Surface Critical Exponents of Self-Avoiding Walks and Trails on a Square Lattice: The Universality Classes of the θ and θ' Points

Iksoo Chang[1],[2] and Hagai Meirovitch[1]

[1]*Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-4052*

[2]*Research Center for Dielectric and Advanced Matter Physics and Department of Physics, College of Natural Science, Pusan National University, Pusan, Korea*

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Using the scanning method we carry out for the first time extensive simulations of trails and self-avoiding walks (SAWs) terminally attached to an adsorbing linear boundary on a square lattice. A bulk attraction energy is also defined for a self-intersection of a trail and a pair of nonbonded nearest-neighbor monomers of a SAW. The chains are simulated at the special point. Our critical exponents differ significantly from the exact values of Vanderzande, Stella, and Seno [Phys. Rev. Lett. **67**, 2757 (1991)] for the θ' model. Thus, their conjecture, that the θ and θ' points belong to the same universality class, is not supported.

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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 importance (e.g., protein folding [4]). 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 [5] and conformal invariance [6]. The θ-point behavior has been usually modeled by self-avoiding walks (SAWs) on a lattice, where an attractive interaction energy is defined between a pair of nonbonded nearest-neighbor (nn) monomers [7,8]. In a seminal work, Duplantier and Saleur (DS) [9] proposed the exact tricritical exponents of a collapsing polymer in 2D. In the bulk they calculated the shape exponent ν, the partition function exponent γ, and the crossover exponent ϕ. They also obtained the free-energy surface exponents for a tricritical polymer that is terminally attached to a nonadsorbing impenetrable boundary (the ordinary point), $\gamma_1 = \gamma$ and $\gamma_{11} = \nu$. These exponents have been derived for a special model of SAWs on a hexagonal lattice with randomly forbidden hexagons. However, it has been pointed out [10–12] that 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 [13]. A related question, raised by Shapir and Oono [14], concerns the universality class of trails, which are walks with a weaker excluded-volume restriction than that of SAWs [15]. They have argued that at tricriticality (unlike at infinite temperature) trails and SAWs may belong to different classes [16–20].

The numerical results for the θ point (i.e., for SAWs with nn attractions) and for tricritical trails mostly agree with the DS value $\nu = \frac{4}{7}$ while the values for γ are slightly smaller than the DS value $\frac{8}{7}$. On the other hand, the central values for ϕ are larger than the DS value $\frac{3}{7} \sim 0.43$ (see Refs. [21–23] and references cited therein); for the most reliable Monte Carlo studies they range from 0.48 to 0.60 for SAWs [12,21,22] and from 0.68 to 0.80 for trails [17,18]. This suggests that the θ and θ' points and trails belong to different universality classes. However, the strongest discrepancy was found for the tricritical surface exponents of both SAWs [21,24] and trails [18], where the numerical values are dramatically smaller than those of DS, i.e., $\gamma_1 \sim 0.6$ and $\gamma_{11} \sim -0.50$, vs ~ 1.143 and ~ 0.571, respectively.

Recently Vanderzande, Stella, and Seno (VSS) [25] have shown that within the framework of the θ' model, the DS surface exponents, $\gamma_1 = \frac{8}{7}$ and $\gamma_{11} = \frac{4}{7}$, are not related to the ordinary point but to the special one, i.e., the multicritical point at which an adsorption transition of a θ' chain occurs, and that the corresponding surface crossover exponent is $\phi_s = \frac{8}{21}$. They also derive $\gamma_1(\theta') = \frac{4}{7}$ at the ordinary point, which is compatible with numerical data for SAWs [21,24,25]. Thus (ignoring the above data for ϕ in the bulk), they have conjectured that the θ and θ' points are in the same universality class. In this paper we examine this conjecture by calculating the critical exponents of SAWs and trails on a square lattice at the special point; our study also provides new information about the relation between SAWs and trails. We use the scanning simulation method which has been found very efficient to handle such problems [17,18,22].

The trails and SAWs consist of N steps (bonds) (i.e., $N+1$ monomers) and they start from the origin located on an adsorbing impenetrable linear boundary on the square lattice. A trail may intersect (or touch) itself only once at an already visited site, but its bonds are not allowed to overlap [14]. An attractive bulk energy ϵ_b ($\epsilon_b < 0$) is assigned to each self-intersection and an attractive surface energy ϵ_s ($\epsilon_s < 0$) is defined for each monomer that is located on the surface. For SAWs an attractive energy ϵ_b is defined for two nn nonbonded monomers and an attractive surface energy ϵ_s is assigned to each bond (rather than a monomer, as for trails) on the surface. This nontraditional definition of the surface interaction [26] is consistent with recent numerical stud-

ies of this model [24,27].

Three different microscopic energies can be defined for configuration i: the bulk energy $E_i^b=\epsilon_b m_i^b$, where m_i^b is the number of self-intersections and nn pairs of monomers for trails and SAWs, respectively; the surface energy, $E_i^s=\epsilon_s m_i^s$, where m_i^s is the number of monomers or bonds on the surface for a trail or a SAW, respectively; and the total energy, $E_i=E_i^b+E_i^s$. Two partition functions Z_α are defined:

$$Z_\alpha=\sum_i{}^{\alpha}\exp(-E_i/k_BT)\,, \tag{1}$$

where k_B is the Boltzmann constant, T is the absolute temperature, $\alpha=1$ denotes the usual partition function, while $\alpha=11$ means that the summation is carried out only over the subgroup of chains which also end on the surface. The Boltzmann probability is

$$P_i^\beta=\exp(-E_i/k_BT)/Z_1\,. \tag{2}$$

Thus, the average surface energy E_s per ϵ_s reads

$$E_s=\epsilon_s^{-1}\sum_i P_i^\beta E_i^s\,. \tag{3}$$

It proves convenient to define the bulk and surface reciprocal temperatures, $K_b=-\epsilon_b/k_BT$ and $K_s=-\epsilon_s/k_BT$, where their critical values are denoted by K_b^* and K_s^*, respectively.

With the scanning method [28], a chain is generated step by step with the help of transition probabilities which are obtained by scanning all the possible chain continuations in b future steps. Thus, the construction probability $P_i(b)$ of chain i is known. For a small b, the future can be scanned only partially; therefore a construction of a chain may fail and in this case it is discarded. However, $P_i(b)$ is biased, i.e., it is not equal to P_i^β [Eq. (2)]; an unbiased estimation $\bar{F}_\alpha$ of the exact free energies $F_\alpha=-k_BT\ln Z_\alpha$ can be obtained from a sample of size n_α, generated with $P_i(b)$, where n_0 is the number of chains attempted [29],

$$\bar{F}_\alpha=-k_BT\ln\left[n_0^{-1}\sum_{t=1}^{n_\alpha}\frac{\exp\{-E_{i(t)}/k_BT\}}{P_{i(t)}(b)}\right]. \tag{4}$$

An appropriate equation can also be defined for the energy E_s [Eq. (3)]. The bias can also be removed by a procedure due to Schmidt [30], in which an effectively smaller sample (the accepted Boltzmann sample) is extracted from the biased one. Thus, n_{accept}, the number of *different* chains accepted to the unbiased sample, serves as the effective sample size for the importance-sampling results.

We generated with the scanning method trails of length $N=240$ using $b=4$, and SAWs of $N=200$ with $b=3$. In order to investigate the dependence of various properties on N, their importance-sampling values were calculated and accumulated for the partial chains of lengths 10,20,.... As in previous studies, the search for K_s^* is based on the fact that with the scanning method, results at *many* different temperatures can be obtained from a *single* sample simulated at a given temperature. The number of attempted chains for each model is relatively large, $n_0\sim40\times10^6$; however, the number of accepted chains n_{accept} becomes significantly lower as N increases; for trails and SAWs of $N=200$ it is $\sim2.6\times10^6$ and $\sim0.9\times10^6$, respectively. The sample for trails was generated at $(K_b^*,K_s)=(1.086,0.690)$ where the value of K_b^* was taken from Refs. [17] and [18] and results were calculated for the 30 temperatures $K_s=0.650,0.653,\ldots,0.737$ and also at $K_b=1.082$ and 1.090 which define the error bars for K_b^*. The sample for SAWs was calculated at $(K_b^*,K_s)=(0.658,0.810)$ (K_b^* was taken from Ref. [22]) and results were obtained for the 34 temperatures, $K_s=0.760,0.763,\ldots,0.859$ and $K_b=0.654$ and 0.662, which define the error bars for K_b^*. The surface critical temperature K_s^* was determined from the behavior of the surface energy E_s [Eq. (3)] at (K_b^*,K_s^*) [31,32],

$$E_s\sim N^{\phi_s}\,. \tag{5}$$

Therefore, at this point one expects $E_s(2N)/E_s(N)=2^{\phi_s}$ (if corrections to scaling are ignored). These ratios for $N=10,20,\ldots$ can be plotted as a function of K_s where the intersection point defines both K_s^* and ϕ_s [33]. In Fig. 1 such a plot is presented for SAWs, where the results for $N=10$ and 20 and for 90 and 100 were omitted since they show strong corrections to scaling and large statistical errors, respectively [34]. A careful analysis (which gives a larger weight to the results of the longer chains) leads to the following values:

$$K_s^*(\text{SAWs})=0.805\pm0.012\,,$$

$$\phi_s(\text{SAWs})=0.483\pm0.022\,.$$

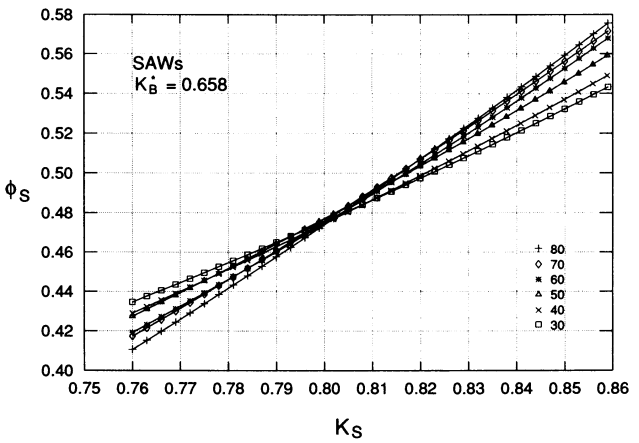

FIG. 1. Plots of $\log[E_s(2N)/E_s(N)]/\log 2$ vs the surface temperature K_s for SAWs of $N=30,40,\ldots,80$ at the critical bulk temperature $K_b^*=0.658$. The intersection point defines both K_s^* and ϕ_s.

where the errors here and in the rest of the paper are 95%-confidence limits. The central value of ϕ_s is an average over the different results for ϕ_s obtained at $K_s^* = 0.805$ (the lines do not meet exactly at a point). In order to obtain the error bars, results for K_s^* have been calculated from similar plots based on a smaller number of lines (e.g., $N = 30$-80, 40-80, 50-80), not only at $K_b^* = 1.086$ but also at 1.082 and 1.090. The errors of ϕ_s also take into account the error in the surface temperatures. A similar analysis for trails leads to

$$K_s^*(\text{trails}) = 0.686 \pm 0.012, \quad \phi_s(\text{trails}) = 0.453 \pm 0.025 .$$

As expected, the above result, $K_s^*(\text{trails}) = 0.686$ is significantly larger than the exact value 0.405... for a random walk on the same lattice [26]. $K_s^*(\text{trails}) < K_s^*(\text{SAWs})$ is also expected due to the fact that it is more difficult to attract a SAW to the surface than a trail. It is important to note that the values of ϕ_s for the two models are equal within the error bars and that both are significantly larger than the value $\frac{8}{21} \sim 0.38$ obtained by VSS for the θ' model at the special point; therefore our results do not support their conjecture that the θ' and θ points belong to the same universality class.

The partition functions Z_a [Eq. (1)] can be obtained by Eq. (4) where at (K_b^*, K_s^*) one expects

$$Z_a = B_a \mu^N N^{\gamma_a - 1}, \tag{6}$$

where B_a is a prefactor and μ, the growth parameter, has the same value as for tricritical chains in the bulk. In order to calculate μ and γ_1 we used the same method as for K_s^* and ϕ_s. Thus, at (K_b^*, K_s^*) one obtains from Eq. (6) (for $a = 1$) $2Z(2N)/Z(N)\mu^N = 2^{\gamma_1}$. Therefore, one can calculate for each pair $(N, 2N)$ the values of $2Z(2N)/Z(N)\mu^N$ for different values of μ, where the intersection point of these lines should define both γ_1 and the correct μ. In Fig. 2 such a plot is presented for trails

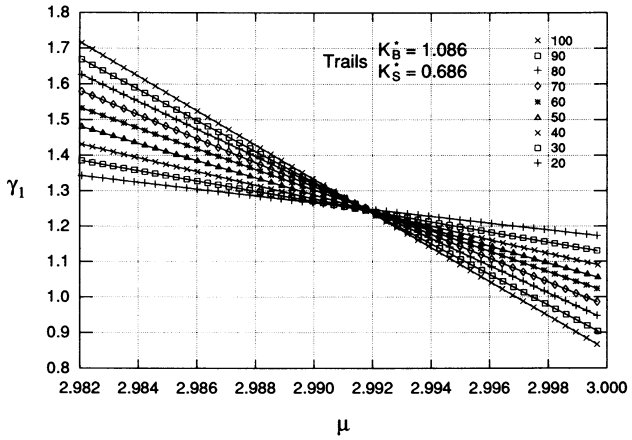

FIG. 2. Plots of $\log[2Z_1(2N)/Z_1(N)\mu^N]/\log 2$ vs the growth parameter μ for trails of $N = 20, 40, \ldots, 100$ at the critical temperatures $(K_b^*, K_s^*) = (1.086, 0.686)$. The intersection point defines both the correct μ and γ_1.

at the transition temperatures (1.086,0.686) for $N = 20, 30, \ldots, 100$ and a well-defined intersection point is observed. A detailed analysis for trails and SAWs leads to

$$\gamma_1(\text{trails}) = 1.265 \pm 0.048,$$

$$\mu(\text{trails}) = 2.9914 \pm 0.0036 ;$$

$$\gamma_1(\text{SAWs}) = 1.265 \pm 0.053 ,$$

$$\mu(\text{SAWs}) = 3.213 \pm 0.009 .$$

Again, the error bars have been obtained by carrying out similar calculations at $(K_b^* \pm D_b, K_s^* \pm D_s)$, where D_b and D_s denote the errors in the corresponding critical temperatures. As expected, the above values of μ are equal, within the error bars, to those obtained for SAWs and trails in the bulk and at the ordinary point. The values of γ_1 for the two models are equal within the error bars to 1.265 which is significantly larger than the VSS prediction $\frac{8}{7} \sim 1.143$. We also estimated the exponent γ_{11}. As expected, the samples of chains that also end on the surface are relatively small, which makes it difficult to use the method described above for γ_1 and μ. Therefore, γ_{11} has been estimated from the values of μ obtained above and best fitting the data for F_{11} by Eq. (6) over various ranges of chain lengths $(N_{\min}, N_{\max})$; the smallest value of $N_{\min}$ is 20 and the largest values of $N_{\max}$ are 60 for SAWs and 80 for trails. Thus,

$$\gamma_{11}(\text{SAWs}) = 0.72 \pm 0.06, \quad \gamma_{11}(\text{trails}) = 0.78 \pm 0.06 .$$

The errors have been obtained by carrying out such calculations at $(K_b^* \pm D_b, K_s^* \pm D_s, \mu \pm D_\mu)$, where D_μ is the error in μ. For each model, the above values of γ_1 and γ_{11} satisfy, within the error bars, the Barber [35] surface scaling relation, $2\gamma_1 - \gamma_{11} = \gamma + \nu$; for the DS values $\frac{8}{7} + \frac{4}{7} = \frac{12}{7} \sim 1.71$. For trails the fit is better than for SAWs, where $2\gamma_1 - \gamma_{11} = 1.75 \pm 10$, and 1.81 ± 10, respectively. This probably stems from the fact that the samples of chains that also end on the surface are larger for trails than for SAWs [36].

In summary, this work provides the first Monte Carlo estimation of critical exponents of trails and SAWs on the square lattice at the special point. Our results for ϕ_s, γ_1, and γ_{11} (like previous results for γ and ν in the bulk) have been found to be the same, within the error bars, for the two models. However, the present results do not support the VSS conjecture that the θ and θ' points belong to the same universality class [37]. We hope that our study will motivate further theoretical work in this still controversial but exciting subject.

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