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1989 J. Phys. A: Math. Gen. 22 3137

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Externally induced phase transition for random inhomogeneous polymers

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Received 31 August 1988

Abstract. We consider an ensemble of frozen linear sequences with intrachain long-range interactions in the good solvent region. The sequences are made up of two kinds of monomers and they are subject to the influence of an external attractive field. We study the phase transition caused by adsorption of the coil below a critical temperature. Making use of the replica method to average over macroscopic samples, we get the temperature dependence for the dispersion of polymer sizes.

1. Introduction

The statistical mechanics of phase transitions for linear polymers made up of different kinds of elementary constituents is of paramount importance for its biological implications [1]. A folded state is required in a biopolymer for a specific function. Often the folding process is externally induced by trapping the coil in a potential well by means of an attractive field which causes adsorption [2, 3]. In previous work along these lines (see, for example, [4]) elastic heteropolymers with no intrachain interactions were considered. Thus, the ‘beads-on-the-string’ transition-operator formulation holds. We shall examine a more realistic situation with intrachain volume-excluded interactions in the good solvent region. In this case, the bending of the chain becomes a non-Markovian process [4–6]. The basic aim is to study the temperature dependence of the polymer statistics by a process of averaging over macroscopic samples. This is done in order to characterise the two fluctuation regimes which depend on the spatial correlation range for the ensemble of polymer strands.

The transition-operator formalism as applied in our context poses some non-trivial problems due to the non-Markovian nature of the problem. The operators and sequence of Green functions on which they act are not statistically independent, as is the case for an elastic chain subject only to interaction with the field [4].

2. The replica method

We shall resort to the standard conformational space-functional integral formalism proposed by Edwards [7]. The Hamiltonian for the disordered chain is made up of

five contributions:

$$H(\mathbf{x}(t)) = H^e + H^{(2)} + H^{(3)} + H^F + H^f \quad (1)$$

$$H^e = \frac{1}{2} \int_0^N dt \left(\left\| \frac{\partial \mathbf{x}(t)}{\partial t} \right\| \right)^2 \quad (2)$$

$$H^{(2)} = \frac{1}{2} \int_0^N \int_0^N dt dt' v(t, t') \delta(\mathbf{x}(t) - \mathbf{x}(t'))$$

= two-body volume-excluded interactions

(3)

$$H^{(3)} = \frac{C}{3!} \int_0^N \int_0^N \int_0^N \delta(\mathbf{x}(t) - \mathbf{x}(t')) \delta(\mathbf{x}(t) - \mathbf{x}(t''))$$

= three-body interactions

(4)

$$H^F = \int_0^N (F_t(\mathbf{x}(t))/T) dt = \text{attractive external field term} \quad (5)$$

$$H^f = \int d\mathbf{R} f(\mathbf{R}) \delta(\mathbf{x}(N) - \mathbf{R}) = \text{virtual field contribution.} \quad (6)$$

Here, t is the contour variable indicating the position of the chain, $\mathbf{x}(t)$ denotes the position vector of the chain segment located between t and $t + \delta t$, $v(t, t')$ is the bare two-body volume-excluded coupling constant, C is the bare Flory interaction constant for the three-body contribution, $F_t(\mathbf{x}(t))$ is the external field exerted at position t on the chain and $f(\mathbf{R})$ is the virtual field controlling the endpoint of the chain (the only relevant case consists in taking the limit $f = 0$).

For simplicity, we shall consider the case of two different kinds of monomers only. The strands are assumed to be randomly constructed. Thus, a specific primary sequence is determined unambiguously by a specific realisation of the random variable $s(t)$, defined by

$$\langle s(t) \rangle = 0 \quad (7)$$

and

$$\langle s(t)s(t') \rangle = \begin{cases} 1 & \text{if the monomer in the segment of the chain} \\ & \text{containing } t \text{ is of the same kind as that in} \\ & \text{the segment containing } t' \\ 0 & \text{otherwise} \end{cases} \quad (8)$$

where $\langle \rangle$ denotes average over the ensemble of primary structures and we have assumed that $s(t)$ can only take the values ± 1 depending on the kind of monomer at position t .

The Hamiltonian depends on the specific realisation of $s(t)$. Consequently, we define

$$v(t, t') = v + A(s(t) + s(t')) + Bs(t)s(t') \quad (9)$$

where A and B are unrenormalised constants. A localised field representing the trapping of the coil by the adsorption well is given by

$$F_t(\mathbf{x}(t))/T = -\ln[1 + T^{-1}(F_{\text{eff}} + \Lambda s(t))\delta(\mathbf{x}(t))] \quad (10)$$

i.e. the field is localised at $x=0$. The constants F_{eff} and Λ have the dimensions of temperature. The external field must obviously be attractive in order to induce a phase transition. As the temperature is raised beyond a certain critical value T_c , the well F_i/T no longer holds the chain and a different correlation range regime (CRR), the coil, emerges.

The fixed-end partition function is

$$Z(N) = \int_{\mathbf{x}(0)=0} d\mathbf{m}(\mathbf{x}(t)) \exp(-H(\mathbf{x}(t))) \quad (11)$$

where $m(\mathbf{x}(t))$ is a measure in the space of paths. Thus, the Green function $G(N, \mathbf{R})$ is given by

$$\partial Z(N)/\partial f(\mathbf{R})|_{f=0} = G(N, \mathbf{R}) = \overline{\delta(\mathbf{x}(N) - \mathbf{R})} \quad (12)$$

where the bar indicates an average over all conformations for a given configuration (thermal average).

We shall denote by $Z(N)^M$, M positive integer, the partition function for M identical replicas of an arbitrarily chosen strand. This function can be extended analytically for M real. The following relation will prove very useful:

$$\begin{aligned} \langle \ln Z(N) \rangle &= \lim_{M \rightarrow 0} (1/M) (\langle Z(N)^M \rangle - 1) \\ &= (\partial/\partial M) \langle Z(N)^M \rangle|_{M=0}. \end{aligned} \quad (13)$$

The replica symmetry-breaking thus appears in the computation of $\langle Z(N)^M \rangle$. Let α, β be dummy indices labelling replicas, then we have

$$\langle Z(N)^M \rangle = \prod_{\beta=1}^M Z_{\text{eff},\beta}(N) \quad (14)$$

where $Z_{\text{eff},\beta}$ is the partition function for an effective Hamiltonian corresponding to a homopolymer, i.e. it contains no disorder. Thus, the effective Hamiltonian is [6]

$$\begin{aligned} H_{\text{eff}} &= H^c + H_{\text{eff}}^F + H^I + \frac{1}{2} V_{\text{eff}} \int_0^N \int_0^N dt dt' \delta(\mathbf{x}(t) - \mathbf{x}(t')) \\ &+ \frac{C_{\text{eff}}}{3!} \int_0^N \int_0^N \int_0^N dt dt' dt'' \delta(\mathbf{x}(t) - \mathbf{x}(t')) \delta(\mathbf{x}(t) - \mathbf{x}(t'')) \end{aligned} \quad (15)$$

where

$$C_{\text{eff}} = C - 3A^2 \quad (16)$$

and

$$V_{\text{eff}} = v + 2A^2 \lim_{M \rightarrow 0} \int_0^N \frac{\partial \ln \tilde{Z}_t^M}{\partial f(\mathbf{R}_\alpha)} \Big|_{f=0, \mathbf{R}_\alpha=0} dt. \quad (17)$$

The function \tilde{Z}_t^M for M integer is the partition function averaged over the ensemble of primary structures for M replicas of a strand of length t whose endpoints coincide.

In order to determine the CRR for the effective Hamiltonian, we need to introduce a different representation. We start by discretising the domain of the contour variable, introducing a partition:

$$\mathbf{x}(j) = \mathbf{x}_j \quad (j = 1, 2, \dots, N). \quad (18)$$

We also introduce transition operators \hat{W}_j defined by

$$\hat{W}_j G(j-1, \mathbf{x}_{j-1}) = G(j, \mathbf{x}_j). \tag{19}$$

Thus, for $j = 1, 2, 3, 4$, we have

$$\hat{W}_j G(j-1, \mathbf{x}_{j-1}) = \exp(-\bar{F}(\mathbf{x}_j)/T) \int d\mathbf{x}_{j-1} g(\mathbf{x}_j - \mathbf{x}_{j-1}) G(j-1, \mathbf{x}_{j-1}) \tag{20}$$

where \bar{F} is a field with $\Lambda = 0$ and the coupling between links is assumed identical:

$$g(\mathbf{x}_j - \mathbf{x}_{j-1}) = (4a^2)^{3/2} \exp\left(-\frac{1}{4a^2} (\mathbf{x}_j - \mathbf{x}_{j-1})^2\right). \tag{21}$$

Here a is the average distance between adjacent links. For $j \geq 4$, the transition operators are different since we must consider long-range interactions of the repulsive type (we denote them by \hat{W}_j):

$$\begin{aligned} \hat{W}_j G(j-1, \mathbf{x}_{j-1}) &= \exp(-\bar{F}(\mathbf{x}_j)/T) \int d\mathbf{x}_{j-1} g(\mathbf{x}_j - \mathbf{x}_{j-1}) \\ &\times \int \prod_{\tau=4}^{j-1} [\Omega^{(2)}(\mathbf{x}_j, \mathbf{x}_{j-\tau}) G(j-\tau, \mathbf{x}_{j-\tau}) d\mathbf{x}_{j-\tau}] \\ &\times \prod_{\tau, \tau'=4}^{j-1} [\Omega^{(3)}(\mathbf{x}_j, \mathbf{x}_{j-\tau}, \mathbf{x}_{j-\tau'}) G(j-\tau, \mathbf{x}_{j-\tau}) \\ &\times G(j-\tau', \mathbf{x}_{j-\tau'}) d\mathbf{x}_{j-\tau} d\mathbf{x}_{j-\tau'}] G(j-1, \mathbf{x}_{j-1}). \end{aligned} \tag{22}$$

For clarification, (22) can be rewritten as

$$\hat{W}_j G(j-1, \mathbf{x}_{j-1}) = \hat{W}_j \hat{\Omega}^{(2)} \hat{\Omega}^{(3)} G(j-1, \mathbf{x}_{j-1}) \tag{23}$$

where $\hat{\Omega}^{(2)}$, $\hat{\Omega}^{(3)}$ are the two- and three-body interaction transition operators respectively. Their kernels are given by

$$\Omega^{(2)}(\mathbf{x}_j, \mathbf{x}_{j-\tau}) = \exp(-\frac{1}{2} V_{\text{eff}} \delta_{\mathbf{x}, \mathbf{x}_{j-\tau}}) \tag{24}$$

and

$$\Omega^{(3)}(\mathbf{x}_j, \mathbf{x}_{j-\tau}, \mathbf{x}_{j-\tau'}) = \exp\left(-\frac{C_{\text{eff}}}{3!} \delta_{\mathbf{x}, \mathbf{x}_{j-\tau}} \delta_{\mathbf{x}, \mathbf{x}_{j-\tau'}}\right). \tag{25}$$

We are left with diffusion equations (20) and (22). However, the functions $G(j, \mathbf{x}_j)$ do not form a Markov chain since the operator \hat{W}_j ($j > 4$) and the vector $G(j-1, \mathbf{x}_{j-1})$ are not statistically independent.

The globular state is characterised by the spectrum of \hat{W}_N for N large. The signature for that specific CRR is that the largest real eigenvalue, λ , is not an accumulation point in the spectrum but represents a discrete level. The temperature T_c at which the phase transition between the two CRR occurs is the temperature at which the level λ splits off from the continuum part of the spectrum. The situation of discrete largest eigenvalue is preserved for $T < T_c$. Since the term corresponding to the largest eigenvalue dominates the Green function, the free energy $\Delta F(N, R)$ for the effective homopolymer in

the globular CRR is given by

$$\Delta F(N, R) = -T \ln \lambda^N = -TN \ln \lambda. \quad (26)$$

Thus, the square end-to-end distance averaged over all conformations (thermal average) for the globular CRR is

$$\overline{R^2} = \frac{\int R^2 \exp(-\Delta F(N, R)/T) dR}{Z(N)} \quad (27)$$

whereas for the random coil CRR it is given by

$$\overline{R^2} = - \left. \frac{\partial^2 G(N, p)}{\partial p^2} \right|_{p=0} \quad (28)$$

where $G(N, p)$ is the Fourier transform of $G(N, R)$. The dispersion relation (variance) for R^2 over the ensemble of primary structures, $V(\overline{R^2})$, is a quantity of the utmost importance in the design of light scattering experiments in order to establish the sensitivity of the configuration to the primary sequence. In a neighbourhood of the phase transition we have

$$V(\overline{R^2}) = \langle (\overline{R^2} - \langle \overline{R^2} \rangle)^2 \rangle = \lim_{M \rightarrow 0} \iint dR_\alpha dR_\beta R_\alpha^2 R_\beta^2 \left. \frac{\partial^2 \ln(\langle Z^M \rangle - 1)}{\partial f(R_\alpha) \partial f(R_\beta)} \right|_{f=0}. \quad (29)$$

A perturbative analysis gives, for the random coil regime,

$$V(\overline{R^2}) = \frac{N^2 A^2 (4 + \pi)}{128 \pi^3}. \quad (30)$$

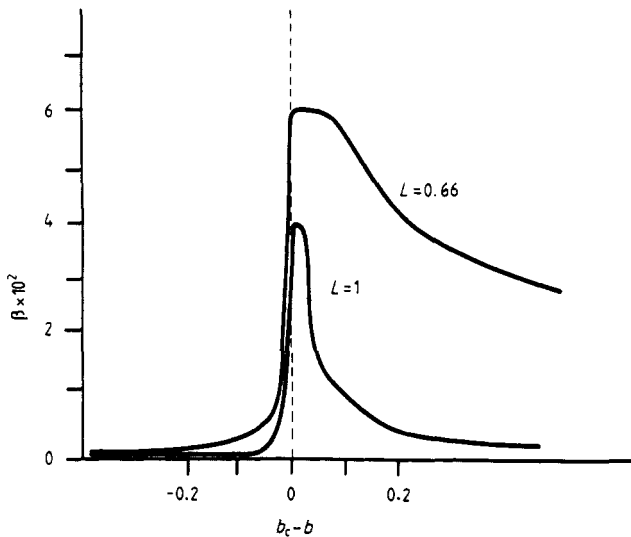


Figure 1. Calculation of the variance for $\overline{R^2}$ over the ensemble of primary sequences. Choice of parameters: $a^2 = 100 \text{ \AA}^2 =$ mean-square length of a link; $N = L \times 10^3$; $u = \frac{1}{2} N^{-1/2}$; $A = \frac{1}{4} N^{-1/2}$; $B = N^{-1}$. External field: $F_{\text{eff}} = 270 \text{ K}$, $\Lambda = 10 \text{ K}$, $T_c = 340 \text{ K}$:

$$b_c - b = (T_c - T)/T$$

$$V(\overline{R^2})^{1/2} / \langle \overline{R^2} \rangle = \beta.$$

3. Phase transition

The relevant order parameter for the phase transition can be taken as the limit for N very large of the distance d_N between $\lambda = \lambda(\hat{W}_N)$ and the continuous part of the spectrum of \hat{W}_N .

Direct inspection of figure 1 provides evidence of the clear distinction between the two correlation range regimes. The globular state, on the RHS of the figure, is far more sensitive to the primary structure, as reflected by the considerably larger value of the relative variance. On the other hand, the coil state is insensitive to changes in the primary structure and its relative variance is almost independent of the length N . The theoretical curves produced are to be regarded as 'thermodynamic' curves. In practice, unless the cooling down is performed with extreme care (approaching a transformation made up of sequential equilibrium states), we would get a 'kinetic' metastable curve. That is so since each sequence will use its specific trick for folding into a metastable state. These states have finite lifetime and will eventually decay to the equilibrium state. It should be stressed that a 'kinetic' folding would lead, in a macroscopic sample, to a higher value of β in the globular state. Thus, a fast-cooling curve should lie above the one presented in figure 1.

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