

Evidence of aging and dynamic scaling in the collapse of a polymer

Suman Majumder* and Wolfhard Janke†

Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany

(Received 4 September 2015; revised manuscript received 16 December 2015; published 28 March 2016)

We investigate a newly framed two-time property for the nonequilibrium evolution dynamics during the collapse of a homopolymer via Monte Carlo simulations of a model polymer. Our results show evidence of aging effects, as observed in the slow dynamics of structural and spin glasses, along with the presence of a dynamic scaling of the autocorrelation function $\sim x^{-\lambda_c}$ (x being the ratio of the cluster sizes at two different times). We estimate the value of λ_c unambiguously by applying a finite-size scaling analysis to the numerical data. The value thus obtained obeys a bound which we predict via general theoretical arguments. The results presented should be of general validity and may trigger direct experimental verification in single-polymer dynamics.

DOI: [10.1103/PhysRevE.93.032506](https://doi.org/10.1103/PhysRevE.93.032506)

I. INTRODUCTION

The ubiquitous nature of aging makes it a fundamental as well as a fascinating topic of research in diverse fields [1–6] including medical science [7,8]. For systems exhibiting slow dynamics upon quenching, e.g., structural glasses [9] (polymer melts) and spin glasses [10], the existence of aging has been realized experimentally [11,12] and theoretically [13–15] as well as numerically [13,16]. Apart from glassy dynamics, aging is also relevant in nonequilibrium coarsening processes [17,18], e.g., in ferromagnetic ordering and phase separation kinetics. In spite of its significant similarities with coarsening processes, aging effects related to the collapse of a homopolymer have rarely been explored [19,20]. The collapse transition bears phenomenological connection with the folding process of a protein, basically a heteropolymer. In fact there is evidence from experiments [21–23] and simulations [24] that the (hydrophobic) collapse precedes the folding of a protein to a compact native state. These facts motivated us to investigate the collapse of a homopolymer following a quench from a good to a poor solvent seeking evidences in favor of aging phenomena and eventually the existence of dynamic scaling behavior.

Unlike the other dynamic aspects where one mainly deals with single-time quantities, aging is probed by multiple-time quantities, e.g., the two-time autocorrelation of a microscopic variable O_i as

$$C(t, t_w) = \langle O_i(t)O_i(t_w) \rangle - \langle O_i(t) \rangle \langle O_i(t_w) \rangle, \quad (1)$$

where t and t_w ($\ll t$) are the observation and waiting times, respectively. Here $\langle \dots \rangle$ denotes averaging over different initial realizations and thermal noise. Slower decay of $C(t, t_w)$ with an increase of t_w is the signature of aging phenomena. For a nonequilibrium process, $O_i(t)$ is generally a quantity reflecting the time evolution of the system, e.g., the time- and space-dependent order parameter in coarsening systems. For spin glasses, Fisher and Huse (FH) [13] predicted a power-law decay of $C(t, t_w)$ in d dimension as

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

where ℓ (ℓ_w) is the corresponding growing length scale at t (t_w) and λ is the dynamic aging exponent. Understanding of such scaling for ferromagnetic ordering is richly developed [17,18], and the FH bound is strictly obeyed [13,25]. There are even efforts to obtain the full form of such scaling functions using local scale invariance [26,27] or via an empirical approach using an effective exponent [28]. However, in fluids the presence of hydrodynamics may lead to an exponential decay [29]. For glasses in particular, one calculates the nonequilibrium incoherent scattering functions by using $O_i = \exp[i\mathbf{q} \cdot \mathbf{r}_i(t)]$ in Eq. (1) where \mathbf{q} is a wave vector and \mathbf{r}_i the position vector. Despite the fact that aging effects in glasses have been extensively studied, to the best of our knowledge, such scaling with respect to a growing length scale has rarely been emphasized [30,31]. The same is the case for the very few existing studies on aging during single polymer collapse, mostly [19] done at very low temperatures.

In this work, we study the collapse of a single polymer via Monte Carlo (MC) simulations and propose an analog of the density-density autocorrelation to probe aging. Our results show the presence of a power-law scaling of the autocorrelation function. We also derive a bound to the aging exponent from very general scaling arguments and apply finite-size scaling analyses for an unambiguous numerical estimate of the exponent.

II. MODEL AND METHODS

We use the bead-spring model, a prototype for flexible polymers in $d = 3$ where nonbonded monomers i and j at distance r_{ij} interact with each other via $E_{\text{nb}}(r_{ij}) = E_{\text{LJ}}[\min(r_{ij}, r_c)] - E_{\text{LJ}}(r_c)$, where

$$E_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

is the standard Lennard-Jones (LJ) potential with σ , the diameter of the monomers and ϵ , the interaction strength which is set to unity for convenience. The cutoff radius r_c ($=2.5\sigma$) is introduced in E_{nb} for faster computation. The connectivity among the successive monomers is maintained via the standard finitely extensible nonlinear elastic (FENE) potential

$$E_{\text{FENE}}(r_{ii+1}) = -\frac{K}{2} R^2 \ln \left[1 - \left(\frac{r_{ii+1} - r_0}{R} \right)^2 \right] \quad (4)$$

*Suman.Majumder@itp.uni-leipzig.de

†Wolfhard.Janke@itp.uni-leipzig.de

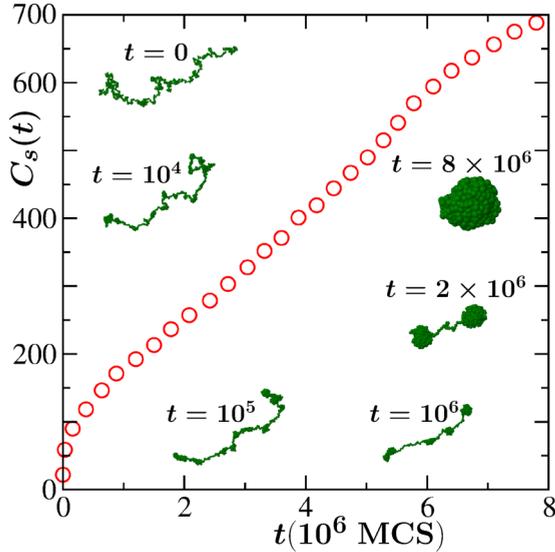


FIG. 1. Snapshots at different times as indicated, illustrating the evolution of a polymer with $N = 724$ after being quenched from $T_h = 10$ in an expanded coil state to $T_q = 1$. The main plot shows the time dependence of the cluster size $C_s(t)$, monitoring the kinetics of the collapse.

with $K = 40$, $r_0 = 0.7$, and $R = 0.3$. We chose $\sigma = r_0/2^{1/6}$ so that the minima of E_{nb} and E_{FENE} coincide. The thermodynamics of this model is well studied, showing nonglassy crystalline ground states [32–34].

Dynamics in the MC simulations is incorporated via the single monomer displacement moves, chosen randomly within $[-\sigma/10, \sigma/10]$, and the trial position of a randomly picked monomer is accepted or rejected according to the standard Metropolis algorithm [35]. This type of local moves shall reproduce the Rouse scaling [36] observed for the dynamics of a polymer chain in viscous solvent neglecting the hydrodynamics. One Monte Carlo step (MCS) consists of N (the number of monomers in the polymer chain) such trial moves which sets the unit of time t . The unit of temperature is ϵ/k_B , where k_B is the Boltzmann constant, also set to unity. We have used polymers with $N = 380, 512$, and 724 , and prepared the initial configurations at high temperature ($T_h = 10$), which were then quenched into the globular phase at $T_q = 1$, well below the collapse transition temperature, $T_\theta (\simeq 2.24)$, for the smallest N . All presented results are averaged over at least 200 independent initial realizations.

III. RESULTS

Figure 1 shows evolution snapshots at different times during the collapse for a polymer with $N = 724$. At $t = 0$ the polymer is in an expanded state where the fluctuations of monomer densities along the chain lead to the formation of nucleation clusters which eventually become stable clusters. Subsequently these clusters withdraw monomers from the bridge connecting the clusters and this way the clusters meet each other, which in the long run gives rise to a single compact globule. The sequence of events observed here is in accordance with the phenomenological picture of Halperin and

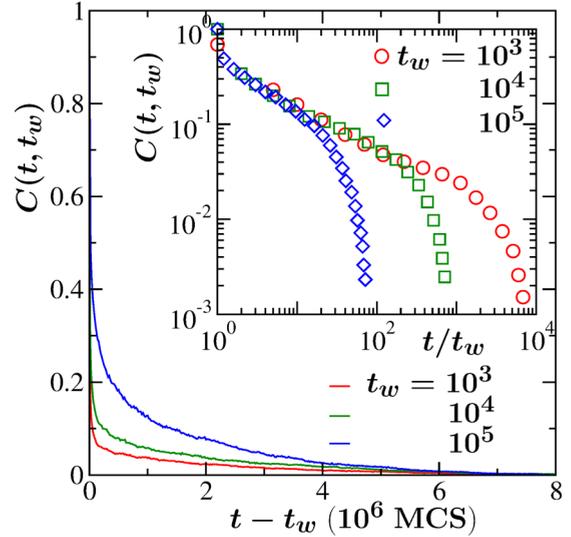


FIG. 2. Plot of $C(t, t_w)$ vs $t - t_w$ for three different waiting times t_w showing the aging during the collapse of a polymer with $N = 724$. The inset shows a double-log plot of the same data plotted against t/t_w depicting the scaling behavior.

Goldbart [37]. In order to monitor the kinetics we have measured the cluster size $C_s(t)$ [$\sim \ell(t)^d$] as the characteristic length scale. A cluster is identified on the basis of the local density around a monomer by counting the number of monomers $n_i = \sum_{j=1}^N \Theta(r_c - r_{ij})$, where Θ is the Heaviside step function. For $n_i \geq n_{min}$, we call it a cluster and remove the overlap via the corresponding Venn diagram to determine the actual number of discrete clusters. Note that the method is independent for any reasonable choice of n_{min} [38] and all the subsequent data are calculated using $n_{min} = 10$. The graph in Fig. 1 shows the variation of $C_s(t)$ with t quantifying the kinetics of cluster growth which is expected to follow a power law. However, the presence of a crossover cluster size makes it difficult to quantify the exponent. For a detailed analysis of the cluster growth we refer to our previous work [38]. Following that, if we do fitting with the form $C_s(t) = C_0 + At^\alpha$ using data for $t \geq 5 \times 10^5$, we get $\alpha = 0.98(2)$ confirming a linear growth as observed in Ostwald ripening.

Next we move on to the central objective of this paper. We probe the two-time property during the collapse by constructing a suitable autocorrelation function that exploits the cluster identification technique. We define the variable O_i in Eq. (1) as a parameter based on the local density around the i th monomer, i.e., O_i takes up the value ± 1 depending on whether the monomer is inside (+1) or outside (−1) a cluster. Thus we have designed a two-time correlation function $C(t, t_w)$ which is analogous to the usual density-density autocorrelation function. In Fig. 2, $C(t, t_w)$ is plotted against $t - t_w$ for different t_w values. The absence of time-translation invariance can be easily seen which is a substantial evidence of aging. Of course one could extract the relaxation time (τ_w) as a function of t_w from these plots to further strengthen this claim. The fact that the higher the value of t_w the larger will be the value of τ_w , is the trademark of aging phenomena. However, here we do not present such an exercise but move on to look for the existence of scaling with respect to t/t_w . The inset of Fig. 2 shows such

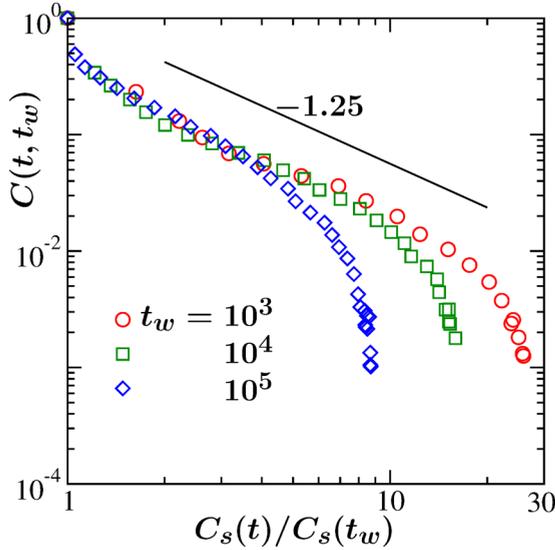


FIG. 3. Plot of $C(t, t_w)$ vs $C_s(t)/C_s(t_w)$ on a double-log scale for three different values of t_w , as mentioned for $N = 724$. The solid line represents a power-law decay with an exponent -1.25 .

a plot of $C(t, t_w)$ vs t/t_w on a double-log scale demonstrating the scaling behavior. The data for different t_w follow each other until they start deviating at late time due to finite-size effects. We have also tested the presence of any special aging by plotting $C(t, t_w)$ vs t/t_w^μ where μ is a nontrivial exponent and $\mu > 1$ (or < 1) refers to super- (or sub-) aging. However, our data do not show any scaling for $\mu \neq 1$, discarding the presence of any special aging. Hence we do not present the data here.

The scaling of $C(t, t_w)$ as a function of t/t_w motivated us to look for the scaling with respect to the ratio of the cluster sizes, i.e., $C_s(t)/C_s(t_w)$. This is executed in Fig. 3 showing a scaling plot of $C(t, t_w)$ as a function of $C_s(t)/C_s(t_w)$ which is analogous to the scaling behavior (2) observed in ordering kinetics [28]. Here also the late time deviation is due to the finite-size effects. The steep decay at very early times is attributed to short-time fluctuations. The solid line there shows the consistency of the data with a power-law decay

$$C(t, t_w) \sim [C_s(t)/C_s(t_w)]^{-\lambda_c} \quad (5)$$

having $\lambda_c = 1.25$. However, at this point it would be naive to conclude about the precise value of the aging exponent λ_c . Before quantifying this exponent more accurately, here we first derive a bound on λ_c from general scaling arguments. As explained earlier, $C(t, t_w)$ is calculated on the basis of local monomer densities along the polymer chain. Hence, as for spin-glass and ferromagnetic ordering [13,25] one can assume $C(t, t_w) \sim \langle \rho(t)\rho(t_w) \rangle$ where ρ is the average density of monomers. Now considering a set of C_s monomers at $t (\gg t_w)$ and assuming that at t_w the polymer is more or less in an expanded coil state, one can write $\rho(t_w) \sim C_s/C_s^{dv}$ where ν is the Flory exponent for the radius of gyration ($R_g \sim C_s^\nu$). Now there are two possibilities. First, at later time t , $\rho(t) = 1$, assuming that all the monomers are inside a cluster. Thus considering the maximum overlap between $\rho(t)$ and $\rho(t_w)$ we get $C(t, t_w) \sim C_s/C_s^{vd} \sim C_s^{-(vd-1)}$. This gives the lower

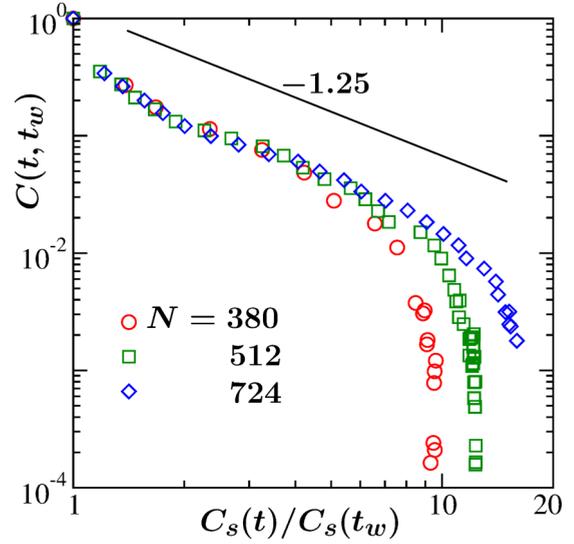


FIG. 4. Double-log plot of $C(t, t_w)$ vs $C_s(t)/C_s(t_w)$ from polymers with $N = 380, 512$, and 724 for $t_w = 10^4$. The solid line shows the power-law decay (5) with exponent $\lambda_c = 1.25$.

bound. Second, if the assumption that the polymer is in an expanded state still holds at time t , then $C(t, t_w) \sim C_s^{-2(vd-1)}$, which gives the upper bound. The obtained bound is thus

$$(vd - 1) \leq \lambda_c \leq 2(vd - 1). \quad (6)$$

The scaling argument presented here is pretty similar to the argument used to propose the FH bound (2). Now by putting $\nu \approx \nu_F = 3/5$ in Eq. (6), where ν_F is the Flory approximation for polymers with excluded volume interaction, one would get $4/5 \leq \lambda_c \leq 8/5$. Inserting the more precise numerical estimate $\nu = 0.587597$ [39], we get $0.762791 \leq \lambda_c \leq 1.525582$. The consistency of our data in Fig. 3 with the line having slope -1.25 shows that this bound is indeed valid. A more precise estimate of λ_c based on a finite-size scaling analysis will be discussed below. Note that our choice of t_w in all the plots is based on the above scaling arguments. We have chosen $t_w \leq 10^5$ following the assumption that the polymer remaining in a more or less expanded state is still valid, which can also be appreciated from the snapshots presented in Fig. 1. The little off behavior of the data for $t_w = 10^5$ in Fig. 3 is indeed due to the fact that at $t = 10^5$ the formation of stable clusters has already initiated. Hence for the finite-size scaling exercise we will use the data for $t_w = 10^4$ from polymers with different N .

In Fig. 4 we have plotted $C(t, t_w)$ as function of $C_s(t)/C_s(t_w)$ with $t_w = 10^4$ for three different N as indicated in the figure. The data for different N follow each other until they encounter the finite-size effects and are again consistent with a power-law decay having the exponent 1.25. Next we introduce the finite-size scaling analysis, a technique widely used in critical phenomena [40,41] by using the data from Fig. 4. We construct our finite-size scaling ansatz by assuming a power-law decay of $C(t, t_w)$ and rewrite Eq. (5) as

$$C(t, t_w) = Ax^{-\lambda_c}; \quad x = C_s(t)/C_s(t_w). \quad (7)$$

We account for the size effect via $NC(t, t_w) = Y(y)$ where $Y(y)$ is the finite-size scaling function and y is the scaling

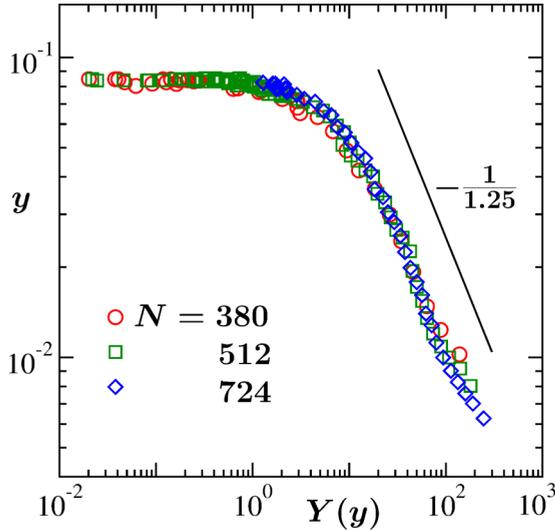


FIG. 5. Finite-size scaling plot on a double-log scale using the data from polymers with different N , as indicated. This plot represents the optimum data collapse, obtained with $\lambda_c = 1.25$. The solid line shows $y \sim Y(y)^{-1/\lambda_c}$.

variable. Now for appropriate choice of $y = x(NA)^{-1/\lambda_c}$ one gets $Y(y) \sim y^{-\lambda_c}$, i.e., $y \sim Y(y)^{-1/\lambda_c}$ in the scaling regime. In the finite-size scaling exercise we fix $A = 1$ and tune the value of λ_c to obtain the optimum collapse of data from different N . We have obtained reasonably good data collapse for $\lambda_c = 1.25(5)$, which is consistent with the predicted bound (6). In Fig. 5 we present a representative of such finite-size scaling plots with $\lambda_c = 1.25$. The data from different system sizes nicely collapse with each other and follow the scaling behavior $y \sim Y^{-1/\lambda_c}$. The flat nature of the data for smaller values of Y is due to the onset of finite-size effects. Finally, recalling the theoretical argument for (6), if one assumes that at time t the polymer is in a theta state (a Gaussian chain with $\nu_\theta = 0.5$), an intriguingly matching value of $\lambda_c = (\nu d - 1) + (\nu_\theta d - 1) = 1.262791$ can be obtained.

IV. CONCLUSIONS

In this paper we have presented results for the evolution dynamics during the collapse of a homopolymer with particular emphasis on two-time properties. As a probe we have designed a two-time correlation function $C(t, t_w)$ in analogy to the density-density correlations, based on the cluster formation during the collapse. Presence of aging behavior is evident from the dynamic power-law scaling as $C(t, t_w) \sim [C_s(t)/C_s(t_w)]^{-\lambda_c}$. For the exponent λ_c governing the decay, we have provided simple scaling arguments to predict a bound $(\nu d - 1) \leq \lambda_c \leq 2(\nu d - 1)$ in relation to the universal Flory exponent ν . Our numerical estimate of λ_c via finite-size scaling analysis gives $\lambda_c = 1.25(5)$, which obeys the predicted bound. A comprehensive study on the validity of this bound for different quenching depths is in progress. Considering the fact that the collapse of the heteropolymer backbone in the early stages facilitates the folding process of an unfolded (expanded) protein to its native structure [42], we feel that a deeper understanding of the collapse based on the framework of our study may lead to new insights into the kinetics of protein folding [24,43–46]. In this regard the simplest task would be to explore heteropolymer models, which we take as a future endeavor.

Since our results neglect hydrodynamics, at first sight they may seem difficult to compare with experiments. However, there are many realistic situations, e.g., polymers adsorbed on fluid surfaces (lipid membranes) [47,48] and in crowded environment [49], where hydrodynamic interactions are negligible. Furthermore recent successful experiments in vacuum (no hydrodynamics or solvent effects) on structure [50,51] and dynamics [52] of single polymers open up the possibility of designing protocols for direct verification of our results.

ACKNOWLEDGMENTS

We thank Subir K. Das for useful discussions. The work was funded by the DFG (German Science Foundation) under Grant No. JA 483/24-3 and SFB/TRR 102 (project B04), and further supported by the EU through the Marie Curie IRSES network DIONICOS under Contract No. PIRSES-GA-2013-612707.

-
- [1] R. Mathieu, P. Nordblad, D. N. H. Nam, N. X. Phuc, and N. V. Khiem, Short-range ferromagnetism and spin-glass state in $Y_{0.7}Ca_{0.3}MnO_3$, *Phys. Rev. B* **63**, 174405 (2001).
 - [2] B. Abou and F. Gallet, Probing a Nonequilibrium Einstein Relation in an Aging Colloidal Glass, *Phys. Rev. Lett.* **93**, 160603 (2004).
 - [3] G. G. Kenning, G. F. Rodriguez, and R. Orbach, End of Aging in a Complex System, *Phys. Rev. Lett.* **97**, 057201 (2006).
 - [4] L. Berthier, Efficient Measurement of Linear Susceptibilities in Molecular Simulations: Application to Aging Supercooled Liquids, *Phys. Rev. Lett.* **98**, 220601 (2007).
 - [5] E. Bouchbinder and J. S. Langer, Shear-transformation-zone theory of linear glassy dynamics, *Phys. Rev. E* **83**, 061503 (2011).
 - [6] J. Bergli and Y. M. Galperin, Logarithmic relaxation and stress aging in the electron glass, *Phys. Rev. B* **85**, 214202 (2012).
 - [7] R. M. Z. dos Santos and A. T. Bernardes, Immunization and Aging: A Learning Process in the Immune Network, *Phys. Rev. Lett.* **81**, 3034 (1998).
 - [8] M. Costa, A. L. Goldberger, and C.-K. Peng, Broken Asymmetry of the Human Heartbeat: Loss of Time Irreversibility in Aging and Disease, *Phys. Rev. Lett.* **95**, 198102 (2005).
 - [9] L. C. E. Struick, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, New York, 1978); W. Kob, Supercooled liquids and glasses, in *Soft and Fragile Matter*, edited by M. E. Cates and M. Evans (IOP, Bristol, 2000), p. 259.

- [10] J.-P. Bouchaud, L. F. Cugliandolo, J. Kurchan, and M. Mézard, Out of equilibrium dynamics in spin-glasses and other glassy systems, in *Spin Glasses and Random Fields*, edited by A. P. Young (World Scientific, Singapore, 1997), p. 161.
- [11] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Excess Wing in the Dielectric Loss of Glass Formers: A Johari-Goldstein β Relaxation?, *Phys. Rev. Lett.* **84**, 5560 (2000).
- [12] P. Lunkenheimer, R. Wehn, U. Schneider, and A. Loidl, Glassy Aging Dynamics, *Phys. Rev. Lett.* **95**, 055702 (2005).
- [13] D. S. Fisher and D. A. Huse, Nonequilibrium dynamics of spin glasses, *Phys. Rev. B* **38**, 373 (1988).
- [14] J.-L. Barrat and M.-L. Klein, Molecular dynamics of supercooled liquids near the glass transition, *Ann. Rev. Phys. Chem.* **42**, 23 (1991); W. Kob, Computer simulations of supercooled liquids and structural glasses, in *Annual Reviews of Computational Physics*, edited by D. Stauffer (World Scientific, Singapore, 1995), Vol. III, p. 1.
- [15] H. E. Castillo, C. Chamon, L. F. Cugliandolo, and M. P. Kennett, Heterogeneous Aging in Spin Glasses, *Phys. Rev. Lett.* **88**, 237201 (2002).
- [16] W. Kob and J.-L. Barrat, Aging Effects in a Lennard-Jones Glass, *Phys. Rev. Lett.* **78**, 4581 (1997).
- [17] M. Zannetti, Aging in domain growth, in *Kinetics of Phase Transitions*, edited by S. Puri and V. Wadhawan (CRC Press, Boca Raton, FL, 2009), p. 153.
- [18] M. Henkel and M. Pleimling, *Non-Equilibrium Phase Transitions, Vol. 2: Ageing and Dynamical Scaling Far from Equilibrium* (Springer, Heidelberg, 2010).
- [19] N. V. Dokholyan, E. Pitard, S. V. Buldyrev, and H. E. Stanley, Glassy behavior of a homopolymer from molecular dynamics simulations, *Phys. Rev. E* **65**, 030801(R) (2002).
- [20] E. Pitard and J.-P. Bouchaud, Glassy effects in the swelling/collapse dynamics of homogeneous polymers, *Eur. Phys. J. E* **5**, 133 (2001).
- [21] L. Pollack, M. W. Tate, A. C. Finnefrock, C. Kalidas, S. Trotter, N. C. Darnton, L. Lurio, R. H. Austin, C. A. Batt, S. M. Gruner, and S. G. J. Mochrie, Time Resolved Collapse of a Folding Protein Observed with Small Angle X-Ray Scattering, *Phys. Rev. Lett.* **86**, 4962 (2001).
- [22] M. Sadqi, L. J. Lapidus, and V. Muñoz, How fast is protein hydrophobic collapse? *Proc. Natl. Acad. Sci. USA* **100**, 12117 (2003).
- [23] B. Schuler, E. A. Lipman, and W. A. Eaton, Probing the free-energy surface for protein folding with single-molecule fluorescence spectroscopy, *Nature (London)* **419**, 743 (2002).
- [24] C. J. Camacho and D. Thirumalai, Kinetics and thermodynamics of folding in model proteins, *Proc. Natl. Acad. Sci. USA* **90**, 6369 (1993).
- [25] F. Liu and G. F. Mazenko, Nonequilibrium autocorrelations in phase-ordering dynamics, *Phys. Rev. B* **44**, 9185 (1991).
- [26] M. Henkel, A. Picone, and M. Pleimling, Two-time autocorrelation function in phase-ordering kinetics from local scale invariance, *Europhys. Lett.* **68**, 191 (2004).
- [27] E. Lorenz and W. Janke, Numerical tests of local scale invariance in ageing q -state Potts models, *Europhys. Lett.* **77**, 10003 (2007).
- [28] J. Midya, S. Majumder, and S. K. Das, Aging in ferromagnetic ordering: Full decay and finite-size scaling of autocorrelation, *J. Phys.: Condens. Matter* **26**, 452202 (2014).
- [29] S. Majumder and S. K. Das, Effects of Density Conservation and Hydrodynamics on Aging in Nonequilibrium Processes, *Phys. Rev. Lett.* **111**, 055503 (2013).
- [30] G. Parisi, An increasing correlation length in off-equilibrium glasses, *J. Phys. Chem. B* **103**, 4128 (1999).
- [31] S. K. Nandi and S. Ramaswamy, How Do Glassy Domains Grow?, *Phys. Rev. Lett.* **109**, 115702 (2012).
- [32] S. Schnabel, T. Vogel, M. Bachmann, and W. Janke, Surface effects in the crystallization process of elastic flexible polymers, *Chem. Phys. Lett.* **476**, 201 (2009).
- [33] S. Schnabel, M. Bachmann, and W. Janke, Elastic Lennard-Jones polymers meet clusters: Differences and similarities, *J. Chem. Phys.* **131**, 124904 (2009).
- [34] S. Schnabel, W. Janke, and M. Bachmann, Advanced multi-canonical Monte Carlo methods for efficient simulations of nucleation processes of polymers, *J. Comp. Phys.* **230**, 4454 (2011).
- [35] D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics* (Cambridge University Press, Cambridge, 2005).
- [36] P. E. Rouse, A theory of the linear viscoelastic properties of dilute solutions of coiling polymers, *J. Chem. Phys.* **21**, 1272 (1953).
- [37] A. Halperin and P. Goldbart, Early stages of homopolymer collapse, *Phys. Rev. E* **61**, 565 (2000).
- [38] S. Majumder and W. Janke, Cluster coarsening during polymer collapse: Finite-size scaling analysis, *Europhys. Lett.* **110**, 58001 (2015).
- [39] N. Clisby, Accurate Estimate of the Critical Exponent ν for Self-Avoiding Walks via a Fast Implementation of the Pivot Algorithm, *Phys. Rev. Lett.* **104**, 055702 (2010).
- [40] M. E. Fisher, The theory of critical point singularities, in *Critical Phenomena, Proc. 51st Enrico Fermi Summer School, Varenna, Italy*, edited by M. S. Green (Academic, London, 1971), p. 1.
- [41] *Finite Size Scaling and Numerical Simulation of Statistical Systems*, edited by V. Privman (World Scientific, Singapore, 1990).
- [42] G. Haran, How, when and why proteins collapse: The relation to folding, *Curr. Opin. Struct. Biol.* **22**, 14 (2012).
- [43] C. M. Dobson, Protein folding and misfolding, *Nature (London)* **426**, 884 (2003).
- [44] J. N. Onuchic and P. G. Wolynes, Theory of protein folding, *Curr. Opin. Struct. Biol.* **14**, 70 (2004).
- [45] K. A. Dill and J. L. MacCallum, The protein-folding problem, 50 years on, *Science* **338**, 1042 (2012).
- [46] P. G. Wolynes, W. A. Eaton, and A. R. Fersht, Chemical physics of protein folding, *Proc. Natl. Acad. Sci. USA* **109**, 17770 (2012).
- [47] B. Maier and J. O. Rädler, Conformation and Self-Diffusion of Single DNA Molecules Confined to Two Dimensions, *Phys. Rev. Lett.* **82**, 1911 (1999).
- [48] H. J. Qian, L. J. Chen, Z. Y. Lu, and Z. S. Li, Surface Diffusion Dynamics of a Single Polymer Chain in Dilute Solution, *Phys. Rev. Lett.* **99**, 068301 (2007).
- [49] C. Echeverria and R. Kapral, Macromolecular dynamics in crowded environments, *J. Chem. Phys.* **132**, 104902 (2010).

- [50] S. Förster and W. Widdra, Structure of single polythiophene molecules on Au(001) prepared by *in situ* UHV electrospray deposition, *J. Chem. Phys.* **141**, 054713 (2014).
- [51] S. Förster, E. Kohl, M. Ivanov, J. Gross, W. Widdra, and W. Janke, Polymer adsorption on reconstructed Au(001): A statistical description of P3HT by scanning tunneling microscopy and coarse-grained Monte Carlo simulations, *J. Chem. Phys.* **141**, 164701 (2014).
- [52] M. Tress, E. U. Mapesa, W. Kossack, W. K. Kipnusu, M. Reiche, and F. Kremer, Glassy dynamics in condensed isolated polymer chains, *Science* **341**, 1371 (2013).