of loops from the core.

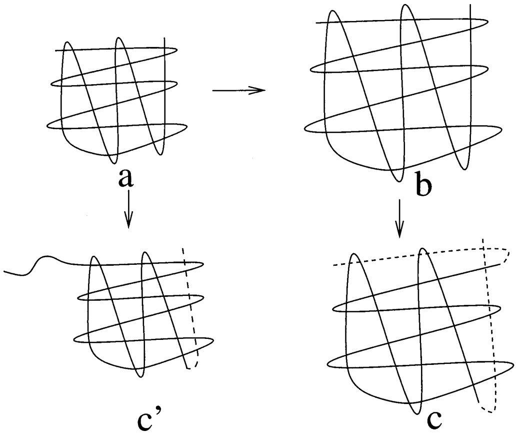

Figure 3. Swelling of an entangled globule. a → c depicts the process of uniform expansion of an entangled wet globule; a → c′ depicts self-disentanglement.

expand. The density of this globule is well equilibrated, but there are no new topological constraints preventing the globule from expanding. We expect that the average geometric distance $\langle r_{ik} \rangle$ between two monomers i, k in a fresh globule scales as $\langle r_{ik} \rangle \sim |i - k|^{1/3}$, for some range of values of $|i - k|$, where $|i - k|$ is the distance between the monomers along the contour of the chain.[20] In an old globule, the complete equilibration of the configuration results in a Gaussian $\langle r_{ik} \rangle \sim |i - k|^{1/2}$ dependence of distance r_{ik} for the close monomers. The price of this equilibration is multiple topological constraints, i.e., entanglements. If equilibrated, the whole globule can be thought as a single large knot. The swelling of unentangled (fresh) and entangled (old) globules should thus be quite different (compare Figure 2a and Figure 3b). Local correlations in both freshly prepared globules and old-entangled globules estimated from direct simulations will be presented in section 4.

The second parameter, measuring the density of solvent inside the globule, allows us to distinguish “dry” and “wet” globules. In a dry globule, the monomers of a polymer are packed so tightly that molecules of solvent cannot penetrate among them. In a wet globule, the space between monomers is large enough for solvent molecules to penetrate. Therefore, in marked contrast to the case of a wet globule, swelling of a dry globule must be dominated by the monomer solvation at the interface.

In the next sections we consider dynamics of swelling for each region, I, II, III and IV, of the phase diagram (Figure 1). In each case we consider the leading dissipation mechanism or other bottleneck constraints which control the dynamics. Then we discuss the results of computer simulations in light of our theoretical predictions.

II. Theory of Swelling of a Fresh (Entanglement-free) Globule

A. Very Fresh and “Not so Fresh” Wet Globules. We will represent the structure of the expanding globule as a closely packed aggregate of n “blobs” of size a. Inside each blob the chain has the structure of a Gaussian random walk containing $(a/b)^2$ monomers, where b is the size of a monomer. The size a is controlled by the number density of the globule: $a = 1/(\rho b^2)$. In the process of swelling of a globule, the size of the Gaussian blobs $a(t)$ is increased with time, until it reaches the size of the whole chain. Later we will consider the special case of a “dry” globule, when $a(0) \approx b$. The entropic price of close packing and folding is about $k_B T$ per blob.

The number of blobs

$$n(t) = \frac{N}{(a/b)^2} \tag{1}$$

decreases with time, and the packing energy nk_BT is dissipated through viscous friction. We find the rate of swelling from the condition that the decrease in packing energy is balanced by the viscous dissipation. The latter is dominated by the flow of solvent inside the globule. The structure of the globule imposes the typical hydrodynamic scale a:

$$k_B T \frac{dn}{dt} = \eta \left(\frac{V}{a}\right)^2 n a^3 \tag{2}$$

and using $V = R/t$, where R is the size of a swelling polymer

$$R = (Nb^2/a^2)^{1/3} a \tag{3}$$

we obtain

$$\begin{aligned} R(t) &= t^{1/5} N^{1/5} \\ a(t) &= t^{3/5} N^{-2/5} \end{aligned} \tag{4}$$

where initial conditions correspond to $t_0 = a_0^{5/3} N^{2/3} = \rho_0^{-5/3} N^{2/3}$. We use dimensionless units $\eta = 1$, $k_BT = 1$, and $b = 1$. To come back to actual units, we should replace $a \to a/b$, $R \to R/b$, and $t \to t/\tau_0$, where $\tau_0 = \eta b^3/k_BT$. The time needed for a swelling chain to reach the

Gaussian size $R \approx N^{1/2}$ is about the Zimm relaxation time:

$$t \approx N^{3/2} \tag{5}$$

The time dependence $R(t) \propto t^{1/5}$ was also found in ref 19. However the physics there is quite different as hydrodynamics is negelected. Hydrodynamics changes the friction law and sets a relevant pore size a smaller than the radius. These two effects happen to compensate at the scaling level.

In this estimate, we used only the most robust feature of the structure of the expanding globule: the density-controlled correlation distance a. This is the only hydrodynamic scale for solvent penetrating inside the expanding globule. Nevertheless, we should note here that the structure of the expanding globule is more complicated and is characterized by one more length scale $\tilde{a}$.

The ideal freshly folded globule may exist only as a theoretical model. Any globule needs some time to be prepared. During that time the folds inside the globule might try to rearrange without crossing each other. These rearrangements result in local Gaussian correlations $\langle r_{ik}\rangle \sim |i - k|^{1/2}$ along the chain beyond the density controlled scale a_0 up to $\tilde{a}_0 = a_0 N_e^{1/2}$. The maximum chain length at which the local Gaussian correlations might be observed is of the order of entanglement length $|i - k| \sim N_e(a_0)^2$. The time needed for this rearrangement is about Rouse−Zimm relaxation time $t \sim N_e^2(a_0)^3$. On shorter time scales, the rearrangement is possible only up to the scale

$$\tilde{a}_0 = (t/a_0^{\,3})^{1/4} a_0$$

This type of local rearrangement is fast compared to swelling process considered above.[20] Simple estimates show that, during the expansion process, the relation between $\tilde{a}$ and a, even if it begins with $\tilde{a}_0 = a_0$ for fresh globule, saturates at

$$\tilde{a} = a N_e^{\,1/2} \tag{6}$$

and holds until a reaches $a = N^{1/2}/N_e^{3/4}$ and $\tilde{a} = N^{1/2}/N_e^{1/4}$. At that moment the structure of the expanding chain can be thought of as a Gaussian walk made of $N/N_e^{1/2}$ monomers folded $N_e^{1/2}$ times. The final process of unfolding these $N_e^{1/2}$ subchains into an equilibrated chain is still described by scaling formulas of eq 4. The reason the structural scale $\tilde{a}$ does not affect dynamics of swelling is simple. The relative velocities of rearrangements of monomers with respect to each other needed for formation of scale $\tilde{a}$ are smaller than the velocity of solvent penetrating the globule, which produces the dynamic bottleneck for the expansion process.

B. Dry-Fresh globule. The above model of expansion in viscous media fails when the globule is so dense that the monomers of solvent cannot penetrate. Instead they can only solvate monomers of the chain one by one, peeling them from the core. In the picture illustrating this process, Figure 2a, only one end of a polymer chain is shown, but configurations with many expanding loops and many wetting centers are also possible, e.g., Figure 2b. We can estimate the wetting rate for one center as $dN_{\text{wet}}/dt \approx \tau_0^{-1}$, where τ_0^{-1} is the molecular diffusion-controlled wetting rate for a single wetting center (i.e., one strand peeling off from the globule) and N_{wet} is the number of wet monomers. In dimensionless units $dN_{\text{wet}}/dt \approx 1$.

A single wetting center is expected when the formation of a wetting center is an activated process with an activation time t_{ac} larger than the wetting time. The wetting center shown on Figure 2b is the source of a chain in a configuration close to Gaussian. In the following, it is assumed that the wet loop is larger than the dense core radius.

To obtain qualitative scaling relations for chain size $R(t)$ and blob size $a(t)$, we simply replace the number of monomers N in eqs 1 and 3 by the number of wet monomers, $N_{\text{wet}} \approx t(dN_{\text{wet}}/dt) \approx t$, and assume $\tau_0 = 1$. A single wetting center is thus expected for an activation time t_{ac} larger than N; hence, this is not for very large globules. After simple estimates, we obtain (in dimensionless units)

$$R(t) \approx t^{2/5}, \quad a(t) \approx t^{1/5} \tag{7}$$

During the wetting process, the loop is found to be slightly compressed as its radius is smaller than the Gaussian size $\propto t^{1/2}$. A concentration profile is anticipated for the wet monomers stored in the loops, and a as given by eq 7 corresponds to the typical distance $r \sim R$ from the center. The power-law relations between R and t, n, and t suggest that the stationary part of the profile ($r < t^{2/5}$) is also a power law $\rho(r)b^3 = (r/b)^{\delta}$. At the outer edge we assume a front, steep enough to be unessential in the integral of the concentration profile. Conservation of polymer then determines the exponent of the concentration profile $\delta = -{}^1/_2$, which leads to the profile

$$\rho(r)b^3 = (r/b)^{-1/2} \tag{8}$$

Note that relaxed Gaussian loops (isolated or in the Daoud and Cotton star-regime with three body interactions) build a profile decaying as r^{-1}. We estimate the time t' needed for the complete wetting of the dry globule to be $t' \approx N$. At this time, all monomers of the initially dry globule become wet, the globule has the size $R = N^{2/5}$, with blobs of size $a = N^{1/5}$. Further swelling of this wet globule proceeds as described by eqs 4 for wet globules.

In the opposite limit, where many wetting centers form without activation, peeling proceeds all over the surface of the globule. The peeled monomers are poorly wet and form a corona with a pore size of a few solvent diameters only. The penetration of solvent through this corona is rate limiting and the whole globule becomes penetrable at a time of order $N^{2/3}$. Though loop condensation takes place, that results in only a few large loops, so this process is irrelevant for the kinetics. The globule subsequently expands over a time $N^{3/2}$ as described by eq 4 for initially wet globules.

III. Theory of Swelling of an Old (Entangled) Globule

At thermodynamic equilibrium, the compacted polymer chain is strongly entangled, and it can be thought as a single large knot. The swelling process is therefore subject to multiple topological constraints. We will estimate below the swelling rates for two most probable mechanisms of swelling: (1) uniform “expansion” of an entangled wet globule, depicted in Figure 3a → Figure

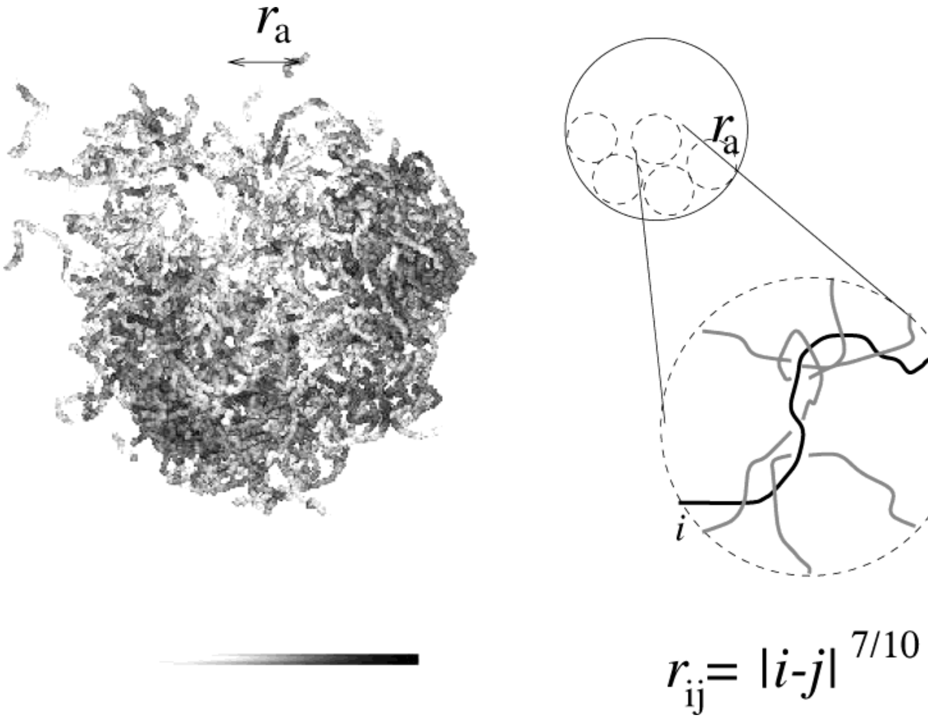

Figure 4. Explanation of the "entangled cell". Snapshot (left) from an MD simulation of a swelling globule ($N = 50\,000$) in the arrested state, showing a hemispherical section of the globule. The entangled cell size is indicated as r_a. The gray scale depicts the degree of constraint on thermal fluctuations of the monomers.[15] Dark regions indicate the accumulation of entanglements. The accompanying schematic (right) depicts the packing of expanded entangled cells and their internal structure.

3c, and (2) reptation of the chain out of the knotted configuration, as shown in Figure 3a → Figure 3c′.

The initial density of the equilibrium globule determines the correlation length $r_0^* \approx c^{-1}$. The presence of entanglements brings the distance between entanglements along the chain $s_e \approx N_e r^*$ as an additional length parameter. The presence of two scales makes the dynamics more complicated: The process of swelling is a two-stage process. In the initial (transitional) stage of swelling, the chain expands as far as it is permitted by the topological constraints. Then, in the second stage of expansion, the slow process of removal of topological constraints governs the dynamics. As the time scales characterizing these two steps are very different, we term the fairly long-lived intermediate state the *arrested* state.

A. Initial Expansion. During this stage, the globule swells from equilibrium to the arrested, stretched configuration, while the number of topological constraints is conserved.

Characterization of Equilibrium and Arrested Configurations. We introduce the notion of an "entangled cell" in the initial equilibrium configuration. This cell contains $N_e^{1/2}$ subchains, each subchain consists of N_e correlation blobs of size r_0^*. Each blob has $(r_0^*)^2$ monomers, and the total number of monomers in an "entangled cell" is $m = N_e^{3/2}(r_0^*)^2$ (see Figure 4). The total energy stored in the interaction of the blobs inside an equilibrium cell is about $N_e^{3/2}$. Before the swelling, the size of the entangled cell is $r \sim N_e^{1/2} r_0^*$. When the entangled cell is allowed to expand, the number of monomers and subchains in a cell remains the same, but the structure of the subchains is changed. This leads to a new cell size r_a in the arrested state (see Figure 4). In the stretched structure, the chain minimizes its free energy under the constraint that the number of entanglements and the number of entangled subchains $N_e^{1/2}$ is conserved. This can be rationalized by a Flory argument balancing the elastic energy and the interaction energy. As in the standard Flory argument for a chain swollen in good solvent,[21] Gaussian elasticity is assumed, and the interaction energy is estimated in the mean-field approximation:

$$F = F_{el} + F_i \approx \frac{N_e^{1/2} r_a^{\,2}}{N_e r_0^{*2}} + \frac{(N_e^{1/2})^2 N_e^{\,2} r_0^{*4}}{r_a^{\,3}} \qquad (9)$$

The estimate is similar to the Flory estimate for single swollen chain, with additional factors $N_e^{1/2}$ and $(N_e^{1/2})^2$ in elastic and interaction energy accounting for $N_e^{1/2}$ chains in the same volume. This leads to the estimate of the stretched cell size $r_a \sim N_e^{7/10} r_0^{*6/5}$. The same type of derivation was used by Pütz for swelling of a weakly cross-linked melt.[22]

Remarkably, this argument can be carried out for scales L smaller than the size of the entangled cell. We should assume that inside a box of size L there are$(L/r_0^*)^{1/2}$ different chains. The number of these chains is conserved during swelling. Under these conditions, on scales smaller than the size of the entangled cell, the structure of the swollen polymer chain is a fractal with exponent $\nu_a = 7/10$ instead of 6/10 as in the original Flory argument for a swollen chain.

Another prediction from the above Flory argument can be made about the monomer/monomer density correlation exponent on scales smaller than r_a. Inside the swollen cell, a test sphere of radius ρ corresponds to an unswollen sphere of radius $\propto \rho^{5/7}$ initially shared by $\propto \rho^{5/7}$ strands that did not separate upon swelling. The total number of monomers inside the test sphere is thus proportional to $m \sim \rho^{15/7}$. This fixes the Hausdorff dimension of the arrested polymer to $D_a = 15/7$. At larger scales the cells are arranged in a dense way and the dimension is $d = 3$. In summary, the arrested globule is described as an array of “entangled cells” characterized by two exponents: An exponent $\nu_a = 10/7$ describing the internal strand structure inside a cell, and an exponent $D_a = 15/7$ describing the (collective) structure inside a cell. (As mentioned in the Introduction, a short account of the structure of the arrested globule including entanglement/entanglement correlations was already given elsewhere.[15])

From a thermodynamical point of view, the chemical potential of the solvent in the globule has again reached its bulk value in the arrested state. The subsequent stages will proceed under vanishing osmotic pressure, the globule being equilibrated under the remaining topological constraints. In the arrested state, the free energy has not yet completely relaxed. Following the Flory estimate, the energy per cell amounts to

$$F_a \sim N_e^{9/10} \tag{10}$$

as compared to $F_a(t = 0) \sim N_e^{3/2}$ in the initial state. Knowing the structure of the quasi-equilibrated stretched configuration, we can estimate the hydrodynamic relaxation time needed to reach this state: In the spirit of eq 2, we balance the viscous dissipation and the decrease of the free energy. The dissipation is dominated by solvent penetration and hence by the largest scale with velocity

$$V_R = \frac{dR}{dt}$$

The incoming solvent sees the globule as a porous medium of pore size the cell size r. The rate equation finally reads

$$\eta(V_R^2/r^2)r^3 = -\frac{dF_a}{dt} \tag{11}$$

The arrested state is thus approached with the terminal time

$$t_a \sim N^{2/3}N_e^{11/10}/F_a. \tag{12}$$

This relaxation is governed by stress diffusion over the globule radius at arrest with the collective diffusion constant

$$D_c \sim \frac{F_a}{\eta r_a}$$

Inserting the estimate of F_a from eq 10 we obtain $t_a = N^{2/3}N_e^{1/5}$.

B. Swelling of the Arrested Globule. To describe the further swelling from the arrested state, we should look for the dominant energy dissipation mechanism. When the entangled globule is expanding, there are two velocities which characterize this motion: the velocity of the radial expansion of the globule in the solvent: $V_R = dR(t)/dt = n^{1/3}(t)\ dr(t)/dt$, and the velocity V_L of different parts of the polymer chain relative to each other, when the chain is threaded through itself. To estimate this velocity, consider swelling of a whole globule when every elementary cell expands from r to $r + \Delta r$. The total tube length of the polymer chain inside of the entangled cells within a globule was $L^{pol} = nrN_e^{1/2}$. After the r to $r + \Delta r$ expansion the length of a tube is increased to $L^{tube} = n(r + \Delta r)N_e^{1/2}$. But the length of a polymer remains about the same. The difference $L^{tube} - L^{pol} = n\Delta rN_e^{1/2}$ gives the distance which the end of the chain should travel inside the globule. During this threading, some knots disappear (as depicted in Figure 3c), and the number of cells is reduced. For the velocity of threading we obtain

$$V_L = n(t)N_e^{1/2}\frac{dr(t)}{dt} \tag{13}$$

which is always larger than V_R.

In the following, we discuss the lifetime t_d of the arrested state for two different dissipation mechanism. First, we assume that the dissipation is dominated by direct contacts between strands. Assuming that the cell is prevented from expansion by N_e entanglements between any two of $N_e^{1/2}$ subchains in this cell, we conclude that energy stored in each entanglement is about $N_e^{9/10}/N_e \sim 1$ in k_BT units. In the following all estimates will be based on the Flory approach; thus the number of contacts is assumed to scale with the Flory energy of a cell, F_a, for consistency. The minimal distance between monomers of two chains forming an entanglement is comparable to their size. This leads to estimate for the rate of energy dissipation, $\eta(V_L^2/b^2)b^3F_a$ per cell. A balance of dissipating energy similar to eq 2 determines the rate equation:

$$\left(\frac{V_L}{b}\right)^2 b^3nF_a = -F_a\frac{dn(t)}{dt} \tag{14}$$

The lifetime of the arrested state t_d is relevant to the early stages of threading:

$$t_d = N^2N_e^{-3/5} \tag{15}$$

We now assume that the dissipation is dominated by hydrodynamic flows induced by the motion of strands relative to each other. The typical velocity gradients during threading are set by the distance between moving threads in a cell. As dissipation is dominated by the larger scale, the relevant distance is given by

$$d_s \sim r/F_a^{1/3} \sim N_e^{2/5} \tag{16}$$

A balance of dissipating energy similar to eq 2 determines the rate equation:

$$\left(\frac{V_L}{d_s}\right)^2 nr^3 = -F_a\frac{dn(t)}{dt} \tag{17}$$

The characteristic time t_d can be inferred directly from eq 17:

$$t_d \sim \frac{\eta N^2N_e^{3/2}}{d_s^2F_a} \tag{18}$$

Using the values of d_s and F_a by eqs 10 and 16, we obtain

$$t_d \sim N^2N_e^{-1/5} \tag{19}$$

With the overall accuracy of Flory estimates used in derivation of the exponents, this estimate gives the same result as the estimate based on direct friction between the chains, by nature N_e is finite and rather small. As shown previously[15] and further discussed in section 4,

$N_e = 30 \ll N$, the dependence on N_e could be disregarded. For long chains the lifetime in the arrested state is much larger than the time for the globule to get trapped. The lifetime t_d as given above does not cross over smoothly to the terminal time t_a as given by eq 12 when the globule contains only one cell. This suggests a sharp transition when self-entanglements become relevant ($N \sim N_e^{3/2}$). We should remember that the Flory argument gives inaccurate estimates for the energy in a good solvent. A more detailed geometrical argument based on the fractal structure does not alter the results significantly.

Inside knots the concentration may be become quite high and local chain structure may matter. Knots can become glassy and trap the globule in the arrested state. This is not accounted for by our theory.

C. Swelling of an Entangled Dry Globule. In the previous section, we assumed that the penetration of solvent into the globule does not control swelling. We had shown that for the wet globule the energy dissipation from the flow of solvent inside the globule is small compared to the energy dissipation from the threading polymer chain. In the case of a dry globule, the distance between monomers of a polymer chain is comparable to the geometrical size of solvent molecules. This kinematic constraint on the penetration of solvents might control the dynamics. We consider first the possibility of the initial stage of swelling, as the result of which the compact globule becomes stretched by a factor $\alpha = N_e^{1/5} \approx 2$. This is the same problem as swelling of a gel with maximum pore size bigger or smaller than the size of solvent molecule. Whether or not solvent molecules penetrate depends on their size relative to the typical distance between chains (i.e., the pore size of a gel).

Consider first the case when penetration of solvent into the globule is possible. The time needed for wetting can be anomalously long, especially in the vicinity of the critical size.[24] When the globule is wet, the swelling dynamics will be the same as described above for the wet entangled globule.

If solvent cannot penetrate into the globule, or if this process is too slow, we should consider the possibility of the self-reptation of the chain out of the entangled configuration. The main question here is whether there is a net external force pulling the chain out of the globule. Naively one might assume that if one end of a polymer chain is outside the globule and another end is inside, then there is a force pulling the external end out of the globule. More careful consideration suggests that the polymer chain can form several protruding loops pulled out of globule, as depicted in Figure 2b with an equivalent entanglement scheme in Figure 5a. One or two ends of the chain could be hidden inside the globule; in this case there would be a net force pulling them out the globule into the nearest loop, and after short a time both ends will be outside, as in Figure 5c. In this case, the sum of all forces acting on the chain is zero and the time needed for the chain to reptate out of entanglements is about the typical reptation time.

$$t = N^3 N_e^{-1} \tag{20}$$

When comparing this time with swelling time of wet entangled globule given in eq 19, the relaxation time for the dry globule is significantly longer. In ref 19, 1-D polymer loops were considered where reptation is irrelevant and exponentially slow dynamics was found. It should be noted that swelling very dense globules as considered in this section is less universal than for wet ones and may depend on the very details of the interaction and local chain structure.

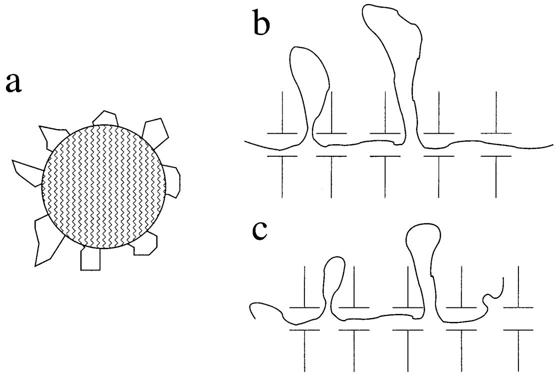

Figure 5. Schematic of the swelling of a dry globule: (a) An initially dry swelling globule consists of a dry core and wet loops. (b) There are forces on a polymer chain pulling toward outside. (c) After some time, both ends of a polymer will be outside and the total force will be zero. The chain then swells according to the self-reptation mechanism.

IV. MD Simulation Results with Comparison to Theory

Here we present MD simulation results on the swelling of globules in different regions of the phase diagram. Our simulation results discussed in section 4.1 covers regions II and IV in the phase diagram shown in Figure 1. To some extent, region III is covered by the Rouse-type simulations presented in section 4.2.

In the following discussion of the simulation methods, standard Lennard-Jones units are employed, with energy in units of $k_B T$. Length is measured in particle diameters, σ, time in $\tau = \sqrt{m\sigma^2/k_B T}$, and mass $m = 1$. Particle pairs which are bonded neighbors along the chain interact through a harmonic potential with a spring constant of 50 $k_B T/\sigma^2$.

A. MD Simulation with Explicit Solvent Particles. 1. Creation of the Initial Dry-Fresh Globule. Dry-fresh globules were created by simulating the collapse of solvated $N = 512$ chains. The collapse simulations were discussed in ref 12. Briefly, 40 individual NVE molecular dynamics (MD) simulations of a single chain in a box of 80 000 solvent particles were performed, with potential parameters chosen such that the equilibrium state is understood to be a collapsed globule. The chains were created as nonreversal random walks with a step length of 0.97σ. All particle pairs (except bonded neighbors) interact via 12−6 Lennard-Jones potentials, which are used to enforce an attractive interaction with a 1$k_B T$ well depth for solvent−solvent and monomer−monomer particle pairs, and pure repulsion for solvent-monomer pairs. For each initial configuration, an MD simulation is run until the radius of gyration of the chain stops changing, indicating a fully collapsed state has been reached. The time step of the simulation is 0.001, and no thermostat was used. Out of these 40, five were chosen at random as “dry-fresh” globules. As size of solvent particle is as large as the size of the monomers, few solvent particles are trapped inside of the collapsed globule; it is therefore “dry”. The initial states for the swelling simulations (described below) are five distinct but statistically equivalent globule conformations immersed in explicit solvent particles.

2. Creation of the Initial Dry-Old Globule. The initial conformation for a dry-old globule was created by growing a random walk of length $N = 512$ in a cubic box that is 30.67σ on a side with periodic boundaries. The walk is grown within a Gaussian confining potential, in which the parameter R_0 represents the "strength"

$$U_{\mathrm{conf}}(r) = \exp\left(-\frac{r^2}{{R_0}^2}\right) \tag{21}$$

where r is the distance of the current particle in the walk from the initial particle. In the growth of the walk, trial steps are accepted or rejected based on a Metropolis criterion. First, the potential at step position r_{i}, $U_{\mathrm{conf}}(r_{\mathrm{i}})$, is evaluated. Then, a uniform random variate X over^{0,1} is chosen. If $X > U_{\mathrm{conf}}(r_{\mathrm{i}})$, then the step is rejected, and new trial steps are attempted (with correspondingly new random variates X) until $X < U_{\mathrm{conf}}(r_{\mathrm{i}})$. After creation of the walk, the confining potential is removed, and 24 000 solvent particles are added at random locations in the box.

After the growth of the walk, the push-off stage MD simulation is performed, while enforcing a time-dependent, radially shifted Weeks−Chandler−Andersen[25] repulsive particle−particle pair potential

$$U_{\mathrm{rs}}(r_{ij}) = \begin{cases} 4\left[\left(\dfrac{1}{r'_{ij}(t)}\right)^{12} - \left(\dfrac{1}{r'_{ij}(t)}\right)^{6} + \dfrac{1}{4}\right] & r'_{ij}(t) < 2^{1/6}, \\ 0 & r'_{ij}(t) \geq 2^{1/6}, \end{cases} \tag{22}$$

where $r'_{\mathrm{ij}}(t)$ is the time-dependent excluded volume radius of pair ij, given as

$$r'_{ij}(t) \equiv r_{ij} + 2^{1/6} b(t) \tag{23}$$

where the factor $b(t)$ decays linearly from unity to zero over the duration of the push-off stage:

$$b(t) = \frac{t_{\mathrm{f}} - t}{t_{\mathrm{f}} - t_{\mathrm{i}}}$$

Here, t_{i} and t_{f} are the initial and final time values of the push-off stage, respectively. During this push-off stage, the Langevin-type thermostat is used, with a friction of $\Gamma = 5.0\tau^{-1}$.[27]

3. Swelling Simulation. For both the dry-fresh and dry-old globules, swelling is simulated using traditional NVE MD. The swelling is initiated by specifying that all particle−particle interactions are repulsive (corresponding to eqs 22 and 23 with $b = 0$), creating an athermal polymer−solvent system for which the equilibrium state is understood to be a coil. The time step in all cases was 0.001τ.

The initial status of the globule can be characterized according to Figure 1. The local correlation function of a globule is related to its age. Local correlations in freshly prepared globules were calculated; the density−density correlations (for brevity, not included) are the same as in a dense liquid. Then we looked at the spatial correlation function $\langle r_{ij}^2 \rangle$ of monomers i and $j = i + s$, which are apart from each other by distance $s = |i - j|$ along the chain. In Figure 6a, the slope of the log−log plot of $\langle r_{ij}^2 \rangle$ vs s depicts the exponent of the internal correlation exponent ν of the fresh globule to be $^2/_3$. Note that at small scales $\nu = 1$, indicating that the corresponding length of segments are equilibrated during the collapse. We expect this equilibrated length scale to grow upon aging. For old entangled globules (which were grown already collapsed rather than "aged"), the initial configurations are Gaussian random walks so that the slope 2ν is 1. The saturation appears due to the finite size of the collapsed globule as the chain segments are reflected at the globule's boundary.

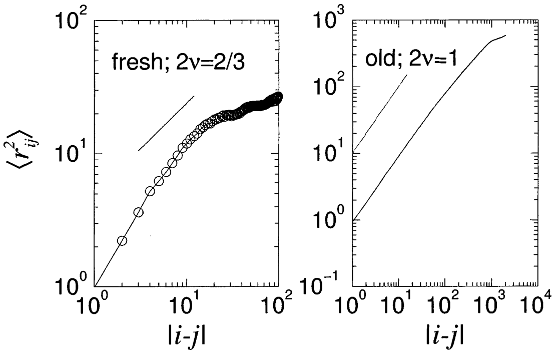

Figure 6. Internal correlation functions, $\langle r^2_{ij} \rangle(t)$, of initial configurations for the fresh (left) and old globule. Shown are lines of slope 2ν.

In Figures 7 and 8, we show the snapshots of swelling fresh and entangled globules ($N = 512$), respectively. Here, the dark spheres are "wet" monomers, defined as those monomers for which the number of contacting solvent particles exceeds N_{c}. For illustrative purposes, we choose $N_{\mathrm{c}} = 8$ for the fresh globule and $N_{\mathrm{c}} = 6$ for entangled globule. As time progresses, in the early stage, the number of wet monomers increases as some loops are formed on the surface of the globule; this behavior is not sensitive to a choice of N_{c} between about 5 and 8. The fresh globule splits into several pieces which are reminiscent of the chain configuration prior to final collapse. The loops on the surface and the bridging monomers between the clusters become wet. Figure 9 shows the slow decay of the wet monomer profile compatible with eq 8 followed by an exponential cutoff (see inset in Figure 9).

In a swelling-entangled globule, loops appear only on the surface of the globule and the whole globule remains as a single piece. The swelling is isotropic. For relatively short chains ($N = 512$), the completely arrested stage is not observed. There are only a few (about three) "entangled cells" per globule on average. In Figure 10, the trace of $R_{\mathrm{g}}(t)$ clearly depicts the difference between the fresh and entangled globule. Swelling of an entangled globule slows down at around $t = 50$ while fresh globule is growing sublinearly ($R_{\mathrm{g}} \sim t^{2/5}$) with respect to time which qualitatively agrees with our prediction (eq 7). The effect of entanglements is less dramatic compared to the larger chain which we will consider in next section. The swelling is arrested in some stretched intermediate state from which the polymer escapes by a slow, albeit effective, self-disentanglement process. One of the five initially prepared aged globules easily escaped from the arrested state. The corresponding $R_{\mathrm{g}}^2(t)$ is shown in Figure 10 between the averaged trajectories of old and fresh globules.

B. Rouse-Type Simulation (No Solvent Particles). Though some slowing down is clearly seen in these explicit-solvent MD simulations, the arrested state

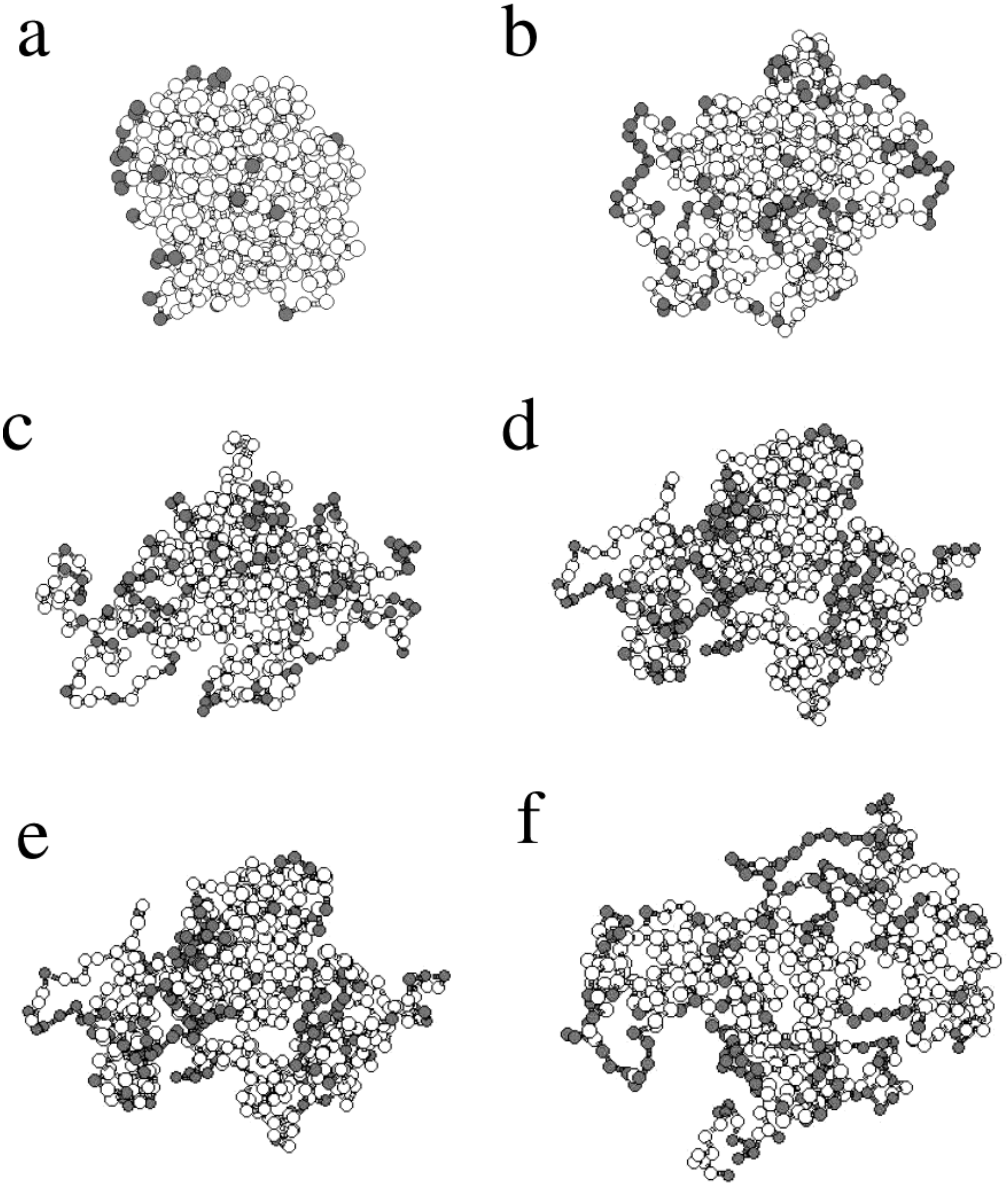

Figure 7. Snapshots of a swelling fresh globule with time interval 100τ. Dark spheres are “wet” monomers, as defined in the text.

attributed to topological constraints reached after swelling of the entangled globule is best seen from the Rouse-type simulations (i.e., without explicitly moving solvent particles) considered in this section, which allow us to simulate chains as large as $N = 100\,000$. No solvent particles were included in the simulations discussed here, which neglects hydrodynamic interactions. The lack of hydrodynamics will obviously influence the disentanglement process. However, the arrested structure itself is not expected to depend on the details of the solvent−polymer dynamics.

We begin with a cubic box with dimension 171σ per side, with periodic boundaries in all directions. We then place the first monomer of the chain at a random location in this box, and define this as the origin. We then grow the random walk from this origin with step size of 0.97σ, with the condition that no step may take the walk beyond a stipulated distance from the origin, R_0. We chose to grow a walk of 100 000 steps in a spherical volume such that the overall particle number density *inside the confining sphere* was $0.85\sigma^{-3}$. Hence, R_0 is 30.4σ. During growth of the walk, if a trial step would lie more than R_0 from the origin, it is thrown out and new trial steps are attempted until one is found that lies within R_0. After the growth of the walk, the push-off stage MD simulation is performed as described previously in section 4.1.2. We examined several push-off stage durations; the one used most commonly was 5000 steps in length, each step 0.01τ for a total time $t_f - t_i$ of 50τ.

In the swelling stage, after the push-off, the full WCA excluded volume potential is used (i.e., $b(t) = 1.0$ in eq 4.1.2). The equations of motion are integrated using the velocity-Verlet algorithm,[26] with a time step Δt of 0.01τ.

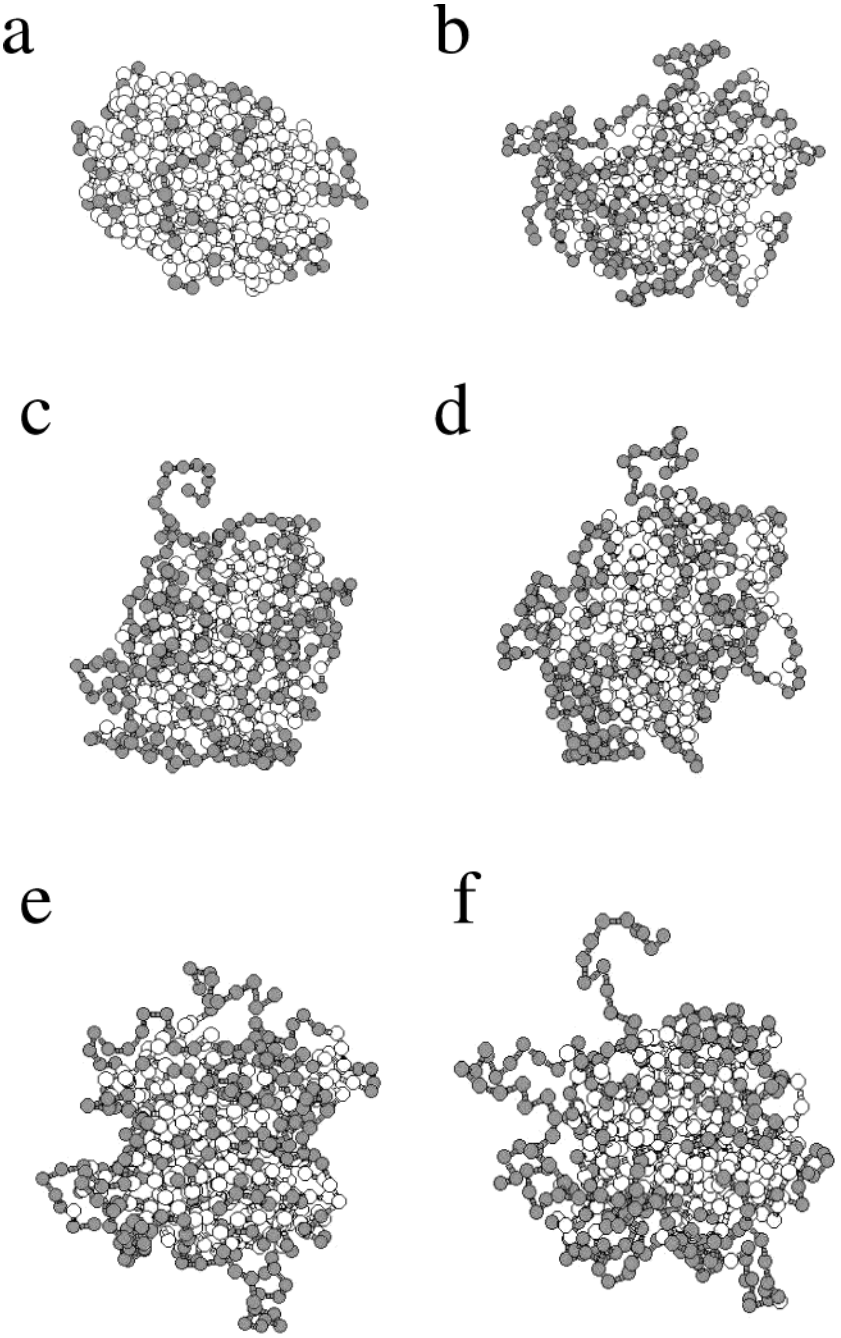

Figure 8. Snapshots of a swelling entangled globule with time interval 100τ. Dark spheres are "wet" monomers, as defined in the text.

In both the push-off and the swelling stages, a Langevin-type thermostat is used to maintain a constant temperature, with friction $\Gamma = 0.5\tau^{-1}$, as before. The set point temperature of the thermostat is 1.0.

Figure 10b shows the squared radius of gyration R_g^2 for this chain ($N = 100\ 000$) as a function of time. After an initially rapid expansion, the globule size saturates at about $t = 4000\tau$, demonstrating the concept of an "arrested state".

In the Introduction, and in our previous work,[15] we pointed out that the structure of the arrested state is characterized by distinct monomer–monomer correlations and entanglement–entanglement correlations. The exponent $\nu_a = 7/10$ describes the internal strand structure via $\langle r_{ij}\rangle \sim |i - j|^{\nu_a}$. We observe excellent agreement with $\langle r_{ij}^2\rangle$ computed from simulation, plotted in Figure 11b, which displays a best-fit exponent of 1.44, giving a computed ν_a of 0.72. The average number of monomers $m(\rho)$ inside the test sphere of radius ρ drawn around a randomly chosen monomer is related to the Hausdorff dimension by $m(\rho) \sim \rho^{D_a}$. The Hausdorff dimension of the entangled cell should be $D_a = 15/7$ up to scale r_a. The structure factor $S(q)$ of the arrested structure is shown in Figure 11a. The Hausdorff dimension is seen only at the intermediate length scale while the large q regime is dominated by surface effects. To avoid the influence of the surface, we compute the real space correlation functions where an average is taken over many test spheres (inside the globule) and arrested globule configurations. At larger scales the globule is a dense packing of cells and the dimension is $d = 3$. The crossover from fractal dimension $D_a = 15/7$ to $d = 3$ is perfectly captured by the simulation results as depicted in Figure 11c.

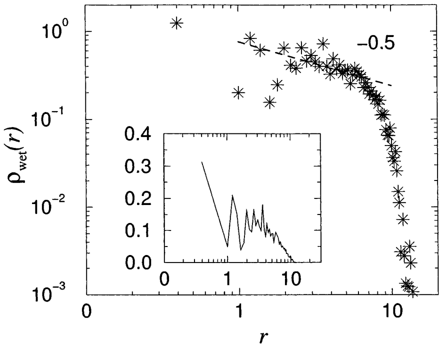

Figure 9. Averaged profile of wet monomers during swelling of freshly prepared globules ($N = 512$, $t = 400\tau$). The semilog inset captures the exponential cutoff.

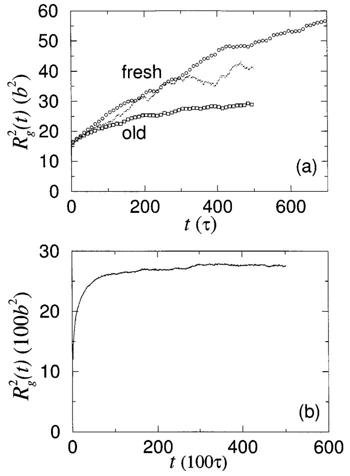

Figure 10. Squared radius of gyration of a swelling chain as a function of time. (a) Initially fresh (○) and old (□) with explicit solvent particles, averaged over five initial globules. The chain length is $N = 512$. R_g^2 for the single "old" globule which most quickly escaped the arrested state is also shown as the dashed curve. (b) The Rouse-type swelling of a chain of length $N = 100\,000$.

This scaling exponent is in excellent agreement with our computer simulation results. This scaling provides a new insight on the nonlocal nature of entanglements. Indeed, if the entanglement could be thought as local constraint, similar to a chemical cross-link, we would expect separation of different chains inside the entangled cell during swelling. Strands would then be stretched ($\nu = 1$) but at a local scale ($\nu = 0.6$). The straight line starting from the monomer size in the scaling data shown in Figure 11 strongly suggests that there is a self-similar picture on all scales below the entangled cell size. This means that during swelling in the presence of topological constraints, separation of different chain strands inside the cell does not occur.

Our data indicate that the number of strands in any given volume is a statistically conserved quantity under the stretching deformation. It is also clear that the picture incorporated in Flory description is oversimplified; structural disorder seen in Figures 4 and 10 indicates that some redistribution of entanglements takes place when they slide and aggregate under stress, as discussed in ref 15.

For such a long chain, the topological relaxation time t_d (eq 18) is by far larger than the computation time, and the chain is never seen to escape from the arrested state.

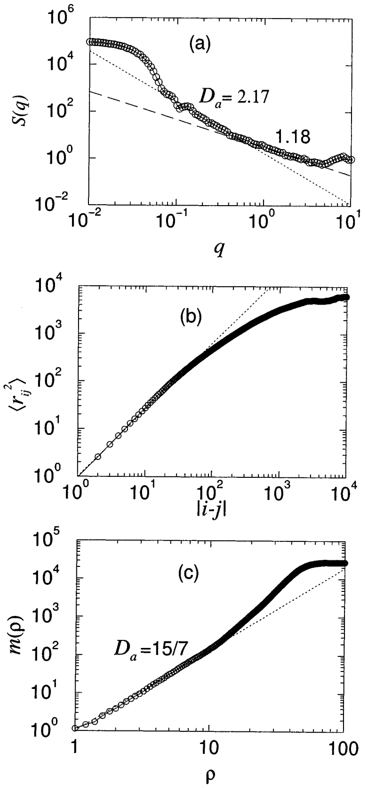

Figure 11. (a) Structure factor $S(q)$ of an $N = 100\,000$ swollen chain at time $t = 50\,000\tau$ computed from MD simulations. The straight line corresponds to the power law $S(q) \sim q^{D_a}$ ($D_a = 15/7$). (b, c) Real space correlation functions of a swelling $N = 100\,000$ globule: (b) single-strand correlation functions at $t = 50\,000\tau$ (arrested), where best-fit value of exponent ν_a from $\langle r^2_{ij} \rangle \sim |i - j|^{2\nu_a}$ is 0.72 and the Flory argument gives $\nu_a = 0.7$ at arrest; (c) number of monomers m vs size of probe sphere ρ showing the collective Hausdorff dimension of $D_a = 15/7$ and the crossover to $D_a = 3$ for the arrested state.

V. Conclusion

We showed that swelling of a collapsed polymer globule is a very intricate problem where aging in the collapsed state and initial compactness play a major role.

A freshly collapsed (fresh) globule has a crumpled structure with internal fractal dimension three and is essentially ready to reexpand. In the simplest fresh-wet case the swelling is homogeneous and the dissipation dominated by the solvent penetration. The swelling time is about the coil relaxation time. A fresh-dry globule is too compact for the solvent to penetrate and only surface monomers are solvated. Swelling proceeds by peeling monomers into loops. The wetting of the initially dry globule is a rather fast process. The wetting step is followed by an expansion step similar to the expansion of an initially wet globule with characteristic time $\propto N^{3/2}$.

The configuration of a polymer chain in an old globule is locally Gaussian with an internal fractal dimension of two. During aging, the density of the globule does not evolve, but the internal structure does. While evolving from crumpled to Gaussian, the globule self-entangles. An old globule can be thought of as a large knot. The additional entanglements formed during aging are topological constraints that are to be released in order to swell the globule back to the coil state. Swelling occurs in two steps. First the globule swells with preserved topology and reaches an arrested state, a step which is relatively fast with a characteristic time increasing as $N^{2/3}$. Subsequently the globule slowly disentangles. We found that the arrested state is characterized by distinct monomer−monomer correlations (with Hausdorff dimension 15/7) and entanglement−entanglement correlations that reflect entanglement sliding.[15] We propose a threading mechanism that allows the wet globule to relax topological constraints in a time proportional to N^2. Finally, the old-dry globule has to disentangle through self-reptation but the dynamics may be dramatically slowed (as it is in glasses).

This work offers several prospects. Structures similar to those in the arrested state exist in swollen, weakly cross-links melts. The behavior of cross-linked entangled gels under tension is also somewhat related as it involves sliding knots. More loosely related problems are healing and coalescence in polymeric systems.

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