

## Unwinding a polymer in a poor solvent

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(Received 5 July 1995)

We consider a collapsed polymer chain in a poor solvent sufficiently below the  $\Theta$  point under the action of a force to unwind it. Using a simple phenomenological mean-field model, we show the polymer coil changes from the collapsed state to the stretched state via a first-order transition as the stretching force is increased. The phase diagram is calculated which consists of a first-order line with a tricritical end point. The lifetimes of the metastable states are also calculated and the hysteresis effects are discussed. Possible connections to molecular gateway and memory devices in chemical engineering are also explored.

PACS number(s): 05.70.Fh, 64.60.Kw, 64.60.My, 61.41.+e

### I. INTRODUCTION

Recent experimental techniques allow the possibility to manipulate and observe the configuration of single DNA macromolecules under external stretching forces using fluorescence microscopy. A magnetic bead is attached to the free end of an end-grafted DNA and subjected to magnetic [1] or hydrodynamic [1,2] forces. Previous analytical treatment [3,4] employing scaling calculations were concerned with the deformation and unwinding of an anchored polymer chain under forces or flows for swollen or ideal polymer chains. These studies found that in these cases, the deformation of the chain is progressive and no sharp coil-stretch phase transition occurs. In this study, we consider another more interesting situation, namely the unwinding of a polymer collapsed in a poor solvent, i.e., much below the  $\Theta$  point. We find that there is a first-order transition from the collapsed globule to the stretched state. By increasing the external unwinding force, the linear dimension of the polymer coil can vary over several orders of magnitude abruptly. This may be useful in some applications on chemical and/or biochemical engineering in designing molecular gateway in which the gate is closed by stretching the polymer chain to block the path. Furthermore, the unfolding of these collapsed macromolecules may provide relevant information on the mechanism of protein folding and other related structures in biomolecules. From the point of view of statistical physics, such a system shows a variety of interesting phase transition phenomena and can provide experimental realizations and testing grounds for these theoretical models. Using a simple Flory-type mean-field theory, we show that if the system is in a sufficiently poor solvent condition, the polymer chain undergoes a first-order transition from the collapsed state to the stretched state. The hysteresis effect associated with the first-order transition is reminiscent of a magnetic system which can be used as a memory device. Thus this phenomenon can be used as a prototype mechanism for chemical engineering in molecular memory devices. Also, such a system may provide possible connections to the memory effects in biological systems such as memory cells.

### II. FLORY MEAN-FIELD CALCULATIONS

We consider a polymer chain with  $N+1$  monomers ( $N \gg 1$ ) collapsed in a poor solvent with one end fixed at

some point in space. A force  $f$  pulls on its free end in the  $z$  direction which tends to unwind the chain. Let  $h$  denotes the end-to-end distance of the chain, then the total phenomenological reduced free energy is composed of three terms corresponding to the elastic free energy, mixing free energy and the potential energy due to  $f$  as follows:

$$\beta F = F_{el} + \frac{1}{a^3} \int d^3r F_{mix}[\phi] - \beta fh, \quad (1)$$

where  $\beta = (kT)^{-1}$  is the inverse temperature,  $a$  is the monomer size,  $F_{el}$  is the elastic free energy due, and  $F_{mix}$  the mixing free energy. In the poor solvent regime, the elastic free energy [5] consists of two terms

$$F_{el} = \frac{1}{a} \int_0^h \mathcal{L}^{-1} \left( \frac{z}{Na} \right) dz + \frac{3}{2} \frac{Na^2}{h^2}, \quad (2)$$

where  $\mathcal{L}(x) = \coth x - 1/x$  is the Langevin function. The first term in  $F_{el}$  takes into account the finite extensibility of the chain [6–8] which is important for strongly stretched configurations and reduces to the usual Gaussian stretching ( $3h^2/(2Na^2)$ ) for small deformations whereas the second term dominates for collapsed configurations.  $F_{mix}$  is taken to be the Flory mixing free energy [6,9]

$$F_{mix}(\phi) = (1-\phi)\ell n(1-\phi) + \chi\phi(1-\phi), \quad (3)$$

where  $\chi$  is the usual Flory interaction parameter and  $\phi$  is the monomer volume fraction. As in the usual Flory mean-field calculation,  $\phi$  is approximated by a constant. In the absence of external force, the chain has a spherical shape and it has been shown that the second-order transition from the swollen state to the collapsed state [9,10] occurs at  $\chi_c = 1/2$ . For  $\chi > 1/2$ , the polymer coil is in a swollen state with a linear dimension  $R \sim aN^{3/5}$ . At the  $\Theta$  point,  $\chi = \chi_c = 1/2$ , the polymer chain behaves like an ideal coil with  $R \sim aN^{1/2}$ . And for  $\chi > 1/2$  the chain has a collapsed configuration with a linear dimension  $\approx aN^{1/3}$ .

As the unwinding force acting on the free end increases from zero, the shape of the collapsed globule will be deformed to an ellipsoid with the dimension in the  $z$  direction being  $h$  while the linear dimension on the  $xy$  plane remains essentially unaltered for small  $f$ . Thus within the mean-field

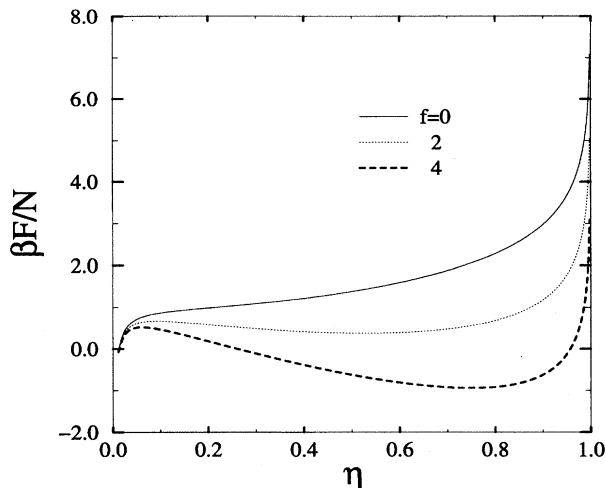


FIG. 1. Reduced free energy as a function of the stretch order parameter  $\eta$  for various values of stretch forces with  $\chi=2$  and  $N=1000$ .  $f$  is in units of  $1/(\beta a)$ .

approximation,  $\phi \approx aN^{1/3}/h$ . Such an approximation breaks down for the stretched state, but in this case the free energy is dominated by stretching free energy [first term in Eq. (4)] and  $F_{mix}$  is negligible, hence it is still legitimate to keep such an approximation in the entire range of  $f$ . The minimum value of  $h$ , denoted by  $h_{min}$ , corresponds to the unperturbed globule,  $h_{min} = aN^{1/3}$ . The collapsed state and the stretched state can be characterized by the stretching order parameter [11]  $\eta \equiv h/(Na)$ . The collapsed state corresponds to  $\eta = \eta_{min} = N^{-2/3}$  and  $\rightarrow 0$  in the long chain limit while  $\eta = 1$  in the fully stretched state. In terms of the order parameter  $\eta$ , the total reduced free energy can be written as

$$\frac{\beta F}{N} = \int_0^\eta \mathcal{L}^{-1}(u) du + \frac{3}{2} \frac{\eta_{min}^3}{\eta^2} + \frac{\eta}{\eta_{min}} \left( \left( 1 - \frac{\eta_{min}}{\eta} \right) \times \mathcal{L} \left( 1 - \frac{\eta_{min}}{\eta} \right) \right) + \chi \left( 1 - \frac{\eta_{min}}{\eta} \right) - \beta f a \eta. \quad (4)$$

Henceforth  $\beta a$  is understood to be absorbed in the unit of  $f$ . The stable state is given by the value of  $\eta$  in the domain  $\eta_{min} \leq \eta \leq 1$  that minimizes the free energy. The poor solvent regime is characterized by  $\chi > 1/2$  and Fig. 1 shows the typical behavior of  $F(\eta)$  for  $\chi=2$ . For small values of  $f$ , the minimum of  $F$  stays at  $\eta_{min}$  corresponding to the collapsed state, while for sufficiently strong  $f$ , a new minimum occurs at a larger value of  $\eta$  corresponding to the stretched state. For  $\chi \gg 1/2$  the transition from the collapsed state to the stretched state is discontinuous as  $f$  increases. The order parameter  $\langle \eta \rangle$  that minimizes  $F$  can be solved numerically from Eq. (4) and is shown in Fig. 2 as a function of  $f$  for  $N=10^3$  and  $10^5$  at  $\chi=2$ . For  $f$  less than some  $f^*$ , the collapsed globule is basically not affected by the unwinding force; as  $f$  increases up to  $f^*$ , the chain is unfolded abruptly resulting in a first-order transition at  $f^*$ . The discontinuous change from the collapsed state (size  $\propto N^{1/3}$ ) to the stretched states (size  $\propto N$ ) covers a change of linear dimension of several orders of magnitude for realistic macromolecular chains

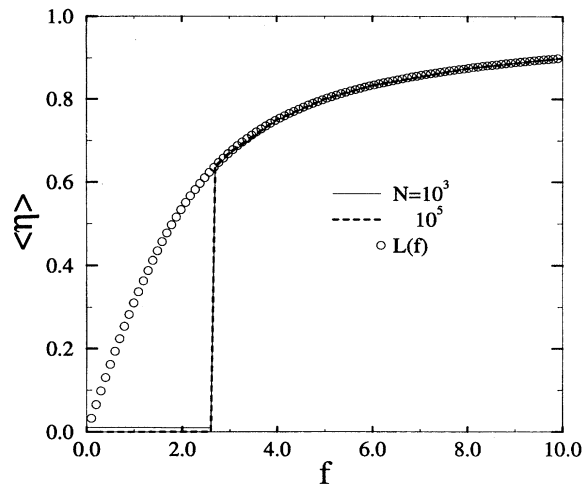


FIG. 2.  $\langle \eta \rangle$  versus  $f$  for  $\chi=2$  with  $N=10^3$  and  $N=10^5$ .  $f$  is in units of  $1/(\beta a)$ . The circle is the Langevin function  $\mathcal{L}(f)$ .

and hence provides a nice open-close switch for a biochemical gateway. For  $f > f^*$ , the chain is gradually stretched further and eventually approaches the fully stretched state. In fact, for  $f > f^*$  the stretching is well described by the Langevin function with  $\eta = \mathcal{L}(f)$ , which is denoted by the circles in Fig. 2. This indicates that once the chain is elongated, the monomer-monomer interactions become negligible and the free energy is dominated by the first and last term in Eq. (4). Figure 3 shows the order parameter  $\langle \eta \rangle$  as a function of  $f$  solved from Eq. (4) for various values of  $\chi$ . For  $\chi < \chi_c = 1/2$ , the coil is in a swollen state and it unwinds progressively without any abrupt change in its size upon an increasing stretching force. More interestingly, a similar behavior of no abrupt change also occurs in the  $\chi_c < \chi < 2\chi_c$  collapsed regime. In fact, in the  $N \rightarrow \infty$  limit  $\langle \eta \rangle$  can be solved analytically from Eq. (4),

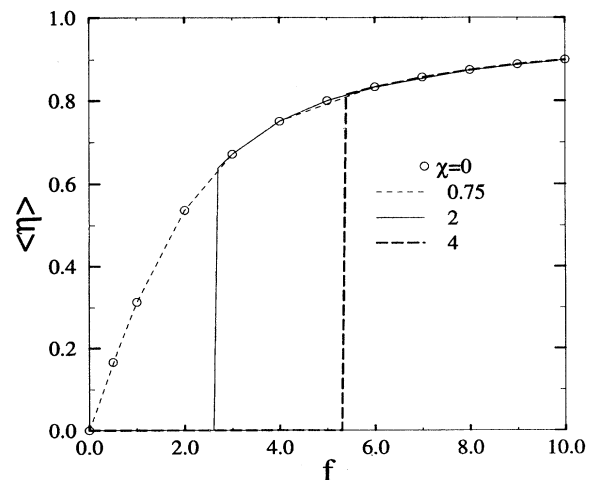


FIG. 3.  $\langle \eta \rangle$  versus  $f$  for  $\chi=0, 0.75, 2$ , and  $4$  with  $N=10^5$ .  $f$  is in units of  $1/(\beta a)$ .

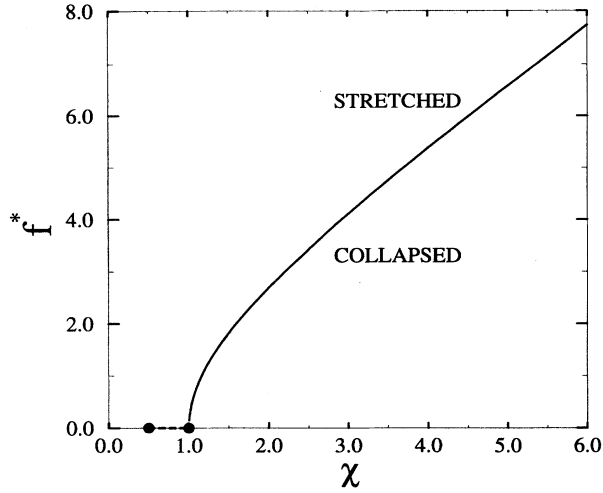


FIG. 4. Phase diagram  $f^*$  versus  $\chi$ . The solid curve is a first-order transition line which ends at the tricritical point at  $f^*=0$  and  $\chi=1$ .  $f^*$  is in units of  $1/(\beta a)$ . The dashed curve denotes a second-order transition line.

$$\langle \eta \rangle = \begin{cases} 0 & \text{for } f \leq f^* \\ \mathcal{L}(f) & \text{for } f > f^*. \end{cases} \quad (5)$$

Furthermore for a given value of  $\chi$ ,  $f^*$  can be solved from the following two equations:

$$F(\eta_{min}) = F(\eta) \quad (6)$$

and

$$\frac{\partial F(\eta)}{\partial \eta} = 0 \quad (7)$$

with two unknowns  $\eta$  and  $f^*$ . In the  $N \rightarrow \infty$  limit, we obtain the equation for the first-order phase transition boundary

$$f^* = e^{1-\chi} \sinh f^*. \quad (8)$$

It is easy to see from Eq. (8) that a positive solution for  $f^*$  exists only for  $\chi > 2\chi_c = 1$ . The phase diagram  $f^*$  versus  $\chi$  is shown in Fig. 4. The first-order line separating the collapsed and stretched states ends at  $\chi = 2\chi_c$  and  $f^* = 0$ . The known second-order transition point [9,10] from the swollen state to the collapsed state at  $f=0$  and  $\chi = \chi_c = 1/2$  is also shown. This collapsed transition at  $f=0$  and  $\chi = 1/2$  has been extensively studied using scaling [12] calculations, renormalization group method [13], and Monte Carlo simulations [14], and it has been well established that the critical phenomenon is governed by a tricritical point. In the present case, there is another tricritical point which is the merging point for the first-order line in the  $f^* > 0$  regime and a second-order line of phase transitions in the  $f=0$  and  $\chi_c \leq \chi \leq 2\chi_c$  regime. A more detailed calculation indicates that  $F(\eta)$  has no local maximum in the  $\chi_c \leq \chi \leq 2\chi_c$  regime. This is demonstrated in Fig. 5 for  $\chi = 0.75$ , which shows that there is only one

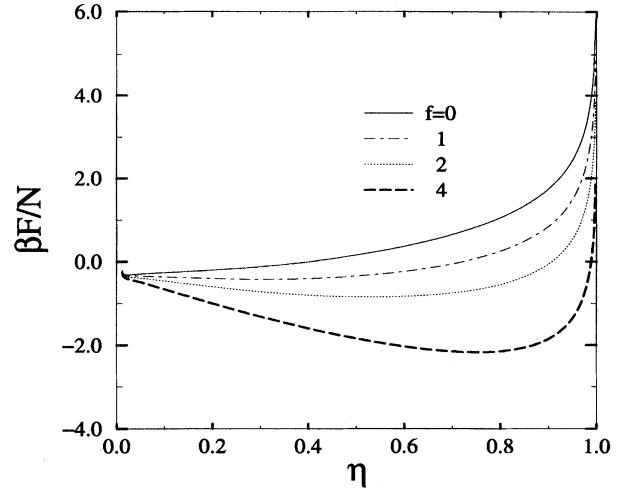


FIG. 5. Reduced free energy as a function of the stretch order parameter  $\eta$  for various values of stretch forces with  $\chi=0.75$  and  $N=1000$ .  $f$  is in units of  $1/(\beta a)$ .

local minimum in  $F(\eta)$  for all values of  $f$ . In the  $N \rightarrow \infty$  limit, the order parameter  $\langle \eta \rangle$  that minimizes  $F(\eta)$  is calculated to be

$$\langle \eta \rangle = \mathcal{L}(f) \quad \text{for all } f \geq 0 \quad \text{and} \quad \chi_c \leq \chi \leq 2\chi_c. \quad (9)$$

Thus the polymer globule is elongated progressively and continuously. In fact, if one extends to the  $f < 0$  region in the  $\chi_c \leq \chi \leq 2\chi_c$  regime, i.e., compressing the coil by bringing the two ends together,  $\langle \eta \rangle$  will remain zero for  $f < 0$ , and for  $f \geq 0$ ,  $\langle \eta \rangle$  follows Eq. (9) with  $f=0$  being a line of second-order transitions.

### III. LIFETIME OF METASTABLE STATES

For  $\chi > 2\chi_c = 1$ , the free energy  $F(\eta)$  possesses two local minima for  $\eta$  in the range  $[\eta_{min}, 1]$  (see Fig. 1) separated by a free energy barrier. The first minimum is at  $\eta_{min}$  while the second one is given by Eq. (7). For  $f < f^*$ , the stretched state ( $s$  state) is a metastable state and the characteristic time for it to transit to the true stable state depends on the free energy barrier height  $\Delta F_{sc}$  via  $\tau_{sc} \sim \exp(\beta \Delta F_{sc})$ , where the subscript  $sc$  denotes transition from the  $s$  state to the collapsed ( $c$ ) state. Similarly for  $f > f^*$ , the time scale for the metastable  $c$  state to transit to the stable  $s$  state goes as  $\tau_{cs} \sim \exp(\beta \Delta F_{cs})$ . The barrier is related to the local maximum of the free energy that occurs at  $\tilde{\eta}$  which can be calculated also from Eqs. (4) and (7). In the large  $N$  limit, we get

$$\tilde{\eta} = \sqrt{\frac{\chi - \frac{1}{2}}{f}} \frac{1}{N^{1/3}} \quad (10)$$

and for  $\chi < \chi_c = 1/2$  no free energy barrier exists, as discussed in the preceding section. The free energy barriers can be calculated from Eq. (4). Figure 6 displays the reduced free energy barrier as a function of  $f$  for  $\chi = 2$ . The free energy barrier is maximal at  $f = f^*$  as expected. Furthermore, Fig. 6 indicates that the collapsed metastable state (in the  $f > f^*$

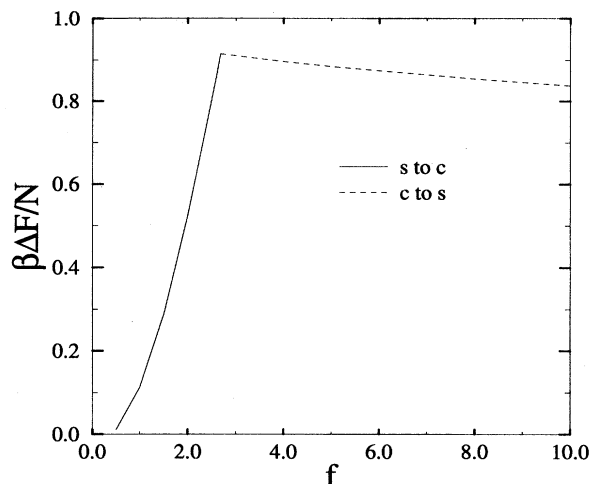


FIG. 6. Reduced free energy barrier versus  $f$  for  $\chi=2$  and  $N=10^5$ .  $f^*\approx 2.68$ .  $f$  is in units of  $1/(\beta a)$ . Solid line is the barrier from the metastable stretched state to transit to the stable collapsed state. Dashed line is the barrier from the metastable collapsed state to transit to the stable stretched state.

regime) has in general a longer lifetime than the stretched metastable state (in the  $f < f^*$  regime). We obtain the free energy barriers in the large  $N$  limit analytically,

$$\frac{\beta\Delta F_{sc}}{N} = \ell n\left(\frac{\sinh f}{f}\right) - \frac{\sqrt{f(\chi - \frac{1}{2})}}{N^{1/3}} \quad (f \leq f^*), \quad (11)$$

$$\frac{\beta\Delta F_{cs}}{N} = \chi - 1 - \frac{\sqrt{f(\chi - \frac{1}{2})}}{N^{1/3}} \quad (f \geq f^*). \quad (12)$$

The existence of metastable states in a first-order transition is manifested experimentally by the presence of hysteresis loop if the observation time is not much greater than the lifetime of metastable states. A strong hysteresis effect is essential for a memory device in complete analogy to a magnetic system. One can imagine the  $s$  state ( $c$  state) corresponds to a “1” (“0”) in some kind of molecular memory device. A “good memory” corresponds to a long lifetime for the metastable state; even the external stretching force is removed. Thus a

knowledge of the lifetime of the metastable states or the height of the free energy barrier is essential in the design of such a molecular memory device. The memory or hysteresis effect can be measured by the maximum of the free energy barrier that occurs at  $f=f^*$ . The barrier increases with  $\chi$  monotonously. Hence the lifetime of the metastable state can be written as

$$\tau \sim \exp[g(\chi)N] \quad (13)$$

for some positive function  $g(\chi)$ . The function  $g(\chi)$  can be calculated analytically in the large  $N$  limit and we have

$$g(\chi) = \chi - 1 - \frac{\sqrt{f^*(\chi - \frac{1}{2})}}{N^{1/3}}. \quad (14)$$

Thus in the  $N \rightarrow \infty$  limit,  $g(\chi)$  is positive for  $\chi > 2\chi_c = 1$  and the lifetime of the metastable state is given by  $\tau = \tau_0 \exp[(\chi - 1)N]$  for some microscopic time scale  $\tau_0$ . Because of the exponential increasing factor in the chain length  $N$ ,  $\tau$  can be macroscopic or even astronomical.

#### IV. SUMMARY AND OUTLOOK

In summary, using the Flory-type mean-field calculation, we found an interesting first-order transition in unfolding a collapsed polymer globule for  $\chi > 2\chi_c = 1$ . This phenomenological mean-field theory, though somewhat crude, yields many interesting physics including a rich phase diagram and information on the lifetime of the metastable states. These results can be readily tested by experiments with setups in Refs. [1,2] and by simulations [15]. We hope our results can stimulate more detailed theoretical work using renormalization group and field-theoretical methods, as well as experiments and designs in chemical engineering. Our mean-field results have been confirmed qualitatively by a separate Monte Carlo simulation using the bond-fluctuation model. The first-order transition signified by the abrupt jump in the stretching order parameter and the associated hysteresis effect are clearly observed in the simulation. These results will be published elsewhere [15].

#### ACKNOWLEDGMENTS

We acknowledge support from the National Council of Science of Taiwan under Grant No. NSC 85-2112-M-008-016.

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