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# An Alternative Indicator for the Collapse Transition: Autocorrelation Time

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**Abstract**

In canonical statistical analysis, it is common to employ response quantities such as the specific heat to identify changes in the thermodynamic behavior of finite systems. However, as a consequence of finite-size effects, conventional thermodynamic quantities do not necessarily exhibit clear indications for pronounced thermal activity. By means of Metropolis Monte Carlo simulations of a coarse-grained model for flexible polymers, we investigate how the integrated autocorrelation times of energetic and structural quantities depend on the temperature. We show that, due to critical slowing down, an extremal autocorrelation time can also be considered as an indicator for the so-called collapse transition, which corresponds to a gas-liquid phase transition.

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## 1. Instruction

The biological function of proteins is often related to their three-dimensional geometric structures and severe illnesses can be caused by the misfoldings of proteins. Therefore, the necessity for a better understanding of general physical principles and mechanisms of structural transitions of polymers such as folding, crystallization, aggregation, and the adsorption at solid and soft substrates has increased rapidly in the past decades. Experimental and computational approaches have been developed to understand these various features. In order to improve the statistical accuracy of estimated expectation values of measured physical quantities, appropriate estimates of the corresponding autocorrelation times are necessary. In the past, most of the studies on analyzing the properties of the autocorrelation times focused on spin models. In the Ising model, the phase transition between ferromagnetism and paramagnetism is of second order. In the thermodynamic limit (i.e., infinite system size), the autocorrelation time $\tau$ approximately satisfies the power law $\tau \propto \xi^z \propto |1 - T/T_c|^{-\nu z}$ in the neighborhood of the critical point $T_c$, where $\xi$ denotes the spatial correlation length, $\nu$ and $z$ denote the critical exponent and dynamic critical exponent, respectively. In computer simulation, $z$ is an algorithm dependent critical exponent. For a system with finite size $L$, $\tau \sim L^z$ at temperatures

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sufficiently close to the critical point [Landau and Binder (2000); Newman and Barkema (1999); Janke (2002)]. The combination of local updates, such as single spin flips, and the Metropolis algorithm [Metropolis et al. (1953)] cause the autocorrelation time to be rather large, since $z \approx 2$ in this case. This effect is usually called critical slowing down which can be reduced to less than unity if non-local update mechanisms, such as Swendsen-Wang, Wolff, and multigrid algorithms are employed [Newman and Barkema (1999); Janke (1998); Sokal (1989, 1992); Kandel et al. (1988, 1989); Coddington (1992)]. For systems exhibiting a first-order phase transition, the dynamics in a canonical ensemble will suffer from the "supercritical slowing down". At the transition temperature, the average residence time the system spends in a pure phase is described by the autocorrelation time $\tau \propto \exp(2\sigma L^{d-1})$, where $\sigma$ is the (reduced) interface tension and $L$ is the projected area of the interfaces. For our study, we investigated the autocorrelation times of different quantities for a coarse-grained, elastic, flexible polymer model with the combination of local monomer displacement and Metropolis Monte Carlo sampling. The reason why we chose this combination is to resemble Brownian dynamics in a canonical ensemble. Our goal is to identify structural transitions and transition temperatures by employing autocorrelation times.

## 2. Model and Methods

We employ a model for elastic and flexible homopolymers [Bachmann (2014)], where the bonds are represented by the finitely extensible nonlinear elastic (FENE) potential [Bird et al. (1987); Kremer and Grest (1990); Milchev et al. (2001)]

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

Non-bonded monomers interact via a truncated, shifted Lennard-Jones potential

$$V_{\mathrm{LJ}}^{\mathrm{mod}}(r_{ij}) = V_{\mathrm{LJ}}(r_{ij}) - V_{\mathrm{LJ}}(r_{\mathrm{c}}). \tag{2}$$

with

$$V_{\mathrm{LJ}}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{3}$$

The total energy of a conformation $\zeta = (\vec{r}_1, \cdots, \vec{r}_L)$ for a chain with $L$ monomers reads

$$E(\zeta) = \sum_{i=1}^{L-2}\sum_{j=i+2}^{L} V_{\mathrm{LJ}}^{\mathrm{mod}}(r_{ij}) + \sum_{i=1}^{L-1} V_{\mathrm{FENE}}(r_{ii+1}). \tag{4}$$

Details of the parametrization are given in Qi and Bachmann (2014).

We employed the Metropolis Monte Carlo Method combined with local displacement updates in our simulation. In a single MC update, the conformation is changed by a random local displacement of a monomer. A chosen monomer is allowed to change its position within a small cubic box with edge lengths $d = 0.3r_0$. Once the update is suggested, we further utilize the Metropolis criterion [Metropolis et al. (1953)],

$$p = \min(1, \exp[-\beta(E_{\mathrm{new}} - E_{\mathrm{old}})]), \tag{5}$$

to decide if the update is accepted. Here, the inverse thermal energy is denoted by $\beta = 1/k_{\mathrm{B}}T$ (we set $k_{\mathrm{B}} \equiv 1$ in the simulations); $E_{\mathrm{old}}$ and $E_{\mathrm{new}}$ are the energies before and after the proposed update, respectively.

Suppose we generate a time series with a large number of data $N$ from an importance sampling MC simulation. For a quantity $O$, the strength of the correlation between two measurements with time displacement $k$ is described by the autocorrelation function

$$A(k) = \frac{\langle O_l O_{l+k}\rangle - \langle O_l\rangle^2}{\sigma_O^2}, \tag{6}$$

where $l$ can be any integer in the range $[1, N-k]$, and $\sigma_O^2 = \langle O_l^2\rangle - \langle O_l\rangle^2 = \langle O^2\rangle - \langle O\rangle^2$ is the standard variance of $O$. As usual, the autocorrelation function is a monotonically decreasing function. The independence of two measurements