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Glassy dynamics in a simple model of a one-dimensional homogeneous polymer

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Abstract

We investigate, using numerical simulations and analytical arguments, a simple one-dimensional model for the swelling or collapse of a closed polymer chain of size N , representing the dynamical evolution of a polymer in a Θ -solvent that is rapidly changed into a good solvent (swelling) or a bad solvent (collapse). In the case of swelling, the density profile for intermediate times is parabolic and expands in space as $t^{1/3}$, as predicted by a Flory-like continuum theory. The dynamics slows down after a time $\propto N^2$ when the chain becomes stretched and the polymer gets stuck in metastable ‘zig-zag’ configurations, from which it escapes through thermal activation. The size of the polymer in the final stages is found to grow as $\sqrt{\ln t}$. In the case of collapse, the chain very quickly (after a time of order unity) breaks up into clusters of monomers (‘pearls’). The evolution of the chain then proceeds through a slow growth of the size of these metastable clusters, again evolving as the logarithm of time. We enumerate the total number of metastable states as a function of the extension of the chain, and deduce from this computation that the radius of the chain should decrease as $1/\ln(\ln t)$. We compute the total number of metastable states with a given value of the energy, and find that the complexity is non-zero for arbitrary low energies. We also obtain the distribution of cluster sizes, which we compare with simple ‘cut-in-two’ coalescence models. Finally, we determine the aging properties of the dynamical structure. The sub-aging behaviour that we find is attributed to the tail of the distribution at small cluster sizes, corresponding to anomalously ‘fast’ clusters (as compared with the average). We argue that this mechanism for sub-aging might hold in other slowly coarsening systems.

1. Introduction

The problem of the dynamics of a single polymer chain has in the past been addressed in many ways, the Rouse model being the simplest theory [1]. In the case where the polymer is not a Gaussian chain, but evolves either towards a swollen or collapsed state, the dynamics can also be studied using more or less elaborate scenarios, either in a phenomenological way (like the ‘sausage’ or ‘necklace’ pictures in the case of the collapse to a compact state [2,3]), via numerics [4] or using analytical methods [5,6]. Although a very common experimental realization of such a dynamical process is the folding or unfolding of proteins as they reach (respectively) their native or denatured state, it has so far been very difficult to test the various theoretical speculations [7].

The dynamics of polymer melts, on the other hand, is much easier to study experimentally [8] and can be compared with some computer simulations [9]. This case exhibits many interesting glassy features, but looks quite different from what happens to a single polymer chain. One can nevertheless learn a lot from these studies, since for a long enough polymer chain that collapses onto itself into a compact conformation, the local environment of a monomer inside a globule is very similar to that of one in a melt. It has recently been speculated that a single homopolymeric [10] or heteropolymeric chain [11] does exhibit some glassy dynamics during the collapse or folding, including aging, at least in an intermediate regime of time before complete folding.

While it is hard to find a satisfactory picture of what happens microscopically as a real polymer chain collapses in three dimensions (either because of the length of computational time for the numerics, or because of the complexity of the analytical approaches involved), one can gain some intuitive understanding by looking at the simpler (but less physical) case of a one-dimensional polymer chain.

In this paper, we investigate theoretically and via Monte Carlo simulations the dynamical behaviour of a single one-dimensional polymer composed of identical monomers that interact via *local* two-body interactions. Our aim is to mimic what happens to a polymeric chain in a good or a bad solvent when it swells towards an expanded coil, or collapses onto a compact globule. We will present some numerical results for both cases, together with some approximate analytical calculations which rationalize these numerical findings. For example, we show that in several situations, the chain constraint (which is difficult to take into account in a rigorous way) can be neglected, and the polymeric chain behaves (at least in some intermediate time region) as an assembly of independent particles ruled by the same type of dynamics.

Finally we will discuss how our results could be compared with real systems that are easier to observe, like polymer melts [9]. The model we present here is in some ways a ‘toy’ model for non-disordered systems where the aggregation interactions are most important, with or without elastic chain constraint. (A realization of this is colloidal gels where glassy cluster patterns appear at high concentrations [12]; however, for this particular experimental case, a scenario in terms of microcollapse events inside the elastic gel structure might be more appropriate [13].)

2. Model and simulations

We consider a string of N particles (monomers), each of which is constrained to live on the sites of a one-dimensional lattice. The elasticity of the chain is enforced by the fact that successive monomers along the chain cannot be at a distance larger than m lattice spacings apart. In our numerical simulations, we have chosen $m = 2$. In our study, the chain is periodic, mainly for practical reasons related to the numerical simulations; the periodic chain and the open chain are expected in our model to behave in the same way, up to some numerical factors. We shall

denote by L the number of sites of the one-dimensional lattice on which the chain actually sits, defining a density of monomers $\rho = N/L$. This length L is actually the measure of the extension of the chain; as we study the dynamics of the chain, this length will evolve with time, and will be referred to as $L(t)$. We assume that the interaction is short range, i.e. two monomers can only interact when they are on the same site. We will call M the number of sites occupied by more than one monomer, and n_i the number of monomers sitting on site i . The total energy E of the chain is therefore

$$E = \frac{v}{2} \sum_{i=1}^M n_i(n_i - 1). \quad (1)$$

where i labels the collection of multiply occupied sites. The interaction parameter v is positive for an excluded volume interaction, which leads to swelling. The ground state and stationary solution of the dynamics is then the fully extended chain, with an end-to-end distance $R \sim N$. For $v < 0$, the interaction is attractive, and we study the collapse of the chain. In this case, the corresponding lowest-lying energy state is a compact 'cluster' of N particles sitting on a unique site. As will be seen in the following, this final state is actually never reached in observable times, as the dynamics slows down dramatically with time.

We shall choose as our initial condition a simple random walk for the chain, corresponding to an equilibrium configuration in the non-interacting case $v = 0$. The typical initial size of the chain is therefore $\sim \sqrt{N}$.

During the Monte Carlo simulation, we do not allow collective motion of monomers but only individual moves. At each step, a monomer is allowed to move to one of its neighbouring sites as long as the distance between its new position and the neighbouring monomers along the chain is $\leq m$. In addition a monomer move is accepted according to a Metropolis criterion: if δE is the energy difference between the new configuration and the initial configuration, then this move is accepted with probability $p = \min[1, \exp(-\delta E/T)]$ where T is the temperature. If one monomer on site i is moved to site j , the energy change δE is given by

$$\delta E = \frac{v}{2} [(n_j + 1)n_j + (n_i - 1)(n_i - 2) - n_j(n_j - 1) - n_i(n_i - 1)] = v(n_j - n_i + 1).$$

In the following we will choose $v = \pm 1$, corresponding respectively to swelling or to collapse. The quantities of interest are primarily based on the density profile $n(x, t) = n_i(t)$, where $x = ia$ (a is the lattice spacing, and i labels here all sites). We will consider for example the radius of gyration, $R(t)$, defined as

$$R^2(t) = \frac{1}{N} \sum_x x^2 n(x, t) - \left(\frac{1}{N} \sum_x x n(x, t) \right)^2.$$

Note that for a fully stretched chain, which is the ground state of the chain in the repulsive case ($v < 0$), the maximum value of R is, for $m = 2$, $(\frac{1}{N} \int_{-N/2}^{N/2} x^2 dx)^{1/2} = N/\sqrt{12} \sim 0.28N$.

3. Repulsive case: swelling of the chain

3.1. Numerical results

We have investigated the behaviour of the gyration radius $R(t)$ for different chain sizes and different temperatures T , including $T = 0$. Interestingly, the different results can be rescaled on top of each other by plotting $r = R/N$ as a function of $\tau = t/N^2$ (see figure 1). There is a well defined regime of time scales where one finds $r \propto \tau^{1/z}$, with $z \simeq 3$, which holds when $r \ll 1$. When r becomes of order 1, the chain becomes substantially stretched, and the

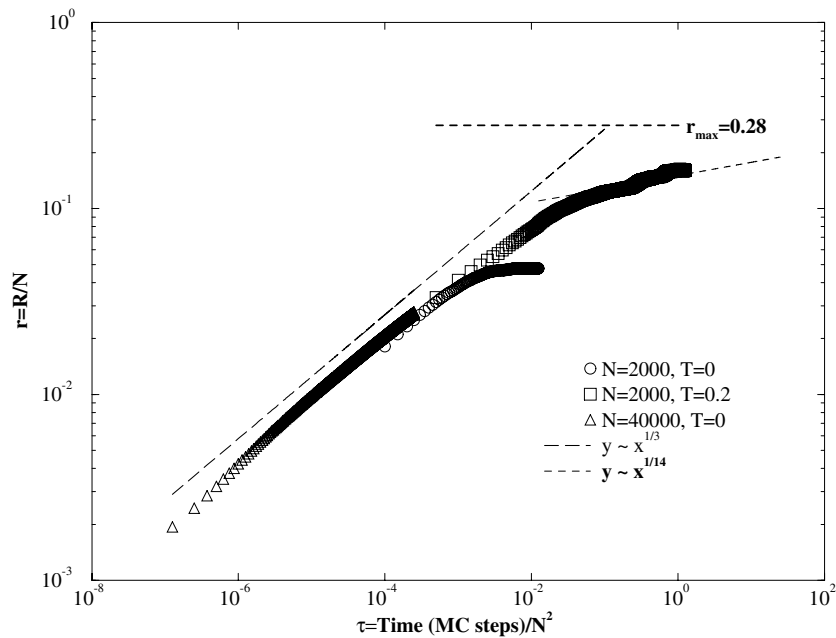


Figure 1. In this graph we plot $r = R/N$ versus $\tau = t/N^2$ for various chain lengths and various temperatures. These are all single runs (no averaging over initial conditions). One can see that there is a well characterized $\tau^{1/3}$ regime for intermediate times. At zero temperature, the chain gets stuck in a metastable state and r saturates to a value much smaller than its maximum value $r_{\max} = 0.28$ (shown as a dashed line). At non-zero temperature, r is in fact logarithmic in time at long times (see section 3.3).

dynamics stops (at zero temperature) or becomes activated (for non-zero temperatures). The scaling $r \propto \tau^{1/3}$ does not hold at very short times either, but sets in after a time $t_c \sim \sqrt{N}$; we observed that the short time behaviour is linear in time. This initial time regime, up to times where $r \sim 1$, is found to be independent of the chain constraint up to a rescaling of time, and can be explained from the simple theories developed below. The chain constraint only starts to play a role when $r \sim 1$, i.e. for $t \sim N^2$.

The dynamics of the whole density profile $n(x, t)$, starting from the initial configuration, is also interesting: after a short transient time t_c (< 100 Monte Carlo (MC) steps for $N = 10\,000$) the profile $n(x, t)$ smoothes to a parabolic form that expands gradually in space (see figure 2). This expansion is self-similar in time and can be well fitted at large times by

$$n(x, t) = n_0(t) \left[1 - \left(\frac{2x}{L(t)} \right)^2 \right] \quad (2)$$

where $\pm L(t)/2$ are the points where the density vanishes. We find that the data are compatible with $z = 3$. This form suggests that $n_0(t) \propto 1/L(t)$, as expected for a scaling profile. For such a parabolic profile, the mean-squared radius is given by $R = L(t)/2\sqrt{5}$.

Again, it is important to note that, except for the very last stages of the swelling, the results are very similar whether the chain constraint is present or not; we will also discuss this feature in the following section.

In the next section, we present different analytical approaches for describing the swelling mechanism in order to account for the above numerical results.

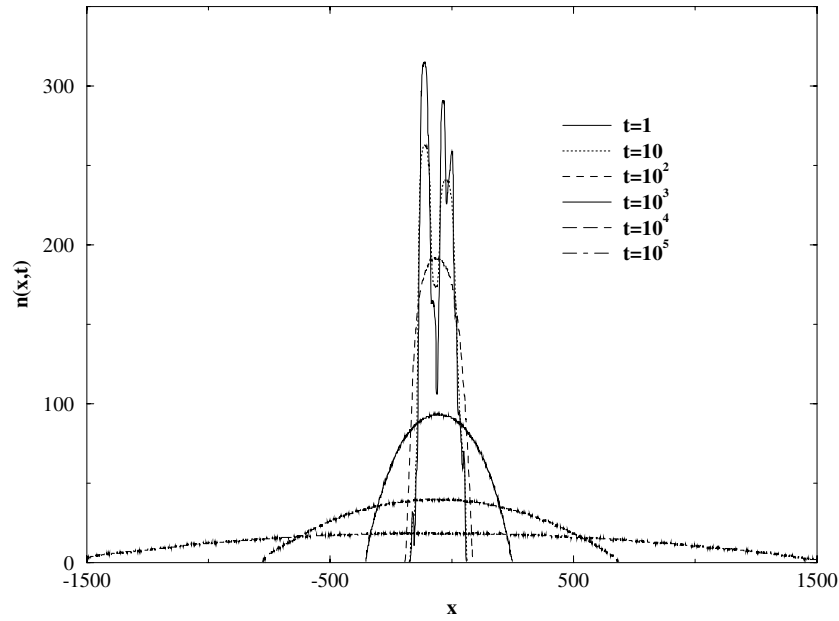


Figure 2. Profiles $n(x, t)$ of the chain as it swells from a random initial configuration, at times $t = 1, 10, 10^2, \dots, 10^5$, with $N = 10\,000$. The profile quickly becomes parabolic and expands in space as $t^{1/3}$.

3.2. Analytical theories for the swelling dynamics

3.2.1. A Flory theory. A very crude analytical approach for the dynamics of the chain can be derived from a dissipative equation of motion for a polymer of size R , combined with a Flory approximation for the free energy $\mathcal{F}(R)$. The Flory free energy is, as usual, written as the sum of an entropic contribution and an excluded volume interaction contribution. The resulting equation reads

$$\frac{\partial R}{\partial t} = -\mu_{\text{chain}} \frac{\partial \mathcal{F}(R)}{\partial R} = -\frac{\mu_0}{N} \frac{\partial}{\partial R} \left(\frac{R^2}{N} + v \frac{N^2}{R^d} \right) \quad (3)$$

where μ_{chain} is the mobility of the chain. It is well known [1] that the mobility for a chain is $\mu_{\text{chain}} = \mu_0/N$, where μ_0 is the mobility of a single monomer. The exact solution for this differential equation can actually be computed, and for an initial condition $R(t=0) = R_0$, reads:

$$R(t) = \exp\left(-\frac{2\mu_0 t}{N^2}\right) \left\{ R_0^{d+2} + \frac{vdN^3}{2} \left[\exp\left(\frac{2(d+2)\mu_0 t}{N^2}\right) - 1 \right] \right\}^{\frac{1}{d+2}}. \quad (4)$$

For an ideal chain initial condition, one has $R_0 \simeq \sqrt{N}$. Therefore, in the regime where $N^{d/2}/v \ll \mu_0 t \ll N^2$, the initial condition term $R(0)^{d+2}$ can be neglected, and one finds

$$R(t) \simeq \left(\frac{d(d+2)}{2} v \mu_0 N t \right)^{\frac{1}{d+2}}. \quad (5)$$

Note that in this time regime the elastic part in the Flory free energy (which comes from the chain constraint) does not play any role and one therefore expects the same scaling to be valid for an ensemble of non-connected repulsive particles, in the intermediate time regime mentioned above. As discussed above, this is indeed what we find numerically, up to a rescaling of time.

In one dimension, the Flory theory predicts a power law behaviour $R(t) \propto N^{1/3}t^{1/3}$ —both scalings in rather good agreement with the numerical results. The very short time behaviour predicted by this approach reads

$$R(t) \simeq R(0) \left(1 + \frac{v \, dN \mu_0 t}{R(0)^{d+2}} \right). \quad (6)$$

In one dimension, the departure from the initial condition is therefore $R(t) = R(0) + \Gamma_F t^{\gamma_F}$ where $\gamma_F = 1$ and Γ_F is independent of the number of monomers N . This approach therefore predicts that for short times $R(t)/\sqrt{N}$ is a function of t/\sqrt{N} , in reasonable agreement with our numerical data.

A slightly more refined theory (but still in the spirit of Flory) actually allows one to understand the parabolic shape of the density profile. One can write a master equation for the number of particles sitting on site i

$$\frac{\partial n_i}{\partial t} = \sum_j W_{ij} n_j(t) - \sum_j W_{ji} n_i(t) \quad (7)$$

where the transition probabilities at finite temperature $T = 1/\beta$ are chosen to be

$$W_{ji} = W_{i \rightarrow j} = w_0 \Theta(n_j - n_i)$$

$$\Theta(n_j - n_i) = \frac{\exp\left(\frac{v\beta}{2}[n_i - n_j - 1]\right)}{\exp\left(\frac{v\beta}{2}[n_i - n_j - 1]\right) + \exp\left(-\frac{v\beta}{2}[n_i - n_j - 1]\right)}.$$

(Here a Glauber type of dynamics is used to ensure that the transition probabilities verify $0 \leq W_{ji} \leq w_0$.)

In the simplest case where we allow moves to both nearest-neighbour sites, we require the condition that $W_{ij} = W_{ji} = 0$ if $|i - j| \geq 2$. We neglect the chain condition, which is expected to be a valid approximation in the short time limit. We also assume (which will be valid in the swelling case), that the density profile is smooth, so that one can expand $\Theta(\Delta n) \simeq \Theta_0 - \beta v \Delta n \Theta_1$. The master equation then becomes, in one dimension ($d = 1$), after taking the continuum limit in space and with $g = \beta v \Theta_1 / \Theta_0$

$$\frac{\partial n(x, t)}{\partial t} = [\nabla^2 n + 2g \nabla(n \nabla n)]. \quad (8)$$

Let us note that the derivation of this continuous equation relies on the assumption that $\beta v |n_{i+1} - n_i| \ll 1$. This may be acceptable in the case of repulsive interactions ($v > 0$), where the profiles $n(x, t)$ turn out to be smooth, so that the number of monomers on neighbouring sites is almost the same. Surprisingly, however, this nonlinear equation also gives a very good description of the zero-temperature results in the long time limit. This is not true in the case of attractive interactions ($v < 0$): the above equation then becomes unstable (this corresponds to a ‘pearling instability’ in the collapse regime described in section 4).

The nonlinear diffusion equation (8) admits a self-similar solution for the profile $n(x, t)$, of the form

$$n(x, t) = \frac{N}{R_s(t)} f\left(\frac{x}{R_s(t)}\right) \quad (9)$$

where $R_s(t) \equiv t^\alpha N^\delta$ is the scaling form for the end-to-end distance of the chain in the intermediate time regime that we study, and f is a scaling function independent of both t and N . Introducing the rescaled variable $u = x/R_s(t)$ in equation (8), we can solve the differential equation for $f(u)$ in the case where the diffusion term can be neglected (this can be checked *a posteriori* to be valid). This fixes the values of both exponents: $\alpha_F = 1/3$ and $\delta_F = 1/3$, which gives back the results of the Flory equation of motion for $d = 1$. Furthermore, the resulting

ordinary differential equation for $f(u)$ has a parabolic solution. The final result, normalized to give the correct number of monomers, is equation (2), with $n_0(t) = N^{2/3}t^{-1/3}(3/64g)^{1/3}$ and $L(t) = 2(9gNt)^{1/3}$, in qualitative agreement with the numerical results of figure 2 (obtained at zero temperature).

3.3. Late stages of the dynamics

It can be observed from the Monte Carlo simulations (see figure 1) that the dynamical evolution becomes frozen at $T = 0$, while it is strongly slowed down at finite temperatures.

It is clear that the chain is trapped for long periods of time in metastable configurations, consisting of fully stretched segments of the chain going alternatively to the left or to the right. If we call the total number of segments $2P$ and ℓ is their average size, the typical extension of the chain in such a configuration is $R \sim \ell\sqrt{P}$. Since $N = 2P\ell$, one has $R \sim N/\sqrt{P}$ or $P \sim r^{-2}$. The dynamics of the chain in the long time region therefore consists of a slow ‘coarsening’, where ‘kinks’ progressively disappear, leading to a decrease of P . The time needed for a hairpin of size ℓ to disentangle can be estimated from the energy barrier to be crossed, which is proportional to ℓ itself. Therefore, one has $\ln t(\ell) \sim \beta v \ell \sim \beta v N r^2$. From this argument, we obtain a logarithmic growth law for the size of the chain in the long time regime

$$R \sim \sqrt{\frac{N}{\beta v} \ln t} \quad (10)$$

in qualitative agreement with the numerical simulations (a good logarithmic fit of the radius of gyration is possible in the last stages of the stretching process). The above estimate assumes that all segment lengths are close to the average value. This is confirmed by an analytical calculation of the number of metastable states of the stretching chain [14].

4. Attractive case: collapse of the chain

4.1. Numerical results

The case of attractive interactions can be studied numerically in the same way as before, except that now the interaction parameter v is negative. In this case, obviously, the ground state of the chain is such that all monomers are located on the same site. As the chain collapses, the profile $n(x, t)$ very quickly becomes discontinuous as monomers aggregate in well separated ‘clusters’ (see figure 3).

These clusters are very slow to coalesce and the dynamics becomes slower and slower as time increases (and as the temperature T decreases). This slowing down is due to the fact that it is energetically very unfavorable to ‘break’ one of these clusters in order to transfer its monomers to larger clusters. The energy needed to remove one monomer from a cluster containing n monomers is equal to $n|v|$ (for large n), corresponding to a time $\propto \exp(\beta|v|n)$. Therefore, the system remains trapped longer and longer in configurations where there are M clusters containing $n \sim N/M$ particles. It is interesting to note that the dynamics of clusters is very close to that of the one-dimensional ‘backgammon’ model introduced in [17] and further studied in [18, 19]: although the barriers are ‘entropic’ in the latter model, the average time needed to empty a cluster also grows exponentially with its size n .

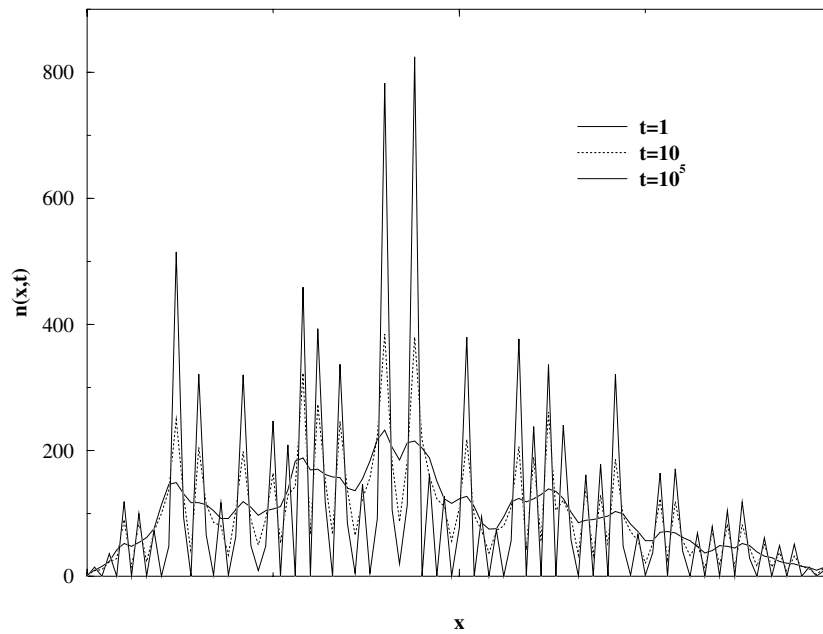


Figure 3. Profiles $n(x, t)$ of the chain as it collapses from a random initial configuration, for $T = 5$, at times $t = 1, 10, 10^5$. The profiles obtained for $t = 10^2, 10^3$ and 10^4 are indistinguishable to the eye from that for $t = 10^5$.

4.2. Calculation of the number of metastable states

A metastable state of lifetime t is a configuration of clusters which remains frozen for a time t . This means that (i) two clusters cannot be nearest neighbours and (ii) the minimum number of monomers in each of the clusters at temperature T is at least equal to $k^*(t, T) = \max(2, T \ln(t))$ since a cluster must contain at least two monomers. How many such configurations are there? This is a combinatorial problem including two steps: first count the number of configurations with N monomers and M clusters each containing more than k^* monomers, then count the number of arrangements of M clusters on a one-dimensional array of L sites, so that all clusters are separated by at least one ‘empty’ site. We will restrict ourselves to the case where the chain constraint is $m = 1$, i.e. two consecutive monomers cannot be at a distance greater than 1. In this case, the number of monomers within a ‘hole’ is exactly equal to 2, because the chain is closed onto itself. Therefore, the total number of monomers belonging to clusters is related to the length L occupied by the chain by

$$\sum_{i=1}^M n_i = N - 2(L - M). \quad (11)$$

We refer the reader to [14] for the details of the calculation. The number of configurations $\mathcal{N}_{k^*}(M|N)$ with at least k^* monomers in each cluster can be calculated using the following formula, and performing a saddle point approximation in the large N limit

$$\mathcal{N}_{k^*}(M|N) = \sum_{n_1=k^*}^N \cdots \sum_{n_M=k^*}^N \delta \left(\sum_{i=1}^M (n_i - 2) - N + 2L \right). \quad (12)$$

Then the number of ways $\mathcal{N}_L(M)$ to arrange M clusters on L sites with all the clusters at least separated by an empty site can be evaluated exactly [14]. We now combine the two

results, and deduce the total number of k^* -stable configurations for a given density ρ

$$\mathcal{N}_\rho(k^*) \equiv e^{N S_\rho(k^*)} = \sum_{M=1}^N \mathcal{N}_L(M) \mathcal{N}_{k^*}(M|N). \quad (13)$$

This is again computed from a saddle point (in M) and leads to

$$S_\rho(k^*) = \left(-1 + \frac{2}{\rho} + \delta(k^* - 2)\right) \ln \left(\frac{1 - \frac{2}{\rho} - \delta(k^* - 2)}{1 - \frac{2}{\rho} - \delta(k^* - 3)}\right) - \delta \ln \left(\frac{\delta}{1 - \frac{2}{\rho} - \delta(k^* - 3)}\right) \\ - \delta^* \ln \left(\frac{\delta^* \rho (1 - \delta^* \rho)}{(1 - 2\delta^* \rho)^2}\right) + \frac{1}{\rho} \ln \left(\frac{1 - \delta^* \rho}{1 - 2\delta^* \rho}\right).$$

In this expression, δ^* is the saddle point value of δ , defined as

$$\frac{[1 - \frac{2}{\rho} - \delta^*(k^* - 2)]^{k^* - 2} [1 - \frac{2}{\rho} - \delta^*(k^* - 3)]^{3 - k^*}}{\delta^*} \frac{(1 - 2\delta^* \rho)^2}{\delta^* \rho (1 - \delta^* \rho)} = 1. \quad (14)$$

At zero temperature, all metastable states are frozen, and the size of the chain L and therefore the density ρ are constant in time. One can estimate the complexity by setting $k^* = 2$ in the previous formulae. We found numerically the solutions of the above equations for $\delta^*(\rho)$ and $S(\rho)$ [14].

It is interesting to draw an analogy with some recent work on the number of metastable states in spin-glasses [15]. As k^* increases, one counts configurations which are more and more stable. Similarly, in spin-glasses, one can introduce k^* -spin flip stable configurations, i.e. configurations the energy of which cannot be lowered by any flip involving at most k^* spins. The complexity of these states was determined for simple spin-glasses by Biroli and Monasson [15]. They show that in mean-field models, inherent states (corresponding to 1-spin flip stable states), pure states and k^* stable states all coincide. But they also show that in finite dimensions (in contrast to infinite connectivity models) all these different concepts are distinct and actually help to visualize the degree of freezing of a glassy system, according to the lifetime of the metastable states relevant after a certain time scale. In the following section, we will show that the analysis of the relevant metastable states of a collapsing polymer allows one to predict how the radius of gyration of the chain decreases with time.

4.3. Consequences for the evolution of the chain at non-zero temperatures

At non-zero temperatures, the relevant metastable states after a time t are such that $k^* \sim T \ln t$. Furthermore, it is reasonable to assume that the chain size is such that the number of metastable states is maximal, that is to say, the chain is in one of its most probable configurations after a time t . We thus maximize the entropy and obtain $\rho(t) = \rho^*(t)$ (and therefore $L(t) = N/\rho^*(t)$) by setting

$$\left. \frac{dS_\rho(k^*)}{d\rho} \right|_{\rho=\rho^*} = 0. \quad (15)$$

Solving for ρ^* and δ^* in the large $u = T \ln t$ limit, we finally find a slow decrease of the number of clusters and an extremely slow decrease of the size of the chain

$$M(t) \sim \frac{1}{T \ln t} \quad L(t) \sim \frac{1}{4 \ln(T \ln t)} \quad S(t) \sim \frac{2 \ln(T \ln t)}{T \ln t}. \quad (16)$$

This last result is quite interesting and is a non-trivial consequence of the present calculation of the complexity of metastable states. It is obviously very hard to check numerically, but suggests an extremely slow contraction of the chain. Numerically, we indeed find that the chain length hardly decreases with time.

4.4. Calculation of the density of metastable states at fixed energy

We now turn to the calculation of the number of metastable states corresponding to a certain degree of freezing k^* , and to a fixed total energy of the system E . The calculation proceeds in much the same way as in the previous section, starting from the expression for the number of k^* -stable configurations with M clusters and N monomers, at fixed energy E

$$\mathcal{N}_{\rho, k^*}(E, M|N) = \sum_{n_1=k^*}^N \cdots \sum_{n_M=k^*}^N \delta \left(\sum_{i=1}^M (n_i - 2) - N + 2L \right) \\ \times \delta \left(\sum_{i=1}^M -\frac{1}{2}n_i(n_i - 1) - (L - M) - E \right).$$

As in section 4.2, the computation is done in the case $m = 1$ and one must therefore distinguish between the contribution of the clusters and the contribution of ‘holes’ containing exactly two monomers. Setting $\epsilon = E/N < 0$, one can solve the problem and find $S_\rho(\epsilon, k^*)$, the complexity per monomer. All curves $S_\rho(\epsilon, k^*)$ for different k^* actually follow a common envelope for a given ρ , and asymptotically approach the following law at very low energies

$$S_\rho(\epsilon) \underset{\epsilon \rightarrow -\infty}{\simeq} -\frac{\ln(-\epsilon)}{\epsilon} \left(1 - \frac{2}{\rho}\right)^2 \\ + \frac{1}{\epsilon} \left(1 - \frac{2}{\rho}\right)^2 \left\{ -1 + \frac{1}{2} \ln \left[\frac{\rho}{4} \left(1 - \frac{2}{\rho}\right)^{3/2} \right] \right\} + \mathcal{O}\left(\frac{1}{\epsilon^2}\right). \quad (17)$$

For large times $\rho \rightarrow \infty$, and we are left with:

$$S(\epsilon) \underset{\epsilon \rightarrow -\infty}{\simeq} -\frac{\ln(-\epsilon)}{\epsilon}. \quad (18)$$

Even for very low energies, the entropy of metastable states never reaches zero: in contrast to the example of spin-glasses, there is no lower cut-off in the energy per monomer below which the number of metastable states is not exponentially large in N .

4.5. Distribution of cluster sizes

Let us define $p(n, t)$ as the distribution of sizes of the clusters, at a given time t and temperature, n being the number of monomers in a given metastable cluster. We further define \bar{n} as the average number of monomers in a cluster. From the above sections, we know that $\bar{n}(t)$ grows slowly (logarithmically) with time. We have studied $\bar{n}p(n, t)$ as a function of $z = n/\bar{n}$ at different times (figure 4). These different curves collapse well onto a single one (note, however, that the range of variation of \bar{n} cannot be very large). The scaling function \tilde{p} is very far from a simple exponential, as a naive maximum entropy argument would suggest. In particular, the tail of \tilde{p} can be fitted as a power law $\tilde{p}(z) \sim (z + z_0)^{-1-\nu}$, with $\nu \simeq 1.9$. For small z , on the other hand, $\tilde{p}(z)$ vanishes rapidly. Although our statistics are not very good, one can fit $\ln \tilde{p}(z)$ as $-(z_1/z)^c$, with $c \sim 1$.

The present cluster dynamics is actually quite similar to the so-called ‘cut-in-two’ model introduced by Derrida *et al* [16] to describe the pattern of coalescing droplets in one dimension. In the latter model, a collection of intervals of different sizes (which represent the droplets) evolves according to the following simple rule: one picks the smallest interval, divides it in two equal parts and sticks the right part to the right neighbour, while the left part coalesces with the left neighbour. In this model, the average size of the intervals grows with time, and the rescaled distribution of interval sizes tends to an asymptotic distribution as shown

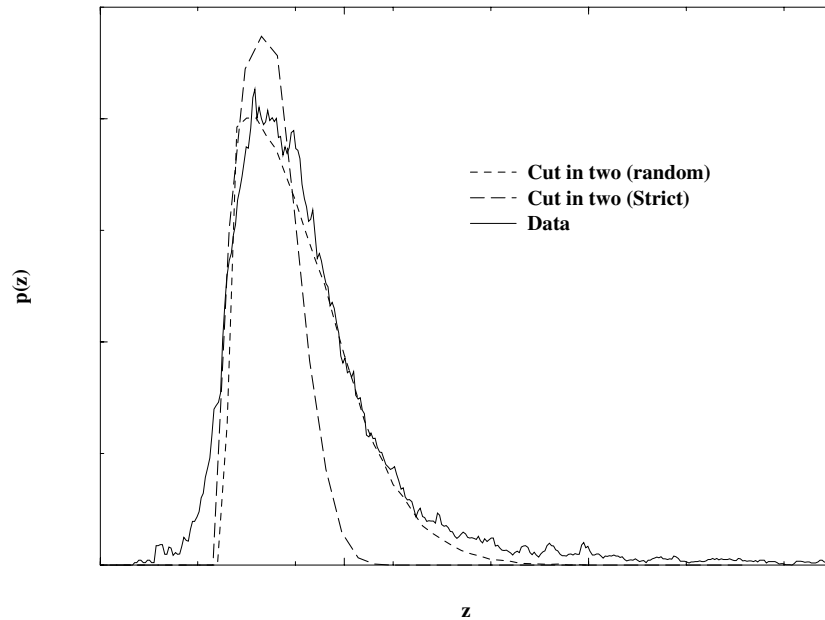


Figure 4. Comparison of the distribution of the cluster sizes in our model with the ones corresponding to a strict cut-in-two model and a randomized cut-in-two model. Note that the density of small clusters strictly vanishes in the latter two models.

in figure 4. The cluster dynamics studied here is similar for the following reason: because the time needed to empty one cluster is exponentially related to its size, the first cluster to disappear will typically be the smallest one available after time t . If one neglects the chain constraint, the smallest cluster empties itself by sending an equal number $n/2$ (on average) of monomers towards its two immediate neighbours. The analogy is not exact, though, since this number is not exactly equal to $n/2$ at each iteration; furthermore, some subtle correlations are induced by the chain constraint. One can nevertheless take the simple ‘cut-in-two’ model, or a randomized version where a random fraction f is pasted to the left and $1 - f$ to the right, as a benchmark with which we can compare our results. This is performed in figure 4. The agreement is only fair, and is better for the randomized model than for the strict cut-in-two version, for which $\tilde{p}(z)$ is known to decay exponentially for large z [16]. Note, however, that the density of small clusters strictly vanishes below a certain value z_c in the cut-in-two model, whereas it is finite in the present dynamics. This is due to the fact that although small clusters are typically the first ones to disappear, fluctuations can persist and keep some small clusters alive, whereas by definition they systematically disappear with a cut-in-two rule. The excess density of small clusters has the interesting consequence, discussed below, of giving rise to a sub-aging behaviour.

4.6. Aging at long times

Another manifestation of the long-lived metastable states is the aging phenomenon, which we have investigated numerically by computing the following age-dependent *structure factor*:

$$C_q(t + t_w, t_w) = \frac{1}{N} \sum_{i=1}^N \langle \exp\{iq[x_i(t + t_w) - x_i(t_w)]\} \rangle \quad (19)$$

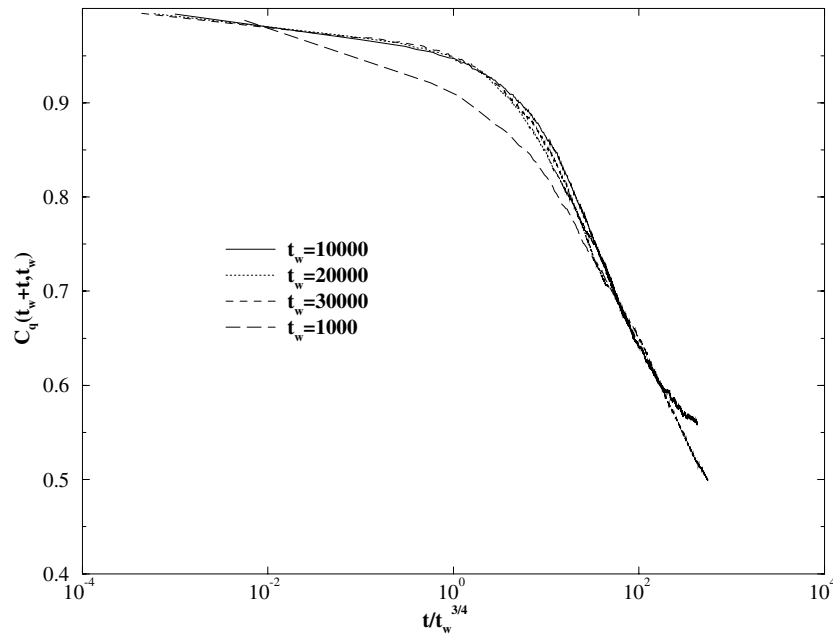


Figure 5. Evidence for aging in the structure factor, for $N = 10\,000$, $q = 5$, $T = 5$, averaged over ten initial conditions. The curves for $t_w = 10^4$, 2×10^4 and 3×10^4 superimpose when plotted as a function of $t/t_w^{3/4}$. The curve with $t_w = 1000$, however, has a different shape. The mechanism proposed in the text suggests that the scaling in t/t_w^μ should indeed only be approximate.

where x_i is the position of monomer i . This quantity is expected to depend both on t_w and t (violation of time translation invariance) in the out-of-equilibrium regime where $T \log t_w \ll N$. As can be seen from figure 5, obtained for $T = 5$, $N = 10\,000$ and averaged over 10 initial configurations, the relaxation becomes slower and slower as t_w increases. As is often observed experimentally [20–22], we have found that the data can be rescaled in the variable $s = t/t_w^\mu$, with $\mu < 1$ (sub-aging). Within the time regime probed by the MC, $\mu \sim 0.75$ for $q = 5$ and 10. This means that the characteristic relaxation time grows more slowly than the waiting time itself. In the present situation, this can be interpreted following the above remark about the small- z behaviour of $\tilde{p}(z)$: the presence of clusters much smaller than the average size \bar{n} means that some clusters will evolve on a time scale much shorter than $t_w = \exp(\bar{n}/T)$. More precisely, one can approximate the short time behaviour of $C_q(t + t_w, t_w)$ by

$$1 - C_q(t + t_w, t_w) \simeq t \int dz z \tilde{p}(z) \exp(-z\bar{n}/T). \quad (20)$$

The above equation is obtained by assuming that each cluster of size n contributes to the correlation function as $n \exp(-t/\tau(n))$ where $\tau(n) = \exp(n/T)$. If $\ln \tilde{p}(z)$ behaves as $-(z_0/z)^c$ for small z , a saddle-point approximation of the above integral leads to

$$1 - C_q(t + t_w, t_w) \propto \frac{t}{t_w^\mu} \quad \mu = \left(1 + \frac{1}{c}\right) \left(\frac{cz_0^c}{\ln t_w}\right)^{\frac{1}{1+c}}. \quad (21)$$

This scenario therefore leads to a sub-aging behaviour for large t_w , albeit with a (slowly) time-dependent exponent μ . The absence of ‘small’ clusters would correspond to the limit $c \rightarrow \infty$, such that $\tilde{p}(z < 1) = 0$. In this case, one finds $\mu = 1$ as expected. The rescaled function

$C_q(s)$ can be fitted by $K/(s_0 + s)^w$, where K is a numerical constant and $w \simeq 0.18$ for $q = 5$ and $w \simeq 0.10$ for $q = 10$.

The above mechanism for sub-aging might be much more general, and hold for other slowly coarsening systems such as the random field Ising model. Suppose that the distribution of domain sizes scales with an age-dependent average length $\bar{R}(t_w)$, such that $t_w \sim \exp(\bar{R}^\psi/T)$ [23]. Then the presence of domains smaller than $\bar{R}(t_w)$ will correspond to relaxation times much shorter than t_w , and therefore to the possibility of sub-aging effects.

5. Summary and conclusion

We have investigated a simple one-dimensional model for the swelling or the collapse of a closed polymer chain of size N , representing the dynamical evolution of a polymer in a Θ -solvent that is rapidly changed into a good solvent (swelling) or a bad solvent (collapse).

The system studied here falls into the category of non-disordered, finite-dimensional models exhibiting glassy dynamics. The list of such models keeps increasing with time [24], although the present model is quite realistic (no *ad hoc* dynamical rules or long-ranged interaction). Actually the chain constraint does not play a very important role in the dynamics of collapse which is, as mentioned above, quite close to the one-dimensional version of the backgammon model.

In real polymeric systems, the presence of a chain would change quantitative features such as diffusion coefficients. Polymer melts have been shown to behave very similarly to structural glasses such as binary mixtures of Lennard-Jones particles [9]. These polymeric systems are out of equilibrium at long times and attempts have been made to describe them within the framework of the mode-coupling theory [9, 11].

A limitation of the present model in the collapsing regime is the unrealistic nature of the interaction potential: there is no hard-core constraint, and the range of the attractive part is finite. For realistic potentials, the total energy of a cluster containing n monomers will eventually grow like n for large n and not like n^2 . Correspondingly, the energy barrier to remove one monomer from a large cluster is finite, instead of being of order n . Furthermore, the long-ranged part of the attractive potential can speed up the dynamics by making the large clusters move towards each other, an effect absent in the present model. Nevertheless, the model used here could be justified for colloidal particles of the type studied in [12]. In this system, clusters of particles form and slowly coalesce, which leads to a very clear aging of the dynamical structure factor. A closer comparison between our model and such experiments has been performed in [13] and requires the inclusion of elastic deformations, as suggested in [12].

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