Free energy of a long, flexible, self-avoiding polymer chain in a tube

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The confinement free energy of a long, flexible, self-avoiding polymer chain, fluctuating in d spatial dimensions in an infinitely long cylindrical tube with diameter L, is given by $\Delta F \approx A k_B T L^{-1} R_\parallel$ for $R_\parallel \gg L$. Here $R_\parallel$ is the length of tube occupied by the chain, and A is a universal amplitude. We show how to determine ΔF and $R_\parallel$ from the correlation length $\xi_L(t)$ of the n-vector model of magnetism in the limit $n \to 0$, defined on the cylindrical volume, near the critical temperature $t_c(L)$ where ξ_L diverges. Using this correspondence, we estimate A in two dimensions from transfer-matrix data for self-avoiding walks on strips of width L with free, critically absorbing, and periodic boundaries. Our results for the universal amplitudes A and $B \approx L R_\parallel^{-1} \langle w^2 \rangle$, where w is the winding number, are in excellent agreement with Monte Carlo simulations of Frauenkron, Causo, and Grassberger for strips with periodic boundaries. [S1063-651X(99)12105-6]

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I. INTRODUCTION

Squeezing a long, flexible polymer chain with excluded-volume interactions into a narrow tube with repulsive ''hard walls'' decreases the conformational entropy. External work is required, i.e., the free energy of confinement ΔF is positive. However, if the interaction between the monomers and the tube walls is sufficiently attractive, the energetic advantage of confinement outweighs the entropic disadvantage, and ΔF is negative.

An illuminating discussion of the free energy of confinement with repulsive monomer-tube interactions in mind is given in de Gennes' book [1]. For a chain of N monomers fluctuating in d dimensions in an infinitely long cylindrical volume with diameter or other [2] characteristic size L, simple scaling arguments imply

$$\lim_{N\to\infty} \frac{\Delta F}{R_\parallel} \approx A \frac{k_B T}{L}, \tag{1}$$

$$\lim_{N\to\infty} \frac{N}{R_\parallel} \approx \alpha \left(\frac{L}{a}\right)^{1/\nu} \frac{1}{L} \tag{2}$$

in the regime $L \gg a$. Here $R_\parallel$ is the length of tube occupied by the chain, a is the mean distance between consecutive monomers, and A and α are dimensionless amplitudes. The quantity A is universal, i.e., the same for all flexible, self-avoiding polymer chains, but does depend on the spatial dimension and the universality class of the monomer-tube interaction. The other amplitude α is nonuniversal. de Gennes' scaling picture does not predict the values of A and α. How to calculate these amplitudes is the main topic of this paper.

The equivalence of polymers or self-avoiding walks and the n-vector model of magnetism for $n \to 0$, first pointed out by de Gennes [3], is an extremely valuable theoretical tool, that makes the powerful techniques of critical phenomena available for polymer problems [1,3–6]. Long polymer chains correspond to long correlation lengths in the magnetic system, i.e., near-critical temperatures. In Sec. II of this paper we show that the fundamental relations (1),(2) for a polymer in a tube also follow from the polymer-magnet correspondence. We relate A and α to the amplitude $\Lambda(L)$ and critical temperature $t_c(L)$ in a one-dimensional transition in which the correlation length $\xi_L(t)$ diverges as

$$\xi_L(t) \approx \Lambda(L)[t - t_c(L)]^{-1}, \quad t \searrow t_c(L), \tag{3}$$

but there is no corresponding thermal singularity in the free energy. In contrast, in the d-dimensional bulk

$$\xi_\infty(t) \approx \Lambda_{\rm bulk}[t - t_c(\infty)]^{-\nu}, \quad t \searrow t_c(\infty), \tag{4}$$

and the free energy has a thermal singularity $\sim [t - t_c(\infty)]^{d\nu}$. Equivalently, we relate A and α to the largest eigenvalue $\lambda_L^{(0)}(t)$ of the transfer matrix for self-avoiding walks with monomer fugacity e^{-t} near $t = t_c(L)$, where the eigenvalue equals 1. Using finite-size scaling theory for magnetic systems, we also confirm in Sec. II that A is universal and α is not.

The results of Sec. II provide a convenient starting point for calculating A with field theory or numerical finite-size scaling. In Sec. III we estimate A in two dimensions from numerically exact transfer-matrix results for self-avoiding walks on infinitely long strips of square lattice with L rows, where $L = 2,3,\ldots,11$. Three universality classes, corresponding to free, critically absorbing and periodic boundaries, are considered. In the case of periodic boundaries, Monte Carlo simulations have been carried out by Frauenkron, Causo, and Grassberger [7]. Our results for A and another universal amplitude B related to the winding number are in excellent agreement with their estimates.

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II. STATISTICAL MECHANICS OF A POLYMER IN A TUBE

The grand canonical partition function of a self-avoiding walk or polymer between points $\mathbf{r}_1$ and $\mathbf{r}_2$ of a d-dimensional lattice with lattice constant a and a cylindrical boundary of diameter L is defined by

$$Z_L(\mathbf{r}_1,\mathbf{r}_2,t)=\int_0^\infty dN e^{-Nt}\mathcal{N}_L(\mathbf{r}_1,\mathbf{r}_2,N). \tag{5}$$

Here $K=e^{-t}$ is the fugacity per step, and $\mathcal{N}_L(\mathbf{r}_1,\mathbf{r}_2,N)$ is the number of distinct walks with N steps between $\mathbf{r_1}$ and $\mathbf{r_2}$. Anticipating the limit $N\to\infty$ in Eqs. (1) and (2), we integrate rather than sum over integer N in Eq. (5). As noted by de Gennes [1,4–6], the partition function $Z_L(\mathbf{r}_1,\mathbf{r}_2,t)$ is formally identical with the spin-spin correlation function of a system of n-component spins with ferromagnetic nearest-neighbor coupling $K=J/k_BT=e^{-t}$ on the lattice in the limit $n\to 0$. This is the basis of the polymer-magnet correspondence. The quantity t increases monotonically with T and plays the role of a temperature variable in the magnetic model.

The canonical partition function of a polymer or self-avoiding walk with a fixed number of monomers and fixed end points equals the quantity $\mathcal{N}_L(\mathbf{r}_1,\mathbf{r}_2,N)$ on the right side of Eq. (5). It is related to the grand canonical partition function by the inverse Laplace transformation

$$\mathcal{N}_L(\mathbf{r}_1,\mathbf{r}_2,N)=\int_{c-i\infty}^{c+i\infty}\frac{dt}{2\pi i}e^{Nt}Z_L(\mathbf{r}_1,\mathbf{r}_2,t). \tag{6}$$

The free energy of confinement ΔF introduced in Eq. (1) is defined by

$$\Delta F=-k_BT\ln\frac{\mathcal{N}_L(\mathbf{r}_1,N)}{\mathcal{N}_\infty(\mathbf{r}_1,N)}, \tag{7}$$

where

$$\mathcal{N}_L(\mathbf{r}_1,N)=\rho\int d^dr_2\mathcal{N}_L(\mathbf{r}_1,\mathbf{r}_2,N) \tag{8}$$

is the total number of distinct walks of N steps originating from site $\mathbf{r}_1$ in the cylindrical volume, and ρ is the density of lattice sites.

For a polymer in a tube with $r=|\mathbf{r}_1-\mathbf{r}_2|\gg L$ the integral relationship (5),(6) between the canonical and grand canonical partition functions can be greatly simplified. de Gennes' fundamental equations (1) and (2) hold in the large-N limit with r, $\ln\mathcal{N}_L$, and $\ln Z_L$ proportional to N. In this limit the asymptotic form of the integrals in Eqs. (5) and (6) follows from steepest-descent integration, which yields

$$\ln\mathcal{N}_L(r,N)=\ln Z_L(r,t)+Nt, \tag{9}$$

$$t=\frac{\partial}{\partial N}\ln\mathcal{N}_L(r,N),\quad N=-\frac{\partial}{\partial t}\ln Z_L(r,t). \tag{10}$$

Here we have introduced the simpler notation $Z_L(\mathbf{r}_1,\mathbf{r}_2,t)\to Z_L(r,t)$, $\mathcal{N}_L(\mathbf{r}_1,\mathbf{r}_2,t)\to\mathcal{N}_L(r,t)$. The grand canonical and canonical free energies of a long polymer in a tube are related by a Legendre transformation. There is an obvious similarity with the ordinary thermodynamics of fluids. The end-to-end distance r and the force $(k_BT)^{-1}\partial\ln\mathcal{N}_L/\partial r$ exerted by the ends of the polymer are analogous to the volume and pressure, respectively, of the fluid.

It is useful to expand the grand canonical partition function of Eq. (5) in the form

$$Z(\mathbf{r}_1,\mathbf{r}_2,t)=\sum_i c_L^{(i)}(\mathbf{r}_{1\perp},\mathbf{r}_{2\perp})\lambda_L^{(i)|x_1-x_2|/a}, \tag{11}$$

where the $\lambda_L^{(i)}(t)$ are eigenvalues of the transfer matrix of a slice of system perpendicular to the cylinder axis with thickness a. Here we have introduced cylindrical coordinates $\mathbf{r}_i=(x_i,\mathbf{r}_{i\perp})$. For $r=|\mathbf{r}_1-\mathbf{r}_2|\gg L$ the dominant term in the sum over i comes from the largest eigenvalue, and

$$\frac{1}{r}\ln Z(r,t)=\frac{1}{a}\ln\lambda_L^{(0)}(t)=-\frac{1}{\xi_L(t)}, \tag{12}$$

where $\xi_L(t)$ is the correlation length of the magnetic system.

For finite L, $\lambda_L^{(0)}(t)$ is an analytic, monotonically decreasing function of t, as expected from Eqs. (5) and (12). From Eq. (12) we see that $\xi_L(t)$ diverges with critical exponent 1, as in Eq. (3), when $\lambda_L^{(0)}$ approaches 1, with

$$\lambda_L^{(0)}(t)\big|_{t=t_c(L)}=1, \tag{13}$$

$$\frac{1}{\Lambda(L)}=\frac{d}{dt}\frac{1}{\xi_L(t)}\bigg|_{t=t_c(L)}=-\frac{1}{a}\frac{d}{dt}\lambda_L^{(0)}(t)_{t=t_c(L)}. \tag{14}$$

Although the correlation length and susceptibility diverge in this ''transition,'' there is no spontaneous symmetry breaking nor any anomaly in the spectrum of eigenvalues of the transfer matrix. We refer to the transition as one-dimensional, since it also exists on a one-dimensional lattice [8].

From Eqs. (9), (10), and (12) it is simple to show that

$$N=-\frac{r}{a}\frac{d}{dt}\ln\lambda_L^{(0)}(t), \tag{15}$$

$$\frac{\partial}{\partial r}\ln\mathcal{N}_L(r,N)=\frac{1}{a}\ln\lambda_L^{(0)}(t), \tag{16}$$

$$\frac{\partial^2}{\partial r^2}\ln\mathcal{N}_L(r,N)=-\frac{1}{ar}\frac{[(d/dt)\ln\lambda_L^{(0)}(t)]^2}{(d/dt)^2\ln\lambda_L^{(0)}(t)}. \tag{17}$$

The most probable end-to-end distance $R_\parallel$ is the value of r that maximizes $\ln\mathcal{N}_L(r,N)$ for fixed N. At extrema of $\mathcal{N}_L(r,N)$ the derivative in Eq. (16) vanishes, and $\lambda_L^{(0)}=1$. Equations (5) and (12) imply negative and positive first and second derivatives, respectively, of $\ln\lambda_L^{(0)}(t)$ with respect to t. From this and Eq. (17) it follows that the single extremum at $\lambda_L^{(0)}=1$ is an absolute maximum. As noted in Eq. (13), $\lambda_L^{(0)}=1$ at $t=t_c(L)$, where the correlation of the magnetic system diverges as in Eq. (3).

Setting $t=t_c(L)$ and $\lambda_L^{(0)}=1$ in Eqs. (9),(12),(15)–(17) and expanding $\ln\mathcal{N}_L(r,N)$ in a Taylor series about $r=R_\parallel$ yields

$$N=-\frac{R_\parallel}{a}\frac{d}{dt}\lambda_L^{(0)}(t)\bigg|_{t=t_c(L)}, \tag{18}$$

$$\ln\mathcal{N}_L(r,N)\approx Nt_c(L)-\frac{(r-R_\parallel)^2}{2aR_\parallel} \times\frac{[(d/dt)\ln\lambda_L^{(0)}(t)]^2}{(d/dt)^2\ln\lambda_L^{(0)}(t)}\bigg|_{t=t_c(L)}+\cdots. \tag{19}$$

The second relation implies typical fluctuations in $r-R_\parallel$ of order $(aR_\parallel)^{1/2}\sim N^{1/2}$.

To calculate the free energy of the confined polymer, we substitute Eq. (19) and the bulk result [1]

$$\ln\mathcal{N}_\infty(\mathbf{r}_1,N)=Nt_c(\infty)+\mathrm{O}(\ln N) \tag{20}$$

into Eqs. (7) and (8). The dominant contribution to the integral over $\mathbf{r}_2$ comes from the maximum at $r=R_\parallel$. We also rewrite $(d/dt)\lambda_L^{(0)}[t_c(L)]$ in Eq. (18) in terms of $\Lambda(L)$ using Eq. (14). In this way we obtain

$$\Delta F=k_BTN[t_c(\infty)-t_c(L)], \tag{21}$$

$$R_\parallel=\Lambda(L)N \tag{22}$$

to leading order for large N. Comparing these two equations with de Gennes' fundamental relations (1) and (2) yields our main results

$$A=\lim_{L\to\infty}\frac{L}{\Lambda(L)}[t_c(\infty)-t_c(L)], \tag{23}$$

$$\alpha=\lim_{L\to\infty}\frac{L}{\Lambda(L)}\left(\frac{a}{L}\right)^{1/\nu}, \tag{24}$$

for the amplitudes A and α, with $\Lambda(L)$ given by Eq. (14).

That the limits in Eqs. (23) and (24) exist and are universal and nonuniversal, respectively, follows from the finite-size scaling form [9,10]

$$\xi_L(t)=L\mathcal{F}\left[\left(\frac{L}{\Lambda_{\mathrm{bulk}}}\right)^{1/\nu}[t-t_c(\infty)]\right] \tag{25}$$

from critical phenomena, valid for large L and small $t-t_c(\infty)$. The function $\mathcal{F}(x)$ is universal and has the asymptotic behavior

$$\mathcal{F}(x)\approx\begin{cases}y_0(x+x_0)^{-1}, & x\to-x_0\\ x^{-\nu}, & x\to\infty,\end{cases} \tag{26}$$

which reproduces the divergent behavior (3) and (4) of the correlation length for finite and infinite L, respectively, with

$$\Lambda(L)=y_0L\left(\frac{\Lambda_{\mathrm{bulk}}}{L}\right)^{1/\nu}, \tag{27}$$

$$t_c(L)=t_c(\infty)-x_0\left(\frac{\Lambda_{\mathrm{bulk}}}{L}\right)^{1/\nu}. \tag{28}$$

Substituting Eqs. (27) and (28) into Eqs. (23) and (24), we obtain

$$A=\frac{x_0}{y_0},\quad \alpha=\frac{1}{y_0}\left(\frac{a}{\Lambda_{\mathrm{bulk}}}\right)^{1/\nu} \tag{29}$$

for the amplitudes A and α in Eqs. (1) and (2). Since the entire scaling function $\mathcal{F}(x)$ is universal, x_0 and y_0 are also universal constants. However, the dimensionless amplitude $a^{-1}\Lambda_{\mathrm{bulk}}$ of the correlation length, with Λ_{bulk} defined by Eq. (4), is nonuniversal, depending, for example, on the type of lattice. Together with Eq. (29) this establishes the universality of A and nonuniversality of α.

III. TRANSFER-MATRIX RESULTS FOR TWO DIMENSIONS

Some of the most precise numerical estimates of the scaling indices of self-avoiding walks in two dimensions have been obtained with a transfer-matrix finite-size method [11–14] due to Derrida [11]. The largest eigenvalue of an exact transfer matrix for self-avoiding walks on strips of infinite length and finite width L is determined numerically. Then the sequence of numerically exact results for finite L is extrapolated to $L=\infty$. Convergence accelerating algorithms [15,16] have proved very useful in extrapolating the data. These algorithms involve subtraction of numbers with small relative differences and require data accurate to many significant figures.

In this section self-avoiding walks on infinitely long two-dimensional strips of square lattice with lattice constant $a=1$ and with $L=2,3\ldots,11$ rows are analyzed with the transfer-matrix approach just described. We work in the grand canonical ensemble and for free and critically-absorbing boundaries introduce distinct surface and bulk fugacities

$$K_s=e^{-t_s},\quad K=e^{-t} \tag{30}$$

for a step along either edge and for all other steps, respectively. The transfer matrix is the same as in Refs. [11,14].

A. Free boundaries

In the semi-infinite geometry with free (hard-wall) boundaries, the surface fugacity K_s is an irrelevant variable. We have obtained numerical results both for strips with $K_s=K$ and $K_s=K_{\mathrm{free}}^*=0.2675$, where we estimate [14] that the leading irrelevant surface variable, which has scaling index $y=-1$, vanishes. In the latter case one expects (and finds) faster convergence of the finite-size estimates as the system size increases.

For both these choices for K_s the critical fugacity $K_c(L)=\exp[-t_c(L)]$ at which ξ_L diverges was determined from the condition (13) that the largest eigenvalue of the transfer matrix equal 1. Our results for $K_c(L)$ with $L=2,3,\ldots,11$ are listed in Table I and shown by full and empty circles in Fig. 1. The data seem compatible with the $L^{-1/\nu}=L^{-4/3}$ dependence implied by Eq. (28) for large L. Extrapolating the two sequences to $L=\infty$ with the van den Broek–Schwartz algorithm [15,16], we obtain $K_c(\infty)=0.380\pm0.001$, consistent with the best estimate

TABLE I. Transfer-matrix results for free boundary conditions. The entry for $K_c(\infty)$ is the value in Eq. (31). The entries for $A(\infty)$ were obtained with the van den Broek–Schwartz extrapolation algorithm.

	$K_s=K$		$K_s=0.2675$	
L	$K_c(L)$	$A(L)$	$K_c(L)$	$A(L)$
2	0.6180 3399	1.351 2016	2.7383 178	2.896 9275
3	0.5222 9500	1.540 2518	0.6965 6501	2.111 1681
4	0.4790 9131	1.654 9658	0.5433 0133	2.078 3113
5	0.4547 5926	1.732 2575	0.4876 3388	2.080 1182
6	0.4392 9415	1.787 8753	0.4590 4147	2.085 6608
7	0.4286 7323	1.829 8051	0.4417 3491	2.091 0148
8	0.4209 7265	1.862 5388	0.4301 9228	2.095 5531
9	0.4151 6014	1.888 7978	0.4219 8094	2.099 2892
10	0.4106 3411	1.910 3269	0.4158 6327	2.102 3569
11	0.4070 2125	1.928 2964	0.4111 4399	2.104 8913
∞	0.3790 5228	2.12 ± 0.01	0.3790 5228	2.12 ± 0.01

$$K_c(\infty)=0.379\,052\,28 \tag{31}$$

of Guttmann and co-workers [17,18].

The transfer-matrix data for the quantity

$$A(L)=L\Lambda(L)^{-1}[t_c(\infty)-t_c(L)]$$
$$=LK\lambda_L'^{(0)}(K_s,K)\ln\frac{K}{K_c(\infty)}\bigg|_{K=K_c(L)} \tag{32}$$

on the right side of Eq. (23) are also listed in Table I. Here we have expressed $\Lambda(L)$ in terms of the largest eigenvalue of the transfer matrix $\lambda_L^{(0)}$ using Eqs. (14) and (30). In the cases $K_s=K$ and $K_s=K^*_{\rm free}$, $\lambda_L'^{(0)}(K_s,K)$ denotes the ordinary and partial derivative, respectively, of $\lambda_L^{(0)}$ with respect to K. According to Eq. (23) the $A(L)$ approach the universal amplitude A in Eq. (1) in the limit $L\to\infty$. Extrapolating the two sequences of $A(L)$ in Table I to $L=\infty$ with the van den Broek–Schwartz algorithm, we estimate $A_{\rm free}=2.12\pm0.01$. The two sequences of $A(L)$ and our prediction for the limiting value are shown in Fig. 2. The sequence with $K_s=K$ is compatible with the expected [19] form $A(L)-A(\infty)\sim L^{-1}$ for large L.

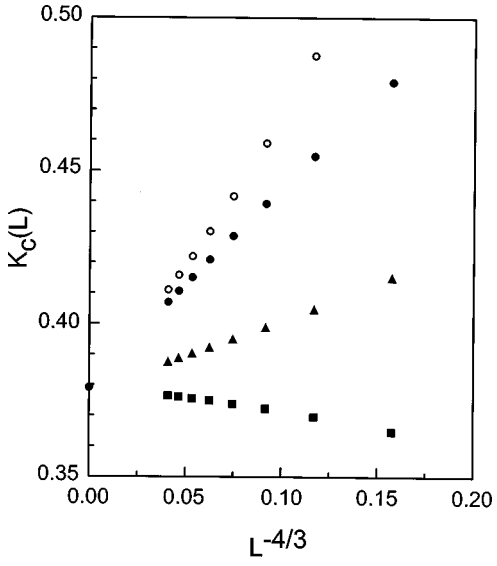

FIG. 1. Critical monomer fugacity $K_c(L)=\exp[-t_c(L)]$ for free boundaries with $K_s=K$ (full circles) and $K_s=K^*_{\rm free}=0.2675$ (empty circles), critically absorbing boundaries (squares), and periodic boundaries (triangles). The point on the vertical axis is the estimate (31) of $K_c(\infty)$ obtained in Refs. [17,18].

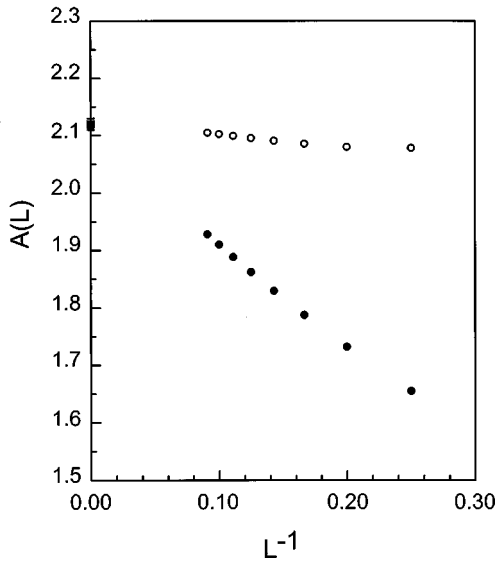

FIG. 2. The quantity $A(L)$ defined in Eq. (32) for free boundaries with $K_s=K$ (full circles) and $K_s=K^*_{\rm free}=0.2675$ (empty circles). The square point with error bars on the vertical axis is our van den Broek–Schwartz estimate $A_{\rm free}=2.12\pm0.01$.

B. Critically absorbing boundaries

Here we follow the same procedure as for free boundaries, except that K_s is replaced by the estimate $K^*_{\rm crit\ ads}=0.7736$ of the critical edge fugacity for adsorption of a self-avoiding walk [14]. The corresponding transfer-matrix data for $K_c(L)$ and $A(L)$ are listed in Table II. The L dependence of the $K_c(L)$, shown by square points in Fig. 1, seems compatible with the asymptotic behavior (28), and our van

TABLE II. Transfer-matrix results for critically adsorbing boundary conditions. The entry for $K_c(\infty)$ is the value in Eq. (31). The entry for $A(\infty)$ was obtained with the van den Broek–Schwartz extrapolation algorithm.

L	$K_c(L)$	$A(L)$
2	0.2926 5770	-0.1171 2598
3	0.3524 5370	-0.1182 4475
4	0.3647 7772	-0.1195 3242
5	0.3697 1263	-0.1206 9628
6	0.3722 8653	-0.1217 2166
7	0.3738 3657	-0.1226 1591
8	0.3748 5892	-0.1233 9830
9	0.3755 7708	-0.1240 8819
10	0.3761 0545	-0.1247 0203
11	0.3765 0822	-0.1252 5310
∞	0.3790 5228	-0.129 ± 0.001

TABLE III. Transfer-matrix results for periodic (cylindrical) boundary conditions. The entry for $K_c(\infty)$ is the value in Eq. (31). The entries for $A(\infty)$ and $B(L)$ were obtained with the van den Broek–Schwartz extrapolation algorithm.

L	$K_c(L)$	$A(L)$	$B(L)$
2	0.5000 0000	0.8308 0188	0.2500 0000
3	0.4367 4647	0.7503 6112	0.3635 0534
4	0.4151 1681	0.7142 1136	0.4137 4660
5	0.4047 4907	0.6976 9258	0.4372 7019
6	0.3987 6231	0.6895 1490	0.4494 5193
7	0.3948 9044	0.6850 3908	0.4564 6874
8	0.3921 9437	0.6823 5214	0.4609 0605
9	0.3902 1775	0.6806 1558	0.4638 9589
10	0.3887 1234	0.6794 2868	0.4660 3173
11	0.3875 3155	0.6785 8229	0.4676 4803
∞	0.3790 5228	0.676 ± 0.001	0.474 ± 0.001

den Broek–Schwartz estimate $K_c(\infty) = 0.379 \pm 0.001$ is consistent with Eq. (31). Extrapolating the sequence of $A(L)$ in Table I to $L = \infty$ with the van den Broek–Schwartz algorithm, we obtain $A_{\text{crit ads}} = -0.129 \pm 0.001$. Note that $A_{\text{crit ads}}$ is negative. The narrower the strip, the lower the free energy of confinement, due to the greater fraction of the monomers on energetically favored boundary sites.

C. Periodic boundary conditions

The case of periodic boundaries corresponds to a square lattice of L rows on the surface of an infinitely long cylinder. The $A(L)$ are given by Eq. (32), with $\lambda_L'^{(0)}(K_s, K)$ replaced by $d\lambda_L^{(0)}(K)/dK$. The transfer-matrix data for $K_c(L)$ and $A(L)$ are listed in Table III. Once again the L dependence of the $K_c(L)$, shown by triangular points in Fig. 1 is compatible with the asymptotic behavior (28), and our van den Broek–Schwartz estimate $K_c(\infty) = 0.380 \pm 0.001$ is consistent with (31). The $A(L)$, shown in Fig. 3, are compatible with the expected [19] form $A(L) - A(\infty) \sim L^{-2}$ for large L. Our van den Broek–Schwartz estimate $A_{\text{periodic}} = 0.676 \pm 0.001$ of the limiting value is in excellent agreement with the Monte Carlo result $A_{\text{period}} = 0.675 \pm 0.002$ of Frauenkron, Causo, and Grassberger [7], indicated by the square point with error bars on the vertical axis.

Frauenkron *et al.* also report a Monte Carlo estimate of the universal amplitude B in the scaling prediction

$$\lim_{N\to\infty} \frac{\langle w^2 \rangle}{R_\parallel} \approx \frac{B}{L}, \quad L \gg a \tag{33}$$

for the second moment of the winding number w of self-avoiding walks on the surface of a cylinder. Here w is defined as the number of times a walk winds around the cylinder, with positive and negative w corresponding to clockwise and counterclockwise directions.

To calculate $\langle w^2 \rangle$, we include fugacities e^{τ} and $e^{-\tau}$ for each clockwise and counterclockwise step, respectively, of the walk perpendicular to the cylinder axis in both the canonical and grand-canonical ensembles. Since there are L rows parallel to the symmetry axis of the cylinder, a complete clockwise rotation has weight $e^{L\tau}$. In the large-N limit the free energies in the two ensembles are again related by a Legendre transformation similar to (9), (10), and $\langle w^2 \rangle$ satisfies

$$L^2 \langle w^2 \rangle = \frac{\partial^2}{\partial \tau^2} \ln \mathcal{N}_L(r, N, \tau)\Big|_{r=R_\parallel,\ \tau=0} = R_\parallel \frac{\partial^2}{\partial \tau^2} \ln \lambda_L^{(0)}(t, \tau)\Big|_{t=t_c(L),\ \tau=0}. \tag{34}$$

Combining Eqs. (13), (33), and (34), we obtain $B = \lim_{L\to\infty} B(L)$, where

$$B(L) = \frac{1}{L} \frac{\partial^2}{\partial \tau^2} \lambda_L^{(0)}(t, \tau)\Big|_{t=t_c(L),\ \tau=0}. \tag{35}$$

The transfer-matrix data for $B(L)$ are listed in Table III and shown in Fig. 4. The $B(L)$ are compatible with the expected [19] form $B(L) - B(\infty) \sim L^{-2}$ for large L. Our van den Broek–Schwartz estimate $B = 0.474 \pm 0.001$ of the limiting value is in excellent agreement with the Monte Carlo result $B = 0.475 \pm 0.004$ of Frauenkron *et al.*

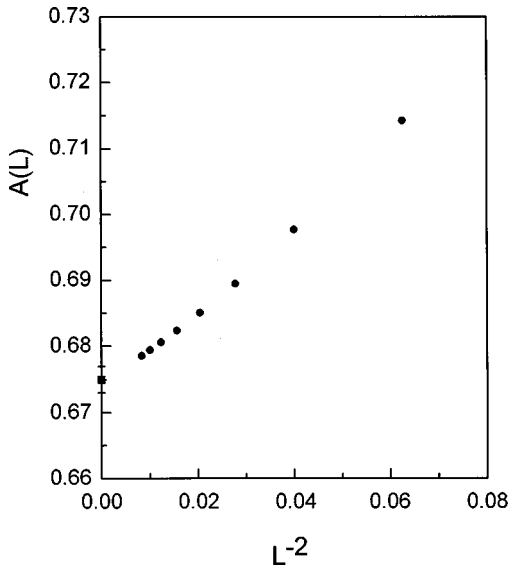

FIG. 3. The quantity $A(L)$ defined in Eq. (32) for periodic (cylindrical) boundary conditions. The square point with error bars on the vertical axis is the Monte Carlo estimate $A_{\text{period}} = 0.675 \pm 0.002$ of Ref. [7].

IV. CONCLUSIONS

Simple scaling arguments given in de Gennes' book determine the the free energy of a long flexible polymer in a tube apart from a dimensionless universal constant A. Since the early 1970's one has known that long polymer chains are related to the magnetic n-vector model near criticality. We were interested in learning whether A can be expressed in terms of well-known universal exponents and amplitudes in critical phenomena. Our main results, given in Eqs. (3), (14), and (23), relate A to the correlation length of the magnetic model and to the largest eigenvalue of the polymer transfer

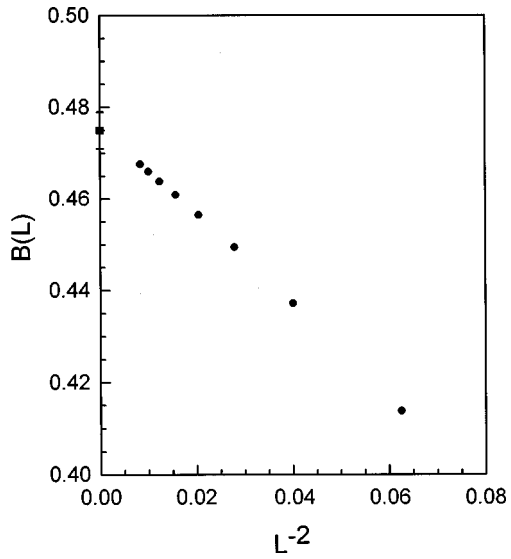

FIG. 4. The quantity $B(L)$ defined in Eq. (35) for periodic (cylindrical) boundary conditions. The square point with error bars on the vertical axis is the Monte Carlo estimate $B=0.475\pm0.004$ of Ref. [7].

matrix. From these formulas A does not appear to be one of the familiar universal quantities in critical phenomena. However, standard finite-size scaling for the correlation length implies that A is indeed universal.

Equations (14) and (23) provide a useful starting point for calculating A with transfer-matrix finite-size scaling. For self-avoiding walks on the surface of a cylinder we obtain $A_{\text{period}}=0.676\pm0.001$ and $B=0.474\pm0.001$ for the universal constants defined in Eqs. (1) and (33), in excellent agreement with Monte Carlo results [7]. For free (hard-wall) and critically absorbing boundaries we predict $A_{\text{free}}=2.12\pm0.01$ and $A_{\text{crit ads}}=-0.129\pm0.001$. That $A_{\text{free}}>A_{\text{period}}$ is physically reasonable, since hard walls confine the polymer more tightly confined than periodic boundaries, resulting in a lower conformational entropy. For critically absorbing boundaries $A_{\text{crit ads}}<0$, i.e., the energetic advantage of confinement outweighs the entropic disadvantage.

We are unaware of any estimates of the universal amplitude A in three dimensions. Milchev *et al.* [20] have carried out Monte Carlo simulations of a polymer chain in a three-dimensional tube with a square cross section. They show how an attractive short-range interaction between the monomers and tube walls affects the longitudinal and transverse dimensions of the polymer and the monomer density profile. Stilck [21] has recently analyzed the density profile of two-dimensional polymers on strips with a numerical transfer-matrix approach similar to our own.

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