Pulling self-interacting polymers in two dimensions

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We investigate a two-dimensional problem of an isolated self-interacting end-grafted polymer, pulled by one end. In the thermodynamic limit, we find that the model has only two different phases, namely a collapsed phase and a stretched phase. We show that the phase diagram obtained by Kumar *et al.* [Phys. Rev. Lett. **98**, 128101 (2007)] for small systems, where differences between various statistical ensembles play an important role, differs from the phase diagram obtained here in the thermodynamic limit.

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I. INTRODUCTION

The physics of single polymer chains in a poor solvent is still not very well understood. Away from the θ temperature, we know that a polymer will be in either a collapsed or a swollen state [1]. The mean-square radius of gyration $\langle R^2\rangle_g$ scales with chain length N as $\langle R^2\rangle_g \sim \text{const}\times N^{2\nu}$, where ν is a critical exponent. At low temperatures, when the polymer is in the collapsed state, $\nu=1/d$ while at high temperatures an "extended" or "swollen coil" state exists where $\nu=1,3/4,0.588\ldots,1/2$ for $d=1,2,3,4$ [1], respectively. These values are believed to be exact for $d=1,2$ and, with a logarithmic correction, for $d=4$. At high temperatures stretching a polymer should produce a state where $\nu=1$ which we shall refer to as the "stretched" state. Although there are many theoretical [2–4] as well as experimental [5] works on pulling of a collapsed chain, it seems that some issues remain to be fully understood.

Recently Kumar *et al.* [6] studied a simple model of interacting self-avoiding walks on the square lattice using exact enumerations. They presented results for the force-induced unfolding of a polymer in two dimensions in the context of modeling single molecule experiments. For finite systems, they proposed a phase diagram, which has three phases, namely a collapsed phase, an extended phase, and a stretched phase (in addition there is a swollen phase which only occurs at $F=0$ above the θ temperature). They found a transition line between the stretched state and the extended phase. The proposed phase diagram is presented in Fig. 1. The lower phase boundary was obtained in both the constant force and constant temperature ensembles, and indicates a phase-transition line where the polymer goes from the collapsed phase to the extended state. However, the upper phase boundary was seen only in the constant force ensemble and it was proposed that this represents a transition line where the polymer goes from the stretched state to the extended state.

In this paper we focus our attention on the true nature of the phase diagram for the model in the thermodynamic limit. We present some further studies of the series data trying to gauge the scaling behavior of the model at different points in the phase diagram. While somewhat inconclusive, our analysis does indicate that the true phase diagram (for nonzero force) has only two distinct phases for nonzero forces and not three as originally conjectured. The extended phase does not exist for nonzero forces and the upper phase boundary is a finite-size effect only present when the model is studied at fixed force with a variable temperature.

Hence to really delineate the phase diagram we have also performed Monte Carlo simulations using the FlatPERM algorithm [7]. We investigate several hypothetical phase diagrams. In particular, we consider the possible scenario that the phases seen are two types of stretched phase: one where the polymer is maximally stretched in a rodlike conformation and the other where $\nu=1$ though the polymer is not maximally stretched. Using the simulation results we are able to confidently deduce that there is no evidence of any additional phase or phase transition in the thermodynamic limit.

We would like to emphasize that the "phase diagram" obtained by Kumar *et al.* [6] for small systems may still be relevant in the context of experiments on biopolymers. In real systems of finite size, differences between various statistical ensembles do play an important role as evidenced not only by this previous study but also by recent experimental work [8]. We thus see our discovery of a discrepancy between the finite size "phase diagram" and the true infinite

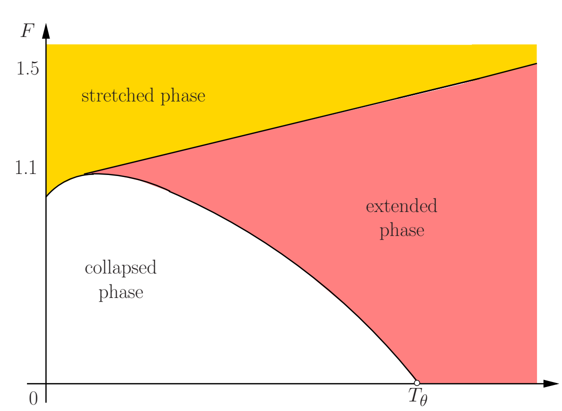

FIG. 1. (Color online) Schematic phase diagram proposed by Kumar *et al.* [6].

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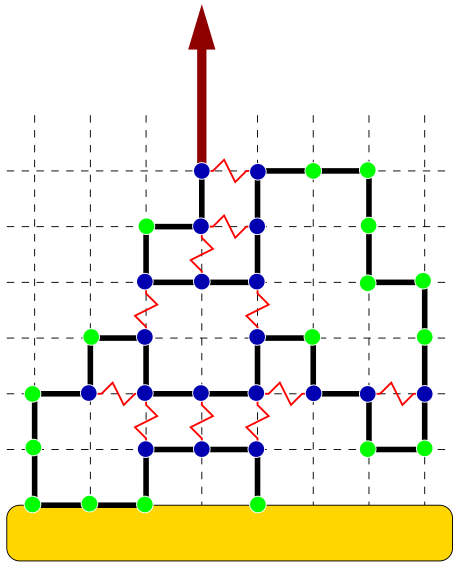

FIG. 2. (Color online) The model of a polymer on the two-dimensional square lattice pulled by the last monomer. The arrow indicates the direction of the pulling force. The dark (blue) filled circles on lattice sites denote monomers interacting via nearest-neighbor interactions.

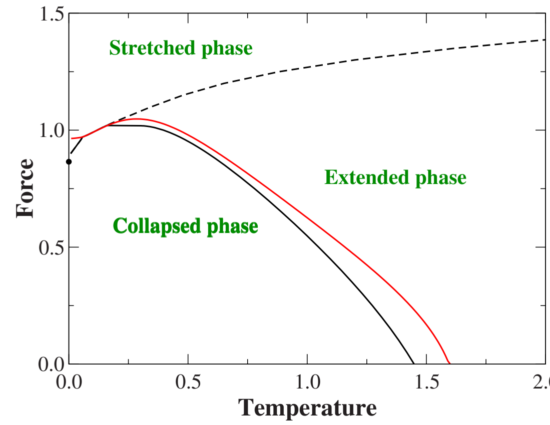

FIG. 4. (Color online) The finite-size phase diagram for flexible chains as obtained from the position of the peak in the contact fluctuation curves for $N=55$. The solid black curve and the dashed curve are obtained by fixing the force and varying the temperature.

size phase diagram as an important contribution to a better understanding of the types of finite-size effects that may be of importance to the interpretation and understanding of experimental results on small systems.

In Sec. II we define the model. In Sec. III we first briefly review the evidence presented using series analysis to support the conjectured phase diagram [6,9] and then present further results from a more thorough and extensive analysis of the series data casting doubt on the upper phase boundary of the proposed phase diagram. In Sec. IV we present the conclusive results of the Monte Carlo simulations which do not support the existence of any additional phase transitions: we carefully consider various possible scenarios. Finally, in Sec. V we summarize our final conclusions.

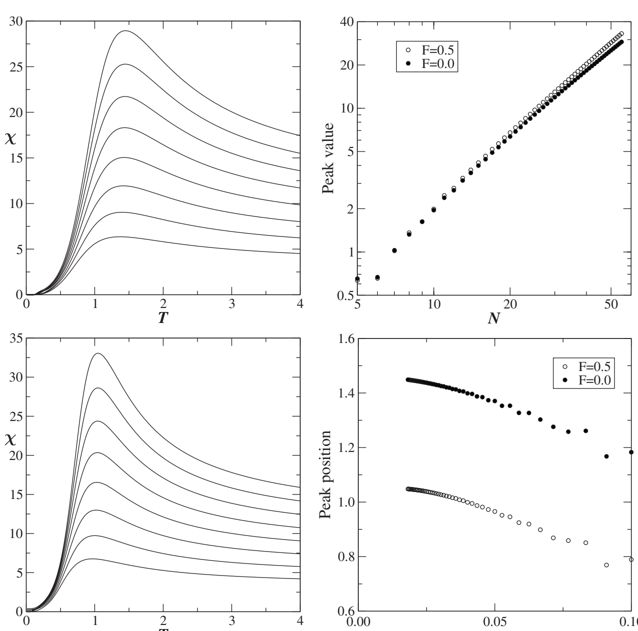

FIG. 3. The fluctuations in the number of contacts as a function of temperature for fixed force $F=0.0$ (upper left panel) and $F=0.5$ (lower left panel). Each panel contains curves for ISAWs of length (from bottom to top) $N=20,25,\ldots,55$. In the upper right panel we show a log-log plot of the growth in the peak value of the fluctuation curve with chain length N. The lower right panel shows the peak position (critical temperature value) vs $1/N$.

II. MODEL

We model the polymer chains as interacting self-avoiding walks (ISAWs) on the square lattice as shown in Fig. 2. Interactions are introduced between nonbonded nearest-neighbor monomers. In our model one end of the polymer is

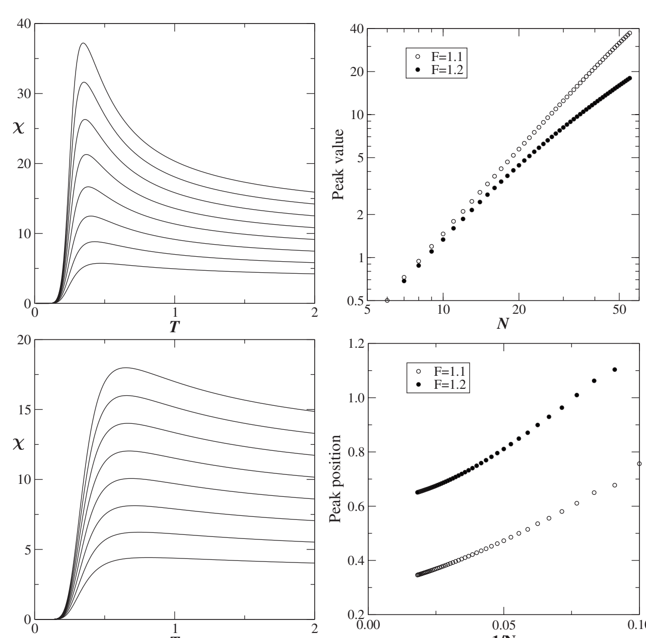

FIG. 5. Same as in Fig. 3 but for fixed force $F=1.1$ (upper left panel) and $F=1.2$ (lower left panel).

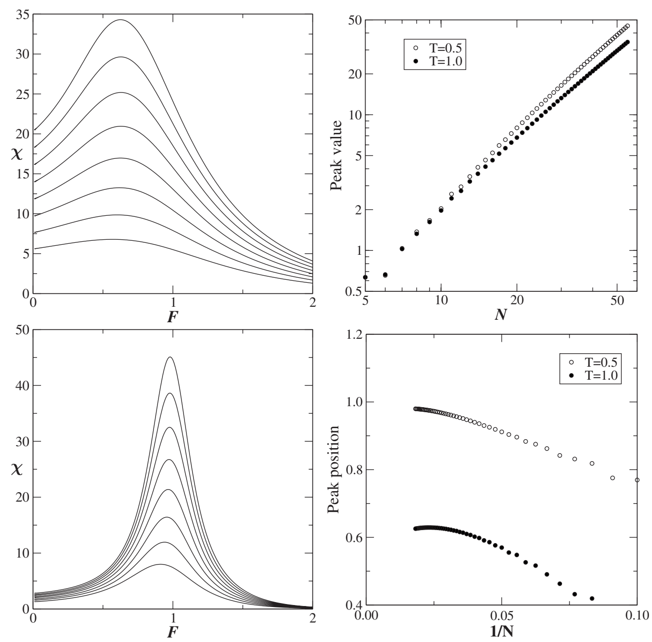

FIG. 6. The fluctuations in the number of contacts as a function of force for fixed temperature $T=1.0$ (upper left panel) and $T=0.5$ (lower left panel). Each panel contains curves for ISAWs of length (from bottom to top) $N=20,25,\ldots,55$. In the upper right panel we show a log-log plot of the growth in the peak value of the fluctuation curve with chain length N. The lower right panel shows the peak position (critical force value) vs $1/N$.

attached to an impenetrable neutral surface (there are no interactions with this surface) while the polymer is being pulled from the other end with a force acting in the direction perpendicular to the surface. Note that the ISAW does not extend beyond either end point so the y coordinate y_j of the jth monomer is restricted by $0=y_0\leqslant y_j\leqslant y_N=h$.

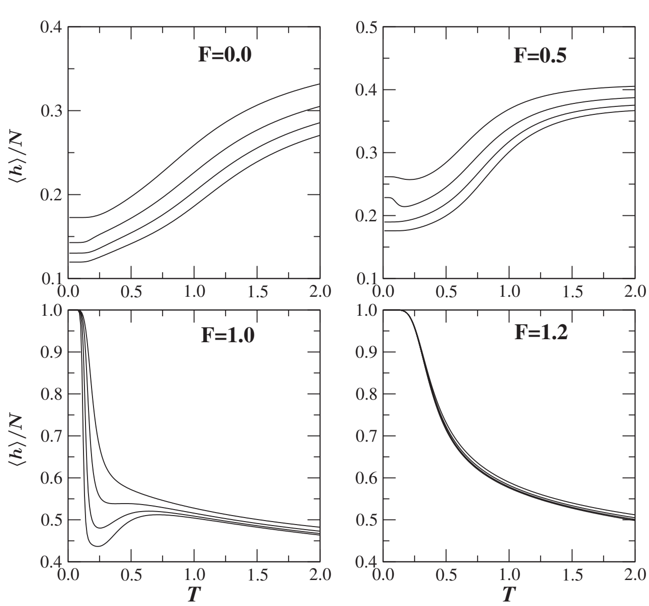

FIG. 7. The average extension per monomer $\langle h\rangle/N$ as a function of temperature T for different values of the force. Each panel contain four curves for, from top to bottom, $N=25$, 35, 45, and 55.

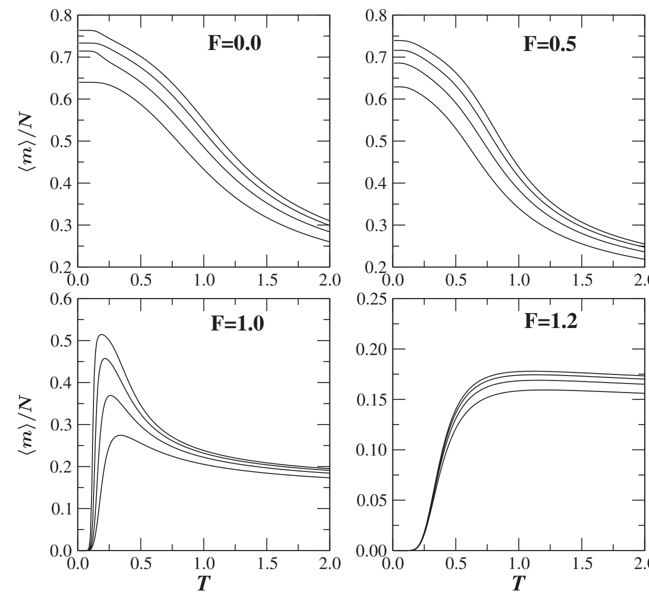

FIG. 8. The average number of contacts per monomer $\langle m\rangle/N$ as a function of temperature T for different values of the force. Each panel contain four curves for, from bottom to top, $N=25$, 35, 45, and 55.

We introduce Boltzmann weights $\omega=\exp(-\varepsilon/k_{\mathrm{B}}T)$ and $u=\exp(F/k_{\mathrm{B}}T)$ conjugate to the nearest-neighbor interactions and force, respectively, where ε is the interaction energy, k_{B} is Boltzmann's constant, T is the temperature, and F is the applied force. In the rest of this study we set $\varepsilon=-1$ and $k_{\mathrm{B}}=1$. We study the finite-length partition functions

$$Z_N(T,F)=\sum_{\text{all walks}}\omega^m u^h=\sum_{m,h}C_{N,m,h}\omega^m u^h, \tag{1}$$

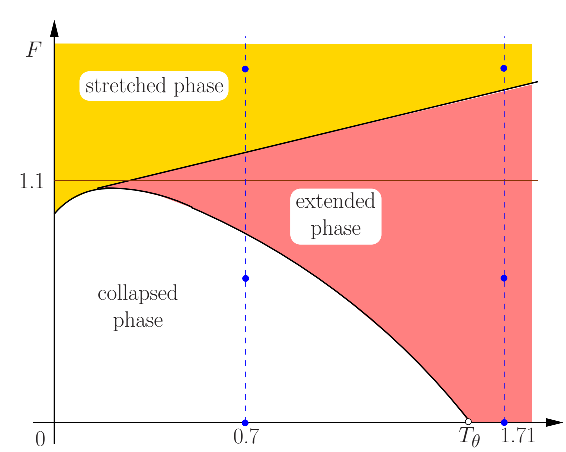

FIG. 9. (Color online) Schematic phase diagram conjectured by Kumar *et al.* [6,9]. The conjectured phase diagram has three different phases: "collapsed," "extended," and "stretched." We have performed simulations of the whole phase space up to length $N_{\max}=128$. The dashed lines at fixed temperatures $T=0.7$ and $T=1.71$ display lines along which simulations were performed for walk lengths up to $N_{\max}=1024$. The six points displayed are those at which we have focused our attention.

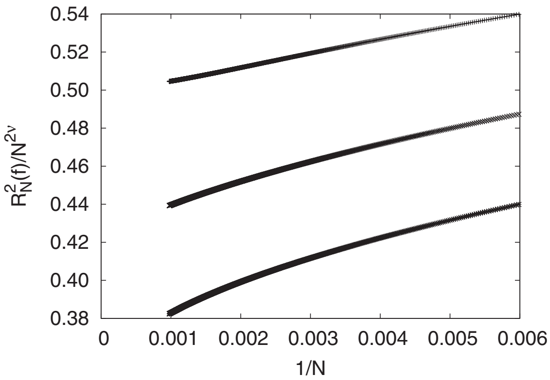

FIG. 10. End-to-end distance divided by $N^{2\nu}$ against $1/N$ for the point $(T,F)=(2.0,0.0)$ with, from top to bottom, $2\nu=1.48$, 1.50, and 1.52. We see that $2\nu=1.5(2)$. This point is thus in the extended phase.

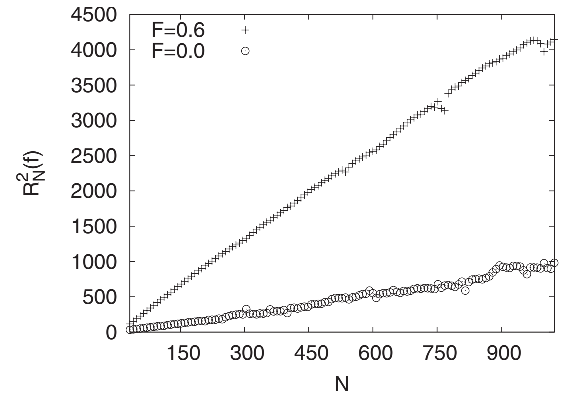

FIG. 11. End-to-end distance divided by $N^{2\nu}$ against N for two points, $(T,F)=(0.7,0.0)$ and $(T,F)=(0.7,0.6)$, for lengths up to $N=1024$. A clear linear dependence is seen implying $2\nu\approx 1$. These points are in the collapsed phase and this exponent result is consistent with this assumption.

where $C_{N,m,h}$ is the number of ISAWs of length N having m nearest-neighbor contacts and whose end point is a distance h from the surface.

III. SERIES ANALYSIS

A. Fluctuation curves and the conjectured phase diagram

To begin, let us recall the type of analysis presented by Kumar *et al.* [6,9]. At low temperature and force the polymer chain is in the collapsed state and as the temperature is increased (at fixed force) the polymer chain undergoes a phase transition to an extended state. The value of the transition temperature (for a fixed value of the force) can be obtained from the fluctuations in the number of nonbonded nearest-neighbor contacts. The fluctuations are defined as $\chi=\langle m^2\rangle-\langle m\rangle^2$, with the kth moment given by

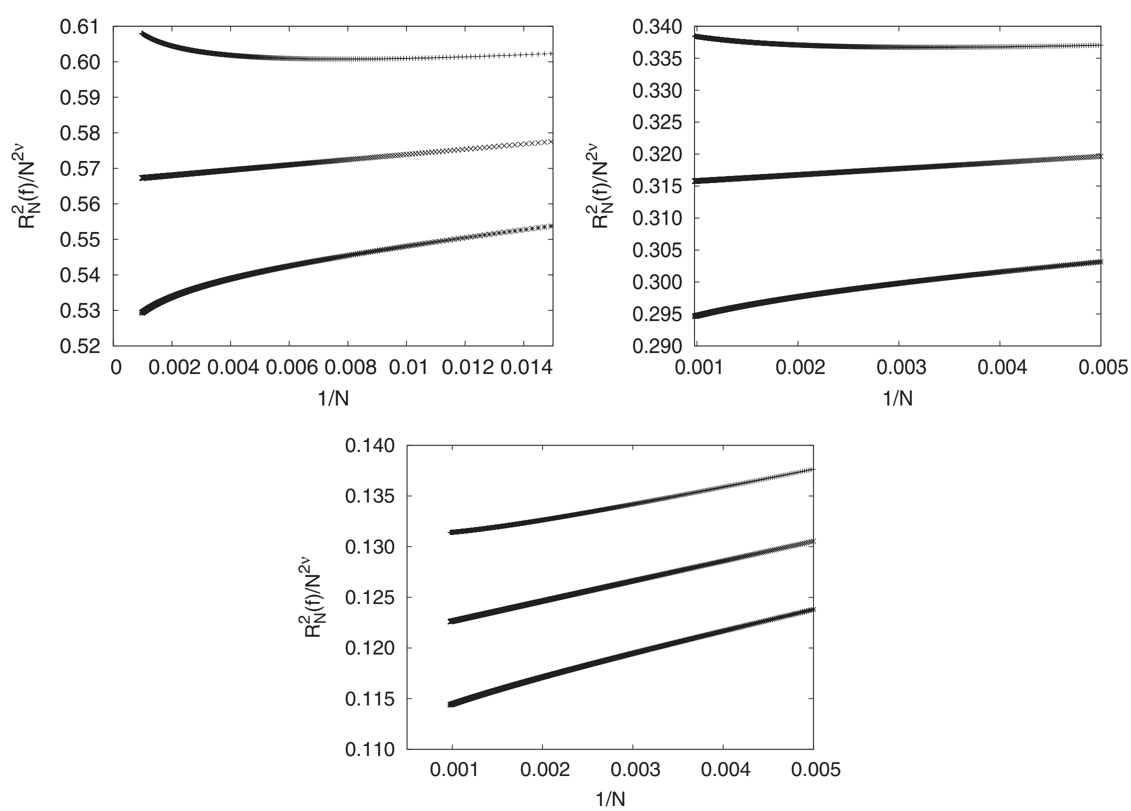

FIG. 12. End-to-end distance divided by $N^{2\nu}$ against $1/N$ for three points, $(T,F)=(0.7,1.5)$, (1.71, 1.5), and (1.71, 0.6) with, from top to bottom, $2\nu=1.99$, 2.00, and 2.01 for chain lengths up to $N=1024$. We conclude that all these points belong to a stretched phase of the same type where $\nu=1.0$.

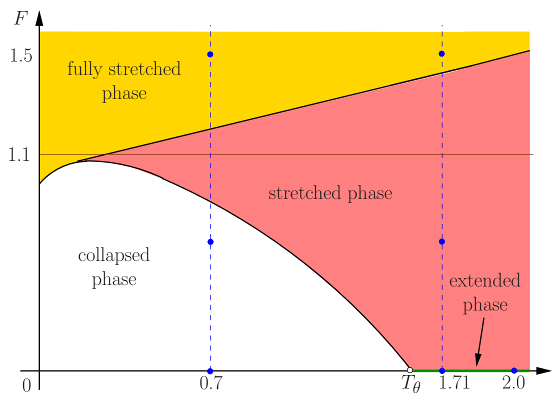

FIG. 13. (Color online) Here is a second possible phase diagram assuming there are two phases for nonzero forces, both with $\nu=1$. Instead of extended and stretched we have fully stretched and stretched. In such a hypothesized fully stretched phase the polymer is effectively in a rodlike conformation where the average height is approximately equal to the length of the polymer.

$$\langle m^k \rangle = \frac{\sum_{m,h} m^k C(N,m,h)\omega^m u^h}{\sum_{m,h} C(N,m,h)\omega^m u^h}.$$

In the panels of Fig. 3 we show the emergence of peaks in the fluctuation curves with increasing N at fixed force $F=0.0$ and $F=0.5$. In the top right panel we show the growth in the peak value as N is increased. Since this is a log-log plot we see that the peak values grow as a power law with increasing N; this divergence is the hallmark of a phase transition. In the lower right panel we have plotted the position of the peak (or transition temperature) as a function of $1/N$. Clearly the transition temperature appears to converge to a finite (nonzero) value but the data exhibit clear curvature which makes an extrapolation to infinite length difficult.

In Fig. 4, we show the force-temperature phase diagram for flexible chains as obtained from the peak positions for the finite chains. However, the true phase diagram should be obtained by extrapolating the data to the $N\to\infty$ limit. In Fig. 4 we have shown the transitions as obtained by fixing the force (black curves). One of the most notable features of the phase diagram is the *re-entrant* behavior but this has been studied and explained in previous papers [6,9]. The other notable feature is that in the fixed force case we see an apparent new transition line from the extended state to the fully stretched state which is solely induced by the applied force (the dashed line in Fig. 4).

B. Further series analysis results

In Fig. 5 we have plotted the fluctuation curves for force $F=1.1$ and $F=1.2$. The curves for $F=1.1$ (including the plot of the peak height) look very similar to the plots (see Fig. 3) for low values of the force. For force $F=1.2$ the peak is not very pronounced and we are hesitant to even call it a peak. Also when we look at the peak height vs N it appears that the curve has two different behaviors for small and large N, respectively. This could be a sign of a crossover behavior.

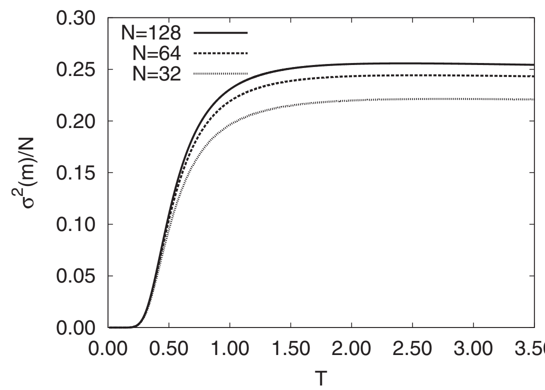

FIG. 14. The fluctuations in the number of contacts m for $F=1.4$ fixed plotted against temperature T. There is no sign of any growing singularities which would indicate a phase transition in the thermodynamic limit.

One can also study the same transition phenomenon by fixing the temperature and varying the force. In the panels of Fig. 6 we show the emergence of peaks in the fluctuation curves with increasing N at fixed temperature $T=1.0$ and $T=0.5$. Again we observe the power-law divergence of the peak value. The only other noteworthy feature is that in the plots of the peak position (critical force value) we observe not only strong curvature but we actually see a turning point in the curves as N is increased. This feature would make it impossible (given the currently available chain lengths) to extrapolate these data. However, we *do not* observe the upper transition line in this study where we have fixed the temperature and varied the force. Indeed this is clear from Fig. 6 where at fixed $T=0.5$ and 1.0 we see only a single peak (giving us points on the red curve in the phase diagram Fig. 4).

In Fig. 6 the value of the force extends up to $F=2.0$ and the upper transition (dashed line in the phase diagram) should appear (if present) as a second peak in the fluctuation curves of Fig. 6. The absence of any evidence of a second peak is what leads us to conclude that we do not see this second transition in the fixed T varying F study and hence confirm that the two ensembles are not equivalent for finite N.

In Fig. 7 we have plotted the average extension per monomer $\langle h \rangle/N$ as a function of temperature. In the case of a fixed force $F=1.2$ (lower right panel) we note that curves for different values of N more or less coincide showing that the average extension scales like N for all temperatures. We contend that this observed behavior shows that the upper boundary is a crossover effect supporting the finding reported recently by Kumar and Mishra [10].

In Fig. 8 we have plotted the average number of contacts per monomer $\langle m \rangle/N$ as a function of temperature. In the case of a fixed force $F=1.2$ (lower right panel) we note that curves for different values of N more of less coincide showing that the average extension scales like N for all temperatures.

IV. SIMULATION RESULTS

Our more detailed analysis of the series indicates that the upper phase boundary is not a genuine phase transition. To

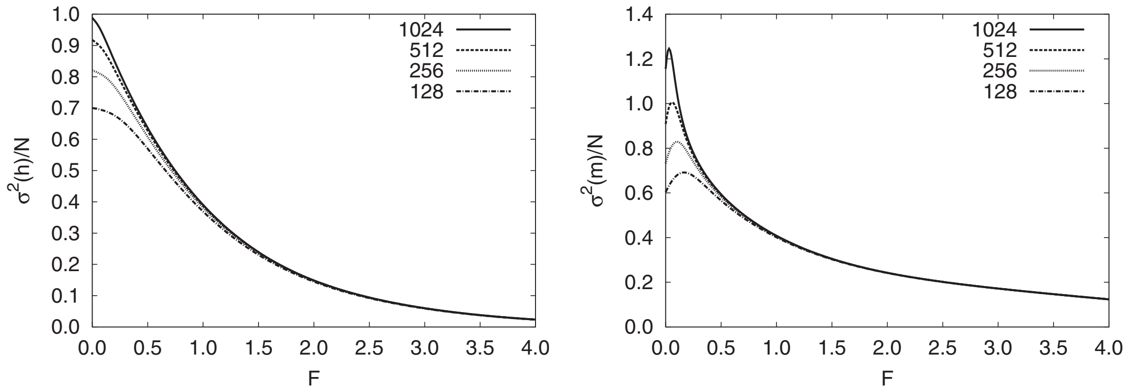

FIG. 15. Plots of the fluctuations against force F for the high temperature $T=1.71$. The chain lengths are, from top to bottom, $N=1024$, 512, 256, and 128.

further investigate the model we have turned to Monte Carlo simulations that allow analysis of longer polymer chains. We have chosen to use the FlatPERM algorithm [7] to simulate the model. One advantage of FlatPERM, as a "flat histogram" technique, is the ability to sample the density of states uniformly with respect to a chosen parametrization, so that the whole parameter range is accessible from one simulation. This allows us to "see" the phase diagram from one set of results. The cost of this, however, is that the chain lengths that can be simulated accurately are still fairly modest. We have performed "whole phase space" simulations up to length $N=128$. On the other hand, by restricting interest to submanifolds of the parameter space longer chains can be analyzed. We have performed simulations along various lines and at points in the phase diagram using walks up to length $N=1024$. The schematic phase diagram conjectured by Kumar *et al.* [6,9] is shown in Fig. 9 along with special lines considered in our simulations.

To demonstrate what is estimated in a FlatPERM simulation consider for a moment a general polymer model with microscopic energies $-\varepsilon_1$, $-\varepsilon_2$, etc., associated with configurational parameters $m_1, m_2, \ldots$, respectively. Let the density of states be $C_{N,m_1,m_2,\ldots}$. Then the partition function is given by

$$Z_N(\beta_1,\beta_2,\ldots)=\sum_{m_1,m_2,\ldots} C_{N,m_1,m_2,\ldots} e^{\beta_1 m_1+\beta_2 m_2+\cdots}, \qquad (2)$$

where $\beta_1=\beta\varepsilon_1$, $\beta_2=\beta\varepsilon_2$, etc., and $\beta=\frac{1}{k_B T}$, with k_B Boltzmann's constant. FlatPERM can estimate $C_{N,m_1,m_2,\ldots}$ or any sum of the $C_{N,m_1,m_2,\ldots}$ over any number of the m_j for a range of lengths $N \leqslant N_{\max}$. If one finds $C_{N,m_1,m_2,\ldots}$ then one can estimate average quantities over this distribution for any values of $\beta_1, \beta_2, \ldots$. In our model we have $m_1=m$ and $m_2=h$ with $\beta_1=1/T$ and $\beta_2=F/T$. We have performed simulations over the complete space of the variables m and h for $N \leqslant N_{\max}=128$. In this way we have estimated the density of states $C_{N,m,h}$. We performed ten different runs with this parametrization for lengths up to $N_{\max}=128$. We have estimated the average number of contacts per monomer $\langle m\rangle/N$ and the average extension per step $\langle h\rangle/N$ and their fluctuations $\sigma^2(m)/N$ and $\sigma^2(h)/N$.

Previous work (see [11] and references therein) has estimated the θ point to be around $T=1/0.663=1.51$. With this in mind we have also performed one-parameter simulations with T fixed at $T=0.7$ and at $T=1.71$. The temperatures chosen were to ensure that one temperature was below and one was above the θ temperature as shown in Fig. 9. We also

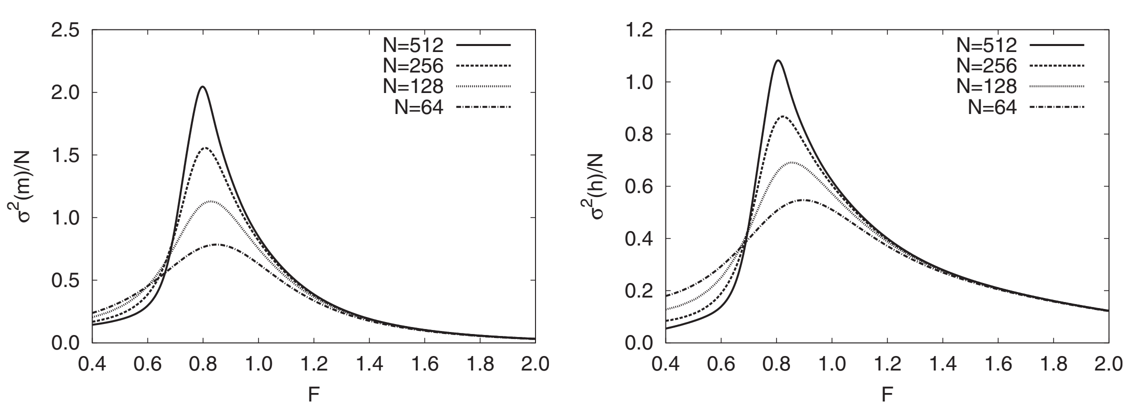

FIG. 16. Plots of the fluctuations against force F for the low temperature $T=0.7$. At the peak the chain lengths are, from top to bottom, $N=512$, 256, 128, and 64.

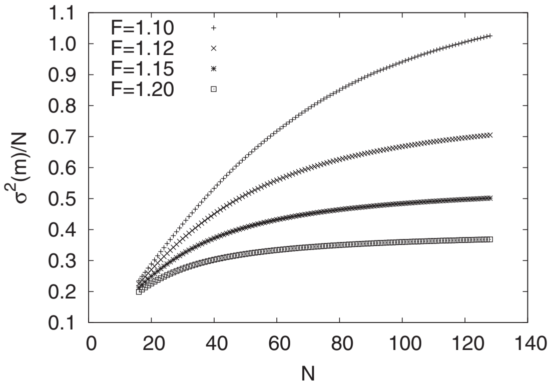

FIG. 17. The maximum of the fluctuations in the number of contacts m for lengths from $N=32$ up to $N=128$ for four different forces (from top to bottom $F=1.10$, 1.12, 1.15, and 1.20) in the region where the original series data analysis detected a phase transition.

studied the temperature $T=2.0$ with $F=0$ as a high temperature point.

In order to delineate the possible phases we considered the points $F=0.0, 0.5, 1.5$ for $T=0.7$ and 1.71 and also the point $T=2.0$, $F=0$. In particular, we analyzed the scaling of the end-to-end distance R_N^2 which gives an estimate of the exponent ν. Let us start with $F=0$. For $T=2.0$ we expect that the polymer is in the extended phase with $2\nu=1.5$ and in Fig. 10 we find precisely that. For $T=0.7$ we expect the polymer to be in the collapsed phase with $2\nu=1.0$ and once again our data in Fig. 11 confirm this expectation. Now let us move to $F=0.5$. For the low temperature $T=0.7$ the series data place this point in the collapsed phase and the data in Fig. 11 bear this out.

However, for the point $F=0.5$ with $T=1.71$ the conjectured phase diagram of Fig. 9 predicts this point to be in the extended phase, which implies $2\nu=1.5$, while we find that $2\nu=2.00(2)$, so this point is in a stretched phase. For $F=1.5$ and for $T=0.7$ and $T=1.1$ the conjectured phase diagram predicts a stretched phase with a value of $2\nu=2$ and we confirm this as seen from Fig. 12.

It is clear that the conjecture of an extended phase with $\nu=3/4$ for $F>0$ is incorrect. However, considering the series results perhaps three phases still exist for $F>0$, with two types of "stretched" phases. It is possible that the phase labeled as "extended" is indeed stretched with $\nu=1$ for $F>0$, while the stretched phase is really a "fully stretched" phase where in addition to $\nu=1$ the average height per step converges to unity:

$$\lim_{N\to\infty} \frac{\langle h \rangle}{N} = 1. \tag{3}$$

That is, the configurations of the polymer are essentially rodlike (with subdominant fluctuations). For such rodlike configurations one would also expect in this phase that

$$\lim_{N\to\infty} \frac{\langle m \rangle}{N} = 0. \tag{4}$$

A revised conjectured phase diagram is drawn in Fig. 13, along with our lines of longer length simulations and the points at which we have focused our analysis. The series data in Figs. 7 and 8 for the low temperature regions when F

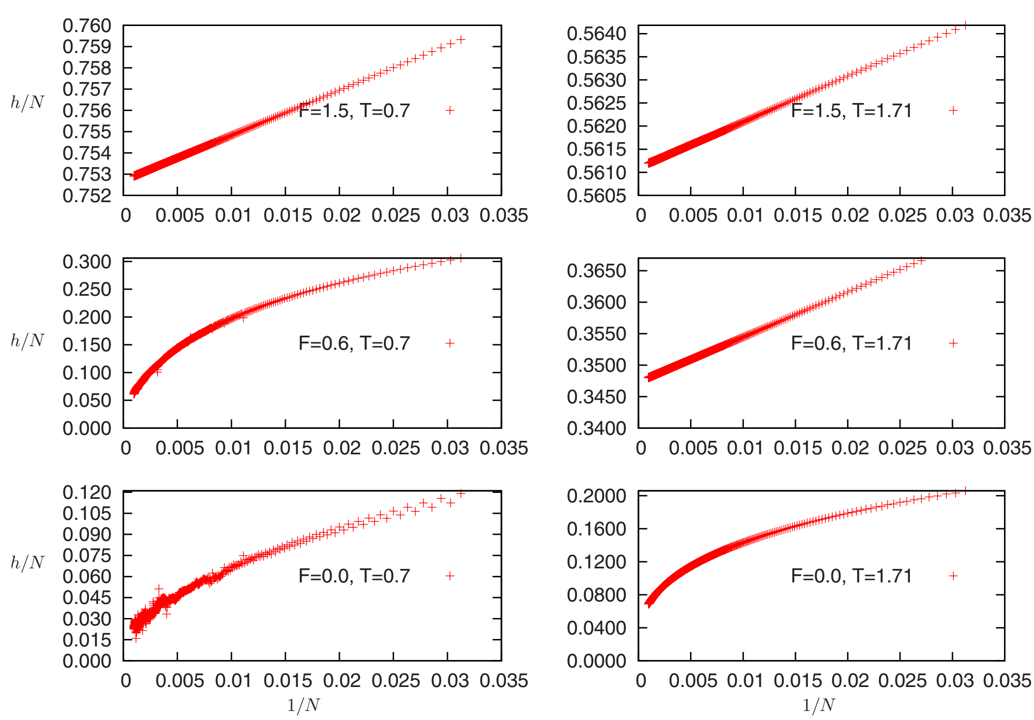

FIG. 18. (Color online) The height of the last monomer at six different points depicted in Fig. 9. We see that in all cases the height of the last monomers does not converge to 1, which we would expect for a fully stretched phase for figures at $F=1.5$, $T=0.7$, and $T=1.71$ and for $F=0.6$, $T=1.71$.

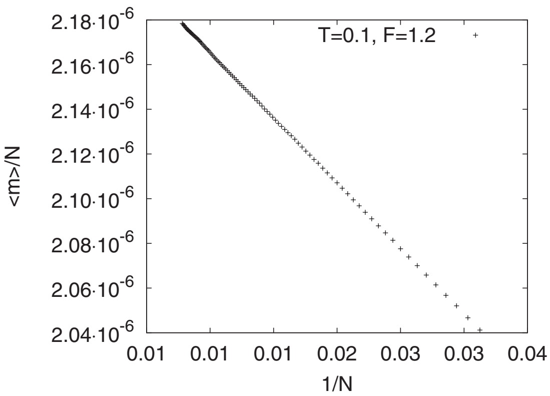

FIG. 19. The behavior of the average number of bulk contacts $\langle m \rangle$ for length $N=32$ up to $N=128$ for the point $T=0.1$, $F=1.2$ as a function of $1/N$. We observe an increase in the average number of contacts $\langle m \rangle$ with N even for very low temperatures.

$=1.2$ display behavior resembling that delineated above for a possible fully stretched phase.

To search for possible phase transitions we have estimated the fluctuations in the number of contacts and fluctuations in the height. For fixed force $F=1.4$ the plot of the fluctuation against temperature in Fig. 14 shows no sign of a growing singularity for lengths up to $N=128$ as seen in the series data for shorter lengths and smaller forces. Now we consider the fixed temperature lines at $T=1.71$ and $T=0.7$. For $T=1.71$ the only sign of a singularity appears near $F=0$ (see Fig. 15), that is, the expected sign of the transition from the extended phase at $F=0$ to the stretched phase at $F>0$. For $T=0.7$ again there is only a sign of a single phase transition in either the fluctuations of m and h (see Fig. 16).

Now the question may be asked about the nature of the peaks in the fluctuations seen at low temperatures at forces just above $F=1$. In Fig. 17 we plot the maximum in the fluctuations at fixed force for various values between $F=1.1$ and $F=1.2$. We note that while these peaks do exist they are not indicative of any divergences. Of course there may still be a weak phase transition. We now turn our attention to any possible difference in the conformations of the polymer in the regions labeled stretched and fully stretched.

To test the hypothesis on which the revised conjectured phase diagram (Fig. 13) rests we consider the scaling of the average height of the last monomer. In Fig. 18 we plot the height of the last monomer at six different points for temperatures $T=0.7$ and $T=1.71$. We observe that at the three points $(T,F)=(0.7,1.5)$, (1.71, 1.5), and (1.71, 0.6) the average height converges to a nonzero, and importantly, nonunity value. Also, at the remaining three points, while there are clear nonlinear corrections to scaling, the average converges to zero. In other words no indication of a fully stretched phase can be found. A further test of the hypotheses leading to the revised conjectured phase diagram (Fig. 13) can be carried out. We assumed that for very low temperatures and large finite forces the average number of contacts per step goes to zero. To test this we have plotted $\langle m \rangle$ against $1/N$ for $F=1.2$ with $T=0.1$ in Fig. 19. While small (of the order of 10^{-6}) this quantity is strictly increasing with length and clearly converges to a (small) nonzero value.

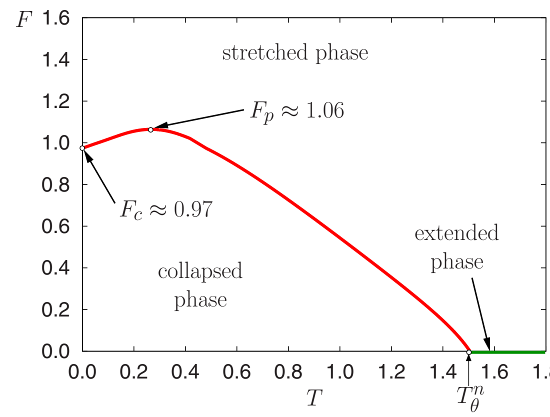

FIG. 20. (Color online) The finite-size phase diagram of a self-interacting self-avoiding walk under tension in two dimensions for length $N=128$. We have estimated the position of the maximum force F_p, and the force F_c for $T=0.0$. The $T_\theta^N \approx 1.47$. One would expect that $F_c=1.0$ in the thermodynamic limit.

We therefore conclude that the upper phase boundary proposed in [6,9] does not exist in the thermodynamic limit and the revised phase diagram in the thermodynamic limit is shown in Fig. 20 which is qualitatively similar to the one proposed by Kumar and Giri [12].

Finally we attempt to measure the exponents associated with the collapse to stretched phase transition. This seems to be a second order phase transition with divergent specific heat. In Fig. 21 we plot the logarithm of the fluctuations in the number of contacts per monomer m/N against $\ln(N)$. The data in this plot are obtained at $T=0.074$ and at the force F for which the fluctuations are maximal. From the data we obtain estimates of the specific heat exponent $\alpha=0.62(10)$ and the crossover exponent $\phi=0.72(6)$. The divergence of the finite size specific heat is expected to be controlled by the exponent $\alpha\phi$ and the two exponents are expected to be related via the scaling relation $2-\alpha=1/\phi$.

V. SUMMARY

In summary we have shown that for a model of self-interacting polymers pulled away from a surface in two di-

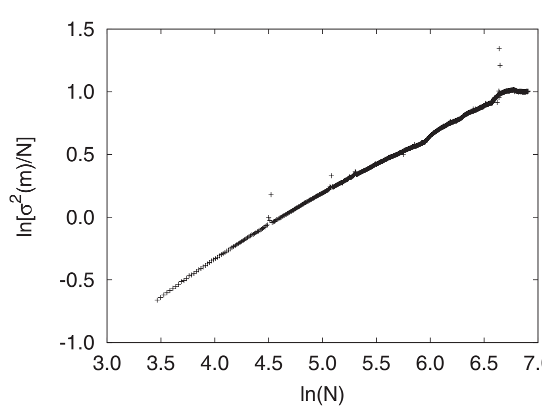

FIG. 21. The logarithm of the fluctuation in the number of contacts per monomer m/N against $\ln(N)$ at $T=0.074$ for the force F at which the fluctuations are maximal. From this curve we can estimate the exponents $\alpha=0.62(10)$ and $\phi=0.72(6)$, which we note are not those of the two-dimensional θ transition.

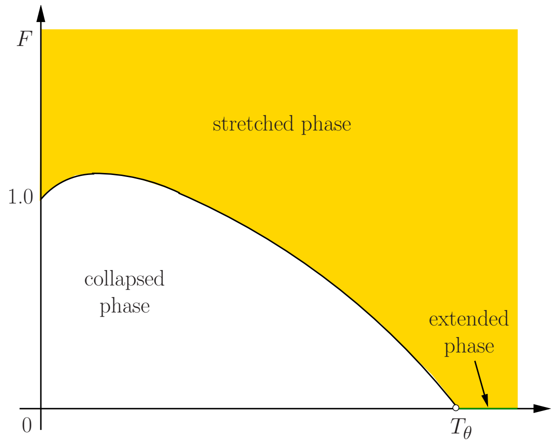

FIG. 22. (Color online) The final conjectured phase diagram for a two-dimensional self-interacting polymer under a stretching force arising from our analysis in this work.

mensions there are only two different phases for nonzero forces in the thermodynamic (infinite length) limit. We therefore conjecture a generic phase diagram as in Fig. 22. One of the phases is the collapsed phase, which is driven by the temperature at small forces. The other is a single stretched phase which occurs whenever the force is applied for temperatures higher than the θ temperature, and for large enough forces for small temperatures. Importantly, the polymer is only in a fully stretched state at zero temperature for forces $F \geqslant F_c = 1$ or when the applied force is infinite. These findings are in agreement with previous numerical studies such as [13] and exact solutions such as those obtained for partially directed walks on the square lattice [14].

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