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# Global Persistence Exponent of the Helix-Coil Transition in Polypeptides

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The dynamical exponent  $\theta_g$  that governs the behavior of the global persistence probability is obtained through short-time Monte Carlo simulations of the helix-coil transition. Our simulations are based on a detailed, all-atom representation of the molecules and an implicit solvation model to approximate the interaction with the surrounding solvent. Our results obtained for the polyalanine and the 34-residue human parathyroid fragment PTH(1-34) are in good agreement each other, and indicate universality of the helix-coil transition in proteinlike molecules.

## 1 Introduction

After the works by Janssen, Schaub, and Schmittmann<sup>1</sup> and Huse<sup>2</sup>, much attention has been devoted to study of phase transitions and critical phenomena of dynamical systems at the early stage of its time evolution. By using renormalization group techniques and numerical calculations, respectively, they showed that universality and scaling behavior are already present in this stage (henceforth named as short-time stage) after quenching from high temperatures to the critical one.

The values of the critical indices obtained through this technique<sup>3,4</sup>, have shown that short-time Monte Carlo simulations are very efficient and can be used to estimate, with good precision, the static exponents and the dynamical exponent  $z$ .

Far from equilibrium, another dynamic critical exponent was proposed by Majumdar et al.<sup>5</sup> studying the behavior of the global persistence probability  $P(t)$  that the order parameter has not changed its sign up to the time  $t$ . The global persistence probability  $P(t)$  can be defined as

$$P(t) = 1 - \sum_{t'=1}^t \rho(t'), \quad (1)$$

where  $\rho(t')$  is the fraction of the samples that have changed their state for the first time at the instant  $t'$ .

At criticality,  $P(t)$  is expected to decay algebraically as

$$P(t) \sim t^{-\theta_g} \quad (2)$$

where  $\theta_g$  is the global persistence exponent. Since then, the study of the persistence behavior have attracted much interest, playing an important role in the study of systems far from equilibrium<sup>6-8</sup>.

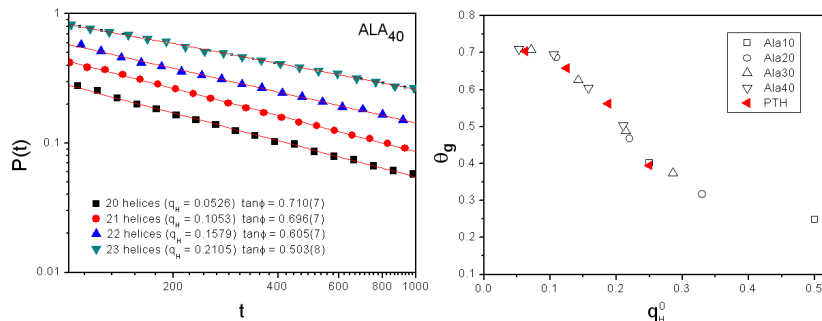


Figure 1. Left: Log-log plot of the time series of the global persistency  $P(t)$  for  $Ala_{40}$  and various initial order parameter values  $q_H^0$ . Right: Persistence exponent as a function  $q_H^0$ . Open symbols are the values for polyaniline and the filled symbols are the values for PTH(1-34).

In this work, we have studied the dynamic critical behavior of helical proteins via short-time Monte Carlo simulations. We evaluated the dynamic critical exponent  $\theta_g$  for  $(Ala)_N$  chains ( $N=10, 20, 30$  and  $40$ ) to verify the effects of finite size. Our investigation is later extended toward the 34-residue human parathyroid fragment PTH(1-34).

## 2 Model

Our short-time MC simulations of the helix-coil transition are based on a detailed, all-atom representation of proteins. The interaction between the atoms is described by a standard force field, ECEPP/2 (Empirical Conformational Energy Program for Peptides) as implemented in the program package SMMP (Simple Molecular Mechanics for Proteins)<sup>9</sup>. The interactions between our polypeptides and surrounding water are approximated by means of an implicit water model, which assumes that the solvation (free) energy is proportional to the solvent accessible surface area and utilizes the parameter set of Ref. 10 that is often used in conjunction with the ECEPP force field.

Crucial for our analysis is the definition of an order parameter. Our analog to the magnetization in spin systems is the number of helical residues  $q_H = 2 * \langle n_H(T) \rangle / (N - 2) - 1$ . Here we define a residue as helical if its backbone dihedral angles  $(\phi, \psi)$ , take values in the range  $(-70^\circ \pm 30^\circ, -37^\circ \pm 30^\circ)$  (their common values in an  $\alpha$  helix), and the residue exhibits the hydrogen bonding pattern observed in  $\alpha$  helices. The normalization factor  $N - 2$  ( $N$  the number of residues) is chosen because the flexible terminal residues are usually not part of an  $\alpha$  helix. Our definition ensures that  $-1 \leq q_H \leq 1$  and  $q_H(T_c) = 0$ .

## 3 Results

We start our investigation of dynamic critical exponent  $\theta_g$  in the helix-coil transition by simulating polyaniline chains of lengths  $N=10, 20, 30$ , and  $40$  in your respectively critical temperatura  $T_c = 315, 415, 450$  and  $470$  which were found in our earlier works<sup>11, 12</sup>. Our results are averaged over 5000 independent runs. Errors are estimated by dividing these

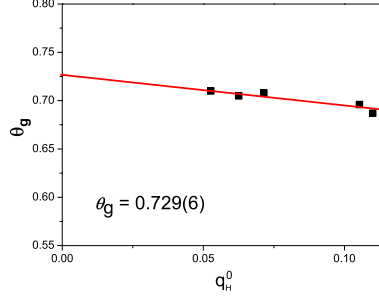


Figure 2. The scaling obtained for the 5 smaller  $q_H^0$ . The persistence exponent found is  $\theta_g = 0.729(6)$ .

5000 runs in bins of 100 runs and calculating the fluctuation of the averages calculated for each bin.

In order to estimate the exponent  $\theta_g$  one needs to prepare the initial states carefully to obtain precise values of the initial  $q_H^0 = q_H(t = 0)$ . The exponent  $q_H^0$  is obtained from Eq. 2. Figure 1 (Left) shows the corresponding log-log plots of  $P(t)$  for  $Ala_{40}$  and various initial values of  $q_H^0$ . This value, and the ones corresponding to polyaniline chains of length  $N = 10, 20$  and  $30$  are listed in Tab. 1.

$q_H^0$	$Ala_{10}$	$q_H^0$	$Ala_{20}$	$q_H^0$	$Ala_{30}$	$q_H^0$	$Ala_{40}$
0.25	0.402(6)	0.11	0.687(7)	0.0714	0.708(7)	0.0526	0.710(8)
0.50	0.248(7)	0.22	0.469(7)	0.1429	0.626(6)	0.1053	0.696(7)
		0.33	0.317(8)	0.2143	0.488(7)	0.1579	0.605(7)
				0.2857	0.374(7)	0.2105	0.503(7)

Table 1. Global persistence exponent  $\theta_g$  for polyaniline chains of length  $N = 10, 20, 30$  and  $40$ .

$q_H^0$	$PTH(1-34)$
0.0625	0.705(6)
0.125	0.658(7)
0.1875	0.562(6)
0.25	0.395(7)

Table 2. Global persistence exponent  $\theta_g$  for the 34-residue human parathyroid fragment  $PTH(1-34)$ .

The general behavior of the global persistence for each polyaniline indicate that when  $q_H^0$  decreases, the value for the persistence exponent  $\theta_g$  increases. In Fig 1 (Right) we show the  $\theta_g$  of all polyaniline as a function of the  $q_H^0$ . We can observe that the value of

$\theta_g$  increase quickly, with the decrease of the  $q_H^0$ , but tends to stabilize by  $\theta_g = 0.7$ . We also estimate the persistence exponent for the PTH(1-34),  $T_c = 545$  (Tab. 2). In Fig 2 we show that the values de  $\theta_g$  for PTH(1-34) (closed simbols) have the same behavior those the polyalanine (open simbols). From the 5 smaller  $q_H^0$  the persistence exponents  $\theta_g = 0.729(6)$  was estimated for this helical protein.

## 4 Conclusion

The behavior of exponent  $\theta_g = 0.729(6)$  for polyalanine and the 34-residue human parathyroid fragment PTH(1-34) are in good agreement each other, and indicate universality of the helix-coil transition in proteinlike molecules.

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Two of the authors (E.A. and J.R.D.F.) acknowledge support by Capes and CNPq (Brazil), and another author (U.H.E.H.) was supported by a research grant from the National Science Foundation (CHE-0313618).

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