Glassy effects in the swelling/collapse dynamics of homogeneous polymers

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Abstract

We investigate, using numerical simulations and analytical arguments, 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 $\Theta$-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, that we compare to simple ‘cut-in-two’ coalescence models. Finally, we determine the aging properties of the dynamical structure. The subaging behaviour that we find is attributed to the tail of the distribution at small cluster sizes, corresponding to anomalously ‘fast’ clusters (as compared to the average). We argue that this mechanism for subaging might hold in other slowly coarsening systems.

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1 Introduction

The problem of the dynamics of a single polymer chain has been addressed in many ways over the past, the Rouse model being the simplest theory [2]. 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 [3],[4]), via numerics [5] or in an analytical way [6],[7]. 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 been so far very difficult to test the various theoretical speculations [8].

The dynamics of polymer melts, on the other hand, is much easier to study experimentally [9] and can be compared to some computer simulations [10]. This case exhibits many interesting glassy features, but looks quite different from what happens to a single polymer chain. However, one can 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 the one in a melt. It has recently been speculated that a single homopolymeric [11] or heteropolymeric chain [12] 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 intuition 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 to real systems easier to observe, like polymer melts [14]. The model we present here is in some way a toy model for non-disordered systems where the aggregation interactions are most important, with or without elastic chain constraint (a realization of that being colloidal gels where glassy cluster patterns appear at high concentrations [13]).

2 Model and simulations

We consider a periodic string of $N$ particles (monomers), each of which 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 in space. In our numerical simulations, we have chosen $m = 2$. If one allows $m = \infty$ then the system is no more an elastic chain but an assembly of $N$ independent particles. The polymer is constrained on a segment
of \( L \) sites, 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 stand on the same site. (The influence of longer ranged interactions on the physical picture obtained below will be discussed in the conclusion). We will call \( M \) the number of sites occupied by more than one monomer, and \( n_i \) is the number of monomers sitting on site \( i \). The total energy \( E \) of the chain is therefore:

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

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 dramatically slows down 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 \( \delta E \) is the energy difference between the new configuration and the initial configuration, then this move is accepted with probability \( p = \min[1, \exp(-\frac{\delta E}{T})] \) where \( T \) is the temperature. If one monomer on site \( i \) is moved to site \( j \), the energy change \( \delta E \) 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 often 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). For example, one can study the participation ratios \( Y_q(t) \), defined as:

\[
Y_q(t) = \sum_x n(x, t)^q.
\]

Obviously, \( Y_1 = N \) and \( E = v(Y_2 - Y_1)/2 \). \( Y_0 \) can be taken as a measure of the size of the chain. Alternatively, we will consider the gyration radius \( R(t) \) 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, the maximum value of \( R \) is, for \( m = 2 \), \( N/\sqrt{12} \sim 0.28N \).
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 Fig. 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 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 $t_c \sim \sqrt{N}$, as can be seen from Fig. 2 where we have plotted $[R(t) - R(t = 0)]/\sqrt{N}$ as a function of $(t/\sqrt{N})$ for short times and different values of $N$. The short time behaviour is linear in time. This initial time regime is found to be independent of the chain constraint, up to a rescaling of time. This is expected 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 $n(x, t)$ from the initial configuration is also interesting: after a short transient time $t_c (< 100$ MC steps for $N = 10000)$ the profile $n(x, t)$ smooths to a parabolic form that expands gradually in space (see Figure 3). This expansion is self-similar in time and can be well fitted at large times by:

$$n(x, t) = n_0(t) \left[1 - \left(\frac{2x}{L(t)}\right)^2\right], \quad (3)$$

where $\pm \frac{L(t)}{2}$ are the points where the density vanishes. We find, for $N = 50000$, $n_0(t) \simeq 725 t^{-0.3}$ and $L(t) \simeq 56.8 t^{0.35}$, compatible with $z = 3$. This form suggests that $n_0(t) \propto 1/L(t)$, as expected for a scaling profile. The participation ratios indeed read in this case:

$$Y_q = \frac{2^q q^2}{(2q + 1)!} n_0^q(t) L(t) \propto t^{(1-q)/3}. \quad (4)$$

In particular, $Y_1 = N = 2n_0(t)L(t)/3$, whereas the energy is expected to relax as $t^{-1/3}$, a result that can be checked numerically independently. 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 discuss this feature also in the following section. The final regime towards the completely expanded configuration of the chain is hard to study numerically as the chain gets trapped in some metastable states. The relaxation towards the completely swollen state is slower and slower, as can be seen on Figure 1.

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

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 the size of the polymer $R$, combined with a Flory approximation for the free
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 $r_{\text{max}} = 0.28$ (shown as a dashed line). At non zero temperature, the long time regime is logarithmic in time. We have also shown, for comparison, the $\tau^{1/14}$ behaviour predicted by the dynamical effective length method discussed below in section 3.2.2.
Figure 2: Initial time regime, where $(R - R_0)/\sqrt{N}$ is plotted as a function of $t/\sqrt{N}$ for different values of $N$. One sees a first regime linear in $t$ crossing over for $t \sim \sqrt{N}$ to the $t^{1/3}$ regime. The dot-dashed line shows a fit to the simple Flory theory described below, Eq. (1). Note that the curves are single runs, which explains the differences for short times.
Figure 3: Profiles $n(x,t)$ of the chain as it swells from a random initial configuration, at times $t = 1, 10, 10^2, ..., 10^5$, with $N = 10000$. The profile quickly becomes parabolic and expands in space as $t^{1/3}$. 
energy $F(R)$. 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:

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

where $\mu_{\text{chain}}$ is the mobility of the chain. It is well known \(^2\) that the mobility for a chain is $\mu_{\text{chain}} = \frac{\mu_0}{N}$, where $\mu_0$ 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:

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

For large times, $R(t)$ converges exponentially fast towards the equilibrium Flory radius $R_F = (vdN^3/2)^{\frac{1}{d+2}}$:

$$R(t) \approx R_F \left[ 1 - \frac{1}{d+2} e^{\frac{2(d+2)\mu_0 t}{N^2}} \right].$$

For an ideal chain initial condition, one has $R_0 \approx \sqrt{N}$. 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:

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

Note that in this time regime, the elastic part in the Flory free energy (that comes from the chain constraint) does not play any role and one therefore expects the same scaling to be valid for an assembly 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 behavior $R(t) \propto N^{1/3} t^{1/3}$ – both scalings in rather good agreement with the numerical results. The very short time behaviour predicted by this approach reads:

$$R(t) \approx R(0) \left( 1 + \frac{vdN\mu_0 t}{R(0)^{d+2}} \right)$$

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 $\Gamma_F$ 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 (see Fig. 2).

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 $i$:

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

where the transition probabilities at finite temperature $T = \frac{1}{\beta}$ are chosen to be:

$$W_{ji} = W_{i \rightarrow j} = w_0 \Theta(n_j - n_i) \quad \Theta(n_j - n_i) = \frac{e^{\frac{vd}{T}[n_i - n_j - 1]}}{e^{\frac{vd}{T}[n_i - n_j - 1]} + e^{-\frac{vd}{T}[n_i - n_j - 1]}}$$

\(^{8}\)
In the zero temperature limit, the transition probabilities are simply described by a step function:

\[ W_{ji} = W_{i\rightarrow j} = w_0 \quad \text{if} \quad n_i(t) > n_j(t) + 1 \\
= 0 \quad \text{if} \quad n_i(t) < n_j(t) + 1 \]  

(12)

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. The Master equation then becomes, in one dimension \((d = 1)\):

\[ \frac{\partial n_i}{\partial t} = w_0 n_{i+1}(t) \Theta(n_i(t) - n_{i+1}(t)) + w_0 n_{i-1}(t) \Theta(n_i(t) - n_{i-1}(t)) - w_0 n_i(t) [\Theta(n_{i+1}(t) - n_i(t)) + \Theta(n_{i-1}(t) - n_i(t))] \]  

(13)

Let us assume that the density \( n_i(t) \) is slowly varying in space, so that one can expand the \( \Theta \) function in powers of \( \Delta n = n_{i+1} - n_i \) as: \( \Theta(\Delta n) \approx \Theta_0 - \beta v \Delta n \Theta_1 \). Then,

\[ \frac{\partial n_i}{\partial t} \approx [n_{i+1}(t) + n_{i-1}(t) - 2n_i(t)] + g [n_{i+1}^2(t) + n_{i-1}^2(t) - 2n_i^2(t)], \]  

(14)

where we have rescaled the time by \( w_0 \Theta_0 \), and set \( g = \beta v \Theta_1 / \Theta_0 \). Taking the continuous limit both in space, we end up with the following non-linear conservative diffusion equation:

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

(15)

Let us note that the assumption \( \beta v |\Delta n| \ll 1 \) is crucial in the derivation of this continuous equation. 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 non-linear equation describes also very well 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 correspond to a 'pearling instability' in the collapse regime which we will discuss further in Section 4.

The non-linear diffusion equation (15) admits a self-similar solution for the profile \( n(x, t) \), of the form:

\[ n(x, t) = \frac{N}{R_s(t)} f \left( \frac{x}{R_s(t)} \right) \]  

(16)

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 \( f \) a scaling function independent of both \( t \) and \( N \). Introducing the rescaled variable \( u = x/R_s(t) \), we find the following differential equation for \( u \):

\[ - \frac{\alpha N}{N^\delta t^{\alpha+1}} [f(u) + uf'(u)] = \frac{N}{t^\delta N^\delta} f''(u) + 2g \frac{N^2}{t^{\delta \alpha} N^4} [f^2(u) + f(u)f''(u)] \]  

(17)

We assume that in the regime of time studied here, the diffusion term can be neglected, which is true if \( t^\alpha \ll g N^{1-\delta} \), and can be checked \textit{a posteriori} when \( R_s \ll N \). Then the equation reduces to:

\[ - \alpha N^{1-\delta} t^{\delta \alpha-1} [f(u) + uf'(u)] = 2g N^{2-4\delta} [f^2(u) + f(u)f''(u)] \]  

(18)
This fixes the values of both exponents: $\alpha_F = \frac{1}{3}$ and $\delta_F = \frac{1}{3}$, 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 Eq. (3), with $n_0(t) = N^2/4^{1/3}(3/64 g)^{1/3}$ and $L(t) = 2(9 g N t)^{1/3}$, in agreement with the numerical results of Fig. 3 (obtained at zero temperature).

### 3.2.2 A dynamical variational method

An alternative, approximate method to study the dynamics of swelling and collapse of polymer chains was proposed in [6]. It is based on a dynamical extension of the effective Kuhn length method of Edwards, which is known to reproduce the Flory value for the end-to-end distance exponent. The essence of the method, together with the self-consistent dynamical equations, are recalled in Appendix A. From these equations, the short time and long time dynamics of the chain was obtained in [6]. In the short time limit, one finds that the chain radius grows, in one dimension, as:

$$R(t) = R_0 + \Gamma_v t^{\gamma_v} \quad \gamma_v = \frac{5}{4} \Gamma_v \propto N^0,$$

at variance both with the Flory prediction $\gamma_F = 1$, and with the numerical simulations.

The intermediate self-similar expansion regime was not worked out in [6]. Looking for a self-similar solution of the form $R(t) \propto t^{\alpha} N^{\delta}$, we have found (after some work) the following values for $\alpha$ and $\delta$:

$$\alpha_v = \frac{1}{14} \quad \delta_v = \frac{11}{14}.$$

Quite surprisingly, again, these values differ from the simple Flory prediction and are very far from the numerical result. From the above value of the exponents, one predicts a stretching time of the order of $N^3$ (longer than what is observed numerically, where the stretched regime is obtained when $\tau = t/N^2$ becomes of order 1).

It is intriguing to see that a somewhat more refined theory (but which basically contains also the ingredients of a Flory theory) gives worse results than the simple-minded approach. It seems actually that the Gaussian variational method misses the fact that the dynamics is governed by repulsive interactions but not sensitive (at short times) to the chain constraint. Hence, the ‘effective’ chain approximation is very bad in this region. The approximation might be better at long times, to describe the approach to the swollen state when the chain constraint becomes relevant. We have shown in Fig. 1 the predicted $t^{1/14}$ for comparison; however, as discussed in the next paragraph, a logarithmic growth is probably more adapted to describe this regime.

### 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. In Figure 4, we show snapshots of the configuration of a short chain, with $N = 100$, as it evolves with time.

It is clear that the chain is trapped for long period of times in metastable configurations, consisting of fully stretched segments of the chain going alternatively to the left or to the right. If we call $2M$ the total number of segments and $\ell$ their average size, the typical extension of the chain in such a configuration is $R \sim \ell \sqrt{M}$. Since $N = 2M\ell$, one has: $R \sim N/\sqrt{M}$, or $M \sim r^{-2}$. The dynamics of the chain in the long time region therefore consists of a slow ‘coarsening’, where ‘kinks’ progressively
Figure 4: Snapshots of the configuration of a short chain, with $N = 100$, as it evolves with time. The $x$ axis is the internal coordinate of the monomers, while the $y$ axis is the corresponding position in space. One can see that the long time dynamics consists of the progressive disappearance of ‘kinks’. Inset: The complexity $S$ as a function of $R$. 
disappear, leading to a decrease of $M$. The time needed for a hairpin of size $\ell$ to disentangle can be estimated from the energy barrier to be crossed, which is proportional to $\ell$ 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 of the size of the chain in the long time regime:

$$ R \sim \sqrt{\frac{N}{\beta v}} \ln t, \quad (21) $$

in qualitative agreement with the numerical simulations: We show on Fig. 5 a logarithmic fit of the radius of gyration as the last stages of the stretching occur. The above estimate assumes that all segments lengths are close to the average value. This is confirmed by an analytical calculation of the number of metastable states of the stretching chain, and is explained in detail in Appendix B.

\[ \begin{array}{c}
\includegraphics[width=\textwidth]{figure5.png}
\end{array} \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Logarithmic growth of the chain at the end of the swelling dynamics, for a small chain $N = 100$.}
\end{figure}

It is indeed interesting to count the number $N(M)$ of metastable states of the chain for a fixed value of $M$, i.e., for a given size $R$ of the chain. The problem is actually related to counting the metastable states of the one dimensional Ising model with Kawasaki dynamics; the corresponding calculations are given in Appendix B. The idea is to make an analogy between a segment of the chain going to the right (or to the left) and a domain of plus (or minus) spins. An additional constraint is needed to make the configuration metastable. The chain can only evolve by moving inwards the monomer at the extremity of the hairpin (see Fig. 4). This is possible if the total number of
monomers sitting on the target site is less than the number of monomers at the starting site. If we assume that the local density of monomers is random, the probability for this to happen is equal to $1/2$. Therefore, a zig-zag configuration with $M$ segments is stable with probability $2^{-M}$. The result is that $N(M) \sim \exp(NS(M))$, with a complexity $S$ given by:

$$S = -\delta \ln 2 + (\delta - 1) \ln(1 - \delta) - \delta \ln \delta,$$

with $\delta = 2M/N \sim N/R^2$. This function is plotted in the inset of Figure 4. At the beginning of the swelling, the complexity increases very rapidly with $R$; after a maximum reached for $\delta^* = 1/3$, $S$ then decreases at large $R$.

If one adds all frozen configurations for all possible values of $M$ (or equivalently, $R$), one finds a total number of frozen states which grows as $C^N/\sqrt{N}$ where the complexity per monomer is $C = 3/2$. This must be compared to the total number of configurations, which is equal, for $m = 1$, to the number of closed random walk, i.e. $2^N/\sqrt{N}$.

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 6.

These clusters are very slow to coalesce and the dynamics is slower and slower with time (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 $n$ large), 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. This can be seen for example on the time evolution of the energy $E(t)$: single runs for three different temperatures are shown in Figure 7. By averaging $E(t)$ over several MC runs, we found a logarithmic decay with time, compatible with the estimate $E \sim -Mn^2 \sim -N \ln(t)$, using $n \sim T \ln t$. It is interesting to note that the dynamics of clusters is very close to that of the one dimensional ‘Backgammon’ model introduced [19] and further studied in [21, 22, 20]: although the barriers are ‘entropic’ in the latter model, the average time needed to empty a cluster also grows exponentially with its size $n$.

4.2 Breakdown of the continuum description

Let us come back to the continuous approach developed in the previous section in the case of repulsive interactions. Starting again from the master equation, and considering attractive interactions this time, we find the following equation for $n(x, t)$:

$$\frac{\partial n(x, t)}{\partial t} = \left[ \nabla^2 n - 2|g|\nabla(n \nabla n) \right].$$

(23)
Figure 6: 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 the last one.
Figure 7: Energy of the polymer as a function of time for a single Monte-Carlo run, at $T = 5, 50, 100$: energetic traps can be visualized.
A naive extension of the self-similar solution found in the repulsive case leads to the following equation for the size of the polymer $R_s$:

$$\frac{dR_s(t)}{dt} = -2|g| \frac{N}{R_s(t)}$$

(24)

or $R_s^3(t) = R_s^3(0) - 6N|g|t$, suggesting that all monomers coalesce into a single cluster in a finite time. This clearly does not capture the essential physical feature of the dynamics at late time, namely the activated coarsening of well separated ‘towers’ of monomers.

In fact, Eq. (23) leads to a short wavelength ‘pearling’ instability of initially smooth profiles. Starting from $n(x, t) = n_0 + \delta n(x, t)$, with $\delta n \ll n_0$, one finds:

$$\frac{\partial \delta n(x, t)}{\partial t} = (1 - 2|g|n_0) \nabla^2 \delta n,$$

(25)

which is unstable as soon as $2|g|n_0 > 1$, i.e. for small enough temperatures or when the chain density is large. As observed numerically, a random walk initial condition is indeed immediately unstable for large $N$, since $n_0 \sim \sqrt{N} \gg 1$.

As soon as the chain has entered the pearled state with well separated clusters of monomers, any continuous description is bound to fail. A discussion in terms of metastable states, and jumps between these states, is needed.

### 4.3 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 the number of arrangements of $M$ clusters on a one-dimensional box of $L$ sites, so that all clusters are at least separated by an empty site. We will restrict to the case where the chain constraint is $m = 1$, i.e., two consecutive monomers cannot be at a distance larger 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:

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

(26)

The number of configurations $N_{k^*}(M|N)$ with at least $k^*$ monomers in each cluster can be calculated using the following formula:

$$N_{k^*}(M|N) = \sum_{n_1=k^*}^{N} \ldots \sum_{n_M=k^*}^{N} \delta \left( \sum_{i=1}^{M} (n_i - 2) - N + 2L \right),$$

(27)

which can be transformed into:

$$N_{k^*}(M|N) = \int d\lambda e^{-i\lambda(N-2L)} \left( \sum_{n=k^*}^{N} e^{i\lambda(n-2)} \right)^M = \int d\lambda e^{-i\lambda N} \left( \frac{e^{i(k^*-2)\lambda}}{1 - e^{i\lambda}} \right)^M$$

(28)
We define in the following $\delta = \frac{M}{N}$, $\rho = N/L$ and $z = i\lambda$, and perform a saddle point approximation on the above integrand in the large $N$ limit. We find that at the saddle point, $z^* = \ln \left( \frac{1 - \frac{2}{\rho} - \delta(k^* - 2)}{1 - \frac{2}{\rho} - \delta(k^* - 3)} \right)$. Then, we obtain:

$$\ln \left[ \mathcal{N}_k^*(M \vert N) \right] = \left[ -1 + \frac{2}{\rho} + \delta(k^* - 2) \right] \ln \left( \frac{1 - \frac{2}{\rho} - \delta(k^* - 2)}{1 - \frac{2}{\rho} - \delta(k^* - 3)} \right) - \delta \ln \left( \frac{\delta}{1 - \frac{2}{\rho} - \delta(k^* - 3)} \right).$$ (29)

Now we count 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. This can be done in the following manner, mapping this problem into an antiferromagnetic spin representation. (A more direct combinatorial method can be found in [20]). We define the formal antiferromagnetic hamiltonian:

$$\mathcal{H} = J \sum_{i=1}^{L} \sigma_i \sigma_{i+1}, \quad J > 0,$$ (30)

where $\sigma_i = 1$ by definition if there is at least one monomer on site $i$, and $\sigma_i = 0$ if site $i$ is empty, so that configurations with consecutive occupied sites have a positive energy and the configurations of zero energy are those with at least one empty site between each occupied site. Using the additional constraint that the total number of occupied sites is set to some value $M$, the number of configurations $\mathcal{N}_L(M)$ is given by the following formula:

$$\mathcal{N}_L(M) = \lim_{J \to \infty} \sum_{\{\sigma_i = 0, 1\} \sum_{i=1}^{L} \sigma_i} e^{-\mathcal{H}} \delta(M - \sum_{i=1}^{L} \sigma_i).$$ (31)

This can be rewritten using the integral representation of the $\delta$-function:

$$\mathcal{N}_L(M) = \int d\mu e^{i\mu M} Z_L(i\mu)$$ (32)

where $Z_L(i\mu) = \sum_{\{\sigma_i = 0, 1\} \sum_{i=1}^{L} \sigma_i} e^{-\mathcal{H}} e^{-i\mu \sum_{i=1}^{L} \sigma_i}$. By performing a saddle-point approximation on $\mu$, one has to find $\mu^*$ such that

$$M + \frac{\partial}{\partial(i\mu)} |_{\mu = \mu^*} \ln Z_L(i\mu) = 0.$$ (33)

The quantity $Z_L(i\mu)$ can actually be computed exactly using a transfer-matrix method, and in the limit $J \to \infty$, $Z_L(i\mu) = \left[ \frac{1}{2} \right. (1 + \sqrt{1 + 4e^{-i\mu}}) \left. \right] ^L$. Using the saddle-point equation, $\mu^*$ is easily found to be equal to $\sqrt{1 + 4e^{-i\mu}} = \frac{1}{1 - 2\delta\rho}$. Finally,

$$\mathcal{N}_L(M) \sim e^{L\Sigma(\delta\rho)},$$ (34)

with

$$\Sigma(\delta\rho) = i\mu^* \frac{M}{L} + \ln Z_L(i\mu^*) = -\delta\rho \ln \left( \frac{\delta\rho(1 - \delta\rho)}{(1 - 2\delta\rho)^2} \right) + \ln \left( \frac{1 - \delta\rho}{1 - 2\delta\rho} \right).$$ (35)

One can check in particular that one finds $\Sigma(0) = 0$ and $\Sigma(\frac{1}{2}) = 0$, as it should.
We now combine the two above results, and deduce the total number of \( k^* \)-stable configurations for a given density \( \rho \):

\[
\mathcal{N}_\rho(k^*) \equiv e^{\mathcal{S}_\rho(k^*)} = \sum_{M=1}^{M_N} \mathcal{N}_L(M) \mathcal{N}_{k^*}(M|N).
\]  

(36)

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

\[
\mathcal{S}_\rho(k^*) = (-1 + \frac{2}{\rho} + \delta(k^* - 2)) \ln \left( \frac{1 - \frac{2}{\rho} - \delta(k^* - 2)}{1 - \frac{2}{\rho} - \delta(k^* - 3)} \right) - \delta \ln \left( \frac{\delta}{1 - \frac{2}{\rho} - \delta(k^* - 3)} \right) - \delta^* \ln \left( \frac{\delta^* \rho(1 - \delta^* \rho)}{(1 - 2\delta^* \rho)^2} \right) + \frac{1}{\rho} \ln \left( \frac{1 - \delta^* \rho}{1 - 2\delta^* \rho} \right).
\]  

(37)

In this expression, \( \delta^* \) is the saddle point value of \( \delta \), defined as:

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

(38)

At zero temperature, all metastable states are frozen, and the size of the chain \( L \) and therefore the density \( \rho \), 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 \( \delta^*(\rho) \) and \( \mathcal{S}(\rho) \) and plotted the results in Figure 8. One should note that since each cluster contains at least 2 monomers, the maximum number \( M \) of clusters is \( \frac{N}{2} \), so \( \delta \leq \frac{1}{2} \). Since a metastable state is such that two clusters should be separated by at least one empty site, one also has \( L \geq 2M \), or \( \delta \rho \equiv \frac{M}{L} \leq \frac{1}{2} \).

It is interesting to draw an analogy with some recent work on the number of metastable states in spin-glasses [1]. 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 [1]. 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 (contrarily 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.

### 4.4 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:

\[
\frac{d\mathcal{S}_\rho(k^*)}{d\rho} \bigg|_{\rho=\rho^*} = 0,
\]  

(39)
Figure 8: Entropy of metastable states $S(\rho)$ and the corresponding optimal number of clusters $\delta^*(\rho)$, as a function of the density of monomers $\rho$, at $T = 0$. 
Solving for $\rho^*$ and $\delta^*$ in the large $u = T \ln t$ limit, we find:

$$\rho^*(u) \simeq 4 \ln u \quad \delta^*(u) \simeq \frac{1}{u} - \frac{1}{u \ln u},$$

and the corresponding value of the entropy, to leading order in $u$:

$$S^*(u) \simeq 2 \frac{\ln u}{u} - 2 \frac{\ln(\ln u)}{u} + \frac{1}{u} (4 - \ln 8).$$

These results predict a slow decrease of the number of clusters and an extremely slow decrease of the size of the chain:

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

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 hyper-slow contraction of the chain. Numerically, we find that the chain length indeed hardly decreases with time.

Figure 9: Entropy of metastable states $S^*(u)$ as a function of $u = T \ln(t)$. Inset: Density of the chain as a function of $\ln(u)$ (plain line). The dotted line is the asymptotic result $\rho(u) \simeq 4 \ln(u)$. 
4.5 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 $E$. As was done before in the case of spin-glasses [14] or Josephson arrays [15], we want to understand how the entropy of metastable states behaves as a function of energy at $T = 0$, and we go here further by looking at its dynamical evolution with respect to $k^* = T \ln t$. The calculation proceeds much in the same way as in the previous section (we also restrict ourselves to the case where $m = 1$), starting from the expression of the number of $k^*$-stable configurations with $M$ clusters and $N$ monomers, at fixed energy $E$:

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

(43)

The technical details of the calculation are relegated to Appendix C. Setting $\epsilon = \frac{E}{N} < 0$ and $S_{\rho}(\epsilon, k^*)$ the complexity per monomer, our final result is plotted on Figure 10. We see that all $S_{\rho}(\epsilon, k^*)$ for different $k^*$ follow a common envelope for a given $\rho$, and asymptotically the curves approach the following law at very low energies:

$$S_{\rho}(\epsilon) \simeq_{\epsilon \to -\infty} -\frac{\ln(-\epsilon)}{\epsilon} \left( 1 - \frac{2}{\rho} \right)^2 + \frac{1}{\epsilon} \left( 1 - \frac{2}{\rho} \right)^2 [-1 + \frac{1}{2} \ln \left( \frac{\rho}{4} \right) \left( 1 - \frac{2}{\rho} \right)^{3/2} ] + o(\frac{1}{\epsilon^2})$$

(44)

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

$$S(\epsilon) \simeq_{\epsilon \to -\infty} -\frac{\ln(-\epsilon)}{\epsilon}$$

(45)

Even for very low energies, the entropy of metastable states never reaches zero: contrarily 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 $N$.

4.6 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 $\pi$ as the average number of monomers in a cluster. From the above sections, we know that $\pi(t)$ grows slowly (logarithmically) with time. We have studied $\pi p(n, t)$ as a function of $z = n/\pi$ at different times. These different curves collapse well onto a single one (note however that the range of variation of $\pi$ 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 $z$ small, on the other hand, $\tilde{p}(z)$ rapidly vanishes. Although our statistics is 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. [17] 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
Figure 10: Entropy of metastable states $S_\rho(\epsilon)$ as a function of the energy per monomer. The plain line is the asymptotic law $S(\epsilon) = -\ln(-\epsilon)/\epsilon$. For a given $k^*$, the domain of definition of the entropy is bounded by $\epsilon_{\text{max}}(k^*) = -\frac{1}{2}(k^* + 1) + \frac{k^*}{\rho}$. The successive arches, defined on $[\epsilon_{\text{max}}(k^* + 1), \epsilon_{\text{max}}(k^*)]$, correspond from right to left, to increasing $k^*$ ($= 3, 4, ..$), and follow a common envelope.
interval sizes tends to an asymptotic distribution shown in Fig. 11. The cluster dynamics studied here is similar for the following reason: because the time needed to empty one cluster is exponential in 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 benchmarks to which we can compare our results. This is performed in Fig. 10. 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 $z$ [17]. 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, to give rise to a sub-aging behaviour.

![Figure 11: 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.](image-url)
4.7 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 \[ C_q(t_w, t+t_w) = \frac{1}{N} \sum_{i=1}^{N} \langle e^{iq(x_i(t+t_w)-x_i(t_w))} \rangle \] (46)

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 127, obtained for \( T = 5 \), \( N = 10000 \) and averaged over 10 initial configurations, the relaxation is slower and slower as \( t_w \) increases. As often observed experimentally \[24, 25, 26\], we have found that the data can be rescaled in the variable \( s = t/t_w \mu \), with \( \mu < 1 \) (subaging). Within the time regime probed by the MC, \( \mu \sim 0.75 \) for \( q = 5 \) and \( q = 10 \). 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 \( \bar{\eta} \) means that some clusters will evolve on a time scale much shorter than \( t_w = \exp(\bar{\eta}/T) \). More precisely, one can approximate the short time behaviour of \( C_q(t+t_w, t_w) \) by:

\[ 1 - C_q(t+t_w, t_w) \approx t \int dz \ z\tilde{p}(z) \exp(-z\bar{\eta}/T). \] (47)

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:

\[ 1 - C_q(t+t_w, t_w) \propto \frac{t}{t_w^\mu} \quad \mu = (1 + \frac{1}{c}) \left( \frac{cz_0^c}{\ln t_w} \right)^{1/c}. \] (48)

This scenario therefore leads to a subaging behaviour for large \( t_w \), albeit with a (slowly) time dependent exponent \( \mu \). 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 \( C/(s_0 + s)^w \), with \( w \approx 0.18 \) for \( q = 5 \) and \( w \approx 0.10 \) for \( q = 10 \).

The above mechanism for subaging 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 \( t_w \sim \exp(\bar{R}^\psi/T) \) \[27\]. 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 subaging effects.

5 Summary – 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 \( \Theta \)-solvent that is rapidly changed into a good solvent (swelling) or a bad solvent (collapse).

- In the case of swelling, the initial phase is to a large degree independent of the chain constraint. The density profile is parabolic and expands in space as \( t^{1/3} \). This regime is well described by a
Figure 12: Evidence for aging in the structure factor, for $N = 10000$, $q = 5$, $T = 5$, averaged over 10 initial conditions. The curves for $t_w = 10^4, 2 \times 10^4$ and $3 \times 10^4$ 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 $t/t_w^\mu$ should indeed only be approximate.
Flory-like continuum equation for the monomer density. 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 (that we have enumerated), from which it escapes through thermal activation. The final stage of the stretching is therefore found to be logarithmic in time: the size of the polymer grows as \( \sqrt{\ln t} \).

- In the case of collapse, the chain very quickly (after a time of order unity) breaks up into small ‘pearls’ or clusters of monomers. The evolution of the chain towards the fully collapsed states proceeds through a slow growth of the size of these metastable clusters, again evolving as the logarithm of time. We have enumerated the total number of metastable states as a function of the extension of the chain, and deduced from this computation that the radius of the chain should decrease as a double logarithm of time, i.e. \( 1/\ln(\ln t) \). We have also found the total number of metastable states with a given value of the energy. We also obtained the distribution of cluster sizes, that we compared to simple one dimensional coalescence models. Finally, the aging properties of the dynamical structure factor was investigated numerically. The subaging behaviour that we found was attributed to the tail of the distribution at small cluster sizes, corresponding to anomalously fast clusters. We have argued that this mechanism for subaging might hold in other slowly coarsening systems.

The system studied here falls in the category of non disordered, finite dimensional models exhibiting glassy dynamics. The list of such models keeps increasing with time [28], 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 for 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 [10]. 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 [10, 12].

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 [13]. In this system, clusters of particles form and slowly coalesce, this leads to a very clear aging of the dynamical structure factor. Hints about the presence of ‘micro-earthquakes’, possibly due to the disappearance of large clusters, have been reported. A closer comparison between our model and such experiments would be very fruitful, but might require the inclusion of elastic deformations, as suggested in [13].
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Appendix A: A variational method for the swelling of a polymer chain

In [6] a polymeric chain with given two-body interactions is approximated by a ‘variational’ gaussian chain with a time-dependent Kuhn length. In other words one starts from the original chain with hamiltonian $H$ and its associated Langevin equation:

$$\frac{\partial r}{\partial t} = -\Gamma_0 \frac{\partial H}{\partial r} + \eta(s, t)$$

$$H = \frac{k_B T}{2a_0^2} \int_0^N \left( \frac{\partial r}{\partial s} \right)^2 ds + k_B T V(r(s, t))$$

and then one tries to replace it with another system characterized by $H_v$:

$$\frac{\partial r^{(v)}}{\partial t} = -\Gamma_0 \frac{\partial H_v}{\partial r^{(v)}} + \eta(s, t)$$

$$H_v = \frac{k_B T}{2a^2(t)} \int_0^N \left( \frac{\partial r^{(v)}}{\partial s} \right)^2 ds.$$  

$\eta(s, t)$ is a gaussian noise with

$$\langle \eta(s, t)\eta(s, t') \rangle = 2D\delta(t - t')$$

and $\Gamma_0 = \frac{D}{k_B T}$ where $D$ is the diffusion coefficient.

In order to find the effective Kuhn length that would represent best the initial system, the radius of gyration is chosen to coincide in both models, to first order in $\chi(s, t) = r(s, t) - r^{(v)}(s, t)$ and $W = H - H_v$.

This leads to an implicit equation for $a(t)$:

$$\int_0^N < r^{(v)}(s, t) \chi(s, t) >= 0$$

We have used periodic boundary conditions, introducing $\omega_n = \frac{2\pi n}{N}$.

The whole calculation is discussed in detail in [6], and we only reproduce the final equations which appear in the form $I + II = 0$, with, in the case of two-body interactions:

$$I = -\sum_{n \neq 0} \omega_n^2 \left[ \frac{a_0^2}{N\omega_n^2} e^{-2D\omega_n^2 f(t)} \left( \frac{t}{a_0^2} - f(t) \right) + \frac{2D}{N} \int_0^t d\tau \left( \frac{1}{a_0^2} - \frac{1}{a^2(\tau)} \right) \int_0^\tau d\lambda e^{-2D\omega_n^2 (f(\tau) - f(\lambda))} \right]$$

and

$$II = 2vN \sum_{n \geq 1} e^{-2D\omega_n^2 f(t)} \int_0^1 dU \int_0^t d\tau \frac{1 - \cos 2\pi n U}{\alpha(\tau, U)^{1+\frac{4}{\alpha}}} \left[ \frac{a_0^2}{N\omega_n^2} + \frac{2D}{N} \int_0^\tau d\lambda e^{2D\omega_n^2 f(\lambda)} \right].$$
We have set:
\[ \alpha(\tau, U) = 4 \sum_{p \geq 1} (1 - \cos 2p\pi U) \left[ \frac{a^2_e}{N\omega^2_p} e^{-2D\omega^2_p f(\tau)} + \frac{2D}{N} \int_0^\tau d\lambda e^{-2D\omega^2_p (f(\tau) - f(\lambda))} \right], \tag{57} \]
and
\[ f(t) = \int_0^t \frac{dr}{a^2(r)}. \]

We are interested here in an intermediate time regime, and choose to keep the time dependence in \(a(t)\) such that \(R(t) = a(t)N^{\frac{1}{2}} \ll N^{\frac{3}{2}}\) and look for a power-law scaling: \(a(t) = N^\mu t^\alpha\). Then the reduced variable \(u = \frac{t}{N^\gamma}\) with \(\gamma = \frac{1}{2} \left[ \frac{4-d}{2(d+2)} - \mu \right]\) is the relevant parameter in this time regime; we are interested in the situation where one can take the limit \(N \to \infty\), keeping \(u\) finite and much smaller than unity.

A succession of approximations gives the following behaviours for the quantities \(I\) and \(II\):
\[ I \simeq u^{2-\frac{4d}{2d}} N^{2\gamma + 3\mu - \frac{4}{2}x\gamma}, \quad II \simeq u^{1-(1-\frac{4}{2d})(1+\frac{1}{2}x)} N^{2\gamma - \rho(1+\frac{1}{2})}, \quad \alpha(\tau, U) \simeq N^\rho u^{1-\frac{x}{5}}, \tag{58} \]
where the parameters used above are defined as:
\[ x = 1 - 2\alpha, \quad \rho = \gamma + \mu - \frac{1}{2}x\gamma, \quad v = \frac{\tau}{N^\gamma}. \tag{59} \]

Finally this allows to find the result announced in the main text for the case of repulsive interactions:
\[ \alpha = \frac{12 - d}{2(6 - d)} \quad (d < 2), \tag{60} \]
so that, in \(d = 1\), \(R(t) \simeq t^{\frac{1}{4}} N^\frac{11}{14}\).

**Appendix B: Calculation of the number of metastable states in the 1D Kawasaki Ising model**

Cornell, Kaski and Stinchcombe \[18\] have studied the dynamics of the one dimensional Ising model, using the Kawasaki prescription: the total magnetization is fixed and the only moves allowed are exchanges of two antiparallel nearest-neighbour spins. It is best suited to model binary alloys. At low temperature, the model has been shown to exhibit a glassy-type behaviour. At finite temperature, the system evolves in time by condensation of domains of parallel spins (if \(J\) is the exchange coupling constant, there is an energy gain of \(4J\) for a spin to join a domain by switching sites with its nearest neighbour); conversely, the evaporation of a spin from a domain costs \(4J\). The diffusion of a spin performing a random walk in a domain consisting of spins of opposite sign costs no energy.

At zero temperature, all evaporation processes are frozen and only condensation and diffusion of spins can occur. However, in order for two domains of same sign to coalesce, the evaporation of the boundary spins is necessary; as a consequence, at \(T = 0\), many states are frozen.

The frozen states are in fact very easy to characterize: they consist of alternating positive and negative domains, each of them containing at least two spins. Let \(M\) be the total number of positive domains; for \(i = 1, \ldots, M\), \(n^+_i\) is the number of + spins in the positive domain \(i\). Between two of these domains there exists a domain of negative magnetization. We label also these domains by \(i = 1, \ldots, M\), and \(n^-_i\) is the number of – spins in the negative domain \(i\).
Since \( N \) is the total number of spins and \( Nb \) the total magnetization (the letter \( m \) being used in the text for the chain constraint), we have the two conservation relations:

\[
N = \sum_{i=1}^{M} (n_i^+ + n_i^-); \quad Nb = \sum_{i=1}^{M} (n_i^+ - n_i^-).
\]

The number of frozen states for \( M \) fixed and fixed magnetization is given by the following expression:

\[
N_F(M, b) = \left( \sum_{n_i^+=2}^{N} \ldots \sum_{n_M^+=2}^{N} \right) \left( \sum_{n_i^-=2}^{N} \ldots \sum_{n_M^-=2}^{N} \right) \delta \left( \sum_{i=1}^{M} (n_i^+ + n_i^-) - N \right) \delta \left( \sum_{i=1}^{M} (n_i^+ - n_i^-) - Nb \right).
\]

The calculation can be handled easily by exponentiating the \( \delta \)-functions, and taking the \( N \to \infty \) limit.

\[
N_F(M, b) = \int d\lambda e^{-i\lambda N} \int d\mu e^{-i\mu Nb} \sum_{n_i^+=2}^{N} \ldots \sum_{n_M^+=2}^{N} e^{(\lambda+i\mu)\sum_{i=1}^{M} n_i^+} \sum_{n_i^-=2}^{N} \ldots \sum_{n_M^-=2}^{N} e^{(i\lambda-i\mu)\sum_{i=1}^{M} n_i^-}
\]

Then a saddle point approximation on \( z_1 = i\lambda \) and \( z_2 = i\mu \) leads to a simple expression for the entropy of frozen states at fixed magnetization per spin \( m \) and fixed fraction of domains \( \delta = \frac{2M}{N} \):

\[
\frac{1}{N} \ln N_F(M, b) = S(b, \delta) = \frac{1}{2} (-1 - b + 2\delta) \ln(1 + b - 2\delta) + \frac{1}{2} (1 + b - \delta) \ln(1 + b - \delta) + \frac{1}{2} (-1 + b + 2\delta) \ln(1 - b - 2\delta) + \frac{1}{2} (1 - b - \delta) \ln(1 - b - \delta) - \delta \ln \delta.
\]

We then determine the optimum \( \delta^* \) for \( \delta \) at fixed magnetization \( b \), in order to find the total entropy for a given \( b \). This leads to an implicit equation:

\[
\frac{(1 + b - 2\delta^*)^2(1 - b - 2\delta^*)^2}{\delta^*2(1 + b - \delta^*)(1 - b - \delta^*)} = 1
\]

**Case \( b = 0 \)**

The complexity of the Kawasaki model is then easy to compute,

\[
S^K(b = 0) = (-1 + 2\delta) \ln(1 - 2\delta) + (1 - \delta) \ln(1 - \delta) - \delta \ln \delta,
\]

The sum over \( \delta \) can be performed using a saddle-point approximation, leading to a total number of frozen states:

\[
N_F^K(b = 0) \sim \frac{C^N}{\sqrt{N}},
\]

where the complexity per spin is \( C \approx 1.618 \). This is slightly less than the number of closed random walks for which \( C = 2 \): each metastable configuration in the Kawasaki problem can be seen as a random walk that goes at least twice in the same direction before changing direction.
The case of zero magnetization is of special interest because it allows to give an estimate of the complexity of the polymeric chain in its stretching regime. As was pointed out in section 3.3, as the chain swells, it is trapped in metastable configurations, consisting of fully stretched segments of the chain going alternatively to the left or to the right. It is easy to draw a correspondence between a segment going to the right (respectively, to the left) and a domain of plus (respectively, minus) spins. The constraint that the chain is closed requires that the number of steps to the right is equal to the number of steps to the left, which is equivalent, in the spin language, to \( b = 0 \).

In order to count the total number of metastable states for the chain, one should actually require that each stretched segment must contain at least one monomer, so that the sums in (62) should start at \( n_i^* = 1 \). However, there must be an energetic bias in order for each end of segment to be stuck at its position, namely that the number of monomers on its ‘inward’ neighbouring site along the chain should be more important. As explained in the main text, we assume that this is true with probability \( 1/2 \), and this adds a multiplicative factor \( 1/2^M \) in formula (62). Finally the complexity of the chain is:

\[
S = -\delta \ln 2 + (\delta - 1) \ln(1 - \delta) - \delta \ln \delta,
\]

This relation is illustrated on Fig. 4 as a function of \( R \), given that \( R \sim M^{-\frac{1}{2}} \). The sum over \( \delta \) can be performed using a saddle-point approximation, leading to a total number of frozen states \( N_F \sim C_N/\sqrt{N} \), where \( C = 3/2 \).

To summarize, the calculation reveals an interesting analogy: the number of states of a chain containing at least \( k \) monomers on each stretched segment is the same as the number of the frozen states in the 1D Kawasaki spin model at zero magnetization and zero temperature (with all domains containing at least \( k \) spins), and is in turn equal to the number of one-dimensional closed random walks biased in such a way that one has to walk at least \( k \) times in the same direction before changing direction.

In order to know the number of metastable states of the chain with at least \( k \) monomers on each segment, one must add an energetic bias introduced via the additional factor \( 1/2^M \) in equation (62).

To complete the analogy let us formulate two remarks.

First, the number of closed random walks in one dimension \( (2^N/\sqrt{N}) \) is recovered when one uses the above formula (62) with sums starting at \( n_i^* = 1 \).

Second, one can also vary the degree of bias \( k \) of the random walk by starting the sums in (62) at \( n_i^* = k \). Physically this corresponds to metastable states over a time scale \( t \) such that \( \ln t = \beta v k \). If in addition, we incorporate the energetic bias factor \( 1/2^M \), this allows to follow with time the number of metastable states at finite temperature as the system coarseens, and relate it to the radius of gyration of the chain at long times.

We obtain the following entropy of metastable states, as a function of the parameter \( u = T \ln t \):

\[
S(u) = -\delta \ln 2 + (-1 + u\delta) \ln(1 - u\delta) + (1 - (u - 1)\delta) \ln(1 - (u - 1)\delta) - \delta \ln \delta,
\]

This entropy is maximum at a certain value of \( \delta \), which, to leading order in \( u \) (for \( u \) large), is given by \( \delta^* \simeq \frac{1}{u} \). We expect that the number of zig-zags in the polymer will adjust at this value, corresponding to one of its most probable configurations. As was explained in the main text, \( R \) and \( \delta^* \) are then related by \( \delta^* \sim N/R^2 \), so that \( R \sim \sqrt{N \ln t} \).

Finally, let us mention that the whole calculation is in spirit (and also in the analytical methods involved) very similar to the calculation of the number of metastable states of a collapsing chain, as a function of the degree of freezing \( k^* = T \ln t \); section 4 of this article is devoted to such a description.
Appendix C: Number of collapsed metastable states as a function of the energy

We start by the expression of the number of \( k^* \)-stable configurations with \( M \) clusters and \( N \) monomers, at fixed energy \( E \), given by:

\[
N_{\rho,k^*}(E, M|N) = \sum_{n_1=k^*}^{N} \ldots \sum_{n_M=k^*}^{N} \delta \left( \sum_{i=1}^{M} (n_i - 2) + 2L - N \right) \delta \left( \sum_{i=1}^{M} -\frac{1}{2} n_i(n_i - 1) - (L - M) - E \right).
\]

In the following, we set \( \epsilon = \frac{E}{N} < 0 \) and limit ourselves to the case \( m = 1 \).

Let us first note that for a given \( k^* \), the maximum energy per particle is equal to \( \epsilon_{\text{max}} = -\frac{1}{2}(k^* + 1) + \frac{k^*}{\rho} \). It is reached for a configuration consisting of \( M \) clusters of \( k^* \) monomers each, and the remaining \( L - M \) sites are occupied by 2 monomers, each of these sites contributing with an energy equal to \( -\frac{1}{2} \). The conservation relation \( N = Mk^* + 2(L - M) \) leads to \( \delta_{\text{max}} = \frac{M_{\text{max}}}{N} = (1 - 2/\rho)/(k^* - 2) \), and the energy is calculated accordingly, leading to \( \epsilon_{\text{max}} = -\frac{1}{2}(k^* + 1) + \frac{k^*}{\rho} \). In the following, we will only need to consider values of \( \epsilon \) in the interval \( ] - \infty; \epsilon_{\text{max}} [ \).

From the expression of \( N_{\rho,k^*}(E, M|N) \) above, one may use the integral representation of the \( \delta \)-functions to find that:

\[
N_{\rho,k^*}(E, M|N) = \int dX \int dY e^{-NF(X,Y)}.
\]

with

\[
F(X,Y) = X(1 - \frac{2}{\rho}) + Y(\epsilon + \frac{1}{\rho}) - \delta \ln \Sigma(X,Y),
\]

and

\[
\Sigma(X,Y) = \sum_{n=k^* - 2}^{\infty} e^{Xn - \frac{1}{2}Yn(n+3)}.
\]

Our procedure is to find an estimate of this quantity via a saddle-point approximation, so that the entropy of metastable states at fixed \( \delta \) is given by:

\[
S_{\rho}(\delta, \epsilon) = -F(X^*, Y^*) - \delta \ln \left( \frac{\delta \rho (1 - \delta \rho)}{(1 - 2\delta \rho)^2} \right) + \frac{1}{\rho} \ln \left( \frac{1 - \delta \rho}{1 - 2\delta \rho} \right)
\]

(72)

where the last step is to maximize this expression with respect to \( \delta \) so that the final result is \( S_{\rho}(\epsilon) = S_{\rho}^{\delta^*}(\delta^*, \epsilon) \).

Limit of low energies \( \epsilon \to -\infty \)

In this part, it is more convenient to perform a change in variables \( Z = X - 3Y/2 \) and \( Z' = -Y/2 \). Moreover, numerical investigation suggests that for \( |\epsilon| \) large, \( Z^* \) should be small and \( Z'^* \) of the form \( Z'^* \simeq -aZ^2; a > 0 \); so we set in the following \( Z' \simeq -aZ^2; a > 0 \), so \( Z \) and \( a \) are the new variables:

\[
F(Z, a) = Z(1 - \frac{2}{\rho}) + aZ^2(3 + 2\epsilon - \frac{4}{\rho}) - \delta \ln \Sigma(Z, a),
\]

(73)
and:
\[
\Sigma(Z, a) = \sum_{n=k^*-2}^{\infty} e^{-aZ^2n^2+Zn}
\]  
(74)

We then approximate the discrete sum \(\Sigma(Z, a)\) by an integral, which is valid if we find \textit{a posteriori} that \(Z\) is small:
\[
\Sigma(Z, a) \simeq -\frac{1}{Z}G(a), \quad G(a) = \int_0^\infty du e^{-au^2-u}
\]  
(75)

Up to this order in \(1/Z\) the results are independent of \(k^*\). The combined saddle-point equations \(\partial F/\partial Z = 0\) and \(\partial F/\partial a = 0\) lead to the simple relation:
\[
Z^*(1 - \frac{2}{\rho}) = -\delta - 2a^*\delta \frac{G'(a^*)}{G(a^*)}.
\]  
(76)

Continuing the algebra with the assumption that \(a^* \neq 0\) does lead to inconsistent values for \(\delta^*\) \((\delta^* > \frac{1}{2})\). We conclude that the saddle-point solution, if there is one, is stuck at \(a^* = 0\). The rest of the calculation is then straightforward: we obtain \(Z^* = -\delta/(1 - \frac{2}{\rho})\), and since \(G(0) = 1\),
\[
S_\rho(\delta, \epsilon) = \delta[1 + \ln(1 - \frac{2}{\rho})] - \delta \ln \delta - \delta \ln \left(\frac{\delta \rho(1 - \delta \rho)}{(1 - 2\delta \rho)^2}\right) + \frac{1}{\rho} \ln \left(\frac{1 - \delta \rho}{1 - 2\delta \rho}\right)
\]  
(77)

Finally, in order to determine \(\delta^*\), we compute:
\[
\frac{\partial S_\rho(\delta, \epsilon)}{\partial \delta} = \ln(1 - \frac{2}{\rho}) - \ln \left[\frac{\delta^2 \rho(1 - \delta \rho)}{(1 - 2\delta \rho)^2}\right]
\]  
(78)

In the limit \(\epsilon \to -\infty\), the interval allowed for \(\delta\) is \([0; \delta_{\text{max}} = -(1 - \frac{2}{\rho})^2/2\epsilon]\). In this interval, \(S_\rho(\delta, \epsilon)\) is an increasing function of \(\delta\), and therefore reaches its maximum at the upper bound. Therefore: \(\delta^* = \delta_{\text{max}}\). Note that this implies that \(Z^* = (1 - \frac{2}{\rho})/2\epsilon\) is indeed small as was assumed in this approach. We get the final result for the tail of the entropy of metastable states:
\[
S_\rho(\epsilon) \cong_{\epsilon \to -\infty} \frac{\ln(-\epsilon)}{\epsilon}(1 - \frac{2}{\rho})^2 + \frac{1}{\epsilon}(1 - \frac{2}{\rho})^2[-1 + \frac{1}{2} \ln\left(\frac{\rho}{4}(1 - \frac{2}{\rho})^{3/2}\right)] + o(\frac{1}{\epsilon^2})
\]  
(79)

**Limit of high energies** \(\epsilon \to \epsilon_{\text{max}}\).

We start again from the expression for the free energy in terms of the variables \(X\) and \(Y\). We assume that \(Y^*\) to be large, and a good approximation is to keep only the first two terms in the sum \(\Sigma(X, Y)\), corresponding to \(n = k^* - 2\) and \(n = k^* - 1\). Then,
\[
F(X, Y) = X(1 - \frac{2}{\rho} - \delta(k^* - 2)) + Y(\epsilon + \frac{1}{\rho} + \frac{1}{2} \delta(k^* - 2)(k^* + 1)) - \delta \ln(1 + e^{X-k^*Y}).
\]  
(80)

The saddle-point equations \(\partial F/\partial X = 0\) and \(\partial F/\partial Y = 0\) lead to a simple system for \(x = e^X\) and \(y = e^Y\):
\[
\frac{x}{y^{k^*}} = \frac{1 - \frac{2}{\rho} - \delta(k^* - 2)}{\delta(k^* - 1) - 1 + \frac{2}{\rho}}, \quad \frac{x}{y^{k^*}} = \frac{\epsilon + \frac{1}{\rho} + \frac{1}{2} \delta(k^* - 2)(k^* + 1)}{\epsilon + \frac{1}{\rho} + \frac{1}{2} \delta(k^* - 1)(k^* + 2)}
\]  
(81)
From this system we obtain a relation between $X$ and $Y$:

$$X = k^*Y + \ln \left( \frac{1 - \frac{2}{\rho} - \delta(k^* - 2)}{\delta(k^* - 1) - 1 - \frac{2}{\rho}} \right),$$  \hspace{1cm} (82)

as well as a consistency relation between $\delta$ and $\epsilon$:

$$\delta^* = \frac{2\epsilon + \frac{1}{\rho} + k^*(1 - \frac{2}{\rho})}{(k^* - 1)(k^* - 2)}$$  \hspace{1cm} (83)

Let us note that at the upper boundary of the interval studied, i.e. for $\epsilon = \epsilon_{\text{max}} = -\frac{1}{2}(k^* + 1) + \frac{k^*}{\rho}$, this consistency relation gives $\delta = \delta_{\text{max}} = (1 - 2/\rho)/(k^* - 2)$, which is indeed the exact result. Then the expression for entropy can be computed in a simple way:

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

$$- \delta^* \ln \left( \frac{\delta^*\rho(1 - \delta^*\rho)}{(1 - 2\delta^*\rho)^2} \right) + \frac{1}{\rho} \ln \left( \frac{1 - \delta^*\rho}{1 - 2\delta^*\rho} \right)$$  \hspace{1cm} (84)

This gives an estimate for the entropy of metastable states near $\epsilon_{\text{max}}(k^*)$ for a given $k^*$. Note that the expression found above is actually defined only in the interval $[\epsilon_{\text{max}}(k^* + 1) = -\frac{1}{2}(k^* + 2) + \frac{k^* + 1}{\rho}; \epsilon_{\text{max}}(k^*) = -\frac{1}{2}(k^* + 1) + \frac{k^*}{\rho}]$, beyond which the present approximation breaks down.

To summarize, for each $k^*$, or equivalently for each $u = T\ln t$, we found the behaviour of the entropy of metastable states both for very low energies ($\epsilon \rightarrow -\infty$), where it is independent of $k^*$, and in the vicinity of the maximum energy $\epsilon_{\text{max}}(k^*)$. Thus the full curve for $S_\rho(\epsilon, k^*)$ is an extrapolation between these two asymptotic regimes, as shown in Fig. 10.

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