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Exactly solvable model with stable and metastable states for a polymer chain near an adsorbing surface

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We report on the conformational properties and transitions of an ideal polymer chain near a solid surface. The chain is tethered with one of its ends at distance z_0 from an adsorbing surface. The surface is characterized by an adsorption parameter c. The exact expression for the partition function is available. We obtained the distribution of complex zeros of this function. The comparison with the Yang-Lee theory allows the characterization of the phase transitions. A first-order conformational transition from a coil to a (adsorbed) flower conformation occurs at $c^* = 6z_0/N$. The flower is composed of a strongly stretched stem and a pancake that collects the remaining adsorbed segments. The degree of stretching of the coil or of the stem serves as an order parameter which parametrizes the analytical expressions of the Landau free energy. The phase diagram with one binodal and two spinodal lines is presented. The height of the barriers between metastable and stable states is obtained and the lifetime of metastable states is estimated. A two-state ansatz is used to develop scaling arguments to account for the effects of excluded volume.

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I. INTRODUCTION

Polymer chains at an interface can undergo conformational phase transitions. One of the classical examples is the escape transition of a chain end grafted onto a substrate squeezed by a piston [1,2]. The conformations go jumplike from a confined "mushroom" to an inhomogeneously partially confined "flower." The flower has a stretched chain fragment, which is called the "stem," and an undeformed coil-like chain fragment, the "crown," and may be considered as a different type of chain conformation. Other single chain conformational transitions were studied for polymers near a liquid-liquid interface [3]. In the limit of infinite chain length a conformational transition from a confined coil to a partially escaped flower becomes first order. For a system with a first-order phase transition one can typically identify stable and unstable states of the system. The focus in this paper is, however, on states in between these, which are called metastable.

The term "metastable" is a combination of the Greek word *meta*, which means change of state, and the Latin word *stabilis*, which means stable. This terminology was introduced by Ostwald [4] in 1897 for a state of matter which precedes a stable state. Ostwald considered metastable states as a fundamental property of matter. From a thermodynamic point of view metastable states correspond to local minima of the free energy where the system is stable with respect to small fluctuations. This minimum is not the lowest one and a metastable state decays with a finite lifetime albeit that this lifetime may be very long.

As told, the existence of metastable states is usually associated with first-order phase transitions. The decay of a metastable phase proceeds by the formation of nuclei of the stable phase and their subsequent growth. For a supercooled gas, these are liquid droplets. The lifetime of a metastable state is determined by the nucleation kinetics, which is mostly controlled by the nucleation barrier.

Metastable states are especially important for polymer systems. The relaxation of a metastable conformation involves the reorganization of many segments of the chain, and this is intrinsically slow. A rigorous description of metastable states in polymer systems is an outstanding problem of statistical physics. The difficulty lies in finding the stable and metastable domains in a multidimensional phase space as well as the height of the barrier that separates them. A strategic direction in treating these problems involves introducing an order parameter and the Landau free energy [5]. Typically, the order parameter has to be defined as a local fluctuating quantity. According to fluctuation theory of phase transitions, the height of the barrier is associated with the Ginzburg number. The Ginzburg number characterizes the intensity of the interactions of correlated fluctuations of the order parameter. When this number is small, self-consistent-field theory works. In the general case, when the Ginzburg number is not small, the problem becomes mathematically extremely involved. Typically, the functional form of the Landau free energy has always been postulated on very general grounds, i.e., as a series expansion in the order parameter with phenomenological coefficients. An exact analytical calculation for a given model is a route which is followed in extremely few cases in the literature. One of the problems is to identify the order parameter in the problem. There are no general guidelines available for doing this.

The aim of this paper is to present a simple model of an

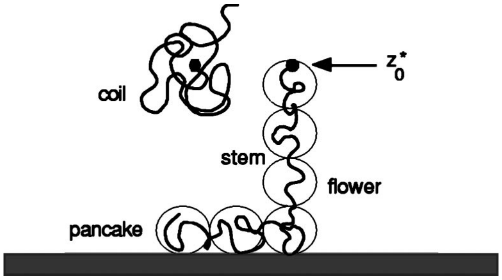

FIG. 1. Illustration of the systems of interest. An isolated Gaussian chain is fixed with one of its ends at a position z_0 above an impenetrable adsorbing surface. The tether points are indicated by the black dots. The (close to) unperturbed coil and the flower conformation are indicated. The flower is composed of a strongly stretched stem and an adsorbed fragment, i.e., the pancake. At some critical coordinate z_0^* two conformations can be equally likely, i.e., the coil and the flower. For $z_0 < z_0^*$ the flower is the preferred state. The thin spheres are drawn to assist the scaling arguments.

ideal chain near a surface. We will show that for this model the stretching of the chain is a useful order parameter. This order parameter characterizes a polymer chain as a whole. As a result the correlations of fluctuations of the order parameter are coupled throughout the whole system and the Ginzburg number is strictly zero. In other words, the system features mean-field behavior. As a result it is possible to elaborate on the route specified above by using the Landau free energy similarly as was done in a very limited number of cases in the literature for closely related problems [3,6,7].

The remainder of this paper is the following. First we will elaborate on various variants of the model that feature conformational coil-to-flower transitions. From the analogy with systems with similar type of conformational transitions, it is possible to conjecture a scaling analysis and account for excluded-volume effects even before the exact results are analyzed. Then we will proceed with presenting results that can be derived from the exact partition functions. Our goal is to collect a complete set of important results for the model. These include the analysis of the distribution of complex zeros. Apart from a rigorous classification of the phase transitions, it gives an idea for the order parameter in the system. Using this order parameter we can elaborate on the Landau function. This will give the full phase diagram and allows us to analyze the barriers between the stable and metastable states, including finite chain length effects. From these barriers it is possible to analyze the lifetime of the system in the metastable states. At the end of the paper we will mention the analogy of the present model with strongly related problems and discuss the chances to measure conformational transitions by AFM experiments.

II. IDEAL CHAIN NEAR ADSORBING SURFACE

Basically we will consider conformational properties of ideal, isolated polymer chains as schematically presented in Fig. 1. In the model, one chain end is fixed to a preset coordinate. We refer to the coordinate for the tethered end as z_0 and choose typically $z_0 > R$, where R is the radius of gyration of the chain, $R = \sqrt{(N/6)}$. Further we take $z_N < z_0$. All other segments in the chain are not confined and therefore the chain of interest can assume many different conformations. Not all possible conformations are equally likely, because there is, in the proximity of the chain, an impenetrable surface with which the polymer chain can interact. We will consider the case in which the polymer segments are attracted to the surface, i.e., that the enthalpic interaction energy exceeds a critical value. The solvent-mediated interaction between the surface and the polymer segments is described by the adsorption parameter c. All the energy parameters are expressed in k_BT units and the segment length b serves as the unit distance.

Let us consider an ideal Gaussian chain consisting of N segments tethered by one end at a distance z_0 from the solid-liquid planar surface and with the other end in z. Only the direction normal to the surface, z axis, is of interest here, since the walk in the x-y plane is unconstrained and therefore described by the standard Gaussian function. The statistical weight $G(N,z_0,z)$ of a chain with the end segments at distances z_0 and z from the interface satisfies the diffusion equation [8]

$$\frac{\partial G(N,z_0,z)}{\partial N} - \frac{1}{6}\frac{\partial^2 G(N,z_0,z)}{\partial z^2} = 0 \tag{1}$$

with the initial condition $G(N,z_0,z) = \delta(z - z_0)$. The short-ranged interaction with the surface is introduced through the de Gennes [9] boundary condition

$$\frac{1}{G(N,z_0,z)}\left.\frac{\partial G(N,z_0,z)}{\partial z}\right|_{z=0} = -c. \tag{2}$$

The physical meaning of c can easily be derived from Eq. (2). When $c < 0$ the function G increases with z and this means that the chain molecule avoids the surface. In the other limit $c > 0$ the polymers stick to the surface and the crossover value $c = 0$ corresponds to the critical conditions. We will consider the strong adsorption case only.

The solution of Eqs. (1) and (2) first found by Lepine and Caille [10] and later by Eisenriegler *et al.* [11] is naturally expressed in reduced variables $Z = z/2R$, $Z_0 = z_0/2R$, and $C = cR$. It can be presented to be composed of two contributions, i.e., one from the coil conformations, G_{coil}, and one from the flower conformations, G_{fl},

$$G(Z_0,Z,C) = G_{coil}(Z_0,Z) + G_{fl}(Z_0,Z,C), \tag{3}$$

where the coil contribution contains all possible conformations of the chain starting at coordinate Z_0 and ending at Z without touching the surface even once,

$$G_{coil}(Z,Z_0) = \frac{1}{2R\sqrt{\pi}}\{\exp[-(Z-Z_0)^2] - \exp[-(Z+Z_0)^2]\} \tag{4}$$

and G_{fl} collects all conformations that touch the surface at least once,

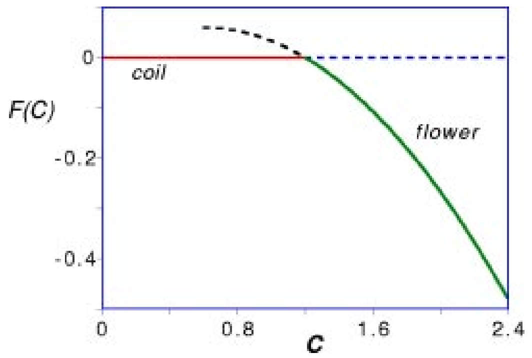

FIG. 2. Free energy of the system as a function of the reduced adsorption energy C. Two branches, coil and flower, of the free energy are drawn. The crossing point, i.e., the binodal, is indicated. The dashed line correspond to the metastable extensions of the free energy. Here we have taken $z_0/N=0.2$.

$$G_{fl}(Z,Z_0,C)=\frac{\exp[-(Z+Z_0)^2]}{R\sqrt{\pi}}[1+\sqrt{\pi}CY(Z+Z_0-C)]. \tag{5}$$

In these equations, the notation of the end-point distribution G has been modified to indicated the use of the reduced variables. For clarity we also introduced the variable C in the arguments of G_{fl} in addition to the arguments used for G in Eqs. (1) and (2). In Eq. (5) the function $Y(x)=\exp(x^2)\mathrm{erfc}(x)$. When $x\gg 1$ we can approximate $Y(x)\approx 1/(x\sqrt{\pi})$, when $x\ll -1$ the limiting behavior is $Y(x)\approx 2\exp(x^2)$, and in between these cases, i.e., when $|x|\ll 1$, $Y(x)\approx 1-2x/\sqrt{\pi}$.

After integration over all coordinates of the Nth segment the partition function $Q(Z_0,C)$ for a chain tethered with one end at Z_0 is found:

$$\begin{aligned} Q(Z_0,C)&=Q_{coil}(Z_0)+Q_{fl}(Z_0,C)\\ &=\mathrm{erf}(Z_0)+\exp(-Z_0^2)Y(Z_0-C). \end{aligned} \tag{6}$$

The partition function $Q_{coil}(Z_0)$ describes the state of a weakly perturbed coil, having no contacts with the adsorbing surface, while $Q_{fl}(Z_0,C)$ describes the sum over all inhomogeneous conformations consisting of an adsorbed part with at least one contact and a stretched stem connecting the grafting point and the adsorbing surface.

The free energy corresponding to the coil and flower partition functions are obtained from Eq. (6). For fixed $Z_0\gg 1$ and $C\gg 1$ we find that the two branches of the free energy cross at

$$C^*=2Z_0 \tag{7}$$

or in the original variables at $c^*=6z_0/N$. This result is identical to the scaling result given above. As the two branches of the free energy cross each other, we expect that the coil-to-flower transition is of the first-order type.

Before moving on it is useful to illustrate graphically the behavior of the free energy and how the transition comes about. In Fig. 2 it is shown that the free energy of the coil is independent of the reduced adsorption energy C. The flower conformation of course decreases with C. The continuous lines in Fig. 2 correspond to the stable parts and the dashed continuations of these lines are metastable branches of the system. The crossing point of the two lines correspond to the binodal condition as given by Eq. (7). At a given adsorption parameter, the lower branch describes the thermodynamically stable state. The analysis of the partition function does not allow us to determine whether the other branch (with a higher free energy) corresponds to a metastable or an unstable state. We will address this question below.

It is well known that when the grafting point Z_0 is placed near the surface and $c\gg 0$, we find

$$F_{ads}(0,C)=-\ln[Q(0,C)]=-c^2N/6. \tag{8}$$

This equation suggests a simple scaling picture. The adsorbed layer can, in a $1k_BT$ per blob ansatz, be presented by $Nc^2/6$ blobs. Each blob consists of $g=6/c^2$ segments. From this we find the physical meaning of the c parameter as the inverse blob size $\xi=1/c$.

It is of interest to mention that Eq. (8) shows that the effect of the adsorbing surface is similar to the effect of an external (adsorption) field u_{ads} felt by *all* the segments: $F_{ads}=u_{ads}N$, where $u_{ads}=-c^2/6$. There is a strong analogy with other systems recently discussed in the literature which have similar characteristics, e.g., the chain confined under a disk featuring the escape transition [1,2,12–19], and the coil-to-flower transition for a chain pinned near a step in the external potential [3,7,20]. From this analogy we know that the conformational transition in the model can be found from a two-state ansatz. It is of interest to briefly present the arguments to obtain the central result.

Within the two-state approach we conjecture that the chain should choose between either the coil or the flower conformation. The coil has a free energy $F_{coil}=0$ as it is the reference state. Let us assume that the flower is composed of a stem with $n=N-m$ segments and thus that there are $m=N-n$ segments in the crown. Then the free energy of the flower is given by a contribution of the stem and the disk. The first part is given by the stretching of the Gaussian chain. For the disk we use the result of Eq. (8):

$$\begin{aligned} F_{flower}(m)&=F_{stem}(N-m)+F_{ads}(m)\\ &=3H^2/2(N-m)-mc^2/6. \end{aligned} \tag{9}$$

Optimization of the free energy of the flower with respect to m gives

$$N-m=3H/c. \tag{10}$$

Inserting this result in Eq. (9) and equating this to zero, i.e., the free energy of the coil, we find that the transition takes place at $H^*=Nc/6$. Also, it is of interest that at the transition the number of segments in the stem is exactly equal to the number of segments in the disk $m^*=N/2$. It is easily shown that the blob size in the stem $\xi_{stem}=1/c=\xi_{ads}$. In Fig. 1 the blobs are indicated by thin spheres. Below we will apply the scaling approach to include excluded-volume effects.

III. COMPLEX ZEROS OF THE PARTITION FUNCTION

At a phase transition point, thermodynamic functions have a singularity, meaning that they or their derivatives have a finite or infinite discontinuity. On the other hand the partition function $Q=\Sigma_i \exp(-E_i/k_BT)$ is just a sum of exponentials and thus has no singularities as a function of external parameters. Since the free energy is the logarithm of the partition function, and the logarithmic function has a singularity at zero argument, the only possibility left is that the partition function should vanish (or at least, in some sense, tend to zero) when the system approaches the transition point. It is obvious though, that the partition function is positive and cannot be zero at any real value of external parameters. It was also realized very early that a true mathematical singularity of the free energy can develop only in the thermodynamic limit, when the number of particles tends to infinity.

The approach pioneered by Lee and Yang [21] related the singularities to complex zeros of the partition function. Their original papers dealt with the liquid-gas transition induced by the change in fugacity, so these were the analytical properties of the grand partition function in the complex plane of the fugacity (the fugacity was represented as a complex number with a real and an imaginary part) that were the object of investigation. Similarly, temperature-induced transitions should be described in terms of the zero distribution for the canonical partition function in the complex plane of the temperature (or $\beta=1/k_BT$). These are commonly called Fisher zeros [22] in order to distinguish them from the Yang-Lee zeros in the fugacity plane. Obviously, the general approach is applicable to phase transitions induced by changing any other external parameter as well.

Lee and Yang showed that for finite N the partition function can have only complex conjugated zeros but no zeros on the real positive axis. As the number of particles increases, the complex zeros come closer and closer to the real positive axis, and eventually, in the $N\rightarrow\infty$ limit, they pinch upon the real axis at the transition point. While the Yang-Lee theorem states that the zeros in the fugacity plane have to be located on a unit circle, there are no general results known for Fisher zeros. Empirical regularities show, however, that they tend to fall on smooth arcs that cross the real axis at a certain angle.

In the thermodynamic limit, the free energy and its derivatives can be represented as integrals over the continuous distribution of zeros characterized by some limiting density function. But the problem of finding the actual distribution of zeros for the partition function of even a simple model proves to be formidable. In practice, for a given model the zeros are calculated numerically for small samples and then some extrapolation is employed [23,24].

There exists a phenomenological approach relating certain features of a phase transition (amplitudes and critical indices) to the characteristics of the distribution of zeros [25], as well as scaling predictions for this distribution [26].

Assuming that the zeros concentrate on two symmetric support lines which cross the real axis at the point $\beta=\beta_c$ making an angle ω with it, Grossmann and Rosenhauer [25] were able to present an extensive classification of phase transitions and to express the main characteristics of a transition (jump magnitudes, critical indices, and amplitudes) by the density of zeros g along the support lines. They assumed that the density of zeros is a power-law function of the coordinate along the imaginary y axis: $g(y)\sim y^{1-\alpha}$. Using this assumption several cases can be distinguished, and among them the following two are relevant for our model.

(1) If $\alpha=1$, i.e., the density of zeros $g(y)$ tends to a constant at small y, then the zeros necessarily approach the real axis at a straight angle $\omega=\pi/2$ and the energy has a finite jump $\Delta E=2\pi g(0)$ upon touching the $\beta=\beta_c$ point. This obviously corresponds to a first order transition with a δ-peak singularity in the specific heat.

(2) If $\alpha=0$, the density of zeros grows linearly with y, and the support lines cross the real axis at $\omega=\pi/4$, the energy is continuous but the specific heat has a finite jump discontinuity, as in a classical mean-field second-order transition.

These predictions were supported by the exact solved model of an ideal Gaussian chain attached by one end to a planar adsorbing surface in the presence of a constant normal force applied to the free end of the chain [6]. Results of the present paper are strongly related to this paper.

From the above, it is clear that the adsorption parameter c is analogous to the inverse temperature β. And therefore it is natural to introduce the complex representation for the adsorption parameter $c=\rho\exp(i\chi)$ (where ρ is the amplitude, χ the polar coordinate, and $i=\sqrt{-1}$) in the partition functions. Here we will review the important results and refer to Appendix A for some more details.

The zeros close to the real axis (i.e., with small χ) can be numbered by an index $k=0, 1, 2, \ldots$:

$$\chi_k=\frac{\pi(2k+1)N}{6z_0^2}, \tag{11}$$

and thus the closest zero is characterized by the polar angle

$$\chi_0=\frac{\pi N}{6z_0^2}. \tag{12}$$

For a fixed value of the ratio z_0/N and increasing N, χ_0 approaches the real axis as N^{-1}. At distances of order $z_0\approx N^{1/2}$ the deviation of the polar angle from zero is on the order of unity and one certainly cannot speak of a first-order transition.

At the point of touching the real axis ($\chi\rightarrow 0$, $\rho\rightarrow 6z_0/N$), i.e., for large N, the density of zeros tends to a constant value $g_0=z_0/(2\pi N)$. According to Grossman and Rosenhauer, this falls into the category of first-order transitions with a finite jump in the energy. The magnitude of the jump must be

$$\Delta E=2\pi g(0)=z_0/N \tag{13}$$

and is a function of the grafting coordinate and the chain length only. This is an interesting result. Let us introduce a shorthand notation for the right hand side of Eq. (13):

$$s\equiv z_0/N. \tag{14}$$

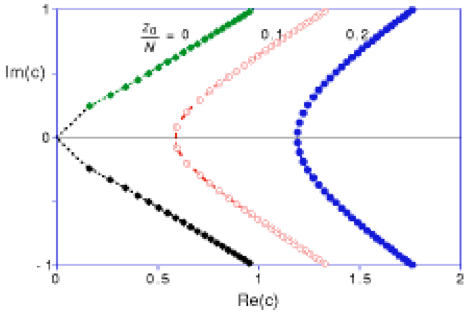

FIG. 3. The distribution of zeros in the complex plane of the adsorption parameter $c = \mathrm{Re}(c) + i\,\mathrm{Im}(c)$. The lines are drawn to guide the eye. The chain length $N=400$ and three values of the tether point $z_0/N=0$, 0.1, 0.2 are indicated. The lines are calculated using Eq. (A3).

Indeed, s can be identified as the level of stretching of the coil when it starts at z_0 and reaches the surface after N steps. In terms of an order parameter, it is known that at a first-order transition the order parameter should jump. Equation (13) indicates that s may be identified by the order parameter in the system. According to Eq. (13) the jump in the energy in the system is accompanied by a jump in the order parameter: it is close to zero when the chain is in the coil state and jumps to z_0/N after the transition. Below we will elaborate on this idea.

On the asymptotic wings of the hyperbola, $\chi \to \pi/4$ and the density of zeros increases linearly with the distance from the transition point along the curve: $g \cong \rho/(6\pi)$.

When the distance from the adsorbing plane to the grafting point, z_0, decreases, so does, accordingly, the density g_0 and the magnitude of the jump in the order parameter. Eventually, at $z_0=0$, the curve degenerates into two straight lines at an angle $\omega = \pm \pi/4$ with the crossing of the real axis at the origin. The density of zeros is then a linear function of the distance from the critical value $c=0$. Hence, the transition becomes second order, which is a well-known result.

An example of the distribution of zeros is given in Fig. 3 for a first-order and second-order transitions. In this figure the grafting distance Z_0 is varied. The complex zeros are, with increasing z_0, distributed along the support line according to the characteristics of a first-order transition. For example, the supporting line, which is drawn to guide the eye, approaches the real axis at an angle of $\pi/2$ and the density of zeros along the line go to a constant $g(0)$.

IV. AVERAGE ORDER PARAMETER

It is essential to elaborate on the selection of the order parameter. In the preceding section it was conjectured that the stretching of the chain can be used as such.

In order to choose the appropriate order parameter it is instructive to visualize a continuous transformation from the initial random coil to the inhomogeneous flower state. First, the coil is stretched so that it can reach the favorable surface. Then, a (nucleation) seed is formed at the surface. This seed grows and forms the pancake (crown) at the expense of the stem until an equilibrium state is reached. In this process, it is the chain stretching parameter that grows continuously. For the deformed coil, the parameter refers to the chain as a whole, while for the flower it refers only to the stem. Hence the order parameter s is defined as follows. For the coil state where the coordinates of the first and last segments are z_0 and z_N, respectively, we have $s=(z_0-z_N)/N$, and for the flower state, $s=z_0/n$, where n is the number of segments in the stem, i.e., the number of segments between the grafting point and the first contact with the $z=0$ boundary.

It should be realized that the number of segments in the stem is fluctuating. The average order parameter has two contributions, one from the coil state with no contacts, and the other from the flower state:

$$\langle s\rangle = \langle s_{coil}\rangle \frac{Q_{coil}}{Q(Z,C)} + \langle s_{fl}\rangle \frac{Q_{fl}}{Q(Z,C)}. \tag{15}$$

For the coil state, the stretching parameter $(z-z_0)/N$ is averaged with $G(Z,Z_0)$ of Eq. (4). The result is

$$\langle s_{coil}\rangle = -\frac{z_0}{N}\frac{\mathrm{erfc}(Z_0)}{\mathrm{erf}(Z_0)}. \tag{16}$$

To obtain the corresponding property for the flower, it is convenient to use $n=N-m$ for the number of segments in the stem. For the flower state, the averaging is performed with the weight $G_{stem}(z_0,n)Q_{ads}(c,N-n)$. Now, G_{stem} is found again from Eq. (4). For sufficient large z_0 and a very small distance $z_n=\delta$ or the second end position, we can rewrite Eq. (4) as

$$G_{stem}(z_0,\delta,n) = \frac{3\sqrt{6}}{\sqrt{\pi}} \frac{z_0\delta}{n^{3/2}} \exp\left(-\frac{3z_0^2}{2n}\right), \tag{17}$$

where $\delta = 1/6$ is an internally consistent choice. The average order parameter in the flower can thus be written as

$$\langle s_{fl}\rangle = Q_{fl}^{-1}\left(\frac{3}{2\pi}\right)^{1/2} z_0 \int_0^N dn \left(\frac{z_0}{n}\right) n^{-3/2} \times \exp\left(-\frac{3z_0^2}{2n}\right) Y(-c\sqrt{N-n}), \tag{18}$$

where Q_{fl} may be presented as

$$Q_{fl} = \left(\frac{3}{2\pi}\right)^{1/2} z_0 \int_0^N dn\, n^{-3/2} \exp\left(-\frac{3z_0^2}{2n}\right) Y(-c\sqrt{N-n}). \tag{19}$$

Combining the integral representation of the partition function Q_{fl} with the closed analytical form of Eq. (6), and using Eq. (40), one can find an exact expression in reduced variables relating the average stretching $S=sR$ to the force:

$$\langle S\rangle = \frac{Z_0}{3} + \frac{1}{3}\left(\frac{1}{\sqrt{\pi}} - Z_0 Y(Z_0) + \frac{Q_{fl}}{2Z_0 Q(Z_0,C)}\right). \tag{20}$$

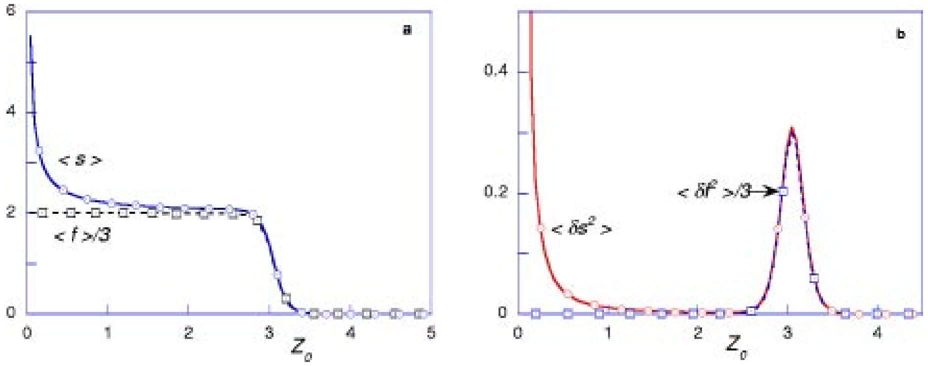

FIG. 4. (a) The average stretching $\langle s\rangle$ (order parameter) and the average (absolute value of the) force $\langle f\rangle/3$ as a function of the reduced distance $Z_0=z_0/2R$ of the grafting point. The second end is unrestricted. (b) The fluctuations of the stretching $\langle \delta s^2\rangle$ and the fluctuations of the force $\langle \delta f^2/3\rangle$ as a function of the separation. Parameters are $N=600$, $c=0.6$.

For a well-developed flower state ($C\gg 1$ and $Z_0<Z_0^*$), expression (20) simplifies to

$$\langle s\rangle \cong \frac{c}{3}\left(1+\frac{1}{cz_0}\right). \tag{21}$$

The main term corresponds to the most probable stem length while the second term represents the correction due to fluctuations. The fluctuation correction damps out with increasing z_0 and the factor $1/c=\xi_{ads}$, the adsorption correlation length, gives the amplitude of the fluctuation contribution.

In Fig. 4(a) the average order parameter (average stretching) is shown as a function of the separation $Z_0=z_0/2R$. Near the transition point the two quantities behave, as explained above, nearly the same. Only for very small grafting coordinates, there is a small noticeable difference [cf. Eq. (20)].

The squared fluctuations of the stretching function s, $\sigma^2=\langle s^2\rangle-\langle s\rangle^2$, can also be found in a closed analytical form, although the expression is quite lengthy. Therefore we choose to present the results in a graphical form only. The fluctuations in the stretching display two maxima: one at $z_0/2R\to 0$, which corresponds to a very short stem, and the other at the transition point $z_0^*/2R=c/6$ (for the parameters used in Fig. 4 this means $Z_0=3$). Here, the chain fluctuates between the coil state with effectively zero stretching and the ordered flower state. In the first region, the fluctuations can be approximated as

$$\sigma^2=\left(\frac{c}{3}\right)^2\left[\frac{\xi}{z_0}+2\left(\frac{\xi}{z_0}\right)^2\right]. \tag{22}$$

The height of the second peak is given by

$$\sigma^2_{peak}\cong\left(\frac{z_0}{N}\right)^2. \tag{23}$$

Apart from the average order parameter, Fig. 4(a) shows the average force acting on the fixed end of the chain. The force can be easily calculated from the partition function from taking the derivative with respect to the distance of the grafting point:

$$f=-\frac{\partial \ln Q(N,z_0,c)}{\partial z_0}. \tag{24}$$

Indeed the force is negative, which means that the the chain is pulled towards the surface. Here and below we will omit the minus sign of the force and present the absolute value of it. Since the average order parameter was introduced as the stretching degree, it is obvious that these two quantities are closely related. However, the properly averaged order parameter is not strictly proportional to the average force. The difference is clearly seen in Fig. 4(a). This is primarily due to the fluctuations in the number of segments that form the stem. These fluctuations are essential when the grafting point is relatively close to the surface, and the stem includes only a small fraction of all the segments. A comparison of the mean-squared fluctuations for the order parameter and the force in Fig. 4(b) demonstrates the same effect: the force fluctuations do not exhibit a maximum at small Z_0 as opposed to the fluctuations in s. The forces are discussed in much more detail below.

V. LANDAU FUNCTION

In the following we will mainly concentrate on the stable and metastable states of the first-order coil-to-flower transitions of a chain near an impenetrable surface.

The first step is to define the Landau free energy [5] in terms of the order parameter s. For the coil we use $s=(z-z_0)/N$ and Eq. (4) can be written as

$$G_{coil}(s)=\sqrt{\frac{3}{2\pi N}}\exp\left(-\frac{3}{2}Ns^2\right). \tag{25}$$

For long enough chains the Landau function $\Phi_{coil}(s)$ reduces to a simple parabolic dependence:

$$\Phi_{coil}(s)=-\frac{1}{N}\ln G_{coil}(s)\cong\frac{3}{2}s^2. \tag{26}$$

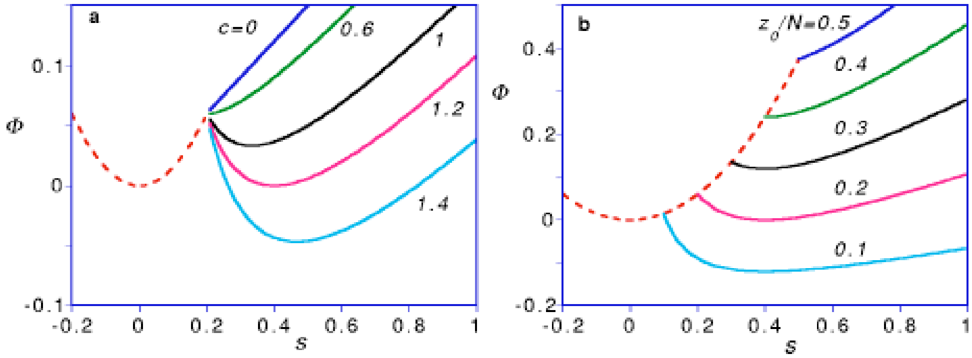

FIG. 5. The Landau free energy as a function of the order parameter s for the coil and flower conformations. (a) For fixed $z_0/N=0.2$ and several values of the adsorption parameter c as indicated. (b) For fixed adsorption parameter $c=1.2$ and for various values of the tether point z_0/N as indicated. $N=1000$ in both cases.

The maximum value of the order parameter in the coil state s_0 is achieved when the free end is just touching the surface, $s_0=z_0/N$.

The flower is an inhomogeneous conformation, and only one part of the chain is stretched. Now the order parameter is associated with the number of segments, n, in the stem, $s=z_0/n$. The Landau function is calculated as $\Phi_{fl}(z_0,n,c)=-1/N\ln[G_{\mathrm{stem}}(z_0,n)Q_{\mathrm{crown}}(N-n_1c)]$, which can be rewritten to give

$$\Phi_{fl}(s,c)=\frac{3}{2}ss_0-\frac{1}{N}\ln\left[Y\left(C\sqrt{\left(1-\frac{s_0}{s}\right)}\right)\right]-\frac{1}{2N}\ln\left(\frac{3Ns_0}{2\pi s}\right). \tag{27}$$

In the thermodynamic limit, the flower branch simplifies to

$$\Phi_{fl}(s,c)=\frac{3}{2}ss_0-\frac{c^2}{6}\left(1-\frac{s_0}{s}\right). \tag{28}$$

The discussion of the Landau function is facilitated by illustrations in graphical form. In Fig. 5(a) results are presented for the Landau free energy as a function of the order parameter for various values of the adsorption parameter and for a fixed grafting coordinate. From this graph it is easily seen that the two branches of the Landau function match at $s=s_0$. Neither the coil state branch nor the point s_0 where two branches meet depend on the adsorption parameter c, while the flower state branch is of course affected by it. With increasing affinity for the surface, the minimum in the flower branch becomes more pronounced.

In Fig. 5(b) the other control parameter z_0 is varied and c is fixed. Again, the Landau function of the coil remains the same, i.e., it does not depend on the control parameter, but now the point where the two branches of the Landau function cross is a function of z_0.

The minimum of the Landau function determines the average value of the order parameter in the (local) minimum of the system. The binodal condition is found when the two minima of the Landau function are equally deep. Of course this condition can be found by either varying z_0 or c.

VI. BARRIER HEIGHTS SEPARATING STABLE AND METASTABLE STATES

The analytical expressions for the Landau function allow us to compute the height of the barrier separating the two minima. The barrier height counted from the coil state minimum is simply given by

$$\Delta_{coil}=\frac{3}{2}Ns_0^2, \tag{29}$$

and barrier height with respect to the flower state minimum is given by

$$\Delta_{fl}=\frac{3}{2}N\left(s_0-\frac{c}{3}\right)^2, \tag{30}$$

provided of course that $c>3s_0$.

It is of interest to note that $\Delta_{coil}=3z_0^2/2N$ is the free energy of stretching the chain F_{str}, while that of the flower contains the combination of the free energy of stretching and that of adsorption

$$\Delta_{fl}=\left(\sqrt{\frac{3z_0^2}{2N}}-c\sqrt{\frac{N}{6}}\right)^2=(\sqrt{F_{st}}-\sqrt{F_{ads}})^2. \tag{31}$$

The importance of the barrier height as counted from the metastable (upper) minimum is related to the kinetic aspect of the problem which we discuss below.

The first spinodal line corresponds of course to $\Delta_{fl}=0$ and thus $c^{**}=3s_0$. Formally, the second spinodal branch should be found from $\Delta_{coil}=0$. This gives $s_0^{**}=0$. This is indeed correct in the thermodynamic limit. Physically, it is obvious that at small grafting distances $z_0\sim R$ the coil can easily touch the adsorbing surface, and the metastability is lost. Therefore, the spinodal condition $s_0^{**}=1/\sqrt{N}$ is more accurate.

The evaluation of the height of the barriers is a central result of this paper. Therefore it is natural to present the predictions of Eqs. (29) and (30) also in graphical form. This is realized in Fig. 6. Some comments on these figures are in order. In Fig. 6(a) the height of the barriers is given as a function of the positional control parameter. At small sepa-

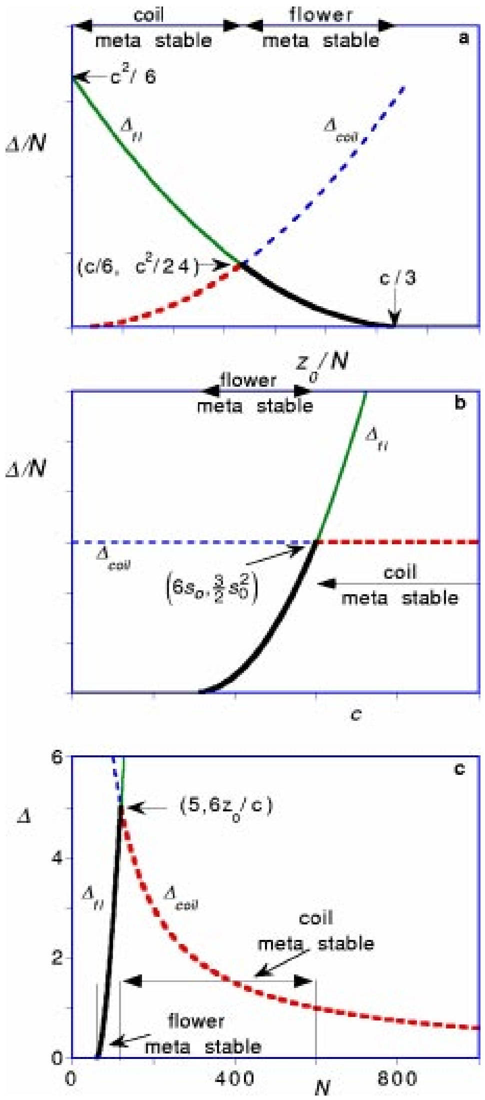

FIG. 6. (a) The reduced height of the barrier Δ/N as a function of the reduced distance z_0/N. The barrier height for the flower Δ_{fl} is drawn by a solid line and that for the coil Δ_{coil} is a dashed line. The thick parts represent the cases where the coil or the flower is stable, the thin lines correspond to the metastable states. (b) The reduced barrier height as a function of the adsorption parameter c. Line choices are similar to graph (a). (c) The barrier height Δ as a function of the degree of polymerization N for a particular choice of $z_0=20$ and $c=1$.

rations the coil is metastable and the barrier height to the other minimum increases with increasing separation. At the same time, the flower state is stable and the height of the barrier decreases with increasing distance. At the transition point (binodal) the height of the barrier is equal as counted from the coil and the flower state. At a distance further out, $z_0/N > c/3$, the barrier for the flower vanishes, and there is just one minimum.

Alternatively, in Fig. 6(b) the adsorption parameter c is the control parameter. From the above we know that the height of the barrier from the coil side does not depend on c. The height of the flower branch increases with increasing c. Again the crossing of the lines correspond to the binodal line. When $c < 3s_0$, there is no barrier for the flower any more. Between $3s_0 < c < 6s_0$ the flowers are metastable and when $c > 6s_0$ the coils are metastable.

There is yet one more variable in the problem. For a fixed value of the adsorption parameter c and grafting distance z_0 it is possible to study the effect of the molecular weight on the barrier height. An example of this is given in Fig. 6(c). The barrier height for the coil is a decreasing function of N, whereas the barrier height increases from the flower side.

The implication of the fact that there exists metastable states is the possibility to have hysteresis effects. Depending on the history of the system, the chain may be temporarily trapped in a metastable state, i.e., it can be in the metastable flower state when the free energy of the coil state is lower. The opposite can also occur, i.e., the system may be trapped in the coil state whereas the flower may be more favorable.

VII. STABLE AND METASTABLE STATES

Let us discuss in some more detail the model from a Landau free energy perspective. Within a certain range of the two governing parameters $s_0 = z_0/N$ and c, there are two minima of the Landau function. The minimum close to $s=0$ corresponds to a weakly perturbed coil and $\Phi(s_{coil}) \approx 0$. The second minimum corresponding to the flower state is found at

$$s^{fl} = c/3. \tag{32}$$

The depth of the minimum is found by inserting Eq. (32) into Eq. (27):

$$\Phi(s_{fl}) = cs_0 - c^2/6. \tag{33}$$

At the binodal condition the two minima are equally deep. This leads to

$$c^* = 6s_0. \tag{34}$$

In the thermodynamic limit $N \to \infty$, this defines the line of the first-order phase transitions. In terms of the original variables c and z_0, the coexistence line equation reads, as we discussed above, $c^* = 6z_0/N$, or in reduced variables, $C^* = 2Z_0$. In the case of $z_0 = 0$ (the chain is attached to the surface), the transition at $c=0$ becomes second order. It was shown in [6] that in the presence of a constant external end force, $c=0$ is a bicritical point.

Going away from the binodal condition by increasing the reduced grafting distance s_0 or by decreasing the adsorption parameter c, the flower state becomes metastable; the depth of the minimum for the flower is not as deep as the minimum of the coil $[\Phi(s_{fl}) > 0]$. Once the position of the flower state minimum s_{fl} coincides with the barrier position s_0, the minimum disappears completely. This gives the equation of one of the spinodal lines:

$$c^{**} = 3s_0, \tag{35}$$

or in reduced variables, $C^* = Z_0$.

To visualize metastable flower states more clearly, it is instructive to find the number of segments belonging to the

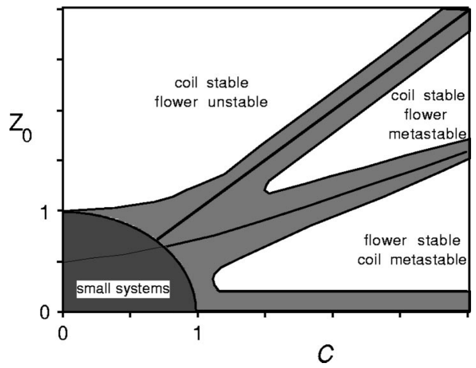

FIG. 7. Phase diagram in the reduced variables C and Z. The binodal line as well as both spinodal lines are indicated. In the region of the gray scaling the finite-size effects are important. There are a number of regions: (1) the coil is stable and the flower is unstable, (2) the coil is stable and the flower is metastable, (3) the coil is metastable and the flower is stable, (4) the coils are unstable and the flowers are stable. These regions are found going from left to right and from top to bottom. The region of small systems is near the origin ($C\leqslant 1, R\leqslant 1$).

stem in the region between the binodal and the spinodal lines. As follows from Eq. (32) and the definition of the order parameter for the flower, $s=s_0/n$, $n_{stem}=z/s_{fl}=3z_0/c$. Along the binodal line this gives $n^*_{stem}=N/2$. Along the spinodal line, $n^{**}_{stem}=N$, which means that the adsorbed crown just did not develop. We conclude that metastable flowers have more than half of the segments in the stem; the smaller the adsorbed part is, the closer we are to the spinodal.

We are now in a position to present the phase diagram of the system including the binodal and spinodal lines. The graphical presentation of this is given in Fig. 7. The binodal line separates the parameter space in regions where the flower is stable (bottom) from that where the coil is stable (top). The top spinodal line is the border line to have metastable flowers, and the bottom spinodal line indicates the loss of metastable coils. In Fig. 7 there is also a gray scaling around the binodal and spinodal lines. These correspond to the finite-size effects discussed below.

VIII. FINITE-SIZE EFFECTS

It is of interest to pay some more attention to the case of finite chain lengths because this is the experimentally accessible case.

All the above is based on the ansatz that a single macromolecule may be treated as a thermodynamic system and certain subsets of conformations are associated with phases. Clearly, one expects some deviations from this thermodynamic picture if the polymerization index is not large. We can expect, e.g., that the transition occurs more gradually. The phase behavior becomes also blurred near the transition line if the interaction parameters are small.

We have an exact analytical expression (6) for the partition function as a function of the two control variables Z_0 and C. It is obvious that the larger the values of the scaling variables are, $Z_0\geqslant 1$ and $C\geqslant 1$, the more pronounced is the phase behavior. In the Z-C phase diagram, we expect the finite-size effects to be quite pronounced in the region near the origin ($Z_0\leqslant 1$, $C\leqslant 1$).

The binodal line (with the finite-size corrections) is found from the condition that $Q_{coil}=Q_{fl}$, to give

$$Z_0^*\cong\frac{C^*}{2}+\frac{\ln 2}{2C^*} \tag{36}$$

for $C^*\geqslant 1$. In the natural coordinates this reads $z_0^*/N\cong c^*/6+\ln 2/(Nc^*)$. In the limit of $C^*\rightarrow 0$, the binodal line (which has only a formal meaning here) intersects the Z_0 axis at $Z^*=0.48$.

The width of the binodal line itself is estimated from the slope of the force distance curve $f(z_0/N)$ at the binodal. The width of the binodal region is given by the ratio of the slope of the force and the magnitude of it. The drop is

$$\Delta Z_0=\frac{\Delta f}{N(\partial f/\partial Z_0)}\sim\frac{1}{Nc^*}, \tag{37}$$

or in scaling variables $\Delta Z_0\sim 1/C^*$ [cf. Eq. (43) below]. Thus the binodal region narrows as one moves away from the origin. In Fig. 7 this is schematically drawn by the thinning of the gray region around the binodal for increasing values of C. Near the origin there is a region where both the width of the binodal as well as the value of Z_0^* is of order unity. This may be called the ‘‘small system’’ region.

The spinodal lines are also characterized by a finite effective width. This width may be estimated from the argument that when the barrier height is of order k_BT it is easily overcome by thermal fluctuations. Taking $\Delta_{fl}=1$ in Eq. (30) we find the width for the first branch of the spinodal:

$$Z_0^{**}=C^{**}+1, \tag{38}$$

or in natural coordinates, $s_0^{**}=c^{**}/3+\sqrt{2/(3N)}$.

As explained above, the finite-size effects are essential for the second spinodal line. It is found by taking $\Delta_{coil}=1$, and from Eq. (29) we find

$$s_0=\sqrt{\frac{2}{3N}} \tag{39}$$

or $Z_0^{**}=1$. Again, the coil becomes unstable once it can easily touch the adsorbing surface. Note that the width of the spinodal regions remain constant everywhere in the C-Z_0 phase diagram, in contrast to the narrowing binodal region (cf. Fig. 7).

IX. CHAIN STRETCHING AND LOCALIZATION FORCE

In the preceding part it was found that when the grafting point $z_0>R$ the coil-to-flower transition is first order. This transition has also consequences for the force needed to maintain the end point at the specified coordinate z_0.

As told above, the force can be easily calculated from the partition function [cf. Eq. (24)]. The result can best be presented in the scaling variables,

$$F=\exp(-Z_0^2)\frac{CY(Z_0-C)}{Q(Z_0,C)}, \tag{40}$$

where $F=fR$. Again, the negative sign was omitted since we are only interested in the magnitude of the force. The asymptotic behavior of the force as a function of c and z_0 in the limit of large N is quite simple:

$$F=\begin{cases} C, & Z_0<Z_0^* \\ F^*-(F^*)^2(Z_0-Z_0^*), & Z_0\approx Z_0^* \\ \pi^{-1/2}(C/Z_0)\exp(-Z_0^2), & Z_0>Z_0^*, \end{cases} \tag{41}$$

where $Z_0^*=C/2$ as before and $F^*=2C/3$ is the force at the transition point. In the thermodynamic limit $N\rightarrow\infty$ the force f exhibits a very simple behavior as a function of the c parameter:

$$f=\begin{cases} 0, & c<c^* \\ c, & c\geqslant c^*. \end{cases} \tag{42}$$

In Fig. 8(a) we give an example of the force needed to keep the chain grafted at the coordinate z_0 for several values of the adsorption parameter c. As the chain end is moved away from the adsorbing surface, the force remains constant until we approach the binodal distance z_0^*. In the vicinity of the transition point $z_0/N=c/6$ the force decreases linearly with z_0:

$$f\approx f^*-\frac{(f^*)^2}{2}(z_0-z_0^*). \tag{43}$$

At larger distances, the chain is effectively unable to reach the adsorbing surface and the force is practically zero. The slope of the force distance relation near the transition is given by $(\partial f/\partial z_0)_{z=z_o}=N(f^*)^2\approx Nc^2$. The transition thus becomes more abrupt with increasing c. The graphs presented in Fig. 8(b) show the force at a fixed (normalized) separation as a function of the adsorption strength. In the flower state, i.e., at high values of c, the force is proportional to c. The drop to virtually zero force takes place when $c<c^*$.

The description in terms of the Landau function allows us to introduce the force associated with metastable states. The force due to a metastable flower conformation is determined by the stem stretching, which is given by the position at the corresponding minimum of the Landau function $s_{fl}=c/3$. Neglecting the fluctuations in the number of segments comprising the stem, we use the simple expression relating the average force to the stretching parameter, $f=3s_{fl}$.

It follows immediately that the force associated with the metastable flower state is the same, $f=c$, as in the case when the flower state corresponds to the true equilibrium. Upon crossing one of the branches of the spinodal line, metastability is lost and the force is determined by the only stable state left. As a result, hysteresis effects can be very pronounced, as illustrated by the dashed arrows in Figs. 8(b) and 8(c).

The change in the force with the adsorption parameter c at fixed grafting distance z_0 is given in Fig. 8(b). The force is small for very small values of c, then jumps at the transition point $c^{**}=c^*/2$, and finally grows linearly with c. If the grafting distance is fixed at large enough values, $z_0\geqslant R$, one of the spinodal branches is never crossed, namely, the coil state never becomes absolutely unstable. Hence the hysteresis loop for the force in Fig. 8(b) is not closed. Both the position of the transition point and the magnitude of the jump in the force are proportional to the reduced grafting distance.

The hysteresis loop in Fig. 8(c) is completely closed. In this graph, c is fixed and the force is plotted as a function of the position of the fixed end. The force in the metastable branches eventually jump either when the coil becomes unstable, i.e., when $z_0<R$, or when the separation is just twice the value corresponding to the binodal.

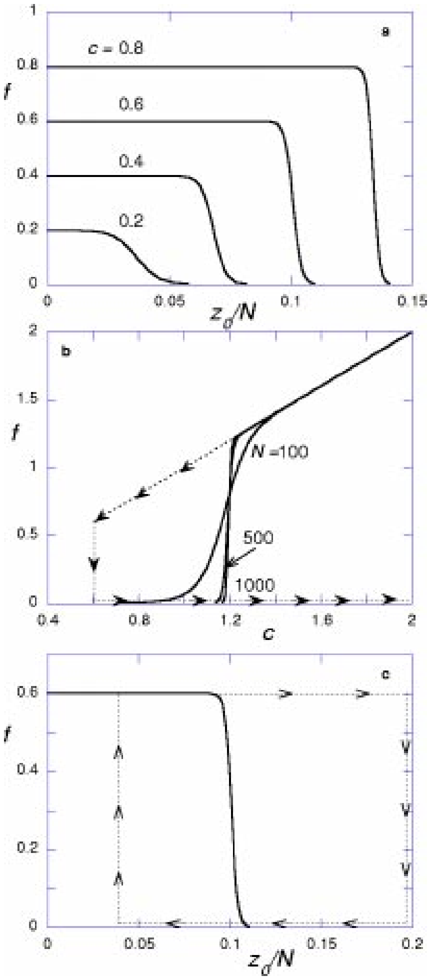

FIG. 8. (a) The force f needed to keep the tethered chain with the end at z_0 versus the reduced distance z_0/N. The sign of the force is in reality negative because the chain is attracted to the surface. Parameters are $N=1000$ and the c parameter is varied as indicated. (b) The force versus the adsorption parameter c for various values of the chain length as indicated and for $z_0/N=0.2$. The dashed lines with the arrows represent the hysteresis effects. (c) Example of a reduced force as a function of the reduced distance is presented for $c=0.6$ and $N=1000$, with special attention to the hysteresis effect indicated by the dashed lines with the arrows.

X. LIFETIME ANALYSIS

As we showed above, there exist metastable states in the vicinity of the binodal line. The spinodal condition and corresponding hysteresis effects are of course of a kinetic nature and depend on the ratio of a typical experimental measurement time and the internal relaxation time.

It is well known that the relaxation time for a process involving a barrier crossing is exponential in the barrier height. The barriers separating metastable states from the stable ones were calculated above. We expect the characteristic lifetime of a metastable coil to be of the order of $\exp(\Delta_{coil})=\exp[(3/2N)z_0^2]$, independent of the adsorption parameter c. For a metastable flower, the lifetime is expected to be of the order of $\exp(\Delta_{fl})=\exp[(N/6)(c-c^{**})^2]$. In this case, the barrier height is controlled by the proximity to the spinodal value of the adsorption parameter c^{**}.

From the point of view of potential applications, the situation when the lifetime of the metastable state is not very large may be of particular interest. In this case the estimates based only on the barrier height become too crude. A general approach for diffusion-controlled processes for polymeric systems has been put forward by de Gennes [27] and later elaborated on by Fredrickson and Leibler [28]. This machinery may be applied to coil-to-flower transitions, however we have chosen to apply the Fokker-Plank equation formalism to find a more accurate estimate for the characteristic decay time of the metastable states. A complete description of the coil-flower transition kinetics would require solving an equation in a $3N$-dimensional configuration space. However, since we are interested in the slowest process only, the problem is simplified drastically. Assuming that the slowest mode is associated with the relaxation of the order parameter and all the other degrees of freedom equilibrate quickly, we can write a one-dimensional Fokker-Plank equation for the probability density $P(s,t)$, with the Landau function $N\Phi(s)$ playing the role of the effective potential:

$$\frac{\partial}{\partial t}P(s,t)=\frac{\partial}{\partial s}D(s)\left[\frac{\partial P(s,t)}{\partial s}+P(s,t)N\frac{\partial \Phi(s)}{\partial s}\right]. \quad (44)$$

Here $D(s)$ is the diffusion coefficient along the configuration space path described by the order parameter s. The Landau function $\Phi(s)$ in the two branches is given by Eqs. (26) and (28).

Standard analysis [29,30] provides an expression for the mean first passage time τ_{coil}, i.e., the time required by the chain initially in the coil state to go to the top of the barrier:

$$\tau_{coil}=\int_0^{s_0}ds\,\frac{\exp[N\Phi_{coil}(s)]}{D(s)}\int_{-\infty}^{s}dq\,\exp[-N\Phi_{coil}(q)], \quad (45)$$

where again $s_0=z_0/N$. The usual way of dealing with this expression is to approximate the internal integral over q by extending the upper limit of integration to s_0. Then, by definition of the Landau function, it has the meaning of the partition function of the coil state, $Q_{coil}=\mathrm{erf}[s_0\sqrt{(3N/2)}]$, which can be taken out of the integral over s. $D(s)$ is the diffusion coefficient along the configuration space path described by the order parameter s.

To understand the meaning of $D(s)$, we start with the conventional translational diffusion coefficient D for the center-of-mass coordinate of a free-draining chain, which is simply given by $D=(N\zeta)^{-1}$, where ζ is the friction coefficient per segment. In this problem, we are dealing with the case that one end of the chain is fixed. For this case a single dynamic variable is associated with the end-to-end distance. The diffusion coefficient to be ascribed to the free end differs from that associated with the center-of-mass motion only by a numerical coefficient of the order of unity, which will be omitted.

Since the time required for a certain displacement is invariant with respect to the choice of the dynamic variable, $dt=(ds)^2/D(s)=(dz)^2/D$. For the coil state, $s=(z-z_0)/N$, and hence $D(s)=N^{-3}\zeta^{-1}$. Further analysis shows that in the simplest approximation, the same expression can be used for the diffusion coefficient $D(s)$ of a metastable flower.

The exponential term $\exp[N\Phi_{coil}(s)]$ is simply the inverse of the Green's function [Eq. (25)]. The final result of the integration is conveniently expressed in terms of the scaling variable Z_0:

$$\tau_{coil}=\frac{\pi}{3}\tau_{Rouse}\,\mathrm{erf}(Z_0)\mathrm{erfi}(Z_0), \quad (46)$$

where $\tau_{Rouse}=N^2\zeta$ is the Rouse fundamental relaxation time, $\mathrm{erfi}(Z_0)$ is the error function on the imaginary axis. For large values of the argument $Z_0>0$, $\mathrm{erfi}(Z_0)\sim(1/\sqrt{\pi}Z_0)\exp(Z_0^2)$. For $Z_0\gg 1$ one obtains

$$\tau_{coil}\cong\frac{\sqrt{\pi}}{3Z_0}\tau_{Rouse}\exp(\Delta_{coil}). \quad (47)$$

The situation with $Z_0\ll 1$ means that the coil state is unstable. The spinodal region corresponds to $Z_0\sim 1$, with τ_{coil} on the order of the Rouse fundamental relaxation time.

In the same approximation of replacing the internal integral by the partition function, the mean first passage time for the chain initially in the flower state, τ_{fl}, has the form

$$\tau_{fl}=\tau_{Rouse}Q_{fl}N\int_{s_0}^{s_{fl}}ds\,\exp[N\Phi_{fl}(s)]. \quad (48)$$

Using the asymptotic expansion of the integral (see Appendix B) one arrives at the following expression in the scaling variables:

$$\tau_{fl}\cong\frac{2\sqrt{\pi}}{3}\tau_{Rouse}\frac{C^{**}}{C}Y(C^{**}-C)Dw(\varepsilon C/2), \quad (49)$$

where $Dw(y)=\exp(-y^2)\int_0^y\exp(t^2)dt$ is the Dawson integral, $C^{**}=Z_0$ is the spinodal condition (excluding finite-N corrections), and $\varepsilon=1-(C^{**}/C)^2$ characterizes the relative deviation from the spinodal. Away from the spinodal, $C-C^{**}\gg 1$, the lifetime contains the expected exponential factor,

$$\tau_{fl} \cong \frac{4\sqrt{\pi}}{3}\tau_{Rouse}\frac{C^{**}}{C^2-(C^{**})^2}\exp(\Delta_{fl}). \tag{50}$$

For $C-C^{**} \leqslant 1$, the lifetime is linear in the deviation from the spinodal:

$$\tau_{fl} \cong \frac{2\sqrt{\pi}}{3}\tau_{Rouse}(C-C^{**}). \tag{51}$$

The fact that τ_{fl} vanishes when $C \rightarrow C^{**}$ simply reflects the situation where the stem comprises nearly all the segments and the adsorbed chain fragment disappears.

XI. ESTIMATION OF THE LIFETIME OF A METASTABLE STATE

It is useful to try to put some numbers to the above predictions. The elementary relaxation time of a segment (ζ, or $\zeta b^2/k_B T$ in standard units) is, for typical segment lengths and typical solvent viscosities, on the order of several nanoseconds, 10^{-8} s. This is what is seen, e.g., in polarized luminescence.

A crude estimate of the lifetime of a metastable state is the following:

$$\tau_{Rouse} \leqslant \tau \leqslant \tau_{Rouse}\exp(\Delta_{\max}), \tag{52}$$

where $\Delta_{\max}=(3/2)N(c/6)^2$ is the maximum barrier height (at the binodal line). This applies to both the metastable coil and the metastable flower.

The lower bound gives an idea of the characteristic time near a spinodal (though the lifetime may be even smaller); the upper bound provides an estimate for the lifetime of a very metastable state (almost stable).

Let us take $c=1$ as a parameter for reasonably strong adsorption, then $\Delta_{\max}=N/24$. Consequently, we arrive at the following bounds:

$$N^2\times 10^{-8}\ \text{s} \leqslant \tau \leqslant N^2\times 10^{-8}\exp(N/24)\text{s}. \tag{53}$$

For $N=100$, we arrive at 10^{-4} s $\leqslant \tau \leqslant 10^{-2}$ s, depending on how far we are from the spinodal. Similarly, for $N=500$, 10^{-3} s $\leqslant \tau \leqslant 10^{6}$ s.

For a much weaker adsorption, $c=0.2$, $\Delta_{\max}\approx(1.7\times 10^{-3})N$, so that for chains with $N<10^3$ we cannot even start to speak about metastability.

XII. EXCLUDED-VOLUME SCALING

Above, it was shown how to construct a scaling picture of the coil-to-flower transition. Again, the flower consists of a stem of n segments and the adsorbed part of $N-n$ segments. In the absence of excluded-volume effects, the free energy of the flower state has the stretching term $3z_0^2/2n$ and the adsorption term $-c^2(N-n)/6$. Minimization with respect to n gives $n=3z_0/c$. The free energy of the flower state is therefore $F_{fl}=-Nc^2/6+z_0 c$. It follows immediately that the degree of stretching of the stem is $z/n=c/3$, while the elastic force is $f=c$. The condition of stability (or metastability) of the flower means that the size of the stretching blob is equal to that of the adsorption blob: $\xi=1/f=1/c$. As the end point is moved further away from the surface, the number of blobs in the stem, z_0/ξ, grows linearly with z_0, while the blob size remains the same. The scaling picture gives the correct value for the equilibrium transition point. Equating the free energy of the flower state to that of the coil, $F_c=0$, one obtains again $z_0^*/N=c/6$. It also follows that at the binodal line, the stem comprises exactly half of the chain: $n/N=1/2$.

The scaling picture is quite useful for estimating the effect of excluded-volume interactions on the coil-to-flower transition. The flower free energy is modified to

$$F_{fl}=-B(N-n)c^{1/(1-\nu)}+A\left(\frac{z}{n^{\nu}}\right)^{1/(1-\nu)}, \tag{54}$$

where A and B are numerical coefficients [$A=3/2$ and $B=1/6$ for an ideal three-dimensional (3D) coil], and ν is the Flory exponent equal to 3/5 for chains with excluded volume and 1/2 for ideal coils. Minimization with respect to n yields

$$n=zc^{-1}\left(\frac{A\nu}{B(1-\nu)}\right)^{1-\nu}. \tag{55}$$

The free energy is given by

$$F_{fl}=-BNc^{1/(1-\nu)}+Kzc^{\nu/(1-\nu)}, \tag{56}$$

where

$$K=A^{1-\nu}B^{\nu}\left(\left(\frac{\nu}{1-\nu}\right)^{1-\nu}+\left(\frac{1-\nu}{\nu}\right)^{\nu}\right).$$

It follows that the adsorbed part still exerts a constant stretching force, which now scales as $f\sim c^{\nu/(1-\nu)}$. The equilibrium transition point (the equation of the coexistence line) reads

$$\frac{z_0^*}{N}=\frac{B}{K}c. \tag{57}$$

One can see that the excluded-volume effects do not affect the scaling form of the coexistence line. The fraction of segments in the stem at the binodal line is found to be $n^*/N=\nu$ and thus the fraction of segments in the adsorbed part equals $(N-n^*)/N=1-\nu$; both still independent of z_0 and c. The value of 1/2 is of course recovered in the Gaussian case. The spinodal conditions are modified correspondingly. One spinodal line associated with the instability of the coil state is obviously given by

$$z_0^{**}\sim R\sim N^{\nu}. \tag{58}$$

The other spinodal line, associated with the disappearance of the flower, is found from the condition that the number of segments in the stem is equal to N. Since the number of segments in the stem is linear in z_0, one can immediately obtain from the combination of Eqs. (55) and (57),

$$\frac{z_0^{**}}{z_0^*}=\frac{1}{\nu}. \tag{59}$$

The binodal and spinodal lines come closer to each other than in the case of Gaussian chains. The region where metastable flowers exist is relatively smaller, since the adsorbed part at the coexistence line comprises only $2N/5$ segments.

XIII. DISCUSSION

It is essential to reiterate that for the presented model, exact analytical results are found. We showed that it is possible to obtain the partition function in a closed form, to evaluate the distribution of the complex zeros of the partition function, and to compute the Landau free energy that controls the distribution of the order parameter. These results are available not only in the thermodynamic limit, but also for finite systems. Why is this possible? What are the main differences between this model and the classical models for low molecular-mass systems?

First, the interaction between monomeric units is taken into account only in terms of enforcing the chain connectivity. This interaction is treated separately from the very beginning and accounted for by the basic differential equation (1) for the partition function that describes a Gaussian random walk. The interaction energy is explicitly assigned to only those units that are in direct contact with the adsorbing surface. The excluded-volume interactions between non-neighboring units is neglected even if they come close to each other in space.

Second, the order parameter is defined not as a local quantity, but for the system as a whole. This is equivalent to completely correlated order parameter fluctuations within the volume of the system. This corresponds to the Ginzburg number being equal to zero.

One of the most critical points in the discussion of the Landau free energy is the identification of the order parameter. The analysis was performed with the stretching order parameter. There is yet another candidate that can serve as an order parameter in the system. Recently a closely related system has been analyzed, which features a coil-to-flower transition [20]. In this system an ideal chain was considered near a step in the external potential. In this paper the system was analyzed in terms of an order parameter, which essentially was the fraction of segments in the favorable region of the space (i.e., on the low potential side of the system). The corresponding property for the present model is the fraction of segments in direct contact with the adsorbing surface (or the number of segments in the pancake). Indeed, it is possible to analyze this quantity analytically. As expected, this quantity is sensitive to the control parameters in the system and it jumps stepwise at the transition. In the coil-to-flower transition of a chain near the stepwise external potential, there were some problems detected associated with the fraction of contacts. More specifically this problem appeared in the rolling transition [3,7]. The rolling transition is the conformational transition that occurs upon the change in sign of the external potential when the chain is grafted exactly at the point where the potential step occurs. The rolling transition is second order, but is still characterized by a jump in the contact fraction. From this it was concluded that the stretching of the chain would be a more appropriate order parameter. Indeed, the jump in s vanishes in the limit where the model features a second-order transition, i.e., when $z_0=0$.

Atomic force microscope (AFM) can be used to investigate the transitions discussed above [31–40]. In such an experiment it is necessary to graft a chain with one end at the AFM tip in such a way that the chain does not adsorb onto this tip. This chain is then brought near an adsorbing surface. Alternatively, one can glue a particle (probe) onto the AFM tip and attach the end of a chain subsequently onto the probe. In this case it is more easy to orchestrate that the chain does not stick to the probe's surface. Then, if the chain does not interact with the probe surface, it will be in a mushroom conformation when the tip is still far from the adsorbing surface. The free energy of a chain in the mushroom conformation is approximately the same as an unperturbed Gaussian chain. This means that the grafting onto the tip or onto the repulsive surface is without any consequences. With the AFM apparatus it is possible to measure the force on the chain as soon as it is in the flower conformation. In effect, the flower bridges the gap between the tip (or probe) and the adsorbing surface. For this reason one can refer to the adsorption coil-to-flower transitions as a bridging transition. The force which is easily picked up by the AFM apparatus is expected to be independent of the separation and is only a function of the adsorption parameter that characterizes the affinity of the chain for the adsorbing surface. In AFM experiments it is possible to control the time of contact (or the time of close proximity of the chain to the adsorbing surface). Therefore, one should expect to observe the hysteresis effects discussed above in full glory.

There are a number of systems that feature conformational transitions of single chains that have received some attention in recent literature. Probably the best known is the escape transition of a chain, which is again end grafted and compressed by a finite-size piston. In this case the chain can jump in a first-order way from a homogeneously confined chain, sitting between the piston and the surface, into an escaped state. The chain in the escaped state has a flowerlike conformation, where a stem is formed from the grafting point to the edge of the cylinder, and a crown collects the remaining segments in a coil-like conformation. Again, it is speculated that it is possible to measure the escape transition in an AFM experiment. However, there are a number of snags that may prevent to unravel details of the escape transition. First of all, the transition is sensitive to the exact geometry [14]. Second, some finite interaction of the polymer chain with the surfaces may seriously frustrate the observation of the escape transition [41]. Finally, the escape transition may be complicated by excluded-volume effects that become more and more important when the chain is gradually more compressed. Therefore, the bridging transition that is described above may be less difficult to detect experimentally.

The coil-to-flower transition that is described for a chain pinned with one end in the unfavorable region of a stepwise external potential is probably an even more closely related system [3,7,20]. In this problem the transition occurs from a coil, which is forced to live in the unfavorable side of the space, to an inhomogeneous conformation composed of a strongly stretched stem and a relatively unperturbed coil. The main difference is clearly with respect to entropic restrictions felt by the crown. In the step-in-external-potential system, the crown is a 3D coil, whereas in the adsorption problem the crown is more like a flat disk. Nevertheless there is a very transparent mapping of all the features discussed above and comparable results in the external potential problem. The analogy may be used to transfer even more results from one problem to the other.

XIV. CONCLUSIONS

Inhomogeneous flowerlike conformations are a rather fascinating state of polymer chains. The flowers typically occur when the chain is tethered by at least one end near an interface. A flower features a stretched chain fragment (stem) and an escaped chain part (crown) that resides in the more favorable region. A Gaussian chain attached near an adsorbing surface exemplifies a class of coil-to-flower transition. In this paper, a number of exact results for this model is obtained. The partition function, the phase diagram (one binodal and two spinodal lines), the analysis of the order of the transitions. the finite-size effects, and the complex zero distributions are among the key results.

One of the central results presented above is the evaluation of the Landau free energy. We argued that the stretching of the coil and the stretching of the stem may serve as the order parameter that parametrizes the exact analytical Landau function. The analysis of the Landau function gives information on the height of the barriers between stable and metastable states. The barriers are responsible for pronounced hysteresis effects. These effects may be found in experiments, when the time scale of the experiment is short with respect to the time needed for the system to cross the barriers from metastable states to stable states. We have estimated these characteristic times: these may be very large indeed. Experimental verification of the coil-to-flower transitions is anticipated.

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APPENDIX A: COMPLEX ZERO DISTRIBUTION

Let us start from the case when the grafting point is on the surface, i.e., $z_0 = 0$. In our model the partition function can be expressed as $Q = Y(-C) = \exp(c^2 N/6)\,\mathrm{erfc}[-c\sqrt{(N/6)}]$. We consider c to be the complex variable. The exponential function has no zeros in the entire complex plane. So we will be interested in the distribution of the zeros of the complimentary error function and particularly its asymptotical form in the limit $N \to \infty$. From a numerical analysis one will find that the zeros condense on two symmetric support lines crossing the real axis at $c = 0$ at an angle $\omega = \pi/4$ with the real axis, and that the density of zeros grows with the distance from the origin. In this limit, i.e., $z_0 = 0$ the system thus features a second-order transition.

Let us now consider the case in which the grafting point is at a positive value $z_0 > 0$. Hence, we will need to analyze $Q(z_0, c) = 0$ with $Q = \mathrm{erf}(Z_0) + \exp(-Z_0^2) Y(Z_0 - C)$ in the complex c plane. For a finite fixed z_0/N and large N this equation is equivalent to $Q = 1 + 2\exp(-zc + c^2 N/6) = 0$. Taking $c = \rho \exp(i\chi)$, we obtain two coupled equations:

$$\begin{gathered} \ln(1/2) = -z\rho\cos(\chi) + \frac{N}{6}\rho^2\cos(2\chi), \\ (2k+1)\pi = -z\rho\sin(\chi) + \frac{N}{6}\rho^2\sin(2\chi), \end{gathered} \tag{A1}$$

where $k = 0,1,2,\ldots$. From the first equation the limiting line of zeros is found by letting $N \to \infty$:

$$\rho = \frac{6\cos\chi}{\cos 2\chi}s, \tag{A2}$$

where $s = z_0/N$ as before.

In Cartesian coordinates, $x = \rho\cos\chi$, $x = \rho\sin\chi$, we can see that this curve is a hyperbola,

$$(x - 3s)^2 - y^2 = 9s^2, \tag{A3}$$

crossing the real axis at $x^* = 6s$ with a straight line.

An equation for the positions of zeros on the hyperbola follows from inserting Eq. (A2) into the second line of Eq. (A1),

$$\frac{(2k+1)\pi}{N} = 3s^2\frac{\sin 2\chi}{\cos^2 2\chi}. \tag{A4}$$

For zeros close to the real axis (i.e., with small χ) this gives

$$\chi_k = \frac{(2k+1)\pi}{6Ns^2}. \tag{A5}$$

The closest zero is characterized by the polar angle

$$\chi_0 = \frac{\pi}{6Ns^2}, \tag{A6}$$

and for fixed s, χ_0 goes to zero in the thermodynamic limit.

Let us calculate the limiting density of zeros

$$g = \lim_{N\to\infty}\frac{1}{N}\frac{\partial k}{\partial l}, \tag{A7}$$

where $dl=\sqrt{(d\rho^2+\rho^2 d\chi^2)}$ is the line element in the complex plane. It follows from the coupled equations (A1) that

$$\left(-s\sin\chi+\frac{\rho}{3}\sin 2\chi\right)d\rho + \rho\left(-s\cos\chi+\frac{\rho}{3}\cos 2\chi\right)d\chi=\frac{2\pi}{N}dk,$$
$$d\rho=\rho(2\tan 2\chi-\tan\chi)d\chi. \tag{A8}$$

After some straightforward algebra expressing $dk/d\chi$ and $dl/d\chi$ in polar coordinates, the final result appears:

$$g=\frac{1}{N}\frac{dk}{d\chi}\frac{d\chi}{dl}=\frac{\rho}{12\pi}\cos 2\chi[1+(2\tan 2\chi-\tan\chi)]^{1/2}. \tag{A9}$$

At the point where the real axis is touched ($\chi\rightarrow 0$, $\rho\rightarrow 6s$), the density of zeros tends to a constant value $g_0=s/2\pi$. According to Grossman and Rosenhauer, this falls into the category of first-order transitions with a finite jump in the energy.

On the asymptotic wings of the hyperbola $\chi\rightarrow\pi/4$, the density of zeros increases linearly with the distance from the transition point along the curve: $g\cong\rho/6\pi$. Along these wings the position of the kth zero follows from Eq. (A2):

$$\rho_k\approx\frac{3}{\sqrt{2}}s+\sqrt{\frac{9}{2}s^2+\frac{2\pi k}{N}}. \tag{A10}$$

This formula simplifies for large k, i.e., $k/N\gg s^2$, to $\rho_k\approx(2\pi k/N)^{1/2}$.

From $g_0=s/2\pi$ we conclude that g_0 goes down when the distance z_0 is decreased, i.e., the jump in the order parameter decreases. Eventually, at $z_0=0$, the curve degenerates into two straight lines at an angle $\omega=\pi/4$ with the real axis crossing the axis at the origin. The density of zeros turns out to be a linear function of the distance from the critical value $c=0$. Here the transition becomes second order, as mentioned above.

We now turn our attention to the finite-size scaling behavior of the position of zeros of the partition function. According to Itzykson *et al.* [26], in the vicinity of the critical point, the distance from the kth zero to the real axis should scale as

$$y_k\sim L^{-1/\nu}k^{1/d\nu}, \tag{A11}$$

or in terms of the total number of units N,

$$y_k\sim\left(\frac{k}{N}\right)^{1/d\nu}\sim\left(\frac{k}{N}\right)^{1/(2-\alpha)}. \tag{A12}$$

Here we have employed the equality $d\nu=2-\alpha$ to pass from parameters d and ν, which do not have a well-defined meaning in our case, to the heat capacity index α. For a second-order transition $\alpha=0$. Taking this value, we arrive at the scaling prediction $y_k\sim(k/N)^{1/2}$, in accordance with the exact analytical result of Eq. (A10). For a first-order transition $\alpha=1$. As from Eq. (A2), $y_k\approx 6s\chi_k$, and using Eqs. (A5) we find $y_k\sim(k/N)2\pi/s$. Indeed this is consistent with the scaling [cf. Eq. (A12)].

The complex zero distribution gives also the possibility to analyze the region where finite-size effects are important and where this is not the case. Above we found that the closest zero is characterized by the polar angle $\chi_0=\pi/(6Ns^2)$. Finite-size effects smooth out the difference between first-order and second-order transitions. For this to be true, even the closest zero should lie not far from the asymptotic wings of the hyperbola: $\chi_0=1$. This means that $Ns_0^2\sim 1$ and thus $s_0\sim N^{-1/2}$. This is in accordance with the finite-size effects analysis given above.

APPENDIX B: LIFETIME OF METASTABLE FLOWER STATE

We start with a rigorous expression for the mean first passage time from the flower state to the barrier top:

$$\tau_{fl}=\int_{s_0}^{s_{fl}}ds\frac{\exp[N\Phi_{fl}(s)]}{D_{fl}(s)}\int_s^{\infty}dq\exp[-N\Phi_{fl}(q)], \tag{B1}$$

where $s=s_{fl}$ is the location of the minimum of the flower branch of the Landau function, and $s=s_0$ is the location of the top of the barrier. Following the standard procedure, we approximate the internal integral over q by a constant, namely, by the value of this integral at the barrier top, $s=s_0$. The vicinity of this point provides the most important contribution for the second integration, while the internal integral changes very slowly with s in this region:

$$\tau_{fl}=Q_{fl}\int_{s_0}^{s_{fl}}ds\frac{\exp[N\Phi_{fl}(s)]}{D_{fl}(s)}, \tag{B2}$$

where $Q_{fl}=\int_{s_0}^{\infty}dq\exp[-N\Phi_{fl}(q)]=\exp(-Z^2)Y(Z-C)$.

Using Eq. (27) for $\Phi_{fl}(s)$ and making the simplest assumption about the diffusion coefficient $[D_{fl}(s)]^{-1}=[D_{coil}(s)]^{-1}=\zeta N^3=N\tau_{Rouse}$, we obtain

$$\tau_{fl}=\tau_{Rouse}N\sqrt{\frac{2\pi}{3z}}\exp(-Z^2)Y(Z-C)\times\int_{s_0}^{s_{fl}}ds\sqrt{s}\exp[-N\Phi_{fl}(s)]. \tag{B3}$$

The next approximation is based on representing $\Phi_{fl}(s)$ by its Taylor expansion around the barrier top:

$$\Phi_{fl}(s)=\frac{3}{2}s_0s-\frac{c^2}{6}+\frac{c^2s_0}{6s}\approx\frac{3}{2}s_0^2-a(s-s_0)+b(s-s_0)^2 \tag{B4}$$

with

$$a=\frac{c^2}{6s_0}-\frac{3}{2}s_0=\frac{1}{2}\left(\frac{c^2}{c^{**}}-c^{**}\right)$$

and

$$b=\frac{c^2}{6s_0^2}=\frac{3}{2}\left(\frac{c}{c^{**}}\right)^2.$$

The upper limit of integration is now taken as the location of the minimum of the approximated Landau function $s_{\min}=a/2b$.

According to the standard procedure of asymptotic integration, the nonexponential term $\sqrt{s}$ in Eq. (B3) is taken as a constant $\sqrt{s_0}$. Changing the integration variable $q=s-s_0$, we arrive at an integral of the form

$$\begin{aligned}\int_0^{a/2b} dq\,\exp(-Naq+Nbq^2) &= \sqrt{\frac{\pi}{4Nb}}\exp\left(-N\frac{a^2}{4b}\right)\operatorname{erfi}\left(\frac{a\sqrt{N}}{2\sqrt{b}}\right)\\ &\equiv \frac{1}{\sqrt{Nb}}Dw\left(\frac{a\sqrt{N}}{2\sqrt{b}}\right),\end{aligned} \tag{B5}$$

where $Dw(y)=\exp(-y^2)\int_0^y dq\,\exp(q^2)$ is Dawson's integral. Substituting

$$\frac{a\sqrt{N}}{2\sqrt{b}}=\frac{1}{2}\sqrt{\frac{N}{6}}c\left(1-\frac{(c^{**})^2}{c^2}\right)$$

in Eq. (B3) we finally arrive at Eq. (49) used above.

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