Scaling of a Collapsed Polymer Globule in Two Dimensions

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Extensive Monte Carlo data analysis gives clear evidence that collapsed linear polymers in two dimensions fall in the universality class of athermal, dense self-avoiding walks, as conjectured by Duplantier [Phys. Rev. Lett. **71**, 4274 (1993)]. However, the boundary of the globule has self-affine roughness and does not determine the anticipated nonzero topological boundary contribution to entropic exponents. Scaling corrections are due to subleading contributions to the partition function corresponding to polymer configurations with one end located on the globule-solvent interface.

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Polymers in solution have been the subject of intense studies for several decades [1]. In the dilute case and in good solvent (high temperature T), excluded volume effects favor swollen configurations for a long linear chain. On the other hand, in poor solvent (low T), effective attractive interactions between monomers dominate, and the typical conformations are those of a compact globule. The transition between swollen and collapsed polymer regimes is marked by the theta point [1,2]. A main achievement of the Coulomb gas [3] and conformal invariance approaches has been the exact characterization of the scaling properties of polymers in the swollen [4,5] and theta regimes [6–8] in two dimensions (2D). On the other hand, the situation is still far from settled as far as the entropic scaling of the collapsed phase is concerned.

A crucial feature expected for a collapsed globule is the presence of a rather sharp boundary separating it from the surrounding solvent. This led Owczarek *et al.* [9] to conjecture the presence of a factor growing like the exponential of the boundary length in the statistical partition sum describing the globule. It was then pointed out by Duplantier [10] that with free boundary conditions such a type of factor appears naturally for models of dense polymers (DP), in which a self-avoiding walk (SAW) covers an assigned region of the lattice visiting a fixed fraction of sites [11,12]. He also argued that a collapsed globule should have the exactly known scaling exponents of DP with a smooth free boundary in 2D. Since DP have only excluded volume effects, this conjecture implies that collapsed configurations should not be sensibly influenced by the attractive interactions. A further, less obvious assumption is that the globule boundary acts as a simple, smooth perimeter confining the polymer [13]. So far, the exponents conjectured in this way have never been confirmed by numerical investigations [14,15].

In this Letter, we show that the entropic scaling of collapsed polymers in 2D is consistent with the universality class of DP. Our analysis elucidates geometrical properties of the globule-solvent interface and the role they play in determining exponents and strong finite size corrections to the asymptotic behaviors.

Let us consider linear SAW's w of $|w| = N$ steps on a square lattice [2] (Fig. 1). If to each pair of nearest neighbor sites visited not consecutively by the SAW (contact) is associated an attractive potential energy $-\epsilon(\epsilon > 0)$, the model undergoes the theta collapse transition upon varying T. This transition can be monitored from the asymptotic behavior of the partition function $Z_N = \sum_{|w|=N} \times \exp[\frac{\epsilon}{T} C(w)]$, where the sum extends to all possible w with an end at a fixed origin, and $C(w)$ is the number of nearest neighbor contacts in w. Below the theta temperature T_Θ, Z_N is expected [9] to have the following asymptotic behavior:

$$Z_N(T) \simeq A\mu(T)^N \mu_1(T)^{\sqrt{N}} N^{\gamma-1}, \tag{1}$$

where A is an amplitude, $\mu(T)$ is a bulk free energy per step depending also on lattice structure, and $\mu_1(T) < 1$ is a boundary term, associated with the existence of a sharp interface separating the typically globular region occupied by the SAW from the rest of the lattice. The factor $\mu_1^{\sqrt{N}}$ implies a boundary contribution to the dimensionless total free energy, $\ln(Z_N)$. Indeed, $\sqrt{N}$ is the average number of SAW steps on the boundary of the globule, under the plausible assumption that this boundary has a fractal dimension equal to 1. If one restricts the sum in Eq. (1) to

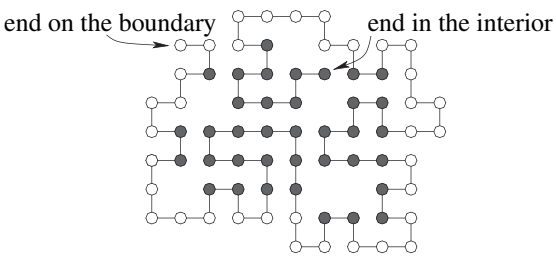

FIG. 1. Collapsed SAW, with sites on the boundary (empty circles) distinguished from sites in the interior (dark circles).

walks which start and end at the origin (polygons), the resulting partition (Z_N^0) has the same asymptotics as in Eq. (1), except for a different exponent γ_0 replacing γ. Both γ and γ_0 could take T-independent universal values in the collapsed polymer regime, as also implied by the conjecture in Ref. [10]. On the basis of the analogy with DP [11,12], Duplantier conjectured $\gamma - \gamma_0 = 19/16$, and $\gamma_0 = 5/6$, implying $\gamma = 97/46$ [10]. This value of γ_0 has a purely topological interpretation and was argued by assuming that for $N \to \infty$ the boundary of the globule becomes a smooth continuous arc without wedges [10]. An analysis of extensive exact enumerations was performed in Ref. [14], in order to determine $\gamma - \gamma_0$ from extrapolations of Z_N/Z_N^0. Considering such a ratio, one expects the exponential and stretched exponential factors in Eq. (1) to simplify in numerator and denominator, leaving an N dependence $\sim N^{\gamma-\gamma_0}$. The estimated $\gamma - \gamma_0 \approx 0.92$ was inconsistent with the conjecture of Ref. [10]. An effort to determine γ was subsequently made on the basis of extensive grand canonical Monte Carlo sampling [15]: The estimate $\gamma \approx 1.09$ again appears to rule out that conjecture.

A correct interpretation of this contradictory scenario and a solution of the puzzle can be achieved once all physical consequences of the existence of a well defined interface between collapsed globule and solvent are elucidated. This interface does not only imply the presence of a stretched exponential factor in the asymptotic partition function in Eq. (1). Indeed, unlike in the swollen regime, the typical configurations of a polymer globule can be naturally partitioned into distinct groups, depending on the location of the chain ends with respect to the boundary. This circumstance provides a natural source of scaling corrections to the asymptotic power law scaling in Eq. (1). For example, imagine one manages to restrict the sum in Z_N to compact configurations in which one end of the chain is located on the globule boundary, while the other one falls in the interior. We ask how the resulting ''-interior-boundary'' partition function Z_N^{ib} should scale compared to Z_N. The fact that scaling should not be influenced by attractive interactions and that the interfacial boundary has fractal dimension equal to 1 suggests that a simple N-dependent geometrical factor should connect the two partition functions: $Z_N^{ib} \sim N^{-1/2} Z_N$. This factor $N^{-1/2}$ represents the probability that one of the ends of a compact chain of N steps (globule area $\sim N$) ends on the globule boundary (length $\sim N^{1/2}$), if one assumes that a chain end falls with equal probability anywhere within the globule.

Of course, we also take into account that the fraction of walks with both ends on the boundary is, in turn, negligible with respect to Z_N^{ib}. Indeed, we can define also a restricted partition sum Z_N^b to which only chain configurations with both ends on the boundary contribute. In this case, the factor relating the restricted partition to Z_N will be N^{-1}, since for large N one should regard as independent events the occurrences of boundary locations for the two ends. Summarizing, if we further define Z_N^i as the partition restricted to configurations with both chain ends in the interior of the globule, the following asymptotics should be expected:

$$Z_N^i \simeq A_i \mu^N \mu_1^{\sqrt{N}} N^{\gamma-1}, \tag{2a}$$

$$Z_N^{ib} \simeq A_{ib} \mu^N \mu_1^{\sqrt{N}} N^{\gamma_{ib}-1}, \tag{2b}$$

$$Z_N^b \simeq A_b \mu^N \mu_1^{\sqrt{N}} N^{\gamma_b-1}, \tag{2c}$$

where A_i, A_{ib}, and A_b are suitable amplitudes, while $\gamma_{ib} = \gamma - 1/2$ and $\gamma_b = \gamma - 1$. Clearly, the sum of the three Z's above must yield Z_N. So the behaviors of Z_N^{ib} and Z_N^b, if confirmed, would also identify scaling corrections to the leading behavior in Eq. (1). The relative magnitudes of the amplitudes will play a key role in determining up to what extent these corrections are important at finite N.

In order to proceed, we need a meaningful definition of the boundary and of the interior of a collapsed configuration. First, from now on we denote as *neighbors* the nearest and second neighbors of a site. For a SAW w, we define as boundary the set of visited sites which are neighbors of at least one nonvisited site in communication with the exterior (Fig. 1). In order to communicate with the exterior, such a nonvisited site must be connected by at least one path of empty neighbor sites to the perimeter of a large lattice box enclosing the globule. The interior is then given by the sites visited by the walk which do not belong to the boundary. This boundary definition resembles that of a percolation cluster hull [2,5,7]. We were able to implement it by sampling long chain configurations via the new pruned enriched Rosenbluth method (nPERM) algorithm with importance sampling [16]. By this algorithm, we evaluated weights proportional to Z_N and to the restricted partition functions defined above, up to $N_{\max} = 1920$. The nPERM is an extremely efficient tool for sampling long compact SAW configurations and was even applied with success to study native structures of lattice proteins [16]. The weight of the subset of configurations in which the SAW comes back to the origin gave an estimate of Z_N^0. We explored the collapsed regime at $\epsilon/T = 0.7$, 0.77, and 0.85. For the case $\epsilon/T = 0.85$, on which we concentrated most efforts, we sampled 2×10^9 configurations for each N (2×10^6 completely independent). This took more than 1 yr of 2 GHz-CPU time.

We first checked how the average number B_N of sites on the boundary [Fig. 2(a)] grows with N. In Fig. 2(a), we show B_N vs N in a log-log scale for $\epsilon/T = 0.85$. The data give clear evidence that asymptotically $B_N \sim N^{1/2}$. Thus, it makes sense to check if the scalings in Eqs. (2) are consistent with the data and also provide the leading scaling correction mechanism to Eq. (1). We considered the ratios of all partition functions with respect to Z_N^0. These ratios are reported as a function of N in the log-log plots in Fig. 3, which give an instructive representation of the role played by the scaling corrections at various N. The logarithmic slope of Z_N/Z_N^0 vs N, which should be $\gamma - \gamma_0$, appears to

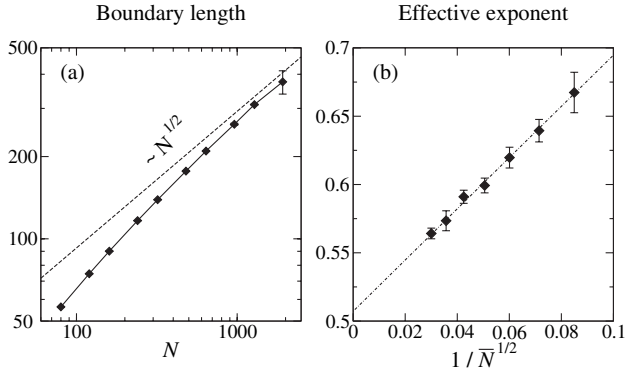

FIG. 2. (a) B_N vs N for $\epsilon/T = 0.85$: Data approach a scaling $\sim N^{1/2}$ (dashed line) for large N. (b) Effective exponent, i.e., the slope of the data in (a), as a function of $\bar{N}^{-1/2}$. The line is a linear fit extrapolating to ≈ 0.5 for $\bar{N} \to \infty$.

have strong corrections which still sensibly bend the curve at the highest values of N. Remarkably, the slope of Z_N^i/Z_N^0 approaches nearly the same value in this extremal region, suggesting that indeed the leading source of corrections is primarily in Z_N^{ib}, as discussed above. The fact that up to $N \approx 1300$ the curve for Z_N^i remains below that for Z_N^{ib} is due to a large ratio A_{ib}/A_i. The extrapolated slopes of the curves are consistent with $\gamma - \gamma_{ib} = \gamma_{ib} - \gamma_b = 1/2$ as anticipated for Eq. (2) (see Fig. 4).

The above results suggest that the asymptotics of the collapsed regime should be best determined by isolating and studying Z_N^i. To confirm this, we evaluated an effective entropic exponent $\gamma - \gamma_0$ using a weighted linear least square fit of $\log_{10}(Z_N/Z_N^0)$ vs $\log_{10}N$ (and similarly for Z_N^i). To quantify the approach to the asymptotic scaling, we consider subsets of four consecutive points (N_1, N_2, N_3, N_4) and fit their slope in Fig. 3. The results are plotted as a function of $1/\bar{N}^{1/2}$ in Fig. 4, where $\bar{N} = (N_1N_2N_3N_4)^{1/4}$. In the case of Z_N, there is much curvature in the plot. Quite remarkably, in the case of Z_N^i, the plot appears pretty linear and extrapolates very close to $\gamma - \gamma_0 = 19/16$ for $N \to \infty$. This linearity clearly indicates that $N^{-1/2}$ represents the leading scaling correction. One can push further the analogy with DP, imagining that the $N' = N - B_N$ monomers in the interior of the globule are representative of the DP phase, the remaining B_N ones just forming a kind of box boundary. In other words, the partition function can also be parametrized by the number N' of monomers in the interior, i.e., $Z_{N'} = Z_N$. Repeating the same analysis with N' in place of N, we obtain effective exponents for $Z_{N'}^i/Z_{N'}^0$ that lie on an almost horizontal straight line (Fig. 4), showing that the scaling correction amplitude has been drastically reduced. This allows a more accurate extrapolation of $\gamma - \gamma_0 = 1.20(3)$, very close to the value $19/16$ expected for DP.

As a further step, we determined individual γ's by directly fitting $\ln Z_N$ with a function of the form

$$N \ln\mu + \sqrt{N} \ln\mu_1 + (\gamma - 1) \ln N + \ln A + A_1/\sqrt{N} \quad (3)$$

and Z_N^0 with a similar one [17]. The term $A_1/\sqrt{N}$ corresponds to the expected scaling correction. With or without this term, we found that, upon removal of the data at smaller N's, the fits are not always stable, again a signal of the presence of a strong correction to scaling. On the other hand, with the $A_1/\sqrt{N}$ term, the best asymptotic estimate of γ is expected when all data are included. On this basis, we estimated $\gamma = 1.18(4)$ and $\gamma_0 = 0.02(7)$, again for $\epsilon/T = 0.85$. We also fitted data for $\epsilon/T = 0.70$. At this temperature, one observes theta point values of γ and γ_0. This means that this temperature is still too close to the critical value $\epsilon/T_\Theta = 0.665$ [18] to observe the DP scaling in chains with $N \lesssim 2000$. However, for $\epsilon/T = 0.77$, one finds results pretty consistent with those found for $\epsilon/T = 0.85$, confirming the expectation that the col-

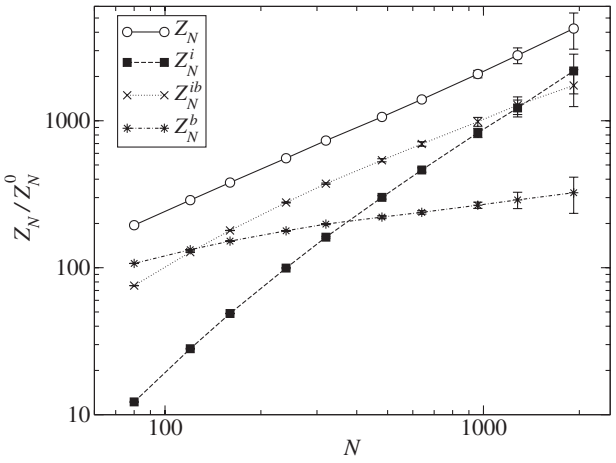

FIG. 3. Partition function ratios for $\epsilon/T = 0.85$. For $N \lesssim 100$, the dominant contribution to Z_N comes from Z_N^b; for $100 \lesssim N \lesssim 1300$, Z_N^{ib} dominates; while Z_N^i becomes the leading term only for $N \gtrsim 1300$. Lines emphasize the trends.

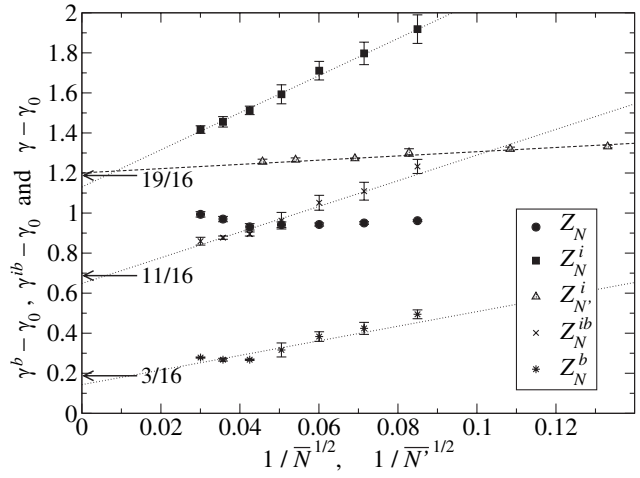

FIG. 4. Effective $\gamma - \gamma_0$ as a function of $\bar{N}^{-1/2}$ (dotted lines) or $\bar{N}'^{-1/2}$ (dashed line) for $\epsilon/T = 0.85$. Fits of $\gamma^{ib} - \gamma_0$ and of $\gamma^b - \gamma_0$ are also shown. Arrows mark the DP value $\gamma - \gamma_0 = 19/16$, and $\gamma - \gamma_0 - 1/2$ and $\gamma - \gamma_0 - 1$.

TABLE I. Estimated and exact exponents.

ϵ/T	Walk: γ		Polygon: γ_0	
	Estim.	Exact	Estim.	Exact
0.7	1.11(3)	$8/7 \simeq 1.14$[a]	$-0.15(5)$	$-1/7 \simeq -0.14$[a]
0.77	1.20(5)	$19/16 \simeq 1.19$[b]	0.00(5)	0[b]
0.85	1.18(4)	$19/16 \simeq 1.19$[b]	0.02(7)	0[b]

[a]Exact entropic exponents of the theta point in 2D [7].
[b]Exponents of DP in 2D [11].

lapsed phase is described by T-independent exponents. Our determinations are reported in Table I. Previous estimates without scaling corrections [15] included $\gamma = 1.09(8)$ at $\epsilon/T \simeq 0.765$ and $\gamma = 1.11(6)$ at $\epsilon/T \simeq 0.788$. While not testing as deeply the collapsed phase, these less sharp determinations are still compatible with ours.

While the direct fits fully confirm the difference $\gamma - \gamma_0$ extrapolated above, consistent with the DP value $19/16$, $\gamma_0 = 5/6$, as conjectured in Ref. [10], appears definitely excluded. The fits indicate a much smaller γ_0, possibly $\gamma_0 = 0$. $\gamma_0 = 5/6$ was predicted in Ref. [10] under the assumption that the globule-solvent interface can be assimilated to a smooth wall without wedges in the DP model. However, the circumstance that the boundary has a fractal dimension $\simeq 1$, as directly verified here, does not rule out other possibilities. As we argue below, one should expect a rough, self-affine boundary. The attractive forces guaranteeing the cohesion of the globule should determine a line tension ($\sim \ln \mu_1$) for the boundary, which is probably the most important factor controlling its length. The fluctuations of the length of the boundary should have a self-affine geometry, so that its average width grows like $B_N^\zeta \sim N^{\zeta/2}$, $\zeta < 1$ being the roughness exponent [19]. In 2D, the roughness exponent of a line tension controlled boundary has $\zeta = 1/2$. One can argue the roughness exponent ζ of the globule boundary again on the basis of the leading scaling correction $\sim N^{-1/2}$ identified in the problem. If the boundary is self-affine, B_N should have a subleading correction $\sim N^{\zeta-1}$, with positive amplitude, due to the rate of growth with N of the average width of the boundary profile. Thus, in our case we should expect $\zeta = 1/2$. This correction is clearly shown by our plot in Fig. 2(b), where the effective exponents of the scaling of B_N are plotted as a function of $\bar{N}^{-1/2}$: They vary linearly as a function of $\bar{N}^{-1/2}$, with positive slope, and extrapolate to 0.507(3) as $\bar{N} \to \infty$ (dotted-dashed line in the figure). A self-affine curve is not differentiable, and the globule boundary cannot be assimilated to a smooth contour for a DP [10]. The theory of DP [11,12], while still valid for the collapsed globule, is not applicable in the form appropriate for polymers within smooth fixed boundaries [20]. Thus, the topological argument leading to $\gamma_0 = 5/6$ for a collapsed globule does not hold. One should expect a smaller γ_0, as the theory predicts that γ_0 is maximal for a DP with a smooth boundary [10]. Indeed, here we find $\gamma_0 \approx 0$, compatible with the hypothesis that a collapsed polymer is statistically equivalent to a DP with a self-affine rough boundary.

In summary, we gave for the first time solid evidence that the entropic scaling of a collapsed polymer globule in 2D falls in the universality class of athermal DP. The existence of the solvent-globule interface appears crucial in several respects. Besides giving rise to the strong scaling corrections which hindered so far the analysis of the problem, with its nontrivial, self-affine stochastic geometry, the interface also determines an unexpected, close to zero value of the γ_0 exponent of collapsed rings.

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