Collapse transition of self-avoiding walks on a square lattice in the bulk and near a linear wall: The universality classes of the θ and θ' points

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Using the scanning method we study by extensive simulations the θ transition of self-avoiding walks with nearest-neighbor attractions in the bulk and near a linear wall on a square lattice. Consistent results for the two models are obtained for the radius of gyration, but not for the end-to-end distance. Our results for the exponents ν and γ agree with those derived by Duplantier and Saleur [Phys. Rev. Lett. **59**, 539 (1987)] for the θ' model. However, our results for the crossover exponent ϕ (which constitute upper bounds for the correct value) are significantly larger than the value of $\phi(\theta')$. At the ordinary point our result for γ_1 is larger (even though not much) than the value suggested by Vanderzande, Stella, and Seno [Phys. Rev. Lett. **67**, 2757 (1991)] for the θ' model.

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The collapse of polymers at the Flory θ point [1,2] and their adsorption on a surface are fundamental phenomena in polymer physics with a wide range of industrial applications [3] and biological significance (e.g., protein folding [4]; protein membrane interactions, etc. [5]). From the theoretical point of view, a great deal of progress has been achieved in recent years in two dimensions (2D), mainly due to the advent of Coulomb-gas techniques [6] and conformal invariance [7]. The θ-point behavior has been usually modeled by self-avoiding walks (SAW's) on a lattice, where an attractive interaction energy is defined between a pair of nonbonded nearest-neighbor (NN) monomers [8,9]. Duplantier and Saleur (DS) [10] have proposed the exact tricritical exponents of a collapsing polymer in 2D, for a special model of SAW's on a hexagonal lattice with randomly forbidden hexagons. However, this model consists, in addition to the NN attractions, also of a special subset of the next-nearest-neighbor attractions and therefore, instead of describing the usual θ point, it might describe a multicritical θ' point [11–13].

The recent numerical results for the θ point and for tricritical trails mostly agree with the DS value $\nu=\frac{4}{7}$ while the estimates of γ are smaller than $\frac{8}{7}$, the DS value [13–21]. On the other hand, the central values for ϕ are larger than the DS value $\frac{3}{7}\sim 0.428$; for the most reliable Monte Carlo studies they range from 0.48 to 0.60 for SAW's [13,16–18] and 0.68–0.80 for trails [19–21], which suggests that the θ and θ' points and trails may belong to different universality classes.

Of interest also are the exponents of a collapsing chain that is anchored to an impenetrable linear surface (the ordinary point). For the θ' model, DS have proposed $\gamma_1=\gamma\sim 1.143$ and $\gamma_{11}=\nu\sim 0.571$ while the numerical results, $\gamma_1\sim 0.6$ and $\gamma_1\sim -0.5$ found for both SAW's [16,18,22,23] and trails [21] are dramatically smaller. This discrepancy has been explained recently by Vanderzande, Stella, and Seno (VSS) [24] who have shown, that within the framework of the θ' model, the DS values for γ_1 and γ_{11} are not related to the ordinary point but to the special one. They have also suggested that $\gamma_1(\theta')=\frac{4}{7}\sim 0.571$ at the ordinary point which was corroborated by exact enumeration study and is compatible with the above-mentioned numerical data. Thus (ignoring the results for ϕ), they have conjectured that the θ and θ' points are in the same universality class. We have recently applied the scanning simulation method to relatively long SAW's and trails at their special point and have found results for γ_1 and ϕ_s that differ significantly from the VSS values for the θ' model [25], however, an exact enumeration study of SAW's supports all the VSS values [23]. Thus, the relation between the θ and the θ' models is as yet not clear and extensive numerical work is needed.

The main aim of the present work is to investigate the ordinary θ point, in particular γ_1. Thus, we simulate with the scanning method significantly longer chains and larger samples than previously studied. The model is a single SAW of N steps (bonds) (i.e., $N+1$ monomers) that starts from the origin located on an impenetrable linear boundary on the square lattice; an attractive energy ε ($\varepsilon<0$) is defined between two NN nonbonded monomers. This model and its bulk version (in which the surface is removed) are expected to share the same tricritical temperature T_t, growth parameter μ [see Eq. (3)], and the exponents ν and ϕ. Therefore, we also carry out a simulation of the latter model which is much more extensive than that previously performed by Meirovitch and Lim (MI) [17].

With the scanning method [26] a SAW is generated

step by step by scanning all the possible chain continuations in b future steps; b is called the scanning parameter. Since not the whole future is scanned, the chain can be trapped in a cul de sac; in this case it is discarded and a new chain is started. Therefore, from n_0 attempted chains only n will survive. Also, SAW i is not constructed according to its Boltzmann probability, P_i^B, but with a biased probability $P_i(b)$, which approaches P_i^B as b is increased. The bias can be removed by importance sampling [27] or with a procedure suggested by Schmidt [28]. With the Schmidt procedure, an *unbiased* sample of n_{accept} accepted SAW's is extracted from the biased one, where n_{accept} provides a measure for the efficiency of the simulation, the larger is b the larger is n_{accept}. A feature that facilitates the determination of T_t is that results at many temperatures can be obtained from a single sample generated at a given temperature. In order to obtain accurate results for the longer chains (up to $N=250$) we used scanning parameter $b=5$ ($b=3$ was employed by ML). The importance sampling results for the various properties were calculated and accumulated for the partial chains of lengths $N=10,20,\ldots,250$. The two samples were generated at the reciprocal temperature $K=-\varepsilon/k_BT=0.654$ (k_B is the Boltzmann constant). For SAW's in the bulk results were calculated at $K=0.634,0.636,\ldots,0.672$, where $n_0=130\times10^6$ (i.e., 4.5 times larger than the ML sample); however, n_{accept} becomes significantly lower as N increases, 5.12×10^6 ($n_{\text{accept}}/n_0=0.039$) for $N=200$ at $K=0.658$. For SAW's near a surface, results were calculated at $K=0.628,0.630,\ldots,0.676$, $n_0=185\times10^6$ and $n_{\text{accept}}(N=200)=3.12\times10^6$ ($n_{\text{accept}}/n_0=0.017$).

In order to determine the tricritical temperature, we rely on the crossover scaling expression of the root-mean-square radius of gyration $\langle G^2\rangle^{1/2}$, denoted G (and the end to-end distance, R) [29],

$$G\propto N^{\nu}f_{\pm}(N^{\phi}\tau)\ , \tag{1}$$

where τ is $|(T-T_t)/T_t|$. For small τ, $f_{\pm}(x)$ behaves as follows:

$$f_+(x)=\begin{cases}x^{(3/4-\nu)/\phi} & x\to\infty\ ,\\ \text{const} & x\to0\ ,\end{cases}\qquad T>T_t\ ,$$
$$f_-(x)=\begin{cases}x^{(1/2-\nu)/\phi} & x\to\infty\ ,\\ \text{const} & x\to0\ ,\end{cases}\qquad T<T_t\ . \tag{2}$$

Therefore, for $T>T_t$, one would expect the slope of $\log G$ vs $\log N$ to be smaller than $\frac{3}{4}$ for small N and to approach this value asymptotically. For $T<T_t$, this slope decreases asymptotically to $D^{-1}=\frac{1}{2}$. At T_t a constant slope is expected which means $G(2N)/G(N)=2^{\nu}$ (if corrections to scaling are ignored). These ratios for $N=10,20,\ldots,$ (for simplicity we shall omit the values of $2N$) can be plotted as a function of K where the intersection point of the lines defines both K_t and ν [30]. In Fig. 1 such a plot is presented for SAW's in the bulk, where the results for $N=10$ and 20 and 30 and for $N>80$ were omitted because of strong corrections to scaling and large statistical errors, respectively. A similar plot for the ordinary point is shown in Fig. 2 (for $N=40$–90). The intersection points define the following values:

$$K_t(\text{bulk})=0.658\pm0.004\ ,$$
$$\nu(\text{bulk})=0.579\pm0.005\ ,$$
$$K_t(\text{ord})=0.656\pm0.004\ ,$$
$$\nu(\text{ord})=0.583\pm0.005\ ,$$

where the errors here and in the rest of the paper are 95% confidence limits [31]. The central value of ν(bulk) is an average over the different results for ν obtained at $K_t=0.658$ (the lines do not meet exactly at a point). We also calculated the maximal and minimal values of ν at $K=0.654$ and 0.662, respectively, where the error is

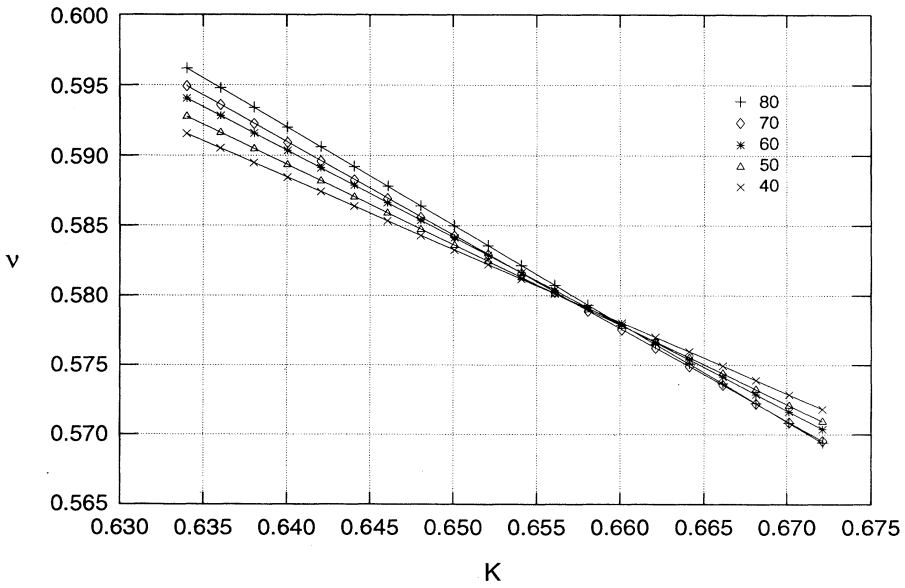

FIG. 1. Plots of $\log[G(2N)/G(N)]/\log 2$ vs the reciprocal temperature K for SAW's of $N=40,50,\ldots,80$ in the bulk. The intersection point defines both K_t and ν.

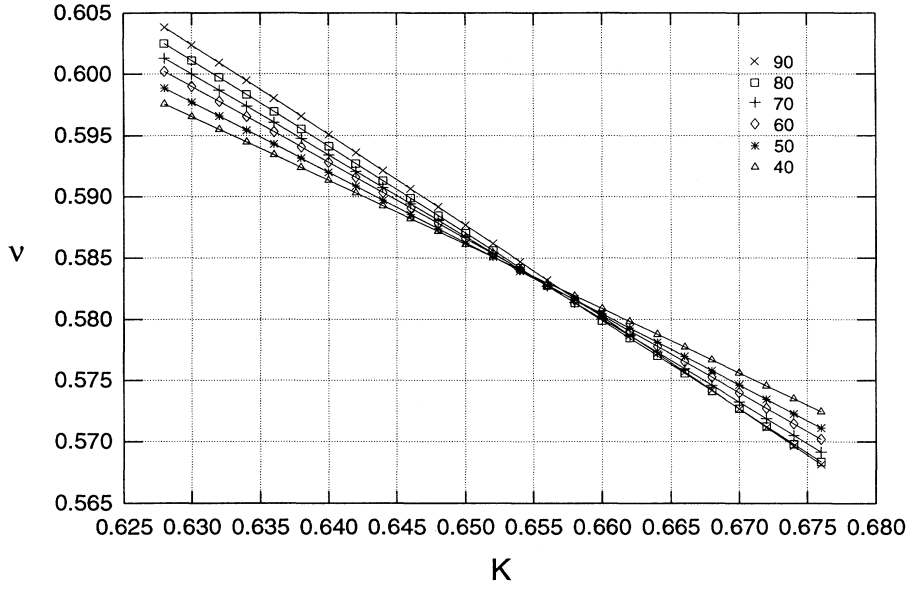

FIG. 2. Plots similar to those of Fig. 1 for SAW's terminally attached to a linear "wall" (the ordinary point).

defined as the maximal deviation of these values from ν (bulk). The same applies to the ordinary point. The present results for K_t(bulk) and ν are equal to the ML values (based on $b=3$), which is an important test for their reliability [26]; our value of ν is slightly larger (within the error bars) than the DS value 0.571; however, in view of the relatively low accuracy obtained for ν by other numerical techniques [13,15,24] we consider our result as a support of the conjecture, $\nu(\theta)=\nu(\theta')$. The result of K_t(ord) is only slightly smaller than that of K_t(bulk), where such a deviation is expected to occur for short chains due to the surface [21,22]; correspondingly, the value of ν(ord) is slightly higher than ν(bulk). Notice that the data for R (unlike those for G) have led to inconsistent results, K_t(bulk)$\sim$0.670 and K_t(ord)$\sim$0.636, which demonstrates strong finite-size effects. This perhaps explains the high value of K_t obtained from a transfer matrix study based on R [15]. We accept the value of K_t(bulk)=0.658 (based on G) as the best estimate of K_t for both models; thus, all the exponents will be estimated at this temperature.

Three partition functions Z_α are defined: For SAW's in the bulk ($\alpha=0$, which will be omitted), for SAW's that start from the surface ($\alpha=1$), and for those that also end on the surface ($\alpha=11$). At K_t the following behavior is expected:

$$Z_\alpha \simeq B_\alpha \mu^N N^{\gamma_\alpha - 1} , \tag{3}$$

where the B_α are prefactors, μ is the growth parameter, and the γ_α are critical exponents. In order to calculate μ and γ_α we use the same method as for K_t and ν. Thus, at K_t Eq. (3) leads to $2Z_\alpha(2N)/Z_\alpha(N)\mu^N=2^{\gamma_\alpha}$. Therefore, one can calculate the results for $2Z_\alpha(2N)/Z_\alpha(N)\mu^N$ for different values of μ, where the intersection point of these lines should define both γ_α and the correct value of μ. In Figs. 3 and 4 such plots are presented at $K_t=0.658$ for SAW's in the bulk ($N=40-120$) and at the ordinary point ($N=30-110$), respectively; the fact that sharp intersection points are obtained for wide ranges of N demonstrates that corrections to scaling are negligible. We obtain

$$\gamma=1.125\pm0.019, \quad \mu(\text{bulk})=3.212\pm0.007 ,$$

$$\gamma_1=0.598\pm0.015, \quad \mu(\text{ord})=3.212\pm0.007 .$$

The central values of γ and μ(bulk) are the average values of results obtained at $K_t=0.658$ from different graphs of $N=40-70$, $40-80,\ldots,40-120$, $50-80$, $50-90,\ldots,50-120$, $60-90$, $60-100,\ldots,60-120$ and $70-100$, $70-120$. Similar calculations were carried out at $K=0.654$ and 0.662 and the maximal deviation from the central value defines the error. The same analysis has also been applied to the ordinary point. The above results for μ are equal and they are close to the ML value 3.213(13), but have smaller error bars. Our result for γ is also defined with the smallest error bars obtained thus far [13–21] which cover (unlike the ML result) the DS value, $\gamma(\theta')\sim1.143$. On the other hand, the VSS value $\gamma_1(\theta')\sim0.571$ is smaller than our estimate for γ_1 (the difference, however, is not large) and than $\gamma_1=0.625\pm0.025$ obtained for self-attracting trails [21]. Previous numerical results, $\gamma_1=0.57(9)$, 0.50(5), 0.571(60), and 0.57(2) (in Refs. [16], [18], [22], and [23], respectively) are significantly less accurate than the present value. The same analysis for γ_{11} has led to a well-defined intersection point, where $\mu\sim3.209$ ($\gamma_{11}\sim-0.38$) is lower than the above bulk value. We therefore calculated γ_{11} by fixing μ at its bulk value 3.212 and obtained

$$\gamma_{11}=-0.46\pm0.06 .$$

Our results satisfy the Barber scaling relation [33]. They

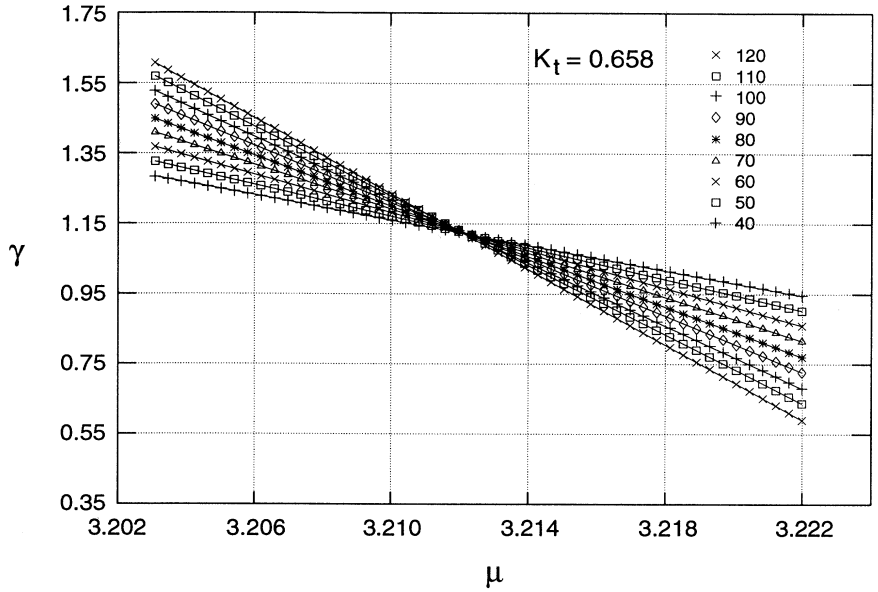

FIG. 3. Plots of $\log[2(Z(2N)/Z(N)\mu^N]/\log 2$ vs the growth parameter μ for SAW's of $N=40,50,\ldots,120$ in the bulk, at the tricritical temperature ($K_t=0.658$). The intersection point defines both the correct μ and γ.

lead to $2\gamma_1-\gamma_{11}=1.66\pm0.075$ which is equal, within the error bars, to $\gamma+\nu=1.714$ (employing the DS values). The crossover exponent ϕ can be obtained from the slope of $\log G'$ vs $\log N$ at K_t where

$$G'=\frac{\partial\langle G^2\rangle}{\partial K}/\langle G^2\rangle$$
$$=(\langle G^2E\rangle-\langle G^2\rangle\langle E\rangle)/\langle G^2\rangle\sim N^{\phi}\ , \qquad (4)$$

and E is the energy [32]. As in previous studies [17,21], these graphs have been found to be strongly concave for small N becoming more straight (but not completely) for large N. Thus, our slopes are based on the results of G' for the longer chains, $N=180-240$ at $K_t=0.658$. We obtain the actually equal estimates

$$\phi(\text{bulk})=0.530\pm0.004,\quad \phi(\text{ord})=0.533\pm0.003\ ,$$

with statistical errors that take into account the uncertainty in K_t. These values should be considered as upper bounds of ϕ due to concavity and as expected they are significantly smaller than the ML result, $\phi\sim0.59$, which is based on shorter chains, $N=70-160$; however, they are still much larger than the DS value, $\phi(\theta')\sim=0.428$. We have also fitted the data to the function, $G'\sim N^{\phi}(1+A/N^x)$, where A is a constant and x is a correction to scaling exponent. Using $x=0.4,0.5,\ldots,1.2$ always resulted in $\phi\sim0.51$ for both models. One would expect a further reduction in the value of ϕ for longer chains and it would be of great in-

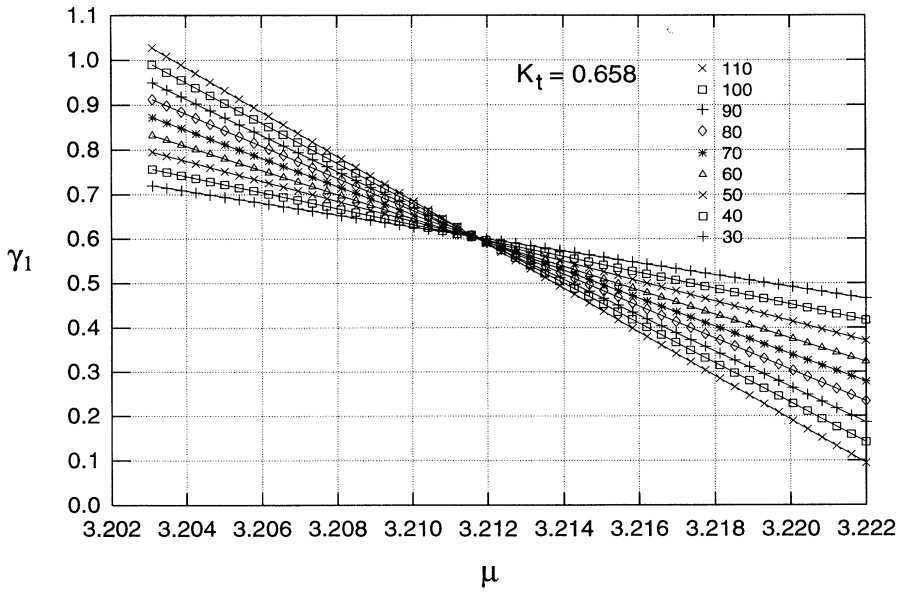

FIG. 4. Plots similar to those of Fig. 3 for SAW's at the tricritical temperature ($K_t=0.658$) at the ordinary point.

terest to test in future studies whether the DS value is reached.

In summary, the results of G (unlike those for R) are consistent for the two models of θ SAW's, i.e., they lead to $K_t \sim 0.658$ and to the same values of ν and ϕ. Our results for ν are close to the DS value of $\nu(\theta')$ and that for γ is equal to the DS value of $\gamma(\theta')$, within the smallest statistical error obtained thus far. On the other hand, the present result for γ_1 is larger (even though not much) than the VSS value of $\gamma_1(\theta')$. Our results for ϕ are significantly larger than the DS value but are smaller than previous results obtained by ML; however, the data show strong corrections to scaling effects and longer chains are expected to lead to a further reduction in the value of ϕ.

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