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**Abstract.** We present results showing aging during the collapse of a polymer chain quenched
from an expanded state to the globular phase via Monte Carlo dynamics of a model
homopolymer. The constructed two-time correlation function, an analogue of the density-
density autocorrelation, shows a power-law scaling with respect to the size of monomer clusters
formed during the collapse. The numerical estimates obtained at different quench temperatures
are in agreement with a theoretically predicted bound for the decay exponent governing the
scaling behavior.

## 1. Introduction

The characteristic feature of aging is that a younger system relaxes faster than an older one.
Considering its realization in diverse fields starting from spin systems to biology makes it an
important as well as interesting topic of research. Aging is quite popular for systems with slow
dynamics, e.g., glasses (both spin glass and structural glass) [1, 2], and especially for ordering
kinetics [3] the theoretical understanding is quite developed [4, 5]. On the other hand, there have
been little efforts in exploring this phenomenon in the dynamics of the collapse of a polymer
chain when it is quenched from its extended state in a good solvent (above the collapse transition
temperature) to the globular phase in a poor solvent (below the collapse transition temperature).

Aging in general is probed by multiple-time properties of an evolving system, e.g., the two-
time autocorrelation function defined as

$$C(t, t_w) = \langle O_i(t) O_i(t_w) \rangle - \langle O_i(t) \rangle \langle O_i(t_w) \rangle, \tag{1}$$

where $t$ and $t_w$ ($\ll t$) are the observation and waiting times, respectively. Here $O_i$ is a parameter
that reflects the spatio-temporal changes during the physical process, e.g., the time- and space-
dependent order parameter for ordering kinetics. For ferromagnetic ordering $C(t, t_w)$ shows a
power-law decay as

$$C(t, t_w) \sim (\ell/\ell_w)^{-\lambda}; \quad d/2 \le \lambda \le d, \tag{2}$$

where $\ell$ ($\ell_w$) is the growing length scale at time $t$ ($t_w$) and $\lambda$ is the dynamical aging exponent.
The bound on $\lambda$ in (2) is known as the Fisher-Huse (FH) bound, first predicted for ordering spin
glasses [6] and later found to be valid for ferromagnetic ordering as well. In the latter case there
exists even detailed theoretical understanding of the full form of the scaling function [7, 8, 9].
Here we exploit the similarities with ordering kinetics [10] to show the presence of aging and
associated dynamical scaling during the collapse of a homopolymer.
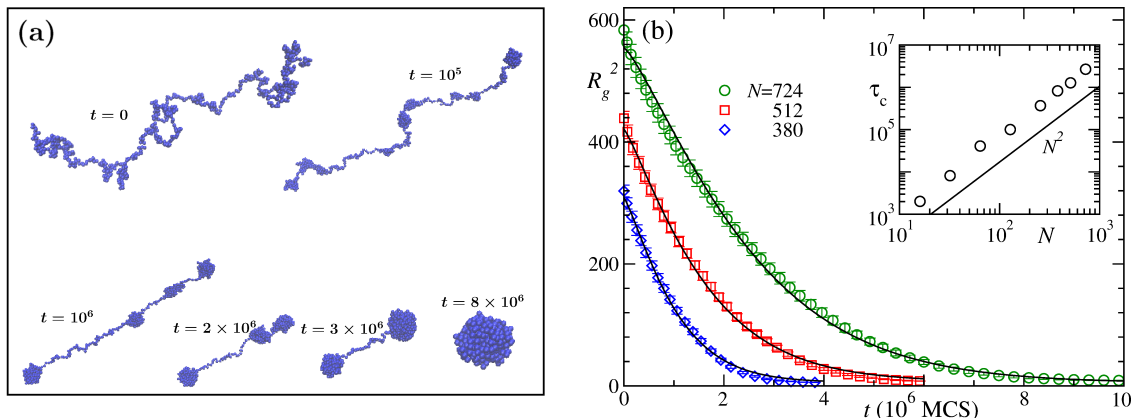
**Figure 1.** (a) Time evolution of a polymer with $N = 724$, after being quenched from $T_h = 10$ to $T_q = 1$. (b) Variation of the squared radius of gyration with time for three different $N$ as indicated. The continuous lines are fits to a stretched exponential decay, described in the text. The inset shows the scaling of the collapse times $\tau_c$ extracted from the fits, as a function of the chain length. The solid line there depicts the Rouse behavior $\tau_c \sim N^2$.

## 2. Model and Methods

We consider the bead-spring model for a flexible homopolymer in $d = 3$ with a nonbonded monomer-monomer interaction energy $E_{\mathrm{nb}}(r_{ij}) = E_{\mathrm{LJ}}(\min(r_{ij}, r_c)) - E_{\mathrm{LJ}}(r_c)$, where $E_{\mathrm{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$ is the standard Lennard-Jones (LJ) potential with $\sigma$ as the diameter of the monomers and $\epsilon$ being the interaction strength which is set to unity. A cut-off radius $r_c$ ($= 2.5\sigma$) is introduced for faster computation. The bond between successive monomers is maintained via the standard finitely extensible non-linear elastic (FENE) potential

$$E_{\mathrm{FENE}}(r_{ii+1}) = -\frac{K}{2} R^2 \ln \left[ 1 - \left( \frac{r_{ii+1} - r_0}{R} \right)^2 \right] \tag{3}$$

with $K = 40$, $r_0 = 0.7$, $R = 0.3$. For these choices and $\sigma = r_0/2^{1/6}$ the thermodynamics of this model is well known with no signature of glassy states [12]. Dynamics in this model is incorporated via Monte Carlo (MC) simulations where displacement moves, chosen randomly within $[-\sigma/10 : \sigma/10]$, are attempted on randomly chosen monomers following the standard Metropolis algorithm [11]. The unit of time is one MC step (MCS) that consists of $N$ such attempted moves where $N$ is the number of monomers present in the polymer chain. The unit of temperature is $\epsilon/k_B$ with the Boltzmann constant $k_B$ set to unity. We have prepared the initial configurations at high temperature ($T_h = 10$) which were then quenched into the globular phase at $T_q$, well below the collapse transition temperature $T_\theta$ ($> T_q$). All presented results are averaged over several hundred initial realizations.

## 3. Results

In Fig. 1(a), we show evolution snapshots at different times during the collapse for a polymer with $N = 724$. Initially at $t = 0$ the polymer is in an expanded state with fluctuations in the density of monomers along the chain. The fluctuations eventually lead to the formation of stable nucleation clusters, evident from the configuration at $t = 10^5$. These clusters then start growing by withdrawing monomers from the bridges connecting them and once the tension in the bridge reaches maximum the clusters coalesce with each other to form bigger clusters as shown in the snapshots at intermediate times. These events continue until they give rise to a single cluster like
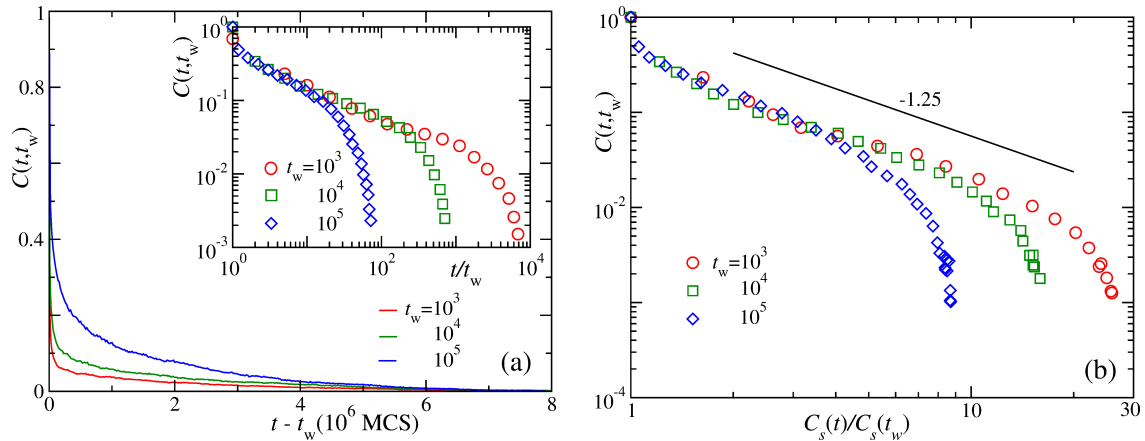
**Figure 2.** (a) Plot of the autocorrelation function $C(t, t_w)$ of a polymer with $N = 724$ for three different values of $t_w$ at $T_q = 1$. The inset shows the scaling of $C(t, t_w)$ as function of $t/t_w$. (b) Demonstration of the dynamic scaling of $C(t, t_w)$ as a function of $C_s(t)/C_s(t_w)$. The solid line corresponds to the power-law decay (4) with an aging exponent $\lambda_c = 1.25$.

in the snapshot at $t = 8 \times 10^6$. The sequence of events observed here looks pretty similar to the phenomenological picture of Halperin and Goldbart [13]. At this point it is worth mentioning that this cluster-growth phase of the collapse bears similarities with usual coarsening systems. To define the appropriate length scale for the cluster growth, we conveniently opt to measure the average cluster size $C_s(t)$ [$\sim \ell(t)^d$]. For that we identify a cluster on the basis of the local density around a monomer $i$, i.e., by counting the number of monomers $n_i = \sum\limits_{j=1}^{N} \Theta(r_c - r_{ij})$, where $\Theta$ is the Heaviside step function. We call it a cluster when $n_i \geq n_{\min}$, where $n_{\min}$ is a threshold value. It has been shown that the method is insensitive to reasonable choices of $n_{\min}$ [10]. Once the total number of discrete clusters is identified we measure the average cluster size, $C_s(t)$, as the average number of monomers present in each cluster. The kinetics of this cluster growth during the collapse has been explored by us elsewhere and was found to show a linear growth with time. As we are here particularly focused on the two-time properties, we shall not discuss the cluster growth further but refer to Ref. [10] for details.

In Fig. 1(b), we show the time evolution of the mean squared radius of gyration, $R_g^2 = \sum\limits_{i,j}(r_i - r_j)^2/2N^2$, for different $N$. The solid lines there are fits to the stretched exponential function $R_g^2 = a_0 + a_1 \exp[-(t/\tau_c)^\beta]$, where $\beta \approx 1.20 - 1.25$ and $\tau_c$ gives a measure of the collapse time. In the inset of Fig. 1(b), we show the scaling of $\tau_c$ with the chain length. The data seem to be quite parallel to the solid line which represents the Rouse scaling behavior ($\sim N^2$), expected for the diffusive dynamics of polymers in highly viscous solvent neglecting hydrodynamics [14].

Moving on to the prime quantity of interest in this work, we use our cluster identification technique to define the parameter $O_i$, in order to calculate the two-time property according to Eq. (1). We assign $O_i = \pm 1$ depending on whether the monomer is inside (+) or outside (−) a cluster [15]. The autocorrelation function $C(t, t_w)$ calculated this way is an analogue of the density-density autocorrelation in particle systems or the order-parameter autocorrelation for spin systems. In Fig. 2(a), the main frame shows plots of such autocorrelations $C(t, t_w)$ as function of $t - t_w$, clearly indicating the absence of time-translational invariance, the evidence for aging. In the inset we show the scaling of $C(t, t_w)$ with respect to $t/t_w$, a signature of simple aging. Note that at late time the abrupt decay is due to the onset of finite-size effects. The
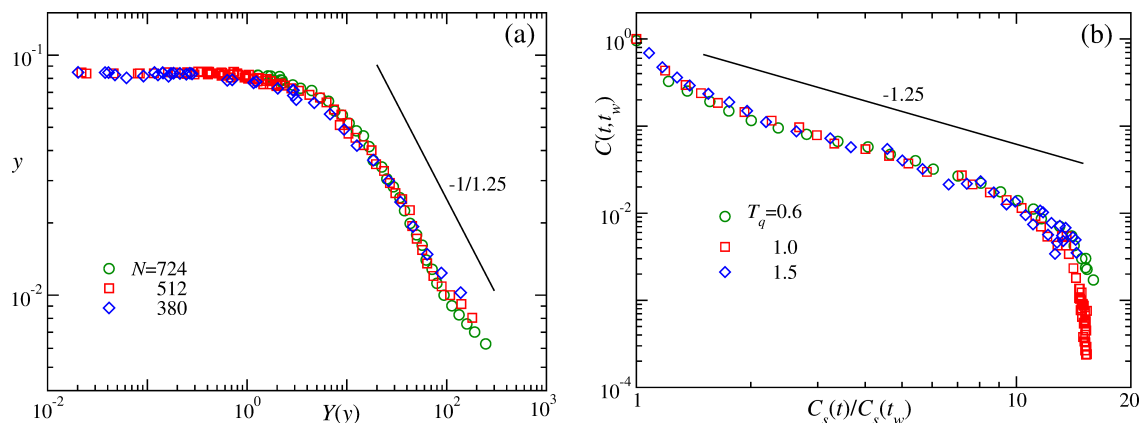
**Figure 3.** (a) Finite-size scaling plots for $C(t, t_w)$ with $t_w = 10^4$ at $T_q = 1$. The solid line shows the expected behavior $y \sim Y(y)^{-1/\lambda_c}$ with $\lambda_c = 1.25$. (b) Scaling plot of $C(t, t_w)$ as a function of $C_s(t)/C_s(t_w)$ for different quench temperatures $T_q$ as mentioned.

observed scaling of the autocorrelations with respect to the growing length scale in ordering kinetics motivated us to look for such scaling also here, of course with respect to the growing cluster size $C_s(t)$, the corresponding relevant quantity. Figure 2(b) shows such a scaling plot of $C(t, t_w)$ as a function of $C_s(t)/C_s(t_w)$. The steep early-time decay is attributed to short-time fluctuations. The linear behavior of the data on a double-log scale suggests that the scaling is power law in nature which can be quantified as

$$C(t, t_w) = A \left[ C_s(t)/C_s(t_w) \right]^{-\lambda_c}, \tag{4}$$

where $\lambda_c$ is the corresponding aging exponent and $A$ is an amplitude that depends on temperature. Below we derive a theoretical bound on $\lambda_c$.

From the fact that $C(t, t_w)$ is an analogue to the density-density autocorrelation it is justified to assume $C(t, t_w) \sim \langle \rho(t)\rho(t_w) \rangle$ where $\rho$ is the average density of monomers. Considering $t_w$ to be an early enough time, one can argue that the polymer is in an extended configuration so that the average density $\rho(t_w) \sim C_s/C_s{}^{d\nu}$ for a set of $C_s$ monomers, where $\nu$ is the Flory exponent for the size, i.e., radius of gyration ($R_g \sim C_s^\nu$) of a polymer chain of $C_s$ monomers. Now in the first limiting situation, at later time $t$, $\rho(t) = 1$, assuming all the monomers to be inside a single cluster and a maximum overlap between $\rho(t)$ and $\rho(t_w)$, provides the lower bound on $\lambda_c$ with $C(t, t_w) \sim C_s/C_s^{\nu d} \sim C_s^{-(\nu d - 1)}$. The other limiting situation of the polymer being still in an expanded state at time $t$, provides the upper bound on $\lambda_c$ with $C(t, t_w) \sim C_s^{-2(\nu d - 1)}$. Combining, we get the bound on $\lambda_c$ as [15]

$$(\nu d - 1) \leq \lambda_c \leq 2(\nu d - 1). \tag{5}$$

Putting $\nu \approx \nu_F = 3/5$ in Eq. (5), where $\nu_F$ is the Flory approximation for polymers with excluded volume interaction, one would get $4/5 \leq \lambda_c \leq 8/5$. The consistency of our data in Fig. 2(b) with the line having slope $-1.25$ shows that this bound is likely to be valid. A more precise estimate of $\lambda_c$ based on a finite-size scaling analysis can be done by writing down $NC(t, t_w) = Y(y)$, where $Y(y)$ is a finite-size scaling function and $y$ is the scaling variable. Now, for an appropriate choice of $y = [C_s(t)/C_s(t_w)] (NA)^{-1/\lambda_c}$, one gets $Y(y) \sim y^{-\lambda_c}$, i.e., $y \sim Y(y)^{-1/\lambda_c}$ in the scaling regime. By fixing the value of $A = 1$ we have tuned the value of $\lambda_c$ to obtain the optimum collapse of data from different $N$. In this exercise a reasonably good data collapse is obtained for $\lambda_c = 1.25(5)$, consistent with the predicted bound (5). A

representative of such finite-size scaling plots with $\lambda_c = 1.25$ is shown in Fig. 3(a). The data from different system sizes collapse onto each other to follow the scaling behavior $y \sim Y^{-1/\lambda_c}$ [15]. The plateau for smaller values of $Y$ is due to the onset of finite-size effects at late times.

In Fig. 3(b) we demonstrate the independence of the autocorrelation function on the quench temperature $T_q$, where the $y-$axis has been multiplied by an appropriate factor in order to take care of the amplitudes $A$ at different $T_q$. The collapse of the data from different $T_q$ onto a single master curve shows that the power-law scaling is independent of the quench depth. Note that in this plot we have used different $t_w$ for different $T_q$ such that the values of $C_s(t_w)$ are approximately the same and consequently the data for all $T_q$ have the same scaling width. The solid line shows the consistency of our data with the value of the aging exponent obtained from the finite-size scaling exercise at $T_q = 1$ and implies that the bound (5) is in fact valid at all temperatures.

## 4. Conclusion
We have presented results from the diffusive dynamics of a homopolymer collapse via Monte Carlo simulation seeking evidences for aging. By constructing a suitable two-time correlation function we have captured the aging during the collapse and also found an associated power-law scaling with respect to the growing clusters of monomers. In addition, for the decay exponent governing the scaling we have derived a theoretical bound which is not only found to be valid when compared with our estimates using finite-size scaling analysis but also appears to be independent of the quench temperatures.

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