Polymer 44 (2003) 2829–2831

polymer

www.elsevier.com/locate/polymer

Polymer communication

Dynamics of stiff polymers mapped from an Ising model

K.K. Müller-Nedebock[a,*], H.L. Frisch[a,b]

[a]Department of Physics, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa
[b]Department of Chemistry, State University of New York at Albany, Albany, NY12222, USA

Received 6 April 2002; received in revised form 18 February 2003; accepted 18 February 2003

In this note we discuss the dynamics of a simple matrix model for stiff polymers. The underlying basis of these models is a mapping of the spatial conformation of a single chain from one-dimensional Ising or Potts descriptions of configurations.

Many of the computations can be performed by drawing upon the knowledge about these one-dimensional magnetic models, i.e. transfer matrices can be used to determine averages. The rotational isomeric state (RIS) model of Flory [1] and the helix-coil model by Zimm and Bragg [2] are well-known and much-used examples of such formalism.

Dynamics for the Ising model were postulated in the seminal works of Glauber [3] and of Kawasaki [4]. Here we shall use these ideas, as summarized in [5], to note briefly what such dynamics imply for the relaxation of the stiff polymers described by matrix models. We note that the dynamics of the helix-coil model has been investigated extensively [6–9]. Recently, atomistic simulations have again investigated aspects of conformational diffusion for helix formation (see [10] and references therein).

The model in Ref. [11] describes a polymer chain of N bonds, to each of which is associated an Ising variable $\sigma = \pm 1$. There are two parts to the mapping of the Ising variables to the three-dimensional spatial form of the polymer. Firstly, we assign meaning to σ: when $\sigma = -1$ we say that the polymer chain segment following the bond described by σ has exactly the same orientation as the segment preceding the $\sigma = -1$ bond. For the case $\sigma = +1$ the orientation of the chain changes. The second part of the model describes how the orientation changes. This is achieved very simply, for example, by stipulating that each time the segment direction changes it changes to the next bond vector in a cyclic sequence of unit vectors $\{\hat{t}_1, \hat{t}_2, \hat{t}_3, \hat{t}_4, \ldots, \hat{t}_1, \hat{t}_2, \ldots\}$. In so doing the polymer configuration is completely described. Together with the usual nearest-neighbor Ising Hamiltonian in homogeneous external field, it is possible to compute the free energy and averages of the conformation of the chain and to derive force-extension relationship with constrained chain-end directions.

If a single Ising spin in the middle of a relatively straight, stiff, and long molecule were to flip the two parts of the chain on either side of the flipped bond would be strongly re-oriented in space (according to the model described above). Such a fast change is clearly unlikely when inertial effects of the molecule are considered and rule out (for the present situation) the types of dynamics considered relevant for the helix-coil model (see, e.g. [6]). It is far more likely that the molecules of our model relax by letting either bends move towards and off the chain ends or by letting bends be added at the ends in order to diffuse to central regions of the molecule. (We do not consider here the more complicated situation of the nucleation of multiple complicated combinations of kinks which would could only affect the overall chain conformation to a little extent.)

Under such very general considerations Glauber dynamics would represent an inappropriate choice for the dynamical behavior of a stiff chain, in that spin flips ('bends' or 'straightenings') could occur anywhere on the molecule with equal probability. In the following paragraphs we make use of well-established results to model the entrance and exit of bends at the ends of the chain (the 'bend bath' approach) and to model the general spin-preserving diffusion within the chain.

For the first scenario we make use of the results of Blender, et al. on hopping diffusion across an interface [12]. In this work transport equations are written down and solved for hopping on two semi-infinite Ising lattices which are joined at the site labeled by 0. The transport equations are given for the occupation number realization of the Ising system $n_i = (1 + \sigma_i)/2$ for the case where there is no

---

[*] Corresponding author. Tel.: +27-21-8083386; fax: +27-21-8083385.
E-mail address: kkmn@physics.sun.ac.za (K.K. Müller-Nedebock).

0032-3861/03/$ - see front matter
doi:10.1016/S0032-3861(03)00195-2

interaction term between neighboring lattice sites. The rate of change of occupation number, for hopping rates α in the region $i>0$ and β for $i<0$, is given by

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \begin{cases} \alpha(n_{i+1}-2n_i+n_{i-1}), & i>0 \\ \alpha(n_1-n_0)+\beta(n_{-1}-n_0), & i=0 \\ \beta(n_{i+1}-2n_i+n_{i-1}), & i<0 \end{cases} \tag{1}$$

The solution of this transport Eq. (1) with the boundary condition

$$n_i(t=0) = \begin{cases} 1, & i \leq 0 \\ 0, & i>0 \end{cases} \tag{2}$$

is readily obtained by Laplace transformation in [12]. The result of Blender, et al. we use, is the time-dependent penetration length $\xi_\pm(t) = \sum_{i=1}^{\infty} i n_{\pm i}(t)$ (given in the Laplace variable s associated with the time t):

$$\tilde{\xi}_+(s) = \frac{\alpha}{s}\tilde{n}_0(s) \tag{3}$$

$$\tilde{\xi}_-(s) = \frac{\beta}{s}\left[\tilde{n}_0(s) - \frac{1}{s}\right] \tag{4}$$

with

$$\tilde{n}_0(s) = \frac{1}{s}\,\frac{\sqrt{s+4\beta}+\sqrt{s}}{\sqrt{s+4\beta}+\sqrt{s+4\alpha}}. \tag{5}$$

The boundary condition (2) could represent the polymer in the region $i \geq 0$, which is originally straight (every $\sigma=-1$) coupled to a 'bath of bends', $i<0$. These bends move into the chain at the chain end reaching a depth given by Eq. (3) after a certain time.

The rate constants α and β must be associated with the original Ising Hamiltonian parameters of the chain model, $H=\sum_i h\sigma_i$. This can be done by comparing statistical mechanical averages to the large time limit of values for the dynamical formalism. Eventually the ratio of the density of bends on the chain ϱ_+ to the density of bends in the bath ϱ_- becomes:

$$\frac{\varrho_+}{\varrho_-} = \frac{\varrho_+}{1/2-\varrho_+} = \lim_{s\to 0^+}\frac{\sum_{i\geq 0} n_i}{\sum_{i\leq 0} n_i} = \lim_{s\to 0^+}\frac{\sum_{i\geq 0}\tilde{n}_0 x^i}{\sum_{i\leq 0}[(\tilde{n}_0 - 1/s)y^i + 1/s]}, \tag{6}$$

with

$$x = \frac{4\alpha}{(\sqrt{s+4\alpha}+\sqrt{s})^2} \tag{7}$$

and

$$y = \frac{4\beta}{(\sqrt{s+4\beta}+\sqrt{s})^2}. \tag{8}$$

Here we have made use of Eqs. (8) and (9) in Ref. [12] and of the fact that the total density equals 1/2. Eq. (6) can be solved for ϱ_+ with the condition that $\varrho_+ = 1/4$ if $\alpha=\beta$:

$$\varrho_+ = \frac{1}{2}\left[\frac{\alpha}{\alpha+\beta}\right]. \tag{9}$$

Comparing this with the result from equilibrium statistical mechanics, where

$$\varrho_{\text{equil}} = \frac{2\sinh h + 1}{4\cosh h} \tag{10}$$

means that we can assign a value to the ratio α/β through:

$$\frac{2\sinh h + 1}{4\cosh h} = \frac{1}{2}\left[\frac{\alpha}{\alpha+\beta}\right]. \tag{11}$$

In the second situation we make use of the results of Kawasaki's model kinetics [4] where nearest-neighbor spins can be exchanged maintaining the total spin and where there is an interaction between these nearest neighbors. We view this process as the motion, somewhere within our polymer chain, of bends. Kawasaki approximates the master equation for the normalized spin distribution function by using a local equilibrium distribution. When the spin density varies slowly in space its resulting expression reduces to a diffusion equation with the diffusion constant (quoted from Ref. [4]):

$$D = \frac{2\alpha}{\chi\zeta}\,\frac{\mathrm{e}^{-K}}{(\cosh K)^2}\sum_{\{\sigma\}_{[12]}} \mathrm{e}^{H_{[12]}} \tag{12}$$

Here the Hamiltonian for nearest-neighbor pairs $\langle ij\rangle$ is $H=\sum_{\langle ij\rangle} K\sigma_i\sigma_j$, the subscript notation $[ij]$ means that all terms with occurrences of σ_i or σ_j are omitted from an expression, $\zeta = \sum_{\{\sigma\}_{[12]}} \exp H$, and the magnetic susceptibility is χ. The lattice constant has been set equal to 1.

In summary, we have argued that stiff polymers modeled by mapping from Ising models and with Glauber–Kawasaki dynamics can show diffusion of bends. For no external magnetic field in the underlying Ising model of the chain the diffusion coefficient is the long-known expression given in Ref. [4]. For no mutual interactions between neighboring spins we have interpreted the results of Ref. [12] for the non-equilibrium properties of bends entering and leaving the ends of the chain. Specifically, these results give a time-dependent penetration depth into a straight chain. The rate coefficients of the master equation are related to one another by referring to the equilibrium state.

Acknowledgements

HLF acknowledges the financial support of NSF Grant DMR 9628224 and a Fulbright Fellowship. KKMN acknowledges the financial support of the National Research Foundation of South Africa.

References

[1] Flory PJ. Statistical mechanics of chain molecules. New York: Wiley-Interscience; 1969.
[2] Zimm BH, Bragg JK. J Chem Phys 1959;31:526.
[3] Glauber RJ. J Math Phys 1963;4:294.
[4] Kawasaki K. Phys Rev 1966;145:224.
[5] Kawasaki K, Phase transitions and critical phenomena, vol. 2. London: Academic Press; 1972. Chap. 11, p. 443.
[6] Baumgärtner A, Binder K. J Chem Phys 1979;70:429.
[7] McQuarrie DA, McTague JP, Reiss H. Biopolymers 1965;3:657.
[8] Poland D, Scheraga HA. J Chem Phys 1966;45:2071.
[9] Tanaka T, Soda K, Wada A. J Chem Phys 1973;58:5707.
[10] Hummer G, García AE, Garde S. Phys Rev Lett 2000;85:2637.
[11] Müller-Nedebock K K, Frisch H L. Submitted for publication.
[12] Blender R, Dieterich W, Frisch HL. Phys Rev B 1986;33:3538.