Novel Phase Diagram for Self-Avoiding Walks (Polymers)

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(Received 10 May 1985)

The analogy between self-avoiding walks and the zero-component magnetic system on a lattice is considered. The magnetic system possesses a natural boundary in the (T-H) plane below which we *cannot* continue it analytically. It is found, however, that we *do not* have to cross this boundary to obtain the semidilute regime. The scaling relation of des Cloizeaux is confirmed. There is also discovered a *new* phase below the boundary which is identified as a *collapsed* phase. This is quite unexpected because no attractive interactions are allowed.

PACS numbers: 05.50.+q, 64.70.−p

Self-avoiding walks (SAW's) have been used extensively as an ideal representation of linear polymer chains. Most of the analytical and mathematical properties of SAW's have been obtained for the case of a single SAW in an infinite-volume limit,[1] where boundary effects are unimportant. If one is interested in long-range properties of polymers, then their chemical details are not very important and the above model seems to be quite appropriate. The scaling behavior of a single SAW is identical with that of a zero-component magnetic system.[2] This analogy was extended by des Cloizeaux[3] to describe a polymer solution (in a good solvent) in the semidilute regime where chains overlap strongly: This regime corresponds to vanishing external magnetic field H just below the critical temperature T_c (see path 1 in Fig. 1). With this observation, he was able to put forward an *important* scaling relation for the osmotic pressure that has been checked experimentally.[4]

The above success of the scaling relation[3] has given rise to an unfounded belief, which has been used extensively to calculate various quantities of interest,[5] that the analogy between SAW's and the $n=0$ magnetic system works everywhere. It should be emphasized that the proof of the above correspondence assumes[6] full $O(n)$ symmetry and, therefore, works only at high temperatures and, at most, up to the critical point T_c. It has been *believed* to work even below T_c, where the $O(n)$ symmetry is explicitly broken. However, it has been shown only recently[6] that such a belief is *unfounded:* For $n<1$, and, in particular, $n=0$, the $O(n)$ model *cannot* be analytically continued below a certain line AC defined by $H\sim\tau^{\Delta}$ (see Fig. 1), where $\tau=(T_c-T)/T_c$. Various pathologies appear just below AC as we analytically continue the theory for $n<1$, which suggests a certain phase transition across AC. Since the path 1, along which the semidilute regime is defined, crosses AC, it throws doubt on the scaling relation proposed by des Cloizeaux, in spite of the fact that it has also been derived by other methods not involving any $n=0$ limit.[7]

The aim here is to consider carefully for the first time the correct analogy between the magnetic system ($n=0$) and the polymer system over the whole range of temperatures. It is shown that the scaling relation of des Cloizeaux is correct, except that it is obtained not along path 1, but along paths lying above ACB, with ACB defined by $|\tau|\sim H^{1/\Delta}$. I introduce a scaling variable X. Below BC, $X\to 0$ as we approach C or the $H=0$ line. This phase is identified with the dilute solutions of polymer chains. The chains are *swollen* and the value of ν is given by $\nu\simeq 3/(d+2)$. Above the curve ACB, X is finite as we approach C. This limit gives us the scaling behavior of overlapping chains in the semidilute regime. Below AC, $X\to\infty$ as we approach C or the $H=0$ line. This phase is identified as a *collapsed* phase or a *compact* phase ($\nu_c=1/d$). This is a *new* phase, never discussed before in the literature, in the context of the magnetic analogy. What is even more *remarkable* is the fact that such a phase can actually occur in the present model which does not allow for any attractive interactions, needed for such a phase. The only interactions allowed in the model are repulsive in nature. The crossover from the dilute regime to the semidilute regime is a smooth one. As a matter of fact, they both represent the *same* phase. However, we must go through a transition as we go from the phase above AC to the phase below, with AC playing the role of a spinodal boundary, below which instabilities appear. It is also found that we *cannot* jus-

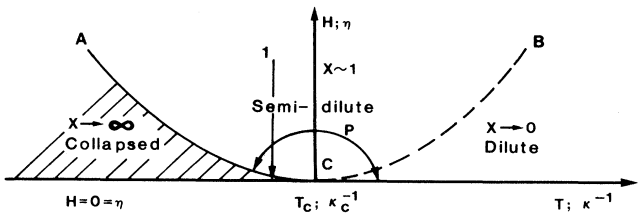

FIG. 1. The analytic continuation of the magnetic system ($n=0$) breaks down below the spinodal boundary AC. The phase below AC represents the collapsed phase of the polymer system. The dilute limit is obtained below BC. The scaling limit of the semidilute regime is obtained by approaching C along a path located in the region above ACB and *not* along path 1.

tify screening which suggests random-walk behavior in the region above ACB as is the current belief. There is only one length scale in the problem in this region and it scales as $|\tau|^{-\nu}$ as we approach C.

Let us briefly summarize the current state of our understanding. We will restrict ourselves to a *lattice*. It is found[8] that the activity κ for a bond and the activity η for an end point of a SAW are related to the ferromagnetic coupling K and the magnetic field H of the corresponding magnetic system ($n=0$). The natural object for study is the following partition function:

$$\hat{Z}=\sum_{p\geq 0}\sum_{l\geq p}\kappa^{l}\eta^{2p}U_{p,l}, \tag{1}$$

where $U_{p,l}$ is the number of ways of putting p different SAW's of total length l on the lattice with N_0 sites. This partition function $\hat{Z}$ has been studied only recently without any $n=0$ limit for all κ and η.[9] The critical point is located at $\kappa=\kappa_c$ ($T=T_c$), $\eta=0$ ($H=0$), and is completely destroyed as soon as $\eta\neq 0$. The phase above T_c is well understood: As $T\rightarrow T_c^{+}$ ($\kappa\rightarrow\kappa_c^{-}$), $H=0$, one is describing the scaling behavior of a single SAW. It is found that the polymerization index $N=\phi_l/\phi_p$ is inversely proportional to $|\tau|$, where ϕ_p is the polymer chain density. The phase below T_c has been investigated only recently[9] and the following picture, valid for $\eta=0$, emerges. The polymer density ϕ_p is zero everywhere. The ground state of the system is basically a single SAW, covering a finite fraction of the lattice sites ($\phi_l\neq 0$) below T_c. As $T\rightarrow T_c$, ϕ_l vanishes like $\tau^{1-\alpha}$ and remains zero above T_c.

When we study the nature of the analytic continuation of the $O(n)$ model[6] for $n=0$ below T_c, the following picture emerges. Let $x=\tau/M^{1/\beta}$ and $y=\tau/H^{1/\Delta}$. It is found that along AC, y is a constant, which is taken to be unity: $y\sim 1$. Along AC, we also find that $x=1$ which indicates that the system achieves its "spontaneous" magnetization $M=M_0$ even if $H\neq 0$. This two-valuedness of the M-H relation is not surprising for the $O(n)$ model for $n<1$.[10] Below AC, the analytic continuation develops various pathologies, which suggests that AC is a *natural boundary* for the analytic continuation of the $O(n)$ model from the high-temperature side. Below AC, we *cannot* learn anything about the polymer problem from the magnetic system. In other words, AC forms a spinodal boundary below which the continuation becomes unphysical. Therefore, it is important to consider the polymer problem without use of the magnetic analogy below AC. However, above AC, we can *safely exploit* the above analogy to its fullest extent. This is what I intend to do here.

Before proceeding further, let me give another argument based on finite-size scaling[11] to support my picture of the ground state. According to finite-size scaling, we expect the correlation length $\xi(N_0)$ to be determined by the linear size $N_0^{1/d}$ of the system, where d is the space dimensionality. In the context of the SAW, the correlation length is the linear size R_0 of the SAW. Therefore, $\xi(N_0)=R_0\sim N^{\nu}\sim N_0^{1/d}\sim|\tau|^{-\nu}$, where N is the length (polymerization index) of the SAW. This gives us the expected relation $N\sim|\tau|^{-1}$. Since the volume occupied by the SAW is $V_0\sim R_0^{d}\sim N_0$, we find that we can have only a *finite* number of P of SAW's as $N_0\rightarrow\infty$. (The number P *cannot* grow as N_0^{σ}, with $0<\sigma<1$.) As we approach κ_c along $\eta=0$, we expect to have only a finite number P of SAW's. Therefore, without loss of generality, we can assume that we have effectively only *one* chain in the system below κ_c. As we begin to increase κ above κ_c, this only increases the length of this single SAW, and gives rise to the ground state described above.

For $\kappa>\kappa_c$, our SAW must cover a *finite* fraction of the lattice sites. This is possible only if the SAW is spread out throughout the lattice: The linear size of the SAW is identical with the linear size $N_0^{1/d}$ of the lattice. Such a walk is known as a *collapsed* or a *compact* SAW. If we define ν_c by $R_0\sim N^{\nu_c}$, we find that, since $N=\phi_l N_0$, $\nu_c=1/d$; i.e., the fractal dimension of the collapsed SAW is equal to the space dimensionality d. It is evident that a collapsed SAW is quite distinct from a swollen SAW observed below κ_c. Moreover, it is also clear that the boundary effects are very important in the collapsed phase, whereas they are basically unimportant in the swollen phase. In a sense, one can envision the *phase transition* at κ_c as a transition from a phase where the boundary effects are unimportant to a phase where they become crucial in determining the ground state. It should be remarked that the boundary contributions are *important* in breaking *supersymmetry*,[12] a symmetry that is expected to be broken at κ_c.[13]

Let us now consider the case of nonzero η. We introduce $V_0=N^{\nu d}$ as the volume occupied by a single SAW of length N, and $V=1/\phi_p$ as the amount of volume available for each chain. (As $\eta\rightarrow 0$, $\phi_p\rightarrow 0$ and V becomes unbounded. Since $N=\phi_l/\phi_p$, V_0 increases in this limit, but the relative magnitudes of V_0 and V depend on whether ϕ_l is zero or not as $\eta\rightarrow 0$.) Let us assume that $V_0\ll V$. In this case, chains are far apart and there is basically no overlap between chains. Evidently, this situation corresponds to the dilute limit of the polymer solution. The chains are swollen as a result of excluded-volume effects and $\nu\simeq 3/(d+2)$. Let us introduce a scaling variable X:

$$X=\phi_p^{*}/\phi_p=(V_0/V)^{1/(d\nu-1)},\quad \phi_p^{*}=\phi_l^{d\nu/(d\nu-1)}, \tag{2}$$

where ϕ_p^{*} is defined as the value of ϕ_p at which $V_0\sim V$. As we change η so that $V_0\sim V$, the chains

begin to overlap considerably. Below AC, as $\eta \to 0$, $\phi_p \to 0$, but ϕ_l is finite and nonzero. Therefore $X \to \infty$. I now show that $X \to 0$ below BC, and takes on some finite and nonzero values in the region above ACB defined by $|\tau| \sim H^{1/\Delta}$, as we approach the critical point C or the $H=0$ line.

As remarked above, we can exploit the magnetic analogy above and on AC. From this analogy, we can write down the scaling form for ϕ_l and ϕ_p as follows: $\phi_l(y) = |\tau|^{d\nu-1} f_l(y)$ and $\phi_p(y) = |\tau|^{d\nu} f_p(y)$. Near $H=0$[8], $\phi_l = \kappa\epsilon$ and $\phi_p = MH/2$, where ϵ is the energy per bond and M is the magnetization per spin of the magnetic system. For $T > T_c$, $M \sim H$ as $H \to 0$. Therefore, $\phi_p \sim H^2$, which is possible if $f_p(y) \sim y^{-2\Delta}$ as $y \to -\infty$. Similarly, $f_l(y) \sim y^{-2\Delta}$ in this limit since $N \sim |\tau|^{-1}$. Therefore, as $H \to 0$ above T_c, we find that $X \sim [f_l(y)]^{1/(d\nu-1)} \to 0$. From (2), we find that $X \to 0$ implies $V_0/V \to 0$, which characterizes polymer solutions in the dilute limit, as we have expected. The scaling form of the osmotic pressure can be written as $\Pi = \phi_p f_\Pi(X)$. As $X \to 0$, $f_\Pi(X) \to 1$ and $\Pi \sim \phi_p = \phi_l/N$. The correlation length ξ behaves as $N^{-\nu}$, as expected.[14]

Let us now consider the region above ACB. For the sake of clarity, let us consider the behavior of $f_l(y)$ and $f_p(y)$ at $T = T_c$ ($\tau = 0$). Here we expect that $\phi_p(y) \sim H^{1+1/\delta}$, suggesting that $f_p(y) \sim |y|^{-d\nu}$ as $|y| \to 0$. Similarly, we expect that $f_l(y) \sim |y|^{1-d\nu}$ as $|y| \to 0$. Therefore, $\phi_l \sim H^{(d\nu-1)/\Delta}$ and $\phi_p \sim H^{d\nu/\Delta}$. The average length N behaves as $H^{-1/\Delta}$ and tends to infinity as $H \to 0$. Moreover, $X = \phi_l^{d\nu/(d\nu-1)}/\phi_p$ also tends to a finite and nonzero value. As a matter of fact, it is not hard to see that y approaches a finite value as we approach C along any path lying in the region above ACB, and that X also approaches a finite and nonzero value in this region. For the sake of convenience, we will express this by writing $X \sim 1$, which is only expected to mean that X is *finite*. Below AC, along any path approaching C or the $H=0$ line, both y and X tend to infinity. However, because of the breakdown of the analytic continuation, we cannot use the magnetic analogy below AC.

Let us consider the osmotic pressure for $X \sim 1$. We expect $f_\Pi(X)$ to be a finite constant[15] and since $\phi_p \sim \phi_p^*$, we have $\Pi \sim \phi_p^* \sim \phi_l^{d\nu/(d\nu-1)}$, which is the famous scaling form of the osmotic pressure proposed by des Cloizeaux in the semidilute regime. Therefore, we can safely conclude that the scaling limit of the semidilute regime is obtained by approaching C in the region above ACB. The correlation length in the semidilute regime is expected to behave as $\xi \sim |\tau|^{-\nu} \sim \phi_l^{-\nu/(d\nu-1)}$ obtained for any finite nonzero y. This again agrees with the scaling behavior of ξ in this regime. The crossover from the swollen phase below BC to the semidilute regime is expected to be completely smooth across BC. However, it should be emphasized that there is really not any *fundamental difference* between the swollen and the semidilute regime, as they both belong to the same paramagnetic phase of the magnetic system. We know that the scaling form for various physical quantities in the paramagnetic phase depends on whether y is finite or infinite. For example, $\chi_L \sim |\tau|^{-\gamma}$ or $H^{1/\delta-1}$, dependent upon the values of y. However, they both describe the same paramagnetic phase. Similarly, in our picture, the dilute and the semidilute regimes are not fundamentally different. In contrast, according to des Cloizeaux the scaling limit of the semidilute regime is identified with the ferromagnetic phase of the magnetic system and, therefore, is supposed to be fundamentally different from the swollen phase.[3,14] In particular, we still have only one length scale, i.e., ξ, in our problem and it must behave as $\xi \sim |\tau|^{-\nu}$. We therefore cannot justify screening, which has been argued to imply[14] that $R^2 \sim N$ in the semidilute limit. In our picture, the scaling limit appears only in the limit $\phi_p \to 0$, as we approach C. Therefore, even the radius of gyration R_0 scales not as $N^{1/2}$ but as N^ν in the scaling limit: We can always write $R_0^2 \sim N\phi_l^{-(2\nu-1)/(d\nu-1)}$, but as we approach C along any path of constant X, it is easily seen that $R_0^2 \sim N^{2\nu}$. This is in conformity with the result derived by Oono without use of the magnetic analogy.[15]

Let us now ask what happens as we cross AC. The ground state along $H=0$ is a single SAW. As ϕ_p reduces to zero, we reduce the number of chains [see (1)] while increasing the average length of each chain. The only *mechanism* that can accomplish this is for two end points of two different chains to join together to produce a longer chain. The probability of finding two end points close together is proportional to ϕ_p^2 and vanishes as $\phi_p \to 0$. If the chains continue to penetrate each other as we reduce ϕ_p, then the number of overlapping chains n_{overlap} must grow as $n_{\text{overlap}} \sim V_0/V \sim X^{\nu d-1}$ [see (2)], so as to maintain a finite bond density ϕ_l. However, there is *no* way that these infinite number of chains, each infinitely long, can join together to yield a single SAW in the ground state since the probability of two end points close together vanishes. Therefore, the chains cannot to penetrate. Since the collapsed phase is physically distinct from the swollen phase, there must be a phase transition across AC. The transition is probably a very weak transition with an essential singularity along AC. Since AC forms a spinodal boundary[6] below which we get a complex solution of the magnetic equation of state for $n=0$, the transition might also be a first-order one with, presumably, a discontinuity in entropy. In view of these heuristic arguments, we can now put forward the following picture. The system undergoes a phase transition from a semidilute regime to a collapsed phase. The nature of the transition is not clear

at present. In the collapsed phase, the chains have their fractal dimension equal to d ($\nu_c = 1/d$), and V_0 is given by $V_0 \sim 1/\phi_p$. We do not require any overlap to yield a finite ϕ_l. As ϕ_p is lowered, each chain begins to grow in length by joining itself with neighboring chains until eventually, at $\phi_p = 0$, we have the ground state of a single chain. The collapsed phase is a critical object having self-similarity at various length scales. This is represented schematically in Fig. 2 by the dark chain configuration ($\phi_p = 0$). The configurations of broken light chains depict the situation of a nonzero ϕ_p below AC. A comparison of the two configurations suggests a possible mechanism that might be going on as ϕ_p is reduced. We should remark that *Hamilton walks*[9] ($\eta \to 0$, $\kappa \to \infty$) must be compact walks and, therefore, also possess self-similarity. It is not hard to understand why we have a collapsed phase when all we have are the repulsive excluded-volume interactions. Let us assume reflecting boundary conditions. The boundaries begin to create a pressure on the chain as it begins to fill the lattice below T_c. It is this pressure that mimics an effective attractive potential producing a collapsed phase. Since such effects are not present above T_c, we always have a swollen phase there. There appears to be a certain amount of similarity between this situation and the one that occurs in hard disks.[16] However, it should be realized that our collapsed phase is intimately related to the connectivity, i.e., topological constraints for chains. This phase is completely disordered and is different from the ordered phase in hard disks.

Let us briefly summarize our results. We have argued that there are three different regions: (i) swollen phase corresponding to $X = 0$, (ii) semidilute regime corresponding to $X \simeq 1$, and (iii) collapsed phase corresponding to $X \to \infty$. This is shown schematically in Fig. 1. We go smoothly from the swollen phase to the semidilute regime. We also argue that this regime is not physically a distinct phase, different from the dilute regime: Both regimes are physically identical. We expect a transition across AC into the collapsed phase. We have been able to recover the scaling relations proposed by des Cloizeaux for II. However, we cannot in our picture justify the appearance of screening in the semidilute regime: In the scaling limit, $R_0 \simeq N^{\nu}$ as we approach C, and not as $R_0 \simeq \sqrt{N}$ as is usually assumed.[14]

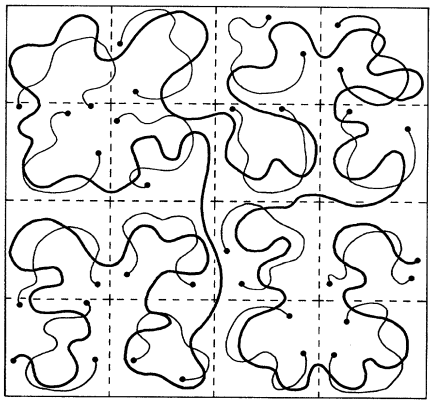

FIG. 2. The thick curve represents the ground-state configuration of a collapsed chain ($\phi_p = 0$). The broken thin curves represent the configuration of many collapsed chains below AC ($\phi_p \neq 0$).

An alert reader might have noticed a certain similarity between our AC and the Thouless-Anderson-Palmer boundary in spin-glasses.[17] I hope that this is not fortuitous and that the present analysis might provide some insight into the spin-glass problems.

I would like to express my thanks to the theory group and to J. des Cloizeaux at Saclay for their kind hospitality where this work was initiated. The financial support from the Research Corporation and a Faculty Research Grant at the University of Akron is gratefully acknowledged.

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