Adsorption of a macromolecule in an external field: An exactly solvable model with bicritical behavior

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We introduce a model of an adsorbing polymer chain in an external field, which admits exact analytical solution for the partition function for a finite number of the units, N. In the thermodynamic limit, the system has an isotropic and two ordered phases, exhibits continuous and discontinuous phase transitions, and has a bicritical point. We obtain exact expressions for the Landau free energy as a function of an order parameter in the vicinity of the first- and second-order phase transition lines, and compare them to the original theory. The Landau free energy is also calculated as a function of two independent order parameters in the vicinity of the bicritical point. The distribution of complex zeros of the partition function is found for both first- and second-order transitions. In the thermodynamic limit it is described by exact analytical expressions, allowing a comparison to the existing phenomenological results within the framework of the Yang-Lee-Fisher approach. An advantage of the model presented is that the partition function can be calculated analytically not only in the thermodynamic limit, but for finite N as well. The ideas of finite-size scaling analysis are checked against the exact solution, in terms of both the functional form of the free energy and the N dependence of the distribution of Fisher zeros. [S1063-651X(97)04908-8]

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I. INTRODUCTION

Historically, the question of whether statistical mechanics is applicable to phase transitions has been debated extensively [1]. Onsager's solution showed that the description of phase transitions is indeed contained in the exact partition function. A lot more has been learned since then about the physics and mathematics of phase transitions. It is remarkable though how modest is the number of exact solutions [2] that would allow one to follow the details of these fascinating phenomena without making *a priori* assumptions. First, there are a few two-dimensional lattice models (Ising, eight-vertex, three-spin, and segnetoelectric). Then there are two somewhat more artificial models: the one introduced by Kac with infinitely weak, infinitely long-range interaction, and the spherical model corresponding to the infinite number of spin components (see [2] for the references). The models mentioned admit exact solution in the thermodynamic limit $N \to \infty$, where N is the number of particles in the system (finite-size corrections are available for the Ising model.) Only some of these models are solved in the presence of the external field.

A number of models from polymer physics can be added. Unlike in the conventional low-molecular-weight systems, the particles in a polymeric material are irreversibly con-nected to form linear chains, thus introducing a "linear memory" effect [3]. Generally speaking this brings about more complications and more possibilities for different kinds of phase transitions. On the other hand, the bonding interactions can be singled out to be treated in a separate way. Once this is done, even most simplified models exhibit nontrivial behavior that could be absent in their low-molecular-weight counterparts. One should also bear in mind that it is physically meaningful to speak of phase transitions even for a single macromolecule, since the number of monomeric units N in it could be very large indeed. Exact solutions describing phase transitions are known for the Zwanzig-Lauritzen model of two-dimensional β-structure formation [4] and for some closely related models of directed polymer adsorption [5]. Another inherently related set consists of the DNA melting model [6] and the model of adsorption of an ideal chain on surfaces of different geometry (planar and cylindrical) [7,8].

Apart from the few exact solutions, more general approaches exist. Ideas of Landau [9] proved invaluable in clarifying the essential background of phase transitions. Although it was recognized early enough that the assumption of analyticity of the free energy as a function of order parameter in the original version is equivalent to the mean-field approximation and is generally incorrect, the Landau-Ginzburg formulation, which incorporates local fluctuations of the order parameter, eventually leads to the fluctuation theory of critical phenomena. On the other hand, the functional form of the Landau free energy has always been postulated on very general grounds, while its exact analytical calculation

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for a given model remains too rare a feat (in fact, we cannot think of any example.)

Another approach goes back to the 1952 paper by Yang and Lee [10], and is based on representing the partition function in terms of its zeros in the complex plane of chemical potential (or temperature, as suggested by Fisher [1]). The theory is mathematically rigorous, which brings about a hefty price to be paid: the problem of finding the actual distribution of zeros for the partition function of even a simple model proves to be formidable. There exists a phenomenological approach relating certain features of a phase transition (amplitudes and critical indices) to the characteristics of the distribution of zeros assumed to be known [11], as well as scaling predictions for this distribution [12]. In practice, for a given model the zeros are calculated numerically for small samples, and then some extrapolations are employed [13].

Relationship between various approaches to phase transitions is not clearly understood and, to the authors' best knowledge, has never been demonstrated on one and the same microscopic model. This is exactly the cause pursued in the present paper. We introduce a model of an adsorbing polymer chain in an external field that admits analytical solution for the partition function. In the thermodynamic limit, the system has an isotropic and two ordered phases (described by two order parameters), exhibits continuous and discontinuous phase transitions, and has a bicritical point. We obtain exact expressions for the Landau free energy as a function of order parameters in the vicinity of phase transition lines, and compare them to the original theory. Moreover, the model allows one to write the Landau free energy as a function of two independent order parameters in the vicinity of the bicritical point. Finally, we find the distribution of complex zeros of the partition function for both the first- and second-order transitions. By the same good fortune, in the thermodynamic limit it is also described by exact analytical expressions allowing a comparison to the existing phenomenological results within the framework of the Yang-Lee-Fisher approach.

Another advantage of the model presented is that the partition function can be calculated analytically not only in the thermodynamic limit $N \to \infty$, but for finite N as well. Therefore, the ideas of the finite-size scaling analysis can be checked against the exact solution, in terms of both the functional form of the free energy and the N dependence of the distribution of Fisher zeros.

We would like to stress that the main interest of the model presented here lies not in some excitingly unexpected new exact results—the model itself is perhaps too simplistic for that (for example, the second-order transitions turn out to be of the mean-field type). Rather, it is the possibility of carrying out analytical results to the very end within the framework of different approaches, and being able to see the inside story of those miraculous workings of nature called phase transitions that make the model ideal for the purposes of instruction and sharpening one's intuition.

II. POLYMER MODEL: PARTITION FUNCTION, SYMMETRY PROPERTY

We consider an ideal Gaussian chain consisting of N segments attached by one end to a planar surface. The translational entropy of the chain as a whole does not come into play. A short-range adsorption interaction exists between the chain segments and the surface. A constant force f normal to the surface is applied to the free end of the chain. Our consideration is based on a random walk model whereby a configuration of a polymeric chain is represented by an N-step walk [14]. 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 a standard Gaussian function. In the continuum limit, the statistical weight $P(N,z)$ of a chain with the Nth segment at distance z from the plane in the absence of the end force satisfies the equation [14,15]

$$\frac{\partial}{\partial N} P(z|N) - \frac{l^2}{6} \frac{\partial^2}{\partial z^2} P(z|N) = 0, \tag{1}$$

with the initial condition $P(z|0) = \delta(z)$ describing the fact that one end of the chain is attached to the plane at $z = 0$. (Of course, there is also the trivial factor equal to the total number of unconstrained N-step random walks.)

The problem can be mapped onto the Schrödinger equation for the Green's function of a quantum particle of mass $3/l^2$ located initially at the plane, by taking $\hbar = 1$, $t = iN$. Henceforth, we take the segment length as the unit length, $l = 1$, and express energy in kT units. The short-ranged interaction with the plane is introduced through the boundary condition [16]

$$\frac{1}{P(z|N)} \frac{\partial}{\partial z} P(z|N) \bigg|_{z=0} = -c, \tag{2}$$

the same as that which appears for the Schrödinger equation in the presence of a δ-functional pseudopotential. Mathematically, adsorption corresponds to the existence of a bound state in the corresponding quantum-mechanical problem. When $c > 0$, the macromolecule tends to stick to the surface; for $c < 0$ it is desorbed. The value $c = 0$ corresponds to what is called the critical adsorption condition. The physical meaning of the c parameter was discussed in Refs. [16, 17].

The solution of Eqs. (1) and (2) for the partition function of the macromolecule with ends fixed was obtained by Lepine and Caille [8] and is naturally expressed in terms of scaled variables $\widetilde{z} = z/2R$, $\widetilde{c} = cR$, where $R = (N/6)^{1/2}$ is the root-mean-square radius of gyration of an ideal chain in an unconstrained state:

$$P(\widetilde{z}|\widetilde{c}) = (\pi R^2)^{-1/2} \exp(-\widetilde{z}^2)\{1 + \pi^{1/2} \widetilde{c} Y(\widetilde{z} - \widetilde{c})\}. \tag{3}$$

Here $Y(t) = \exp(t^2) \mathrm{erfc}(t)$, $\mathrm{erfc}(t)$ being the complementary error function.

The presence of the external end force f will change the statistical weight of every random walk by the Boltzmann factor $\exp(fz)$. Since it is the same for all random walks ending at the same height z, the partition function of the end-force problem is simply $P(\widetilde{z}|\widetilde{c})\exp(fz)$. Positive f corresponds to stretching the chain while negative f presses the free chain end down to the surface. Introducing the scaling variable $\widetilde{f} = fR$, one arrives at

$$P(\widetilde{z}\,|\,\widetilde{c},\widetilde{f}) = (\pi R^2)^{-1/2}\exp[\widetilde{f}^2 - (\widetilde{z}-\widetilde{f})^2]$$
$$\times \{1 + \pi^{1/2}\widetilde{c}\,Y(\widetilde{z}-\widetilde{c})\}. \qquad (4)$$

Integrating P over the position of the free end gives the partition function [17]

$$Z(\widetilde{c},\widetilde{f}) = \frac{\widetilde{c}\,Y(-\widetilde{c}) - \widetilde{f}\,Y(-\widetilde{f})}{(\widetilde{c}-\widetilde{f})}. \qquad (5)$$

The average height of the free end is $\langle z\rangle = R\partial \ln Z/\partial\widetilde{f}$. Since the average number of adsorbed segments (the number of contacts with the plane) is conjugated to the adsorption parameter c [16] one obtains similarly $\langle m\rangle = R\partial \ln Z/\partial\widetilde{c}$. Equation (5) for the partition function of an adsorbing chain with the external field present is remarkably symmetric with respect to interchange of the adsorption parameter $\widetilde{c}$ and the reduced force $\widetilde{f}$. One can say that in a certain strict sense, the effect of adsorption is equivalent to the effect of applying the end force [18]. The average number of adsorbed segments $\langle m\rangle$ as a function of the adsorption interaction parameter c and the force f is the same as the height of the chain end as a function of the interchanged variables: $\langle m\rangle(c,f) = \langle z\rangle(f,c)$. We recall that in terms of conventional units, the dimensionless combinations are m, z/l, cl, and fl/kT.

A stronger consequence of the partition function symmetry is that not only the mean values but all the moments of the probability densities for m and z coincide under the interchange of the conjugated parameters $c\leftrightarrow f$. Therefore, the probability densities themselves, being well-behaved quickly decreasing functions, should coincide under this interchange. The partition function for a given scaled number of adsorbed segments follows from Eq. (4) to be

$$P(\widetilde{m}\,|\,\widetilde{c},\widetilde{f}) = (\pi R^2)^{-1/2}\exp[\widetilde{c}^2 - (\widetilde{m}-\widetilde{c})^2]$$
$$\times \{1 + \pi^{1/2}\widetilde{f}\,Y(\widetilde{m}-\widetilde{f})\}, \qquad (6)$$

where $\widetilde{m} = m/2R$.

A question arises if the symmetry of the partition function could be traced to that of the underlying Hamiltonian. The Hamiltonian of a Gaussian chain interacting with a planar surface via a δ-functional pseudopotential in the presence of the constant end force can be written following Refs. [15, 19]. If the conformation of the chain is specified by the position vector function $\mathbf{r}(s)$, s being the distance along the contour of the chain, then

$$H\{\mathbf{r}(s)\} = \frac{3}{2}\int_0^N ds \left|\frac{d\mathbf{r}}{ds}\right|^2 + \int_0^N ds \left(c\,\delta(z(s)) - f\frac{dz}{ds}\right). \qquad (7)$$

Here, $z(s)$ is the normal component of the vector $\mathbf{r}(s)$. This form of H does not display any obvious symmetry with respect to the interchange of c and f. It would be quite rewarding to find a transformation revealing this symmetry but for now we leave the question open.
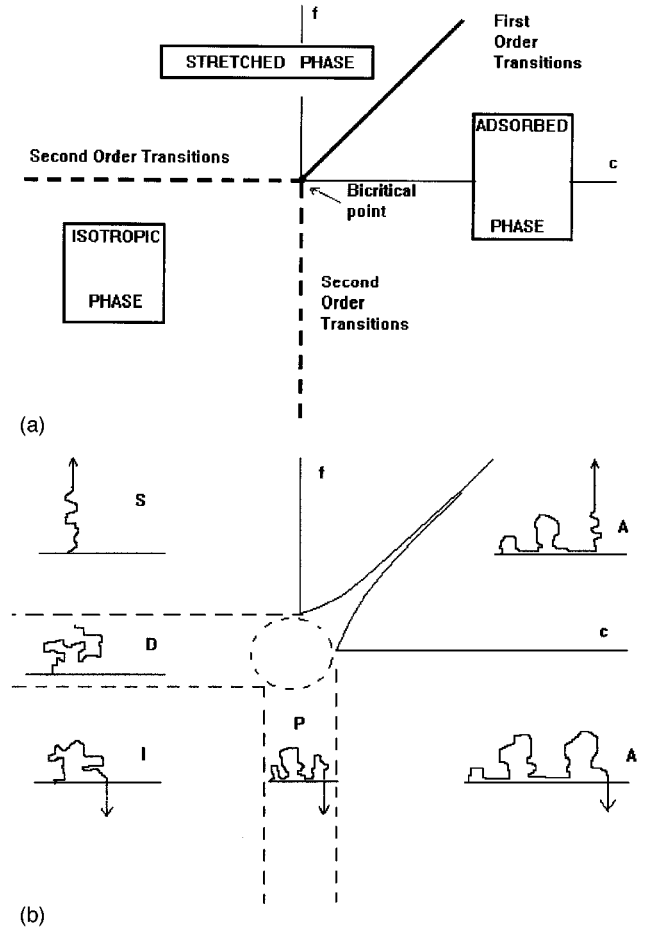

FIG. 1. (a) Phase diagram for an adsorbing Gaussian chain with the end force applied in the thermodynamic limit $N\to\infty$. (b) States of a finite-length chain with typical conformations indicated.

III. PHASE DIAGRAM

The average fraction of adsorbed segments $\theta = \langle m\rangle/N$ is usually taken as an order parameter in the adsorption problem. For an adsorbed chain, a finite fraction of segments (independent of N) are in contact with the plane. In the presence of an effectively repelling surface, the number of contacts is always on the order of one, which means that the chain is desorbed. We recall that one end of the chain is anchored at the surface, eliminating the possibility of floating away from the surface. Accordingly, for the problem of chain stretching it is the average degree of stretching $\zeta = \langle z\rangle/N$ that will naturally serve as the order parameter.

In the thermodynamic limit $N\to\infty$ one can speak of a definite phase state for the macromolecule. Possible states of the chain for various values of the adsorption interaction parameter c and the force f are expressed by the phase diagram, Fig. 1(a). Upward motion along the ordinate corresponds to increasing the stretching force; downward corresponds to pressing the free end of the chain down. Moving to the right means increasing the adsorption strength; moving to the left means increasing the repulsion between the plane and the macromolecule. Three different regions in the diagram correspond to the ''isotropic'' phase ($\theta = \zeta = 0$), the ''stretched'' phase ($\theta = 0$ and $\zeta > 0$), and the ''adsorbed'' phase ($\theta > 0$ and $\zeta = 0$). The dashed lines of second-

order phase transitions come together and pass into the solid line of a first-order transition at the bicritical point $c=f=0$ (according to the standard terminology [20]).

At the transition between absorbed and stretched states of the chain (crossing the solid line $c=f$), the free energy has a discontinuity in the slope and the fraction of adsorbed segments θ as well as the energy of the macromolecule change abruptly. Analysis in terms of the Landau free energy given in the next section turns out to be quite illuminating. In the case when one of the dashed lines of the Fig. 1(a) is crossed, it is the second derivative of the free energy $\partial^2 \ln Z / \partial c^2$ (or $\partial^2 \ln Z / \partial f^2$) that changes discontinuously. These derivatives are related to the specific heat and the susceptibility to the end force, correspondingly.

For chains of finite length N, sharp transitions are blurred and different phase states are separated by crossover regions rather than by lines (see Sec. VI). Transitional regions for finite systems are shown in Fig. 1(b). Typical conformations of the chain in different regions of the diagram are also displayed. We denote the adsorption region of the diagram by A, and the region of stretched conformations in the upper part of the diagram by S. The states to the left from the bicritical point along the line of the second order phase transitions will be called D (desorbed), while their counterparts along the $f=0$ line in the lower region will be called P (pressed down). The third quadrant (isotropic phase) is denoted by I and corresponds to a desorbed macroloop. The vicinity of the point $c=f=0$ is the bicritical region.

It is clear from the diagram that the classical problem of adsorption with no force applied corresponds to moving along the line of second-order transitions from D to A via the bicritical point. An equivalent dual situation is realized when the adsorption parameter is fixed at $c=0$ and the force applied is changed from pressing down to stretching. Adsorption of a chain with the end pressed down (constant $f<0$) is equivalent to stretching of a chain anchored to an inert or repulsing surface, and is also a second-order phase transition, as shown in the next section. Adsorption of a chain under constant stretching force $f>0$ applied is equivalent to tearing off an adsorbed chain under the condition of $c=$const.

The problem of stretching an isolated ideal chain by a constant end force belongs to an introductory statistical mechanics textbook (traditionally, it is also shown to be equivalent to the problem of orienting a set of noninteracting spins by a uniform magnetic field [21]). The dependence of the mean end-to-end distance on the external force is smooth, there being no phase transition whatsoever. We have just seen, however, that the presence of an impenetrable repulsive or attractive surface changes the situation quite dramatically.

IV. COMPARISON WITH THE LANDAU THEORY OF PHASE TRANSITIONS

The phenomenological theory of phase transitions by Landau [9] is based on consideration of the free energy F as a function of the order parameter ϕ. In the vicinity of the second-order transition point, F is expanded in powers of ϕ, only the terms with even powers being present due to symmetry considerations:

$$F(\phi)=F_0+A(T-T_c)\phi^2+B\phi^4+\cdots . \qquad (8)$$

Factors A and B are assumed to be positive and approximately constant in the vicinity of the transition point, so that the coefficient with the quadratic term changes sign at $T=T_c$. Minimization with respect to ϕ gives the equilibrium value $\phi_0=0$ for $T>T_c$, and $\phi_0=(A|T-T_c|/2B)^{1/2}$ for $T<T_c$. In the original model, the specific heat changes discontinuously by $T_c A^2/2B$ at the transition point.

For a Gaussian chain adsorbing onto a planar surface, one has to consider the free energy (per segment) as a function of the fraction of adsorbed segments $\theta=m/N$. Here, the order parameter is not averaged but is allowed to fluctuate. The partition function $P(\theta)$ for the case of zero force ($f=0$) follows from Eq. (6):

$$P(\theta)=\left(\frac{\pi N}{6}\right)^{-1/2}\exp\left(-\frac{3}{2}N\theta^2+Nc\theta\right), \qquad (9)$$

while for the free energy $F=-N^{-1}\ln P$ one obtains

$$F(\theta)=F_0-c\theta+\tfrac{3}{2}\theta^2. \qquad (10)$$

Equation (10) has physical meaning only for $0\leq\theta\leq1$ since the fraction of adsorbed segments is of course non-negative. In the original Landau theory, the free energy is invariant with respect to the change $\phi\rightarrow-\phi$ and is considered analytic in the vicinity of $\phi=0$. Introducing a new variable ϕ so that $\theta=\phi^2$ provides a mapping for the free energy to be defined on the interval $[-1,1]$ and supplies it with the appropriate symmetry. Then

$$F(\phi)=F_0-c\phi^2+\tfrac{3}{2}\phi^4. \qquad (11)$$

In this form, the dependence of F on ϕ exactly coincides with the truncated expansion (8) of the Landau theory. Note that formula (11) is valid not only in the thermodynamic limit, but for finite chains as well.

The behavior of the mean-square fluctuation of the number of adsorbed segments, m, in our model is analogous to that of the heat capacity in the Landau theory, since both are proportional to the second derivative of the free energy with respect to the governing parameter. The quantity analogous to the specific heat is

$$\frac{(\langle m^2\rangle-\langle m\rangle^2)}{N}=\frac{1}{3}+\frac{2\widetilde{c}}{3\pi^{1/2}Y(-\widetilde{c})}-\frac{2}{3\pi Y^2(-\widetilde{c})}\cong\begin{cases}1/(Nc^2), & -\widetilde{c}\gg1 \\ 1/3, & \widetilde{c}\gg1\end{cases}. \qquad (12)$$

It is clear that in the thermodynamic limit the jump in this quantity is indeed equal to 1/3, conforming to the result of the Landau theory $A^2/2B$ with $A=1$, $B=3/2$.

In the case when the chain is adsorbing with its end pressed down ($f<0$), the partition function $P(\theta)$ is given by

$$P(\theta)=\left(\frac{\pi N}{6}\right)^{-1/2}\exp(c^2N/6)\exp[(\theta-c/3)^2 3N/2]\left\{1+\left(\frac{\pi N}{6}\right)^{1/2}fY((3N/2)^{1/2}(\theta-f/3))\right\}. \qquad (13)$$

For not too weak forces, $|f| \gg N^{-1/2}$, the corresponding free energy as a function of ϕ is simplified to

$$F(\phi) = F_0 - c\phi^2 + \frac{3}{2}\phi^4 + \frac{1}{N}\ln\left(1 + \frac{1}{3}|f|\phi^4\right), \quad (14)$$

which is the same as Eq. (11) in the thermodynamic limit $N \to \infty$.

We see that second-order transitions in our model are rigorously described by the Landau mean-field theory. It is well known that for ordinary low-molecular-weight systems Landau theory becomes incorrect in the vicinity of the second-order transition point, due to the strong spatial correlations of the fluctuations of local order parameter. In the polymeric system under consideration, the role of the order parameter is related either to the fraction of adsorbed segments or to the degree of chain stretching. In both cases, the order parameter is defined ''globally,'' for the macromolecule as a whole, and not as a local quantity. Therefore, no correlations of fluctuations are possible at all, and the system always retains mean-field behavior.

The fact that only two terms with ϕ^2 and ϕ^4 are present in the expression (11) is due to the Gaussian elasticity of the chain in the continuum model. Taking into account the finite extensibility will produce higher-order terms in the $F(\phi)$ dependence.

Let us consider in more detail the behavior of the Landau free energy when crossing the line of first-order transitions $c = f$ on the phase diagram, Fig. 1(a). It can be easily shown that this indeed leads to a finite jump in both order parameters (the fraction of adsorbed segments and in the degree of chain stretching), and there exists a latent heat of the transition, as is expected for a proper first-order transition. According to the classical concepts of the Landau approach, the first-order transition corresponds to the case when, within a certain range of external parameters, the free energy $F(\phi)$ has two minima as a function of the order parameter. The deeper minimum gives the equilibrium state, while the other one corresponds to a metastable state. With the change in the governing parameter the relative depth of the two minima changes, and the transition corresponds to switching from one minimum to the other. As a result, the distribution density for the order parameter is bimodal. Accordingly, there should be no pre-transitional fluctuation growth.

We shall see that the first-order transition in our model does not conform to this picture, and the Landau theory fails in a very peculiar way. The Landau free energy can be still derived from the exact formula (6). However, in contrast to the case of second-order transitions, for positive values of f and c one arrives at a function $F(\phi)$ that consists of two branches in the $N \to \infty$ limit:

$$F(\phi) - F_0 = \begin{cases} (f-c)\phi^2 & \text{for } \phi \le \sqrt{f/3} \\ \frac{1}{6}(f^2 - c^2) + \frac{3}{2}(\phi^2 - c/3)^2 & \text{for } \phi \ge \sqrt{f/3} \end{cases} \quad (15)$$

These are a segment of a parabola and a fourth-order curve touching each other at the point $\phi = \sqrt{f/3}$ so that the first derivative remains continuous. The function $F(\phi)$ is explic-
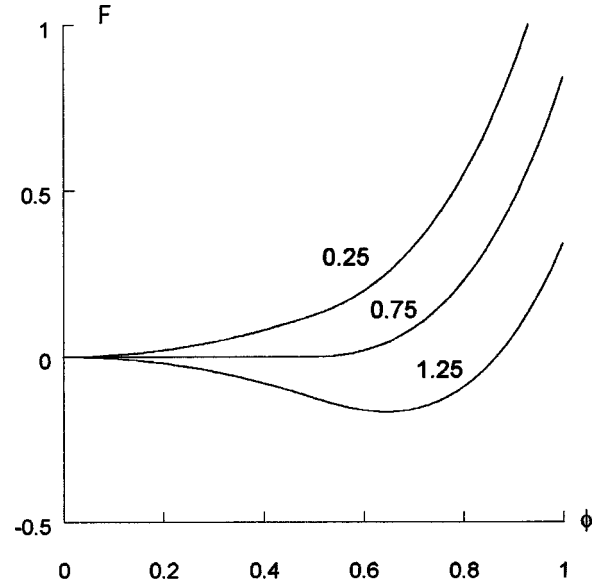

FIG. 2. Landau free energy as a function of the order parameter ϕ upon crossing the first-order transition line: The values of the adsorption parameter c are shown in the figure; the force magnitude is $f = 0.75$. The two analytical branches of F meet at $\phi = 0.5$.

itly nonanalytic (the second derivative is discontinuous at the junction point). Of course, for any finite N, no singularities are present.

It is clear from Fig. 2 that the Landau free energy has always only one minimum so that no bimodality in the order parameter distribution is ever present. At the transition point itself, part of the $F(\phi)$ curve is strictly flat, which brings about a finite jump in the average order parameter. On the other hand, the flattening of the $F(\phi)$ curve in the vicinity of the transition leads also to anomalous pre-transitional fluctuation growth. The origin of this discrepancy with the classical picture is also related to the fact that the order parameter is defined not locally but as pertaining to the system as a whole. At $c = f$ the chain is actually phase separated into a stretched and an adsorbed part, the states with different fractions of segments belonging to each phase being equally probable, hence the flat part of the $F(\phi)$ curve. On the other hand, there is no activation barrier to segregation since there is no interface between the adsorbed and the stretched parts. There is a direct analogy to a gas-liquid mixture in a cylinder kept at a constant pressure exactly equal to that of the saturated vapor. Assuming that we consider the phase separated states with the flat interface of constant area, all these states that differ by the relative vapor-liquid volume fractions have exactly the same free energy. The average density can be therefore considered as fluctuating in the range between that of the saturated vapor and that of the liquid. Infinite compressibility of a phase separated vapor-liquid mixture (considering only strictly equilibrium states) is well known from textbook discussions of the van der Waals equation.

V. JOINT DISTRIBUTION IN TWO ORDER PARAMETERS AROUND THE BICRITICAL POINT

We described the phase behavior of our model in terms of two order parameters θ and ζ and it would be only natural to
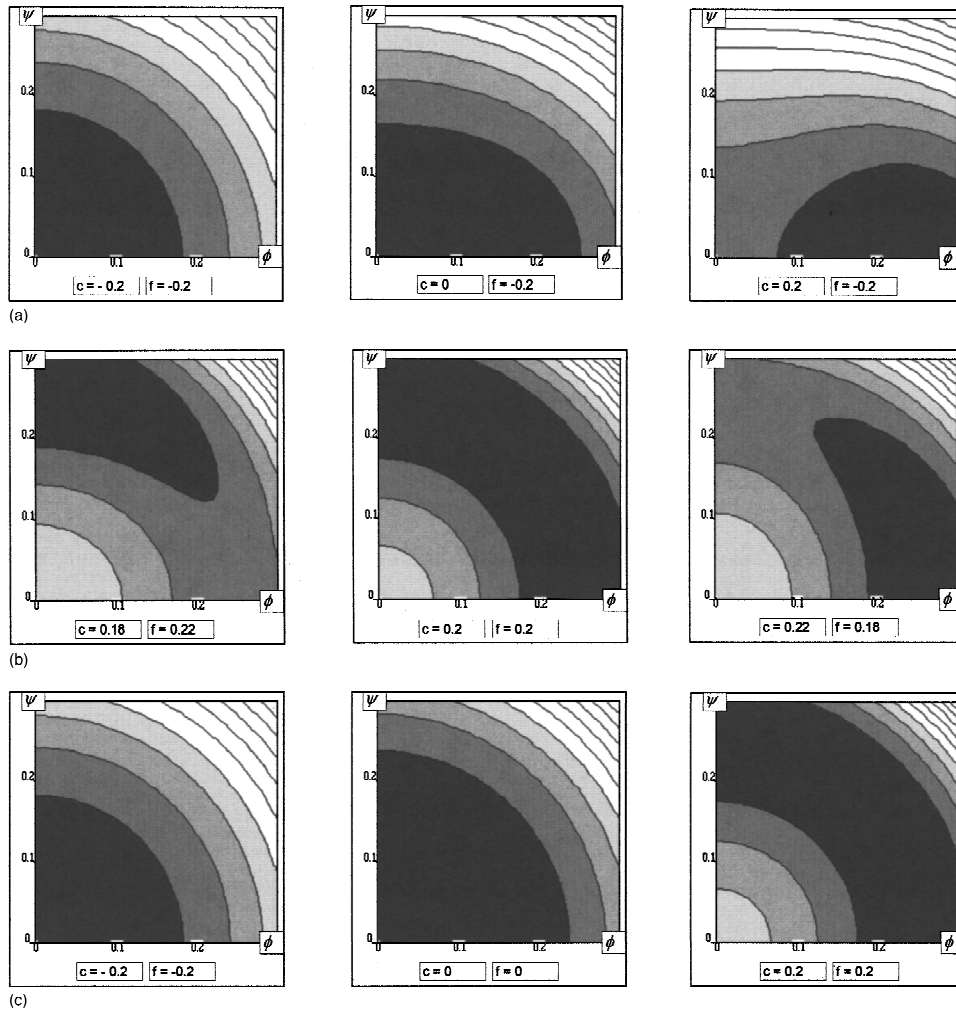
FIG. 3. Contour plots of the Landau free energy as a function of two order parameters: (a) for crossing the second order transition line $c=0$; (b) for crossing the first-order transition line normally to it; (c) for passing through the bicritical point along the $c=f$ line.

try to introduce the Landau free energy as a function of two independent variables $F(\theta,\zeta)$. The probability densities for the free end height and for the number of adsorbed segments, separately, are given by Eqs. (4) and (6). We construct the partition function of a Gaussian chain with the fixed height of the free end z, and the fixed number of contacts with the plane m as follows:

$$P(z,m|N,c,f) = \int_m^N dn \; P(0,m|n,c) P(z,0|N-n,f).$$

$$(16)$$

This is just the sum over different ways to decompose the chain into the adsorbed part consisting of the first n segments, and the tail of $N-n$ segments that has no contact with the surface at all. The next step is to replace the partition function $P(0,m|n,c)$ of a chain with the free end touching the surface with the partition function $P(m|n,c,f\to -\infty)$ of the chain whose free end is not fixed at $z=0$, but rather pressed down to the surface by an infinitely large external force. The latter is given by Eq. (6). Similarly, we take $P(z,0|N-n,f) = P(z|N-n,c\to -\infty,f)$ and employ Eq. (4). Finally, for the Landau free energy we obtain a simple analytical result that is asymptotically exact in the vicinity of the bicritical point $\zeta \ll 1$, $\theta \ll 1$:

$$F(\phi,\psi) = -c\phi^2 - f\psi^2 + 3/2\phi^4 + 3/2\psi^4 + 3\phi^2\psi^2, \quad (17)$$

where $\psi^2 = \zeta$ and $\phi^2 = \theta$

Figures 3(a)–3(c) display the contour plots of the Landau free energy as it changes in various types of phase transitions. The transition between the isotropic and one of the ordered states goes through broadening of the minimum along one axis followed by a gradual shift in its position; see Fig. 3(a). The transition between two ordered states is more peculiar: it involves forming a valley that has exactly the same depth for all the states with the given value of the sum $\varphi^2 + \psi^2$; see Fig. 3(b). If one moves along the line $c=f$ the Landau free energy becomes a function of only one independent variable $t^2 = \varphi^2 + \psi^2 = \theta + \zeta$, as illustrated by Fig. 3(c):

$$F = -ct^2 + \tfrac{3}{2}t^4. \quad (18)$$

The average value $\langle \theta + \zeta \rangle$ is determined by the position of the minimum of the function (18), which changes exactly as in the case of a mean-field second-order transition:

$$\langle \theta + \zeta \rangle = \begin{cases} 0, & c < 0 \\ c/3, & c > 0. \end{cases} \quad (19)$$

On the first-order transition line $c = f$ $(c, f > 0)$, all the states with the given average value $\langle \theta + \zeta \rangle = c/3$ correspond to equilibrium, which allows anomalously large fluctuations in each of the order parameters separately: all the states with θ in the range between 0 and $c/3$ are equally probable.

VI. FINITE-SIZE EFFECTS

The ideas of finite-size scaling [22] stem from a realization that in the vicinity of a transition point the singular part of the free energy should depend on the size of the sample, L, only through the combination L/ξ, where $\xi \sim |T - T_c|^{-\nu}$ is the correlation length, and ν is the corresponding critical index. The common way to write the free energy of the sample is $F = F(|T - T_c| L^{1/\nu})$. Close enough to the critical point where the correlation length ξ becomes much larger than the elementary length l, two different regimes can be identified: (i) in the scaling regime, $L/\xi \gg 1$, the free energy as a function of its argument should have power-law asymptotics; (ii) once L/ξ becomes of the order of one or smaller F tends to a constant, and the critical behavior is smoothed out. The free energy $F(L/\xi)$ should therefore switch from one asymptotic behavior to another at $L/\xi \sim 1$, and this condition defines the range where the finite-size effects are prevalent.

To facilitate direct comparison with the present model we note that here it is not the linear size but the number of units, N, that enters as one of the arguments of the free-energy function. So, instead of the standard way of presenting the free energy we rewrite the argument substituting $L \sim N^{1/d}$ and using the thermodynamic identity $d\nu = 2 - \alpha$, to arrive at

$$F = F(|T - T_c| N^{1/(2-\alpha)}), \quad (20)$$

α being the heat-capacity index. Note that for the model considered here we cannot properly identify the meaning of the linear size of the system, L, or the dimensionality d. However, they do not enter in the final result. One expects the finite-size effects to smear out the transition over the interval

$$\Delta T \sim N^{-1/(2-\alpha)}. \quad (21)$$

In our model, of course, $|T - T_c|$ should be substituted by the deviation from the transition point in terms of the governing parameters c and f.

The explicit dependence of the free energy on the number of chain units, N, is easily extracted from the exact formula (5). For example, if we follow the second-order adsorption-desorption transition at zero force moving along the $f = 0$ line on the phase diagram [Fig. 1(a)], the free energy is given by

$$F = \text{const} + \ln[Y(-\tilde{c})]. \quad (22)$$

Upon crossing the $c = 0$ line of second-order transitions in the lower part of the phase diagram (relatively strong negative force applied), the free energy has a slightly different form:

$$F \cong F_0 + \ln[\tilde{c} Y(-\tilde{c}) + \pi^{-1/2}], \quad (23)$$

where the regular part F_0 contains the dependence on f. In both cases the free energy is indeed an explicit function of the scaling variable $\tilde{c}$ that contains the number of chain elements $\tilde{c} = c(N/6)^{1/2}$. Comparing this to the finite-size scaling form of the free energy $F(|T - T_c| N^{1/(2-\alpha)})$ we have to keep in mind that $|c|$ is exactly the deviation from the critical point $(c_{\text{crit}} = 0)$ and, since the second order transition under consideration is of the mean-field type, the heat-capacity index is $\alpha = 0$. We see, therefore, that the exact solution conforms perfectly to the finite-size scaling ansatz.

Consider now the vicinity of the first-order A-S transition when we increase the force at fixed c eventually tearing the adsorbed chain off the plane. Sufficiently far away from the bicritical region, i.e., $c \gg N^{-1/2}$, $f \gg N^{-1/2}$, the free energy for finite N can be presented as

$$F = \ln\{2t \exp(t^2 + x^2)[x^{-1}\sinh(2tx) + t^{-1}\cosh(2tx)]\}$$
$$= F_0 + \ln\left(\frac{\sinh(2tx)}{tx}\right), \quad (24)$$

where $t = \frac{1}{2}(\tilde{c} + \tilde{f}) \cong \tilde{c}$, $x = \frac{1}{2}(\tilde{c} - \tilde{f})$, and F_0 remains smooth in the vicinity of the transition in the thermodynamic limit. The free energy is a function of the combination $tx \sim |c - f|(Nc)$, where $|c - f|$ is now the deviation from the transition point $f = c$. In the case of the first-order transition the heat-capacity index can be formally taken as $\alpha = 1$ (see also the next section), which leads again to an exact agreement with the ansatz (20).

Returning back to Eq. (21) we conclude that for finite N, second-order transitions in our model are smoothed over the interval $|c| \sim N^{-1/2}$ (A-D transition) or $|f| \sim N^{-1/2}$ (P-S transition). The bicritical region itself has the characteristic size of $N^{-1/2}$ in both directions of the phase diagram. The first-order tearing-off transition has the characteristic width $\Delta f \sim (Nc)^{-1}$. The width of the transition Δf decreases as one moves away from the bicritical point $f = c = 0$.

Similar to the way the magnetization of finite Ising lattices can be presented in a universal scaling form in the coordinates $ML^{\beta/\nu}$ versus $L^{1/\nu}|T - T_c|$, in our model the average number of adsorbed segments is described by universal scaling functions, which we are fortunate to be able to write analytically. Taking $f = 0$ as an example, one obtains

$$\langle m \rangle N^{-1/2} = \left(\frac{2}{3}\right)^{1/2}\left(\frac{1}{\sqrt{\pi}Y(-\tilde{c})} + \tilde{c}\right) \cong \begin{cases} 6^{-1/2}\tilde{c}^{-1}, & -\tilde{c} \gg 1 \\ (2/3)^{1/2}\tilde{c}, & \tilde{c} \gg 1, \end{cases} \quad (25)$$

where $\tilde{c} = c(N/6)^{1/2}$.

The curves are displayed in Fig. 4 in a log-log scale, and it is clear that in the region $\tilde{c} \gg 1$ they are indeed described by power laws similar to magnetic systems, although the values of the indices are, of course, different.
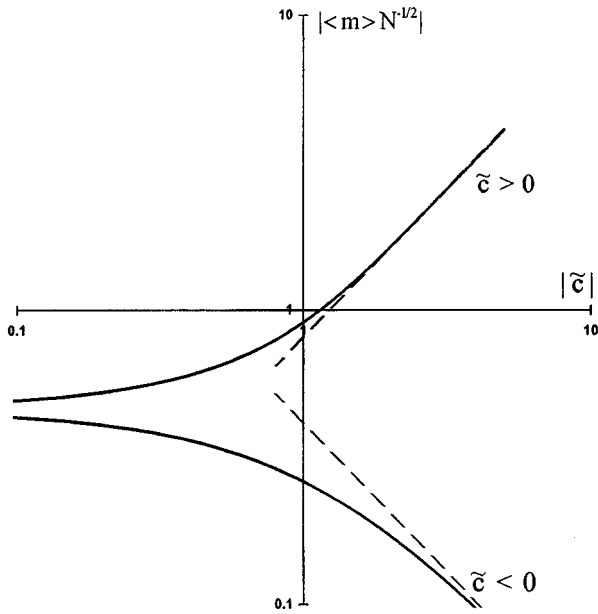
FIG. 4. Log-log plot of the number of adsorbed segments, m, vs the adsorption parameter c in the universal finite-size scaling coordinates. The power-law asymptotics are shown by dashed lines.

VII. 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. The approach pioneered by Yang and Lee [10] related these singularities to 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 fugacity that were the object of investigation. Similarly, the temperature-induced transitions should be described in terms of the zero distribution for the canonical partition function in the complex plane of temperature (or $\beta = 1/kT$). These are commonly called Fisher zeros 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.

Yang and Lee showed that for finite N the partition function can have only complex-conjugate zeros but no zeros on the real positive axis. The only possibility for a phase transition to appear is that as the number of particles increases, the complex zeros come closer to the real positive axis, and eventually, in the $N \to \infty$ 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 that could be characterized by some limiting density function. Assuming that the zeros concentrate on two symmetric support lines that cross the real axis at the point $\beta = \beta_c$ making an angle ω with it, Grossmann and Rosenhauer [11] were able present an extensive classifi-

cation of phase transitions and to express the main characteristics of a transition (jump magnitudes, critical indices, and amplitudes) through the parameters of the linear density of zeros $g(y)$, where y is the coordinate along the imaginary axis. The analysis is based on the following formula for the internal energy (per unit volume) at a given deviation from the critical temperature $\Delta = \beta - \beta_c$:

$$E(\Delta) = 2(1 + \cot^2\omega)^{1/2} \int_0^\infty g(y) \frac{y \cot\omega + \Delta}{(y \cot\omega + \Delta)^2 + y^2} \, dy.$$
(26)

Once the linear density is assumed to be a power function $g(y) \sim y^{1-\alpha}$, the following cases can be distinguished: (1) If the density $g(y)$ tends to a constant at small y ($\alpha = 1$), then the zeros necessarily approach the real axis at a straight angle $\omega = \pi/2$, and the energy has a finite jump $2\pi g(y = 0)$ upon crossing the $\beta = \beta_c$ point. This obviously corresponds to a first-order transition with a δ-peak singularity in the specific heat. (2) If the density grows linearly with y ($\alpha = 0$), 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. (3) If $\alpha = 0$, but $\omega > \pi/4$, or $0 < \alpha < 1$ (arbitrary ω), specific heat diverges at the transition point. This is either a power-law singularity $c_v \sim |\Delta|^{-\alpha}$ in the latter case, or a logarithmic singularity for $\alpha = 0$. In both cases, the value of the angle ω affects only the specific-heat amplitudes on the two sides of the transition point. In particular, the vertical line $\omega = \pi/2$ corresponds to a symmetric transition.

In our model, the governing parameter c (or f) is analogous to the inverse temperature β, while the conjugated variable, the number of adsorbed segments (or the free end height) would be the analog of the energy E. Let us fix the magnitude of the end force $f = f_0$ (it could be negative, zero, or positive, but is still taken as real). Then we should analyze the partition function $Z(c, f_0)$ in the complex plane of the variable c.

We start by considering the distribution of zeros upon crossing the line of the first-order transitions ($f_0 = $ const > 0). The zeros are found from the equation

$$c Y(-c\sqrt{N/6}) - f_0 Y(-f_0\sqrt{N/6}) = 0, \quad c \neq f_0. \quad (27)$$

For large N, and $f_0 > 0$, $|\arg(c)| < \pi/4$ this is reduced to

$$c \exp(c^2 N/6) - f_0 \exp(f_0^2 N/6) = 0, \quad c \neq f_0. \quad (28)$$

Taking $c = \rho \exp(i\chi)$, one obtains two coupled equations:

$$\rho^2 \cos 2\chi + \frac{6}{N} \ln \frac{\rho}{f_0} - f_0^2 = 0, \quad (29)$$

$$\chi + \frac{1}{6}\rho^2 N \sin 2\chi = 2\pi k, \quad k = \pm 1, \pm 2, \ldots . \quad (30)$$

The limiting line of zeros is found by letting $N \to \infty$:

$$\rho^2 \cos 2\chi = f_0^2 \quad (31)$$

or, passing to the Cartesian coordinates $x = \mathrm{Re}(c)$, $y = \mathrm{Im}(c)$,

$$x^2 - y^2 = f_0^2. \quad (32)$$

This curve is easily recognized as hyperbola crossing the real axis at a straight angle at point $x = f_0$, with two asymptotes $y = \pm x$ making an angle $\omega = \pi/4$ with the real axis. The left branch of the hyperbola is irrelevant to the original equation (27).

Combining Eqs. (30) and (31) we obtain an equation for the positions of zeros on the hyperbola:

$$\chi + \tfrac{1}{6} f_0^2 N \tan 2\chi = 2\pi k, \quad k = \pm 1, \pm 2, \ldots . \quad (33)$$

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

$$\chi_k = \frac{6\pi k}{3 + N f_0^2}. \quad (34)$$

The limiting density of zeros $g = \lim_{N \to \infty} 1/N \, dk/ds$, where $ds = \sqrt{d\rho^2 + \rho^2 d\chi^2}$ is the line element, can be calculated exactly everywhere on the hyperbola from Eqs. (31) and (33), to give

$$g(\rho) = \frac{1}{6\pi} \rho. \quad (35)$$

At the point of crossing the real axis $\rho = f_0$, and g tends to the finite value $g_0 = f_0/6\pi$. This falls into category (1) according to the above classification, and indeed gives the first-order transition with a finite jump in the order parameter. The magnitude of the jump was derived in Ref. [11] to be $2\pi g_0 = \tfrac{1}{3} f_0$. This is of course in accordance with the value obtained by direct differentiation of the partition function.

On the asymptotic wings of the hyperbola the distance from the transition point along the curve, s, is the same as ρ, and Eq. (35) shows that the density of zeros increases linearly with it. Taking $s \cong \rho$ and solving for ρ as a function of k one obtains the position of the kth zero

$$\rho_k \cong \left(\frac{12\pi k}{N} \right)^{1/2}. \quad (36)$$

What happens as one crosses the line of the first-order transitions closer and closer to the bicritical point? The focus distance of the hyperbola, f_0, decreases and so do accordingly the density g_0 and the magnitude of the jump in the order parameter. Eventually, at $f_0 = 0$, the curve degenerates into two straight lines at an angle $\omega = \pi/4$ with the real axis crossing it at the origin (see Fig. 5). Here, the transition becomes second order: changing the adsorption parameter c one passes exactly through the bicritical point. Strictly speaking, the asymptotic representation of the Y function used in Eq. (28) is not valid in this case any more. However, the limiting picture of the distribution of zeros does apply.

Indeed, for $f_0 = 0$, the partition function is simplified to

$$Z(c) = Y(-c\sqrt{N/6}) = \exp(c^2 N/6) \operatorname{erfc}(-c\sqrt{N/6}). \quad (37)$$

The exponential function has no zeros in the entire complex plane. So it is the distribution of zeros of the complementary error function, and particularly its asymptotical form in the $N \to \infty$ limit, that we are interested in. Numerical results shown in Fig. 5 suggest that zeroes indeed condense on a support line at an angle $\omega = \pi/4$ with the real axis. This fact
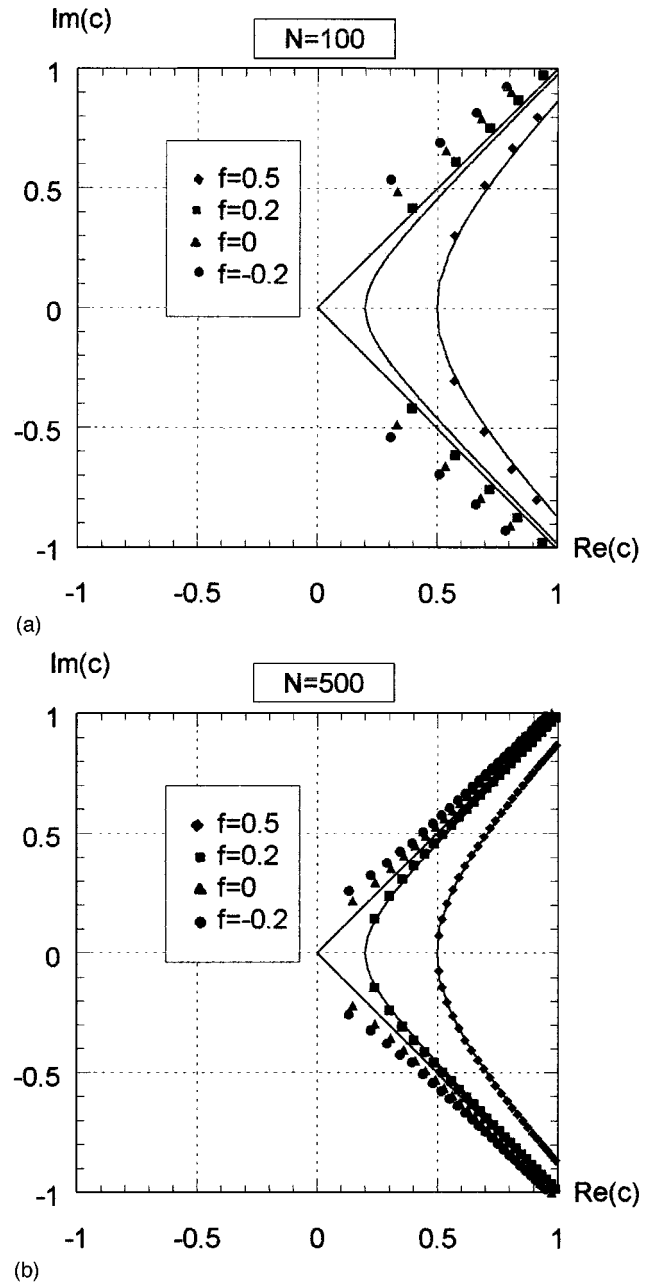

(a)

(b)

FIG. 5. Distribution of zeros of the partition function in the adsorption parameter complex plane for various values of the end-force magnitude, f, indicated in the plot: (a) $N = 100$; (b) $N = 500$. The analytical limiting curves of zeros are shown by solid lines.

can be rationalized if one recalls that along this line the erfc function becomes an integral over a strongly oscillating function:

$$\operatorname{erfc}(t e^{i\pi/4}) = \int_t^\infty (\cos x^2 + i \sin x^2) dx.$$

Due to these oscillations, both the real and imaginary parts of the integral have an infinite number of zeros, the distance between them constantly decreasing as one moves to larger

t. Therefore, it should not be surprising that in the limit of large t, zeros of the erfc function condense on the $|t|e^{i\pi/4}$ line.

The limiting density of zeros can be now evaluated by realizing that the distance δ between two neighboring zeros should correspond to a phase change of 2π in the integrand:

$$(t+\delta)^2 - t^2 \approx 2\pi, \quad \text{and hence} \quad \delta \approx \frac{\pi}{t}.$$

Recollecting that $t = c\sqrt{N/6}$, we recover Eq. (35) for the limiting density of zeros in the c plane: $g(|c|) = |c|/6\pi$.

This case falls into category (2) according to the above classification, and, indeed, results in a second-order transition of a mean-field type with a finite jump in the order parameter fluctuation squared (see Sec. IV). The magnitude of the jump was derived in Ref. [11] to be $2\pi(1/6\pi) = \frac{1}{3}$, where $1/6\pi$ is the coefficient in the density of zeros, Eq. (35). Of course, this coincides with the result obtained directly by differentiating the free energy, Eq. (12).

It is easy to show that the limiting density and the slope of the line of zeros of the partition function upon crossing the line of second-order transitions away from the bicritical point ($f_0 = \text{const} < 0$) are exactly the same: $\omega = \pi/4$, $g(\rho) = \rho/6\pi$. Naturally, this is consistent with the fact that the Landau free energies coincide for both cases in the thermodynamic limit (see Sec. IV). Numerical data for a few first zeros of the exact partition function (27) with $N = 100$ and $N = 500$ for several values of f_0 are displayed in Fig. 5 and support the analytical results for the distribution of zeros.

We now turn our attention to the finite-size scaling behavior of the position of zeros of the partition function. According to the analysis given by Itzykson *et al.* [12], in the vicinity of the critical point the distance from the kth zero to the real axis should scale as

$$y_k \sim L^{-1/\nu} k^{1/d\nu} \tag{38}$$

or, in terms of the total number of units N,

$$y_k \sim \left(\frac{k}{N}\right)^{1/d\nu} \sim \left(\frac{k}{N}\right)^{1/(2-\alpha)}. \tag{39}$$

Here again 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. Taking $\alpha = 0$ for the second-order transition, we arrive at the scaling prediction $y_k \sim (k/N)^{1/2}$, in accordance with the exact analytical result, Eq. (36). On the other hand, for the first-order transition, Eqs. (30) and (34) give $y_k \approx f_0 \chi_k \approx (6\pi/f_0) k/N$. Since the first-order transition should be formally assigned $\alpha = 1$, the scaling prediction (39) is indeed correct.

In particular, we found that the closest zero is characterized by the polar angle

$$\chi_1 \approx \frac{6\pi}{3 + Nf_0^2}. \tag{40}$$

This gives another way of evaluating the region where finite-size effects smooth out the difference between the first- and second-order transitions (i.e., the characteristic width of the bicritical region). For this to be true, even the closest zero should lie not far from the asymptotic wings of the hyperbola:

$$\chi_1 \sim 1, \quad \text{which means} \quad Nf_0^2 \sim 1, \quad f_0 \sim N^{-1/2},$$

in accordance with the estimates of Sec. VI.

It is worth noting that in contrast to the lattice models where the partition function of a finite system is a polynomial and therefore has only a finite number of zeros, the model of the adsorbing chain that we discuss results in a partition function with an infinite number of zeros for any value of N. The reason for this is that we deal with a continuum model as opposed to lattice models with finite sets of discrete states.

VIII. CONCLUDING REMARKS

As we have seen, the model presented allows one to carry out exact analytical results within all the approaches we have employed, be it the direct calculation of the partition function, or finding the Landau free energy that controls the distribution of order parameters, or calculating the distribution of complex zeros of the partition function. These results are available for the first- and second-order transitions, and the vicinity of the bicritical point that the model possesses, not only in the thermodynamic limit, but for finite systems as well. A question naturally arises: Why is this possible? What are the main differences between this model and the classical exactly solvable lattice models?

First, the interaction between monomeric units is taken into account only in terms of their connectivity, i.e., each unit interacts only with two neighbors along the chain. This interaction is separated 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 only to the units in contact with the adsorbing plane. The volume interaction between non-neighboring units is neglected even if they come close to each other in space.

Second, both order parameters are defined not as local quantities, but for the system as a whole. Hence the notion of correlation length for the order parameter fluctuations in this description has no meaning.

Third, the external field was taken as linear in the z coordinate and acting only on the free tail, not on the loops and trains of the adsorbed chain. Together with the planar geometry and the Gaussian property of the random walk, this made the problem effectively one dimensional.

All this separates our model from the classical lattice systems and may prevent any direct extension of the results obtained onto the other unsolved problems that puzzle the brighter theoretical minds of our time. However, for purposes of getting to understand better and teaching the fundamentals of statistical mechanics of phase transitions this model seems to be a very appropriate and useful tool.

[1] M. E. Fisher, in *Lectures Theoretical Physics* (University of Colorado Press, Boulder, 1965), Vol. 70, p. 1.

[2] R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic Press, New York, 1982).

[3] I. M. Lifshits, Zh. Eksp. Teor. Fiz. **55**, 2408 (1968) [Sov. Phys. JETP **28**, 1280 (1969)].

[4] R. Zwanzig and J. I. Lauritzen, J. Chem. Phys. **48**, 3351 (1968).

[5] V. Privman, G. Forgacs, and H. L. Fricsh, Phys. Rev. B **37**, 9897 (1988); F. Igloi, Phys. Rev. A **43**, 3194 (1991); Europhys. Lett. **16**, 171 (1991).

[6] M. E. Fisher, J. Chem. Phys. **45**, 1469 (1966); for a review, see A. A. Vedenov, A. A. Dykhne, and M. D. Frank-Kamenetsky, Sov. Phys. Usp. **105**, 479 (1971).

[7] R. J. Rubin, J. Chem. Phys. **43**, 2392 (1965); **44**, 2130 (1966); A. A. Gorbunov, E. B. Zhulina, and A. M. Skvortsov, Polymer **23**, 1133 (1982).

[8] Y. Lepine and A. Caille, Can. J. Phys. **56**, 403 (1978); E. Eisenriegler, K. Kremer, and K. Binder, J. Chem. Phys. **77**, 6296 (1982).

[9] L. D. Landau and E. M. Lifshits, *Statistical Physics* (Pergamon Press, London, 1969), Chap. 14.

[10] C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952); **87**, 410 (1952).

[11] S. Grossmann and W. Rosenhauer, Z. Phys. **207**, 138 (1967).

[12] C. Itzykson, R. B. Pearson, and J. B. Zuber, Nucl. Phys. B **220**, 415 (1983).

[13] R. B. Pearson, Phys. Rev. B **26**, 6285 (1982); E. Marinari, Nucl. Phys. B **235**, 123 (1984).

[14] P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[15] S. F. Edwards, Proc. Phys. Soc. London **85**, 613 (1965).

[16] P.-G. de Gennes, Rep. Prog. Phys. **32**, 187 (1969).

[17] A. A. Gorbunov and A. M. Skvortsov, J. Chem. Phys. **98**, 5961 (1993).

[18] A. M. Skvortsov, A. A. Gorbunov, and L. I. Klushin, J. Chem. Phys. **100**, 2325 (1994).

[19] M. Adamuti-Trache, W. E. McMullen, and J. F. Douglas, J. Chem. Phys. **105**, 4798 (1996).

[20] M. E. Fisher, Rev. Mod. Phys. **46**, 597 (1974); M. E. Fisher and D. R. Nelson, Phys. Rev. Lett. **32**, 1350 (1974).

[21] R. Kubo, *Statistical Mechanics* (North-Holland, Amsterdam, 1965).

[22] M. E. Fisher, in *Critical Phenomena*, edited by S. E. Green (Academic Press, New York, 1971); M. E. Fisher and M. N. Barber, Phys. Rev. Lett. **28**, 1516 (1972).