

Force-induced triple point for interacting polymers

Sanjay Kumar*

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

Debaprasad Giri†

Physics Section, MMV, Banaras Hindu University, Varanasi 221 005, India

Somendra M. Bhattacharjee‡

Institute of Physics, Bhubaneswar 751 005, India

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We show the existence of a force induced triple point in an interacting polymer problem that allows two zero-force thermal phase transitions. The phase diagrams for two different models of mutually attracting but self-avoiding polymers are presented. One of these models has an intermediate phase and it shows a triple point. A general phase diagram with multicritical points in an extended parameter space is also discussed.

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Soon after the discovery of the double helical structure of double-stranded DNA (dsDNA), its melting by change of temperature or the pH of the solvent was recognized [1]. Only recently it has been realized that there can be a force-induced unzipping transition [2] of a DNA with a force applied solely at one end. In both the thermal and the forced cases, the phase transition takes a double-stranded form to two single strands. The prediction of the unzipping transition based on interacting Gaussian chains [2] was immediately reconfirmed by a dynamical approach [3]. Results on the unzipping transition are now available from extensive exact solutions of lattice models [4–6], simple models of quenched-averaged DNA [7], Monte Carlo simulations of a three-dimensional model with self- and mutually avoiding walks [8], etc., on the theoretical front, and for real DNA from experiments [9]. From the theoretical results, it emerges that the qualitative features of the unzipping transition are insensitive to the dimensionality (d) of the models and are seen even in two-dimensional models. These results include a re-entrance [4–6] in the low temperature region.

In the systems studied so far, there is only one zero force thermal phase transition. In such cases, with two intensive variables, temperature T and force g , there is an unzipping transition line, $g=g_c(T)$, in the g - T plane, demarcating the bound or zipped phase from the unzipped phase. This gives the unzipping phase boundary. In case there are more than one transition, the phase diagram will be influenced by the intermediate phases. A special situation corresponds to the case where the intermediate phase is stabilized by entropy and cannot be produced by a force in the ground state. Our aim is to determine the global phase diagram for the unzipping transition where the existence of such an intermediate phase leads to a triple point in the g - T plane.

We consider two models, A and B, which differ in the

nature of the mutual interaction of the two strands. These models are general enough to be defined in any d though, for computational limitations, we consider the two-dimensional square lattice version only. Let us consider two linear polymer chains which are mutually attracting self-avoiding [10] in nature. On a square lattice, the polymers are not allowed to cross each other as shown in Fig. 1. Monomers (also called bases) are the sites occupied by the polymers and the interactions are among the “bases” so that an interacting pair may also be called a base pair. There is an attractive interaction between monomers or bases only if they are of opposite strands and are nearest neighbors on the lattice. The nearest neighbor interaction mimics the short range nature of the hydrogen bonds. In model A, any monomer of one strand can interact with any monomer of the other strand. In model B, monomer i of one strand can interact only with the i th monomer of the other strand. This model is similar to the models of DNA studied earlier [11] though it does not take into account the directional nature of the hydrogen bonds. A more realistic model incorporating this feature, similar to models in the context of relative stabilities of DNA hairpin structures [12], has also been studied but the results of interest in this paper turn out to be similar to model B. Such modifications are therefore not discussed in detail. The interaction energy in all the cases is taken as $-\epsilon(\epsilon > 0)$ and we shall choose $\epsilon = 1$. In all cases the monomers at one end (index=1) of each

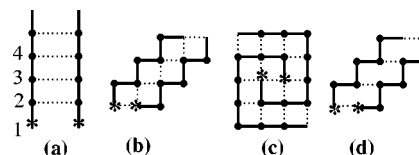


FIG. 1. (a)–(d) represent the possible conformations of models A and B. For model A (a) and (b) are two possible states with (c) representing a possible ground state. For model B, (a) represents the ground state and (d) represents a partial bound state. Note that (d) differs from (b) in the nature of interactions represented by the dotted lines. In model B, (c) has no valid interaction and would represent an open state.

*Electronic address: yashankit@yahoo.com

†Electronic address: dgiri@bhu.ac.in

‡Electronic address: somen@iopb.res.in

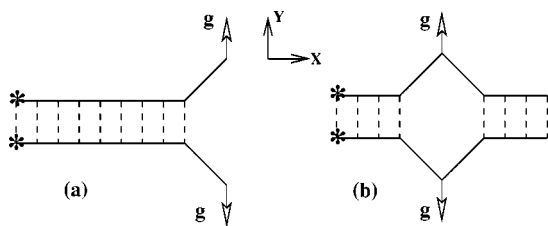


FIG. 2. Schematic figures for a force (a) applied at one end, and (b) applied at the middle. Fixed endpoints are indicated by stars.

strand are always kept fixed occupying nearest neighbor sites on the lattice.

For model A the ground state is a spiral of the type shown in Fig. 1(c) while for model B it is a zipped state as in Fig. 1(a). Because of the constraint of holding the monomers with index 1 at nearest neighbor sites, model A is also equivalent to a diblock copolymer model [13] which has two phase transitions in zero force with increasing temperature. The polymers go from a compact spiral-like phase to a zipped phase (a first order transition) and the zipped phase then melts (continuous transition) at a still higher temperature. It is this intermediate phase that is of interest to us. By introducing a three-body interaction the intermediate phase in model A can be made to disappear so that a multicritical point emerges in the extended parameter space. This case is also considered in the paper. In view of the simple ground state in models B, no such intermediate phases are expected or known.

A force is applied at one end [Fig. 2(a)] or at the middle [Fig. 2(b)] of the chains, in the y direction. The contribution to energy by this force is $-gy$ where y is the absolute distance in the y direction between the two strands at the point of application of the force. A recent study [6] showed a rich phase diagram when a force is applied somewhere in the interior. Furthermore, such situations occur in many processes like gene expression where RNA is formed in bubbles or eye-type configurations on DNA. Motivated by these, we consider the case of a force applied at the midpoint. A low temperature analysis shows that the phase diagram is expected to be different from the end case. We compare the g - T phase diagrams of model A vs model B. In the process we identify the unzipping force as a relevant variable required for complete characterization of the critical and the multicritical points of model A.

The thermodynamic properties associated with the unzipping transition are obtained from the partition function which can be written as a sum over all possible configurations

$$Z_N(\omega, u) = \sum_{n,y} C(m, y) \omega^m u^y. \quad (1)$$

Here N is the chain length of each of the two strands, $\omega = \exp(1/T)$ is the Boltzmann weight associated with each base pair (taking the Boltzmann constant $k_B=1$) and m is the total number of intact base pairs in the chain. Finally u is the Boltzmann weight, $\exp(g/T)$ associated with force. $C(m, y)$ is the number of distinct configurations having m bound base pairs whose end (or mid) points are at a distance y apart. We

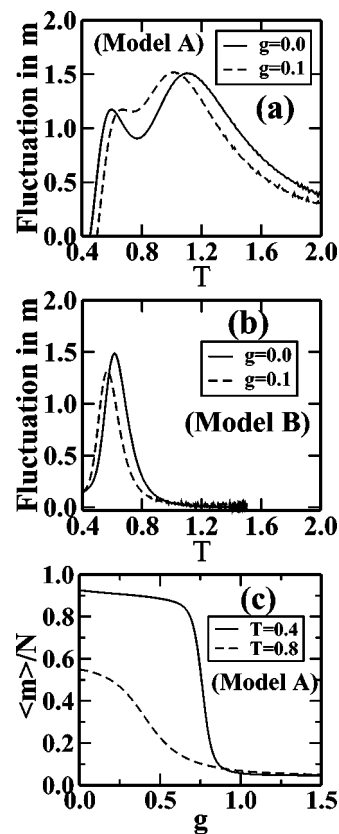


FIG. 3. Variations in fluctuation of m with temperature (T) for $g=0.0$ and 0.1 are shown for model A (a) and model B (b). (c) shows the sharp drop of the fraction of bound base pairs ($\langle m \rangle / N$) for model A ($N=16$) as the force exceeds the critical force at a constant temperature.

have obtained $C(m, y)$ for $N \leq 16$ monomers in two dimension ($d=2$) and analyzed the partition function through series analysis. We prefer this technique because in this case the scaling corrections are correctly taken into account by suitable extrapolation technique. To achieve the same accuracy by the Monte Carlo method, a chain of about two orders of magnitude larger than in the exact enumeration method must be considered [14].

The reduced free energy per base pair is found from the relation $G(\omega, u) = \lim_{N \rightarrow \infty} (1/N) \log Z(\omega, u)$. The limit $N \rightarrow \infty$ is found by using the ratio method [15] for extrapolation. The transition point for zero force (i.e., thermal melting) can be obtained from the plot of $G(\omega, u)$ versus ω or from the peak value of $\partial^2 G / \partial (\ln \omega)^2$. For self-avoiding walk at $u=1$, we find $T_c = 1.1 \pm 0.1$ and 0.61 ± 0.08 for models A and B, respectively. With a force ($u \neq 1$), the phase boundary is obtained from the fluctuation in m . Figure 3 shows the variation of fluctuation of m with temperature for model A and B.

For model A, we see two peaks in the temperature dependence of the fluctuation in m for small g (Fig. 3). The low temperature peak is the transition where the spiral state goes over to the zipped state while the second peak is the unzipping transition. The transition can be seen in Fig. 3(c) where the fraction of the number of bound base pairs $\langle m \rangle / N$ are shown to vanish as the force increases. One therefore finds

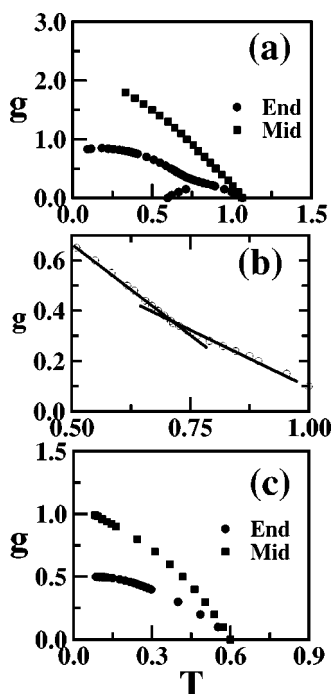


FIG. 4. Force-temperature (g - T) phase diagrams for the end and the midcase, for (a), (b) model A, and (c) model B. The spiral to zipped transition is shown only for the end case. (b) shows the region near the triple point. The crossing point is the location of the triple point.

three transition lines, spiral-unzipped, spiral-zipped, and zipped-unzipped. The unzipped phase is thermodynamically identical to the zero force swollen phase except for stretching by the force. The phase diagrams are shown in Fig. 4. Since the two peaks in Fig. 3(a) approach each other as the force increases, it becomes difficult to locate the spiral to zipped phase boundary at higher force. Therefore, we have higher uncertainties (~ 0.04) in locating the spiral to zipped transition at higher force and so this part of the line is not shown in Fig. 4. It is to be noted that without force the spiral compact phase cannot be directly transformed into the unzipped, swollen phase. We argue that each of these lines are first order in nature so that the meeting point of the three lines is a *triple point*. From thermodynamic stability analysis [16], it is known that the angle between two coexistence lines at a triple point in a phase diagram must be less than π . Therefore, a discontinuity in the slope in the unzipping phase boundary in the g - T plane is expected at the potential triple point. Figure 4(b) shows the meeting of the two unzipping boundaries. From the intersection of the boundaries, our estimate of the location of the triple point is $g_t = 0.35 \pm 0.02$, $T_t = 0.75 \pm 0.02$.

Our results are based on the $N=16$ (32 monomers) enumerations. For this length there is significant surface contribution. The ground state energy is $E_0 = -[2N - O(\sqrt{N})]$ for model A and $E_0 = -N\epsilon$ for model B for a DNA of N monomers (bases). The $O(\sqrt{N})$ correction for model A only comes from the monomers on the boundary. If we ignore the surface contribution (valid for large N) the spiral to zipped state transition temperature T_{c1} may be estimated from a simple

energy balance argument. The spiral state has an energy $E_0 = -2N$ with negligible entropy while the zipped state has the free energy $= -N - NT \ln \mu_b$, where $\ln \mu_b$ is the entropy per base pair of the zipped phase. Equating these two we get $T_{c1} = 1/\ln \mu_b - O(N^{-1/2})$, where the surface correction has also been shown. If we use $\mu_b = 2.6382$, the connectivity constant for the square lattice self-avoiding walk [10], we find $T_{c1} \approx 1.04$ which is close to the value known from other estimates [13]. Our value of $T_{c1} = 0.5$ is consistent with the above form since the surface correction lowers the estimate of T_{c1} .

The zipped state for model A cannot be obtained by energy minimization only nor can it be produced by force at $T=0$ because the end separation remains subextensive going from $O(\sqrt{N})$ in the spiral phase to $O(1)$ in the zipped phase. It is the gain in entropy (with respect to spiral) that gives stability to the zipped phase in the intermediate temperature range (“entropy-stabilized” phase). Since this spiral-zipped phase boundary cannot meet the $T=0$ force axis and since, for large N , the force term cannot affect this transition, one would expect a phase boundary parallel to the g axis. It also follows that the spiral to the zipped state transition remains first order as it is for the zero-force case. It should however be noted that the surface contribution in the spiral state in the form of the extra energy $\sim g\sqrt{N}$ actually helps in the stabilization of the spiral structure over the zipped phase for small g , at least for small N . As a result, the phase boundary obtained for finite N has a finite slope as shown in Figs. 4(a) and 4(b).

To determine the nature of the spiral-unzipped transition, we use a low temperature expansion. At $T=0$, the critical force can be found from a matching of the ground state energy with the energy of the completely unzipped state. If the force stretches the strands completely, the unzipped state has the energy $= -2Ng$ taking the bond length to be unity. Comparing this with the bound state energy E_0 , we see $g_c(T=0) = E_0/2N$. For large N , $E_0 = 2N$ and so we get $g_c(T=0) = 1$, while it is 0.5 for models B. For finite N , if the surface correction is taken into account, then $g_c = 1 - (1/\sqrt{2N}) \approx 0.8232$ for $N=16$. The value shown in Fig. 4 is very close to this estimate rather than the large N value. In absence of large N data, extrapolations have not been attempted for model A. Since the fraction of bound pairs shows a jump from a finite value to 0 as the force exceeds g_c , the $T=0$ force induced transition is first order.

The low temperature phase boundary for the mid-case can be obtained by an extension of the $T=0$ argument given above. Following Ref. [6], let us consider the situation with the force applied at a position sN ($0 < s \leq 1$), from the fixed end. The unzipped state has the energy $= -2sNg$ taking the bond length to be unity. This needs to be compared with the bound state energy $E_0 = -a\epsilon N$ where $a=2$ for model A but $a=1$ for model B. We therefore see $g_c(T=0) = a/2s$. A factor of 2 difference in the end case vs mid-case and model A vs B are seen in Fig. 4.

The phase boundary close to $T=0$ can be obtained by considering configurations where m base pairs for the end case or a bubble of $2m$ base pairs for the mid-case have been unzipped. At T close to zero, the unzipped part of the chains

remain completely stretched with negligible entropy. Consequently the free energy of such configurations with respect to the completely bound state is $\Delta F = \sigma m(a + T \ln \mu_B) - gm$, where $\sigma = 1$ for the end case or 2 for the mid-case, and $\ln \mu_B$ is the entropy per base pair of the bound state which is lost on unzipping the base pairs. For the mid-case a large m is favorable ($m \leq N/2$) if

$$g > g_c(T) \equiv 2(a + T \ln \mu_B)$$

while for the end case, the critical force is given by $g_c(T) = a + T \ln \mu_B$. In either case, a reentrance is possible if $\ln \mu_B > 0$. For both the models studied here, $\ln \mu_B = 0$, and therefore, unlike other DNA problems [4–6], no reentrance is expected. The free energy expression also shows a jump or discontinuity in the number of unzipped pairs across the phase boundary just as at $T = 0$. The transition line in the low temperature region is therefore first order.

For the transition in the small force region at temperatures close to the melting point (but away from the critical region), the entropies of the unzipped single strands need to be considered. This can be done by using polymer statistics. The unbound region is like a two-dimensional SAW of length $2m$ under a stretching force. The probability [10] that a SAW will have an end-to-end separation y is

$$P(y, m) \sim \exp[-c(ym^{-\nu})^\delta],$$

where ν is the polymer size exponent, $\delta = (1 - \nu)^{-1}$ and c is a constant. This gives an extra contribution to the entropy so that the free energy can be written as

$$\Delta F(N, m, y, g) = \Delta F_0(N, m) - gy - c(ym^{-\nu})^\delta,$$

where

$$\Delta F_0(N, m) = m[2f_u(T) - f_z(T)]$$

is the free energy in zero force, $f_{z,u}$ being the free energies of the zipped and the swollen chains ($\epsilon = 0$) in zero force. Since the zipped state is the thermodynamically stable phase, we have $f_z(T) < 2f_u(T)$. Minimization with respect to y then gives $y \sim mg^{1/(\delta-1)}$. Using this, we obtain

$$\Delta F(N, m, g) = \Delta F_0(N, m) - c_1 mg^{1/\nu}$$

using the relation between ν and δ . A further minimization with respect to m then gives $g_c(T) \sim |2f_u(T) - f_z(T)|^\nu$ with a jump in m . It is therefore a first order transition. This argument is valid away from the critical region if the melting is continuous, as in model A, because of the bubble formations of all length scales by thermal fluctuations. But by continuity the transition is to remain first order becoming continuous or critical only at the terminal point in zero field.

The results for model A can be extended to a case with a three-body interaction that stabilizes the spiral phase [13]. Let there be an interaction δ that favors a configuration with a monomer of one strand sandwiched between the monomers of the other strand on the two nearest neighbors on the same axis as shown in Fig. 5(a). Let us call such a contact as a δ contact. This is a three-body interaction so that a δ contact has energy $2\epsilon + \delta$. For corner sharing configurations [an example shown in Fig. 5(a)] there is no three-body interaction.

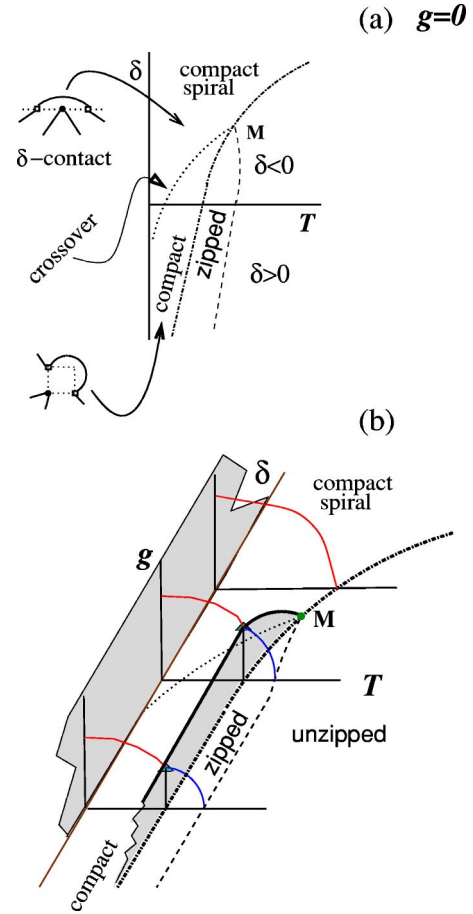


FIG. 5. (Color online) (a) Schematic phase diagram in the δ - T plane in zero force. The δ contact is also shown for the region where it dominates. The dotted line is a crossover line for the two compact configurations distinguished by the nature of contacts as indicated. M is the multicritical point (at zero force) where the zipped phase vanishes. The thick line is the first order line while the denaturation of the zipped phase is a continuous transition (dashed line). (b) Proposed phase diagram in the g - δ - T space. The line connecting the triangles is a line of triple points ending on M . The shaded surface separates the compact phase from the zipped phase and is parallel to the $T = 0$ plane (also shaded for clarity).

Let us first consider the zero force phase diagram. For large negative δ , strong attractive three-body interaction yields a compact spiral ground state dominated by the δ contacts. In this regime, there is only one thermal denaturation transition from the compact spiral phase to the swollen phase. However, for $\delta > 0$, i.e., repulsive three-body interaction, there is an intermediate zipped phase formed via the pairwise attraction. For such δ , the ground state configuration is a compact but nonspiral phase, mostly devoid of δ contacts. The three phases are similar to what we have seen for $\delta = 0$. Therefore, in the δ - T plane at $g = 0$, a multicritical point [M in Fig. 5(a)] occurs with $\delta = \delta_M < 0$. This point M is the meeting of the line of continuous thermal denaturation of the zipped phase and the first-order compact-zipped transition. In the compact case without any δ contact, a mean field estimate of the ground state energy, assuming equal proportion of double and single contacts, gives

$E=-(3/2)N$. By comparing with the energy of the spiral state, namely $-2N+2N\delta$ for $N\rightarrow\infty$, one finds the crossover at $T=0$ to be at $\delta\approx 0.5$. In the δ - T phase diagram, m such a crossover line [dotted line in Fig. 5(a)] should end at M .

Let us now consider the effect of a force at one end. Our results for the $\delta=0$ case suggest that so long as the zipped phase is thermodynamically stable, there is a triple point under a force. Hence, there is a line of triple points in the region $\delta\geq\delta_M$ terminating on M . The g - T - δ phase diagram is schematically shown in Fig. 5(b). The shaded surface separates the compact phase from the zipped phase and has the line of triple points at its edge. The zipped phase is inside the pencil shaped region with M at its tip. Even though in zero force, M resembles a critical endpoint (a second order line ending on a first-order line), actually there is an additional line of triple points ending there. This line exists only when there is a force. We are not aware of any other such multicritical point, especially in polymers. The scaling or univer-

sal behavior at such a multicritical point M remains a major open issue.

To summarize, we have determined the phase diagram of two polymer models under a force and have shown the existence of a force induced triple point when the interactions allow an entropy-stabilized phase before melting. The unzipping force is a relevant term at the continuous meltinglike transition and is therefore important for a complete characterization of the critical behavior. Our results open up the possibility of much richer phase transitions and multicritical behaviors in polymeric systems when subjected to an unzipping force. We hope that single molecule experiments would be able to explore experimentally this area in polymers.

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