

# The competition of hydrogen-like and isotropic interactions on polymer collapse

J Krawczyk<sup>1</sup>, A L Owczarek<sup>1</sup> and T Prellberg<sup>2</sup>

<sup>1</sup> Department of Mathematics and Statistics, The University of Melbourne, Parkville, Victoria 3052, Australia

<sup>2</sup> School of Mathematical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, UK

E-mail: [j.krawczyk@ms.unimelb.edu.au](mailto:j.krawczyk@ms.unimelb.edu.au), [aleks@ms.unimelb.edu.au](mailto:aleks@ms.unimelb.edu.au) and [t.prellberg@qmul.ac.uk](mailto:t.prellberg@qmul.ac.uk)

Received 14 June 2007

Accepted 4 September 2007

Published 24 September 2007

Online at [stacks.iop.org/JSTAT/2007/P09016](http://stacks.iop.org/JSTAT/2007/P09016)

doi:[10.1088/1742-5468/2007/09/P09016](https://doi.org/10.1088/1742-5468/2007/09/P09016)

**Abstract.** We investigate a lattice model of polymers where the nearest neighbour monomer–monomer interaction strengths differ according to whether the local configurations have so-called ‘hydrogen-like’ formations or not. If the interaction strengths are all the same then the classical  $\theta$ -point collapse transition occurs on lowering the temperature, and the polymer enters the isotropic liquid drop phase known as the collapsed globule. On the other hand, strongly favouring the hydrogen-like interactions gives rise to an anisotropic folded (solid-like) phase on lowering the temperature. We use Monte Carlo simulations up to a length of 256 to map out the phase diagram in the plane of parameters and determine the order of the associated phase transitions. We discuss the connections to semi-flexible polymers and other polymer models. Importantly, we demonstrate that for a range of energy parameters, two phase transitions occur on lowering the temperature, the second being a transition from the globule state to the crystal state. We argue from our data that this globule-to-crystal transition is continuous in two dimensions in accord with field-theory arguments concerning Hamiltonian walks, but is first order in three dimensions.

**Keywords:** classical Monte Carlo simulations, phase diagrams (theory), polymers, copolymers, polyelectrolytes and biomolecular solutions

---

**Contents**

|  |           |
|--|-----------|
| <b>1. Introduction</b>   | <b>2</b>  |
| <b>2. Model and simulations</b>  | <b>4</b>  |
| <b>3. Results and discussion</b>   | <b>6</b>  |
| 3.1. Pure hydrogen bonding and the canonical ISAW models . . . . .         | 6         |
| 3.2. Features of the phase diagram . . . . .                               | 7         |
| 3.3. Low temperature phases . . . . .                                      | 8         |
| 3.4. The phase transitions . . . . .                                       | 11        |
| 3.4.1. Swollen coil to folded crystal and swollen coil to globule. . . . . | 11        |
| 3.4.2. Collapsed globule to folded crystal. . . . .                        | 12        |
| 3.5. Summary . . . . .   | 13        |
| <b>Acknowledgments</b>   | <b>14</b> |
| <b>References</b>  | <b>15</b> |

---

**1. Introduction**

The self-avoiding walk (SAW) on a lattice [1, 2] is a key model in statistical mechanics for the study of the static properties of polymers. Incorporating interactions in this model makes it possible to represent many features of real polymers. Regardless of the constraints on the lattice relative to the real world, the model mimics very well many properties of physical systems [3]. The self-avoiding walk on a lattice is a random walk which is not allowed to visit a lattice site more than once. Unless a bending energy is introduced, each visited lattice site is considered to model more than one of the monomers of the polymer chain, thereby taking into account the natural rigidity of real polymers. A modelling, though unnatural, simplification is to consider fully flexible polymers so that each visited lattice site is considered to model only a single monomer. In either case, a common way [2] to model intra-polymer interactions in such a walk is to assign an energy to each non-consecutive pair of monomers lying on the neighbouring lattice sites. This is the canonical ISAW model which is the standard model of polymer collapse using self-avoiding walks. With this modification one studies a polymer in a solvent, where the energy between monomers can be attractive or repulsive and depends on temperature. If the energy is repulsive the polymer behaves as a swollen chain (the so-called excluded-volume state) regardless of temperature and one says that it is in a good solvent. When the energy is attractive, and the temperature is low enough, the chain becomes a rather more compact globule [2, 4], reminiscent of a liquid droplet: this is also known as the poor solvent situation. The transition point between those two phases is called the  $\theta$ -point; it is a well-studied continuous phase transition (see [5] and references therein).

The modelling changes as soon as we want to describe any biological system (e.g. proteins), in which the hydrogen bonding plays an important role [6]. One of the main features of the bonding is that the interacting residues lie on partially straight segments of the chain. Hydrogen-like bonding was first modelled on the cubic and square lattices

using Hamiltonian paths by Bascle *et al* [7]. A monomer acquires a hydrogen-like bond with its (non-consecutive) nearest neighbour if both of them lie on straight sections of the chain (see figure 2). Note that the identification of a single contact of this type with a single hydrogen bond is only valid if fully flexible polymers are considered; otherwise the contact represents an agglomeration of such bonds. The interacting self-avoiding walk modified to have only such interactions will be referred to as the hydrogen-like bonding model, or rather hb-model. The hb-model was studied in mean-field approximation [7] and a first-order transition from a high temperature excluded-volume (swollen) phase to a quasi-frozen solid-like phase was found in both two and three dimensions. Hence this would indicate that it is a different type of transition from the  $\theta$ -point one. Note also that the low temperature hb-phase is anisotropic whereas the collapsed globule of the standard  $\theta$ -point model is isotropic. The hb-model on the square lattice was studied directly by Foster and Seno by means of the transfer matrix method [8] and by Krawczyk *et al* [9] on both the square and cubic lattices using a Monte Carlo method. In both studies a first-order transition was found between an excluded-volume (swollen coil) state and an anisotropic ordered compact phase in two and in three dimensions, again in contrast to the  $\theta$ -point [2].

It is appropriate to compare this difference between the behaviours of the hb-model and  $\theta$ -point models with the difference between the behaviours of interacting semi-stiff polymers and the fully flexible  $\theta$ -point polymers. This is because hydrogen bonding induces an effective stiffness in the polymer between those monomers that are taking part in the interactions. As the temperature is lowered the proportion of the monomers experiencing this stiffness increases, so while not all the segments of the polymer feel this stiffness at high temperatures, the proportion of monomers involved with nearest neighbour hb-interactions increases towards unity as the temperature is lowered. In three dimensions, Bastolla and Grassberger [10] discussed so-called semi-stiff self-avoiding walks, which interact via all nearest neighbours, as in the  $\theta$ -point model, and include a bending energy. They showed that when there is a strong energetic preference for straight segments, this model undergoes a single first-order transition from the excluded-volume high temperature state to a state similar to the low temperature solid-like state of the hb-model. Intriguingly, if there is only a weak preference for straight segments, the polymer undergoes two phase transitions: on lowering the temperature the polymer undergoes the  $\theta$ -point transition to the liquid globule followed at a lower temperature by a first-order transition to the frozen phase. We should point out though that in two dimensions the transition between the globule and the frozen state has only been studied in Hamiltonian walks, and there it seems to be continuous one [11].

To complicate matters further, there is at least one other model using a different definition of interactions which could be regarded as hydrogen-like bonding. This model [12] defines interactions between parallel segments, that is, bonds of the lattice occupied by the walk and so connecting monomers; see figure 2. We will call this model the interacting bond model. Studying this model by means of Bethe approximation, Buzano and Pretti [12] found, in both two and three dimensions, two phase transitions: while decreasing the temperature the  $\theta$ -collapse to an isotropic globule phase is followed by a first-order transition to a solid-like phase. Hence, this is similar to the semi-stiff model for weak stiffness. The interacting bond model in two dimensions has recently been studied by Foster [14] and also displays two transitions. In [13] Buzano and Pretti added isotropic

nearest neighbour monomer–monomer interactions to the interacting bond model, and investigated the phase diagram in three dimensions, again in the Bethe approximation. They showed that the phase diagram is similar to the interacting bond model. However, if the interactions between monomers are repulsive, there is only one first-order phase transition from the swollen coil to the solid-like phase. This is again reminiscent of the semi-stiff model for strong stiffness.

It is therefore of some interest to study an enhanced hb-model where non-hydrogen bond nearest neighbours are also considered. Hence, in this paper we investigate a model of self-interacting self-avoiding walks with two types of nearest neighbour interaction: the hb-interactions and nearest neighbour interactions that are *not* hydrogen bonds, which we denote as nh-interactions. The competition between these two types of interaction (hb versus nh) leads to a three-phase phase diagram, with excluded-volume, globule and frozen phases. Of special interest is the comparison to the semi-stiff model. One key question is whether there can exist two phase transitions on lowering the temperature. The orders of the transitions in two and three dimensions are also of interest. We use a Monte Carlo technique, known as FlatPERM [15], to study self-avoiding walks on the simple cubic and square lattices with interactions as described.

The paper is organized as follows. In section 2 we explain more carefully details of the model. In section 3 the phase diagram in both dimensions is discussed. A discussion of the anisotropy of the model is also given. We conclude with a summary and discuss the similarity of this model to the semi-stiff model.

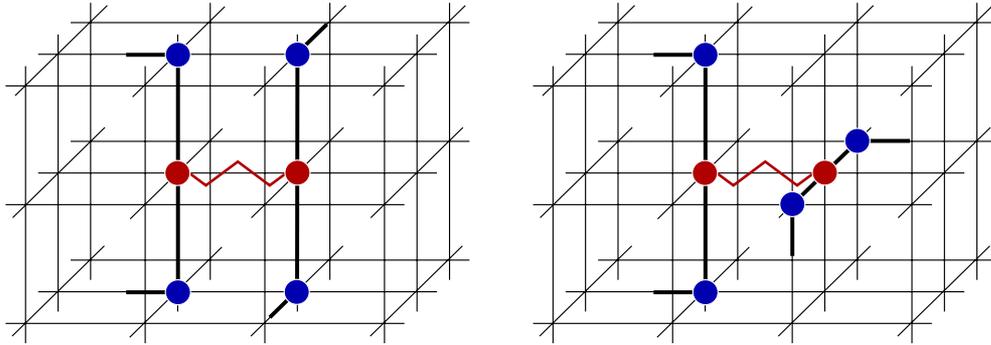
## 2. Model and simulations

The polymer is modelled on a square and simple cubic lattice as a self-avoiding walk with interactions between nearest neighbour monomers of different types: that is monomers that are not consecutive in the walk but nearest neighbours on the lattice. The strength of the interaction depends on the relative position of the monomers involved in the interaction to those next to them on the walk. A segment is defined as a site along with the two adjoining bonds visited by the walk, and we say that a segment is straight if these two bonds are aligned. The ‘hydrogen bonds’ are nearest neighbour interactions that are between monomers where both are part of *straight* segments of the polymer; see figure 1.

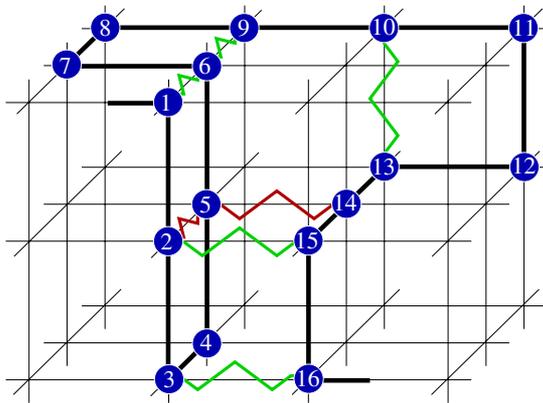
Our model weights the parallel and orthogonal hb interactions equally. Our model also includes all other possible nearest neighbour interactions and assigns them different Boltzmann weight. The two kinds of distinguished interactions are shown in figure 2. As just described, interactions between monomers sitting on straight lines, as in monomer No 5 of the triple of monomers No 2, No 5 and No 14, form the hydrogen bond interactions with like monomers, as in the interacting pairs of monomers 2–5 and 5–14. The energy of those interactions is denoted as  $-\varepsilon_{\text{hb}}$ . The other kind of interaction consists of any nearest neighbour interaction between non-consecutive monomers that are not hydrogen bonds, as in the pairs 1–6 and 10–13 for example. The energy of those interactions is denoted as  $-\varepsilon_{\text{nh}}$ .

Note that the number of all nearest neighbour interactions,  $m$ , is equal to the sum of the numbers of the two types of interaction considered in our model, that is  $m = m_{\text{nh}} + m_{\text{hb}}$ . The energy of configuration  $\varphi_n$  of an  $n$ -step walk is calculated as

$$E(\varphi_n) = -m_{\text{hb}}(\varphi_n) \cdot \varepsilon_{\text{hb}} - m_{\text{nh}}(\varphi_n) \cdot \varepsilon_{\text{nh}}, \quad (2.1)$$



**Figure 1.** The types of nearest neighbour interactions between two straight segments of the polymer involved in the hb-interactions: parallel segments (left) and orthogonal segments (right). In the model studied in this paper these two types are weighted equally. In two dimensions, only parallel interactions are possible.



**Figure 2.** Interactions in a 3D interacting self-avoiding walk. In our model we distinguish two different kinds of interactions, which are denoted by two different colours. The red colour (dark shading) denotes hydrogen-like interactions (hb) (monomers 2–5, 5–14) whereas the green colour (light shading) denotes all other interactions between two neighbouring monomers (nh) (monomers 1–6 and 10–13 for example).

where  $m_{\text{hb}}$  and  $m_{\text{nh}}$  are the number of hydrogen-like bond interactions and that of non-hydrogen-like nearest neighbour interactions, respectively. The inverse temperature is denoted as  $\beta = 1/k_{\text{B}}T$ , where  $k_{\text{B}}$  is the Boltzmann constant and  $T$  the absolute temperature. We define for convenience  $\beta_{\text{hb}} = \beta\varepsilon_{\text{hb}}$  and  $\beta_{\text{nh}} = \beta\varepsilon_{\text{nh}}$ . The partition function is then given by

$$Z_n(\beta_{\text{hb}}, \beta_{\text{nh}}) = \sum_{m_{\text{hb}}, m_{\text{nh}}} C_{n, m_{\text{hb}}, m_{\text{nh}}} e^{\beta_{\text{hb}} m_{\text{hb}} + \beta_{\text{nh}} m_{\text{nh}}} \quad (2.2)$$

with  $C_{n, m_{\text{hb}}, m_{\text{nh}}}$  the density of states. Canonical averages are calculated with respect to this density of states.

Since we will consider simulation results along lines in parameter space at a constant ratio of  $\varepsilon_{\text{nh}}/\varepsilon_{\text{hb}} = \beta_{\text{nh}}/\beta_{\text{hb}}$  we define  $\varepsilon_{\text{nh}} = \gamma$ , and  $\varepsilon_{\text{hb}} = 1 - \gamma$ , so the energy is then given by

$$E = -m_{\text{hb}} \cdot (1 - \gamma) - m_{\text{nh}} \cdot \gamma. \quad (2.3)$$

In our study we will analyse the (reduced) specific heat to investigate the phase diagram: that is,

$$C(T) = \frac{1}{T} \frac{\langle E^2 \rangle - \langle E \rangle^2}{n}. \quad (2.4)$$

We will also consider fixing one of the parameters, either  $\beta_{\text{hb}}$  or  $\beta_{\text{nh}}$ , and varying the other. To analyse the possible phase transitions we then use the fluctuations in the number of monomers of the appropriate type. In the case of  $\beta_{\text{hb}}$  being constant we consider

$$\sigma^2(m_{\text{nh}}) = \langle m_{\text{nh}}^2 \rangle - \langle m_{\text{nh}} \rangle^2. \quad (2.5)$$

When  $\beta_{\text{nh}}$  is constant we consider

$$\sigma^2(m_{\text{hb}}) = \langle m_{\text{hb}}^2 \rangle - \langle m_{\text{hb}} \rangle^2. \quad (2.6)$$

Simulations have been performed with the FlatPERM algorithm [15]. We have simulated the models using a two-parameter implementation (utilizing  $m_{\text{hb}}$  and  $m_{\text{nh}}$ ) for length  $n = 128$  where the simulation directly estimates this density of states  $C_{n,m_{\text{hb}},m_{\text{nh}}}$ . We have also performed one-parameter ( $m_{\text{hb}}$  or  $m_{\text{nh}}$ ) simulations for systems of size 256 where the simulation estimates partial summations of this density of states over one of the variables.

### 3. Results and discussion

#### 3.1. Pure hydrogen bonding and the canonical ISAW models

When  $\gamma = 1/2$  the model becomes the canonical interacting self-avoiding walk (ISAW), which displays the  $\theta$ -transition from coil to globule state. The  $\theta$ -transition is a second-order phase transition in both two and three dimensions. In two dimensions the established crossover exponent is  $\phi = 3/7$  [16], which implies a negative specific heat exponent  $\alpha = 2 - 1/\phi = -1/3$  (the specific heat does not diverge on approaching the transition) [17]. In three dimensions, which is the upper critical dimension for the  $\theta$ -transition, the specific heat is expected to diverge logarithmically [18]. The collapsed state is an isotropic dense liquid-like droplet with a well-defined surface tension [19, 20].

On the other hand, for  $\gamma = 0$  the model becomes the hb-model studied by Foster and Seno [8] on the square lattice and Krawczyk *et al* on the square and simple cubic lattices [9]. In both two and three dimensions, there is a single first-order transition to a folded crystalline state, which is anisotropic.

Using these results as a starting point, one therefore expects there to be at least these three phases (swollen, globule, crystal) in the full two-dimensional parameter space explored here. For  $\gamma > 1/2$ , the hb-interactions are suppressed relative to the non-hb interactions, and the simplest hypothesis would be that the  $\theta$ -transition is not affected. To test this hypothesis, we have considered the line  $\gamma = 1$  below. For  $\gamma$  close to zero, the hb-interactions dominate, and one may expect there to exist some range of values for  $\gamma$

for which the first-order transition of the pure hb-model persists. To test this, we need to consider a small value of  $\gamma$ . We of course then need to consider other values of  $\gamma$  to see whether the two transitions can occur for fixed  $\gamma$  and whether there exist any other phases.

### 3.2. Features of the phase diagram

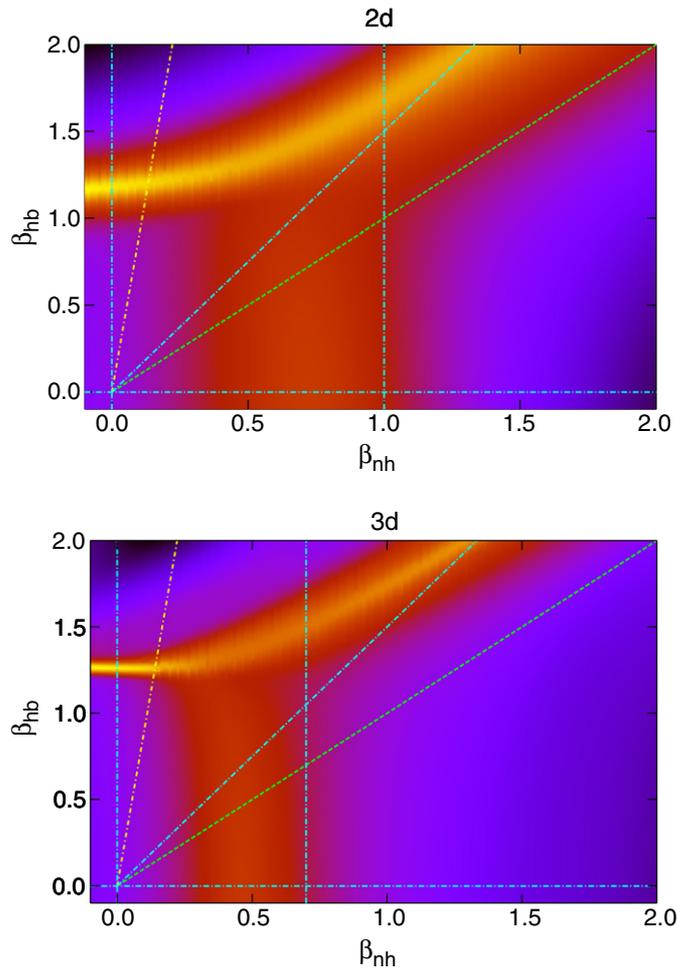
To gain an understanding of which values of  $\gamma$  we may need to consider more closely, we first examine the fluctuations in the numbers of interactions across a wide range of  $(\beta_{\text{hb}}, \beta_{\text{nh}})$ . As in previous work [21, 22, 9], we found the use of the largest eigenvalue of the matrix of second derivatives of the free energy with respect to the parameters  $\beta_{\text{nh}}$  and  $\beta_{\text{hb}}$  most advantageous for showing the fluctuations in a unified manner. Figure 3 displays density plots of the size of fluctuations for  $-0.1 \leq \beta_{\text{nh}}, \beta_{\text{hb}} \leq 2.0$  in two and three dimensions, respectively. The lighter the shade, the larger the fluctuations.

This suggests the presence of three thermodynamic phases separated by three phase transition lines meeting at a single point. From our discussion above, we can therefore identify these three phases as swollen, globule, and crystal. Therefore, for small values of  $\beta_{\text{nh}}$  and  $\beta_{\text{hb}}$ , we expect the model to be in the excluded-volume universality class of swollen polymers, since at  $\beta_{\text{nh}} = \beta_{\text{hb}} = 0$  the model reduces to simple self-avoiding walks. For fixed  $\beta_{\text{hb}}$  and large  $\beta_{\text{nh}}$ , we deduce that the polymer is in a globular state, while for fixed  $\beta_{\text{nh}}$  and large  $\beta_{\text{hb}}$ , we deduce that the polymer is in the anisotropic crystalline state.

A fixed value of  $\gamma$  corresponds to a straight line of slope  $(1 - \gamma)/\gamma$  on the plots in figure 3. The line with  $\gamma = 0.5$  is shown on both plots and it is clear that for any value of  $\gamma \geq 0.5$  (slope less than 1) the system will undergo only one phase transition on lowering the temperature. This transition should be in the universality class of the  $\theta$ -transition. Below, we consider the line  $\gamma = 1$  to verify this. The line with  $\gamma = 0.1$  is shown on both plots and it is clear that there is indeed a range of values of  $\gamma$  around 0 (slope sufficiently large) for which the system will undergo a single first-order hb-model-like transition on lowering the temperature. The figures also suggest that there exists a critical value of  $\gamma$ , say,  $\gamma_c$ , where this scenario ends.

Therefore one may deduce that there exists some range of  $\gamma$  between  $\gamma_c$  and 0.5, not necessarily the whole range, for which the system undergoes two transitions on lowering the temperature. In this region, the polymer starts in the swollen state at high temperatures, undergoes a  $\theta$ -transition to a globular state on lowering the temperature, and on lowering the temperature further, undergoes a further (novel) transition to the crystalline state. We verify this by considering the line with  $\gamma = 0.4$ .

Figure 4 shows the specific heat in two and three dimensions for  $n = 128$  at  $\gamma = 0.1, 0.4$ , and 1.0 as a function of temperature. For  $\gamma = 0.1$  and 1.0, there is one peak in the specific heat which is sharp for  $\gamma = 0.1$  and relatively broad for  $\gamma = 1.0$ . This is consistent with the scenario described above, where at  $\gamma = 0.1$  there should be a first-order transition in the thermodynamic limit, while at  $\gamma = 1.0$  we expect a transition in the  $\theta$ -point universality class. Also as predicted above, for  $\gamma = 0.4$  there are two well-formed peaks in the specific heat. In three dimensions the peak at lower temperature is sharp, while the one at higher temperatures is relatively broad, consistent with a  $\theta$ -like transition from the swollen coil to a collapsed globule at a moderate temperature, followed by a stronger globule–crystal transition at a lower temperature. In two dimensions, there

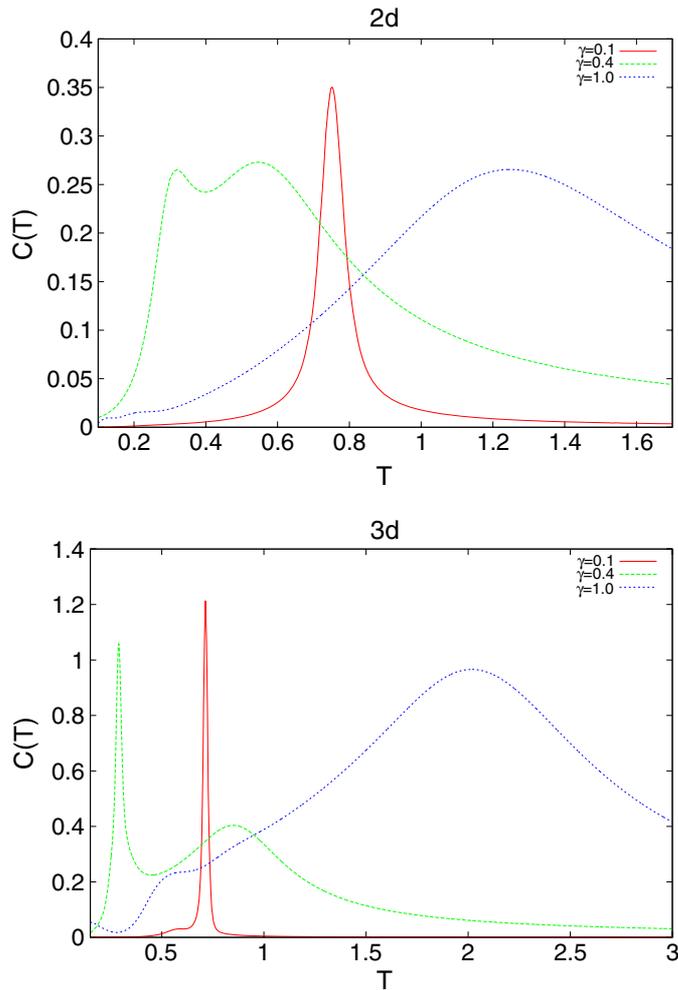


**Figure 3.** Density plots of the logarithm of the largest eigenvalue of the matrix of second derivatives of the free energy with respect to  $\beta_{nh}$  and  $\beta_{hb}$  (the lighter the shade, the larger the value). Both plots are for  $n = 128$ , for two- and three-dimensional systems, top and bottom, respectively. The lines shown indicate cross-sections for which we have performed additional simulations or analysis. In both pictures we show lines with slope  $(1 - \gamma)/\gamma$  for  $\gamma = 0.0, 0.1, 0.4, 0.5$  and  $1.0$ . Displayed are also vertical lines at  $\beta_{nh} = 1.0$  and  $0.7$  in two and three dimensions, respectively.

are two peaks of roughly equal height. However, they are not well separated, which indicates that we need to go to longer lengths to study these transitions.

### 3.3. Low temperature phases

Before considering the order of the phase transitions, especially the globule-to-crystal transition, we verify that the low temperature phases have the properties assumed above. In particular, we demonstrate that while the globular phase displays no orientational order, the phase for large  $\beta_{hb}$  at fixed  $\beta_{nh}$  is a crystal phase which displays strong orientational



**Figure 4.** The specific heat for different values of  $\gamma$  in two and three dimensions for  $n = 128$ . For  $\gamma = 0.1$  and  $1.0$  we see only one maximum in the specific heat, so we expect only one phase transition. For  $\gamma = 0.4$  two maxima occur: upon changing the temperature there are two phase transitions. (The specific heat for  $\gamma = 0.1$  is divided by a factor 15 in three dimensions and 10 in two dimensions to allow us to depict all curves on one diagram.)

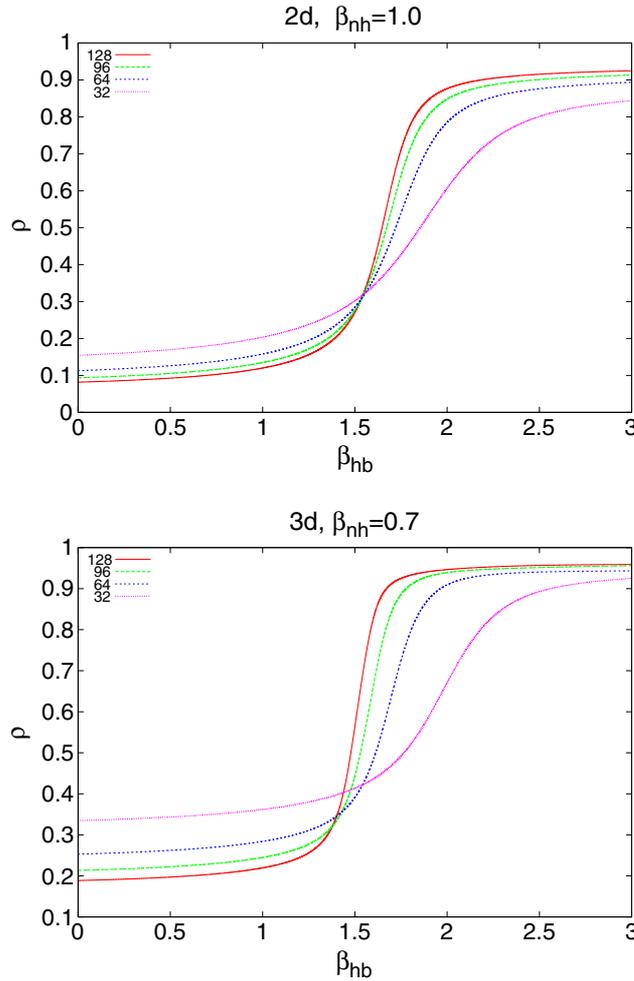
order by showing that in this phase the bonds between monomers prefer to align with one axis of the lattice.

To detect orientational order, we utilize an anisotropy parameter defined in Bastolla and Grassberger [10]. If we denote the number of bonds parallel to the  $x$ -,  $y$ -, and  $z$ -axes by  $n_x$ ,  $n_y$ , and  $n_z$ , respectively, we define

$$\rho = 1.0 - \frac{\min(n_x, n_y, n_z)}{\max(n_x, n_y, n_z)}. \quad (3.1)$$

In a system without orientational order, this quantity tends to zero as the system size increases. A non-zero limiting value less than 1 for this quantity indicates weak

The competition of hydrogen-like and isotropic interactions on polymer collapse

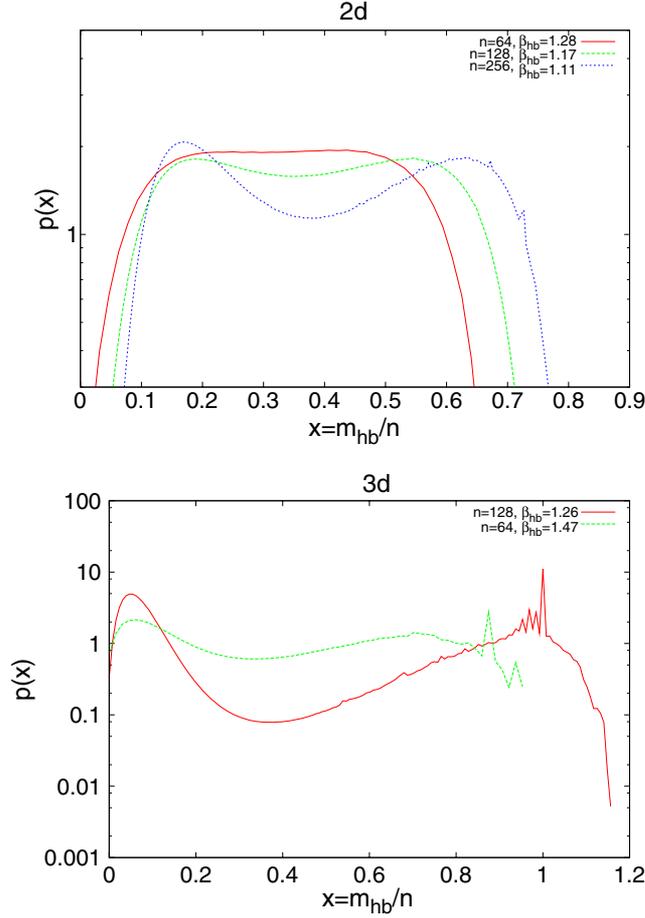


**Figure 5.** The plots display the anisotropy parameter  $\rho$  of the system in two and three dimensions.

orientational order with  $n_{\min} \propto n_{\max}$ , while a limiting value of one indicates strong orientational order, where  $n_{\max} \gg n_{\min}$ .

We consider a fixed value of  $\beta_{nh}$  such that the system is collapsed for any value of  $\beta_{hb}$ . For small values of  $\beta_{hb}$  the polymer is in the globular phase, while for large values it is expected to be in the crystal phase; see figure 3. In two dimensions, we use  $\beta_{nh} = 1.0$ , while in three dimensions we use  $\beta_{nh} = 0.7$ .

Figure 5 shows  $\rho$  as a function of  $\beta_{hb}$  for different lengths ranging from 32 to 128 in two and three dimensions. For small  $\beta_{hb}$ , we find that  $\rho$  converges to zero as  $n^{-1/2}$  as expected if only statistical fluctuations are present. Similarly, for large  $\beta_{hb}$ , we find that  $\rho$  converges to 1 in a corresponding fashion. This indicates the presence of strong orientational order in the large  $\beta_{hb}$ -phase, which we then deduce to be the ordered crystal. Intriguingly, for two dimensions only, there exists a value of  $\beta_{hb}$ , 1.54, at which  $\rho$  seems to be independent of system size. Moreover, by choosing an appropriate exponent ( $\phi \approx 0.75$ ), one can show indications of a scaling collapse of the data near this point. This is our first indication that the two-dimensional and three-dimensional globule-to-crystal transitions are different.



**Figure 6.** Internal energy distribution associated with  $m_{hb}$  at  $\beta_{nh} = 0.0$  in 2D for lengths  $n = 64, 128$  and  $256$  (top) and in 3D for lengths  $n = 64$  and  $128$  (bottom) at values of  $\beta_{hb}$  for which the fluctuations in  $m_{hb}$  are maximal. In both cases we observe a build-up of a bimodal distribution with well-separated peaks as  $n$  is increased.

### 3.4. The phase transitions

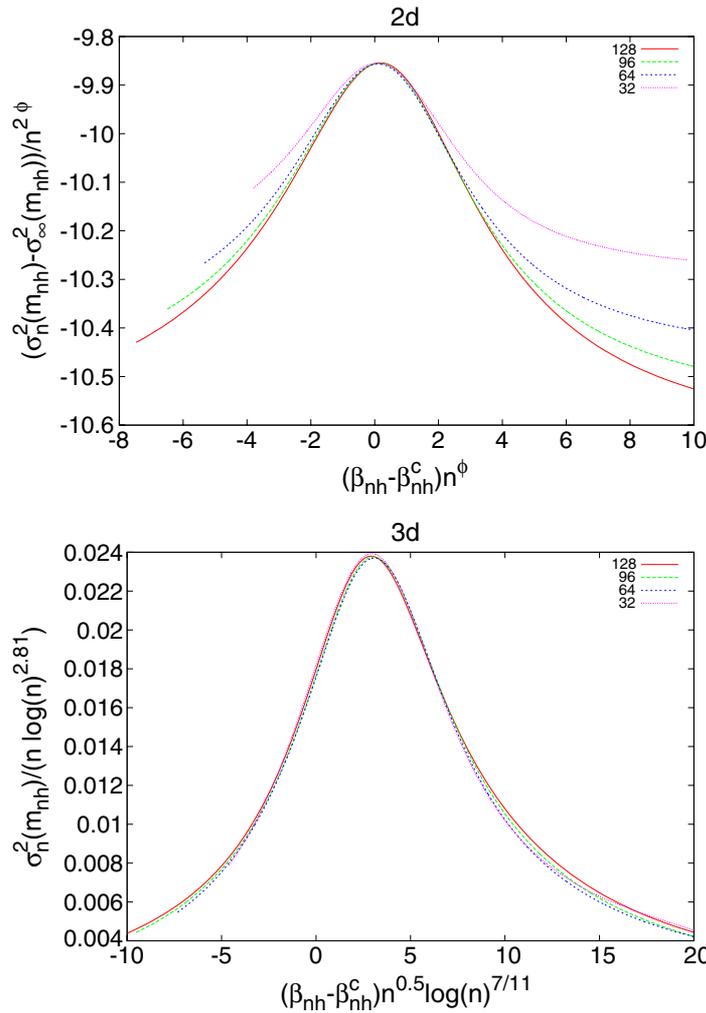
*3.4.1. Swollen coil to folded crystal and swollen coil to globule.* As discussed elsewhere [9], when  $\gamma = 0$ , that is  $\beta_{nh} = 0$ , there is a single phase transition which is first order in both two and three dimensions. We have verified that for small  $\gamma$ , for which we choose  $\gamma = 0.1$ , this scenario remains intact. A bimodal distribution of the internal energy associated with parameter  $m_{hb}$ , see figure 6, can be clearly seen forming as the system size becomes larger very strongly in three dimensions, and more weakly in two dimensions.

To show that the  $\theta$ -transition extends from  $\gamma = 1/2$  to larger values of  $\gamma$ , we can focus on the case of  $\gamma = 1$ , which means that  $\beta_{hb} = 0.0$  and hb-interactions are irrelevant.

In two dimensions the maximum of the fluctuations per monomer for length  $n$  for the  $\theta$ -point behaves as

$$\sigma_n^2(m_{nh}) \sim \sigma_\infty^2(m_{nh}) + a \cdot n^{2\phi}, \quad (3.2)$$

The competition of hydrogen-like and isotropic interactions on polymer collapse

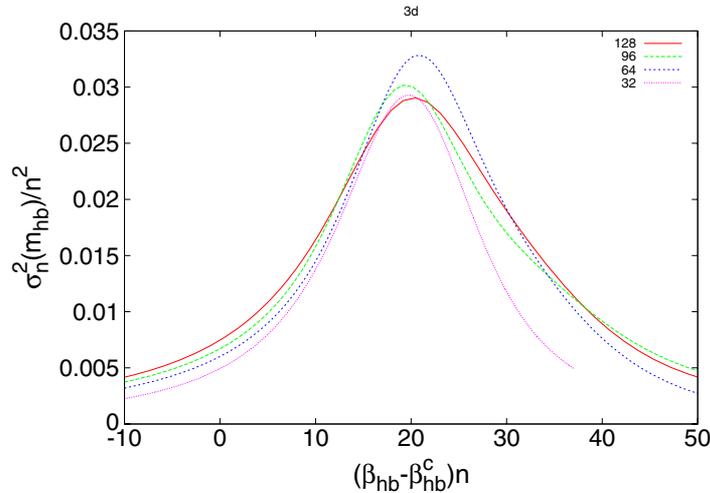


**Figure 7.** Scaling plots for the fluctuations in  $m_{nh}$  for the  $\theta$ -like transitions occurring along the line  $\beta_{hb} = 0.0$ .

where  $\phi = 3/7$ . We have estimated from our data collected at short length that  $\phi = 0.49$ . This is consistent with the observation that for finite system size the effective crossover exponent decreases from a value well above 0.5 [5] to the theoretical value predicted for the  $\theta$ -point  $\phi = 3/7$ . Having extrapolated the limiting value  $\sigma_{\infty}^2(m_{nh})$ , we show in figure 7 a scaling plot of the dependence of the *singular* part of the fluctuations as a function of  $\beta_{nh}$ .

In three dimensions [2, 18] theory predicts  $\phi = 1/2$  and a logarithmic divergence of the maximum of fluctuations. The scaling of the fluctuations around the transition for  $\beta_{hb} = 0$  is shown in figure 7. At short lengths, we find strong corrections to scaling, in accord with the observations in [23, 24]. The effective exponent of the logarithm is equal to 2.8, which is about an order of magnitude more than the value  $3/11$  predicted [18]. However we have checked that the exponent decreases with the system size.

*3.4.2. Collapsed globule to folded crystal.* We begin with the three-dimensional case and return to our simulations at fixed  $\beta_{nh} = 0.7$ . On varying  $\beta_{hb}$  we find a first-order transition



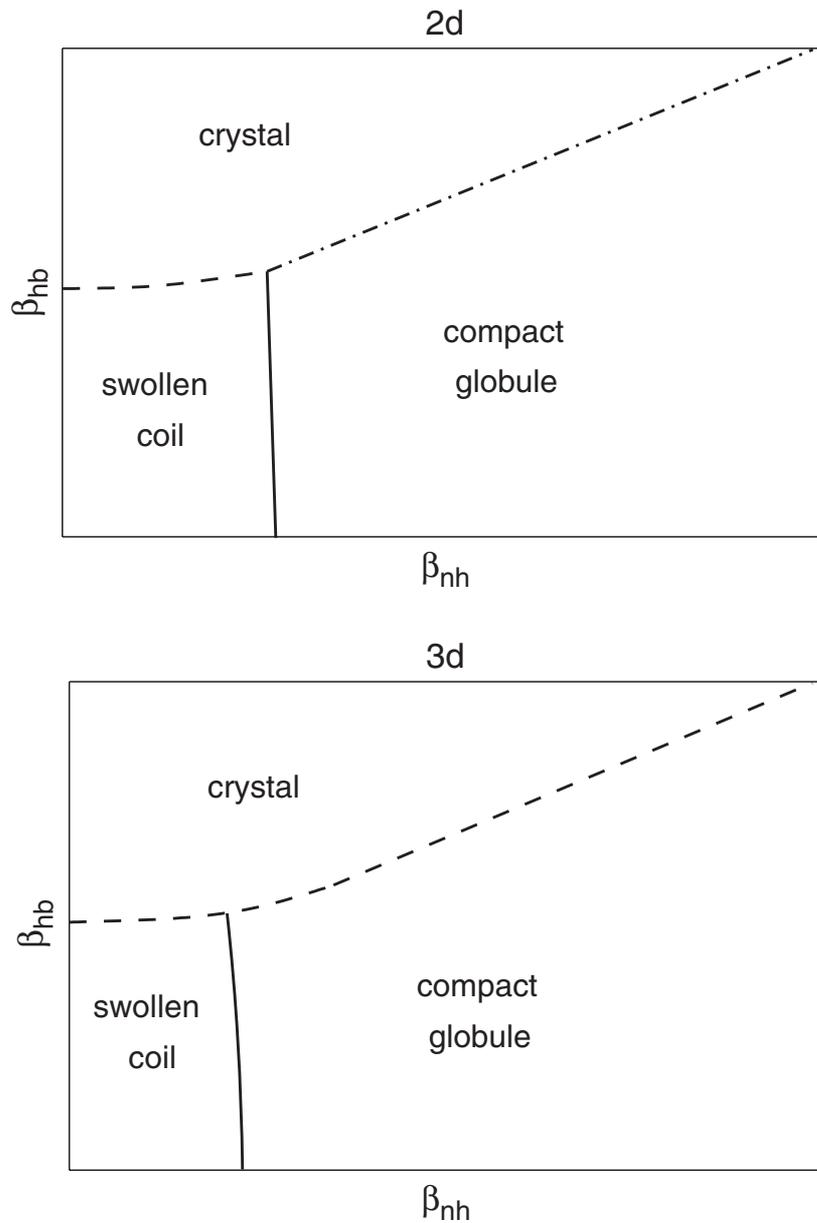
**Figure 8.** A scaling plot for the fluctuations in  $m_{hb}$  for the globule-to-crystal transition occurring along the line  $\beta_{nh} = 0.7$  in three dimensions.

from the globule to the crystal. The maximum of fluctuations per monomer  $\sigma^2(m_{hb})/n$  increases linearly in  $n$ , and the shift of the inverse temperature scales as  $1/n$ , in accord with finite-size scaling of a first-order transition. Figure 8 shows the corresponding scaling collapse, with an extrapolated value of  $\beta_{hb}^c = 1.34$ .

We turn to our simulations of the two-dimensional case at fixed  $\beta_{nh} = 1.0$ . Now, on varying  $\beta_{hb}$  we find a transition which is much stronger than the  $\theta$ -point, but shows no indication of being first order: the maximum of fluctuations per monomer  $\sigma^2(m_{hb})/n$  diverges with an exponent less than one. A scaling plot using a consistent power law is not convincing. Our best estimate for the crossover exponent comes in fact from the scaling of the anisotropy parameter  $\rho$  discussed above, which gives  $\beta_{hb}^c = 1.54$  and a crossover exponent in the vicinity of  $\phi = 0.75$ . The scaling of the fluctuations is not inconsistent with these values.

### 3.5. Summary

We summarize our findings by presenting conjectured phase diagrams in two and three dimensions in figure 9. For large values of the ratio of the interaction strength of hydrogen bonds to that of non-hydrogen bonds, a polymer will undergo a single first-order phase transition from a swollen coil at high temperatures to a folded crystalline state at low temperatures. On the other hand, for any ratio of these interaction energies less than or equal to 1, there is a single  $\theta$ -like transition from a swollen coil to a liquid droplet-like globular phase. For intermediate ratios two transitions can occur, such that the polymer first undergoes a  $\theta$ -like transition on lowering the temperature, this being followed by a second transition to the crystalline state. In three dimensions we find that this transition is first order, while in two dimensions we find that this transition is probably second order with a divergent specific heat. It can be argued using a zero-temperature argument that this scenario arises as soon as the ratio of the interaction energies is greater than 1. In this way the phase diagram described is qualitatively similar to that of the semi-stiff interacting polymer model described in three dimensions by Bastolla and Grassberger [10].



**Figure 9.** The schematic conjectured phase diagrams in two and three dimensions. A dashed line denotes a first-order transition, and a solid line a  $\theta$ -like transition. The dot-dashed line represents a putative second-order phase transition that is not yet completely characterized.

The interesting questions that remain for future work include those of further characterizing the globule-to-crystal transition in two dimensions and also clearly delineating the range of interaction ratios for which two transitions occur.

### Acknowledgments

Financial support from the Australian Research Council and the Centre of Excellence for Mathematics and Statistics of Complex Systems is gratefully acknowledged by the

authors. All simulations were performed using the computational resources of the Victorian Partnership for Advanced Computing (VPAC).

## References

- [1] Flory P, 1971 *Principles of Polymers Chemistry* (Ithaca, NY: Cornell University Press)
- [2] de Gennes P-G, 1979 *Scaling Concept in Polymer Physics* (Ithaca, NY: Cornell University Press)
- [3] Vanderzande C, 1998 *Lattice Models of Polymers* (Cambridge: Cambridge University Press)
- [4] des Cloiseaux J and Jannik G, 1990 *Polymers in Solutions: Their Modelling and Structure* (Oxford: Oxford University Press)
- [5] Prellberg T and Owczarek A L, 1994 *J. Phys. A: Math. Gen.* **27** 1811
- [6] Pauling L and Corey R B, 1951 *Proc. Nat. Acad. Sci.* **37** 235
- Pauling L and Corey R B, 1951 *Proc. Nat. Acad. Sci.* **37** 251
- Pauling L and Corey R B, 1951 *Proc. Nat. Acad. Sci.* **37** 272
- Pauling L and Corey R B, 1951 *Proc. Nat. Acad. Sci.* **37** 729
- [7] Bascle J, Garel T and Orland H, 1993 *J. Physique II* **3** 245
- [8] Foster D P and Seno F, 2001 *J. Phys. A: Math. Gen.* **34** 9939
- [9] Krawczyk J, Owczarek A L, Prellberg T and Rechnitzer A, *A lattice model for parallel and orthogonal beta-sheets using hydrogen-like bonding*, 2007 *Phys. Rev. E* in press
- [10] Bostolla U and Grassberger P, 1997 *J. Stat. Phys.* **89** 1061
- [11] Jacobsen J L and Kondev J, 2004 *Phys. Rev. Lett.* **92** 210601
- [12] Buzano C and Pretti M, 2002 *J. Chem. Phys.* **117** 10360
- [13] Buzano C and Pretti M, 2003 *Mol. Cryst. Liq. Cryst.* **398** 23
- [14] Foster D P, 2007 *J. Phys. A: Math. Theor.* **40** 1963
- [15] Prellberg T and Krawczyk J, 2004 *Phys. Rev. Lett.* **92** 120602
- [16] Duplantier B and Saleur H, 1987 *Phys. Rev. Lett.* **59** 539
- [17] Brak R, Owczarek A L and Prellberg T, 1994 *J. Phys. A: Math. Gen.* **26** 4565
- [18] Duplantier B, 1986 *Europhys. Lett.* **1** 491
- [19] Owczarek A L, Prellberg T and Brak R, 1993 *Phys. Rev. Lett.* **70** 951
- [20] Baiesi M, Orlandini E and Stella A L, 2006 *Phys. Rev. Lett.* **96** 040602
- [21] Krawczyk J, Owczarek A L, Prellberg T and Rechnitzer A, 2005 *J. Stat. Mech.* P05008
- [22] Krawczyk J, Owczarek A L, Prellberg T and Rechnitzer A, 2005 *Europhys. Lett.* **70** 726
- [23] Grassberger P and Hegger R, 1995 *J. Chem. Phys.* **102** 6881
- [24] Hager J and Schäfer L, 1999 *Phys. Rev. E* **60** 2071