

# An exactly solvable model for first- and second-order transitions

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**Abstract.** The possibility of an exact analytical description of first-order and second-order transitions is demonstrated using a specific microscopic model. Predictions using the exactly calculated partition function are compared with those based on the Landau and Yang–Lee approaches. The model employed is an adsorbed polymer chain with an arbitrary number of links and an external force applied to its end, for which the variation of the partition function with the adsorption interaction parameter and the magnitude of the applied force is calculated. In the thermodynamic limit, the system has one isotropic and two anisotropic, ordered phases, each of which is characterized by two order parameters and between which first-order and second-order transitions occur and a bicritical point exists. The Landau free energy is found exactly as a function of each order parameter separately and, near the bicritical point, as a function of both of them simultaneously. An exact analytical formula is found for the distribution of the complex zeros of the partition function in first-order and second-order phase transitions. Hypotheses concerning the way in which the free energy and the positions of the complex zeros scale with the number of particles  $N$  in the system are verified.

## 1. Introduction

For a long time a much debated issue has been whether the statistical mechanics can be used for describing phase transitions [1]. Many authors argued that a phase transition can only be described by calculating the Gibbs free energy for each separate phase, which may require using a distinct model for each phase. Then one must compare these free energies and decide which of the phases occurs in equilibrium, and which may exist as a metastable phase. Onsager [2] demonstrated that the description of phase transitions can be based on the exact partition function common for the entire system, without any additional assumptions.

Great advances in the theory of phase transitions were brought about by the study of exactly solvable models which exhibit nontrivial behavior with phase transitions of the first or the second order, and at the same time permit finding the exact partition function of the system [3]. Usually, such models cannot be directly comparable with experiment; they are useful, however, for understanding the physics of phase transitions. At present, there are surprisingly few exactly solvable models, notwithstanding the immense efforts in this direction.

Most models describe particles or spins located at the nodes of some kind of lattice. Each spin is represented by a  $D$ -dimensional vector. For one-dimensional systems, and for spin interaction with closest neighbors, the problem has been solved for any  $D$ . It has been demonstrated that the system does not exhibit phase transitions at finite temperatures [4] (a phase transition only occurs in the Kac model [5] with infinitely weak forces and an infinitely large radius of interaction). For  $D \rightarrow \infty$ , the problem has been solved exactly for arbitrary magnetic field and interaction between closest neighbors, or for long-range forces [6] (this problem is equivalent to the so-called spherical model [7]). For  $D = 1$  with interaction between closest neighbors on a two-dimen-

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Received 10 July 1997, revised 5 February 1998

*Uspekhi Fizicheskikh Nauk* 168 (6) 719–730 (1998)

Translated by A S Dobrosavl'skiĭ, edited by S N Gorin

sional lattice in the absence of a magnetic field (the two-dimensional Ising problem), a solution was obtained by Onsager [2]. Exact solutions have also been found for the two-dimensional models of ferroelectrics and antiferroelectrics [8]. All these models admit exact solutions only in the thermodynamic limit  $N \rightarrow \infty$  (where  $N$  is the number of particles in the system).

Apart from these models, a number of models from the physics of polymers can be taken. Unlike low-molecular systems, the particles in a polymer molecule are bound in a linear chain (the so-called ‘linear memory effect’ [9]). Even a single polymer chain may be regarded as an individual thermodynamic system if the number of monomer units is large enough [10]. For a linear chain capable of forming a two-dimensional folded  $\beta$ -structure, Zwanzig and Lauritzen [11] obtained an exact solution which describes a phase transition of the second order from a disordered folded structure to a regular arrangement. Further modifications of this model, allowing for the possible existence of coils, were considered in Ref. [12]. Another class of models is concerned with the melting of DNA [13], and with the adsorption of an ideal chain on surfaces of different geometry (planar [14–16] or spherical [17]).

Apart from the exactly solvable models, there are a number of general approaches to the description of phase transitions. The first approach was proposed by L D Landau in 1937 [4]. He assumed that the nonequilibrium free energy of the system depended analytically on the so-called parameter of order. In the neighborhood of a phase transition, where the parameter of order goes to zero, the free energy can be expanded in powers of the parameter of order, which allows constructing the thermodynamics of the system. Later it was demonstrated that Landau’s theory is equivalent to the mean-field approximation. The inclusion of local fluctuations of the order parameter has led to the construction of the fluctuation theory of second-order phase transitions [18]. Note that, to the best of our knowledge, the functional form of Landau’s free energy has always been postulated rather than calculated exactly for a particular model.

Another method of description of phase transitions, proposed by Yang and Lee [19] in 1952, is based on the analysis of complex zeros of the partition function. If a phase transition is feasible in the system, then in the thermodynamic limit  $N \rightarrow \infty$  the zeros come infinitely close to the real axis. There is a phenomenological approach which relates the critical exponent and the amplitude of heat capacity for different phase transitions to the distribution of complex zeros [20] and gives scaling predictions for such distributions [21]. Being mathematically rigorous, the Yang–Lee theory does not simplify the solution of the problem, since finding the distribution of zeros is no easier than getting the exact expression for the partition function. In practice, for each particular model the distribution of zeros was calculated numerically for a certain number  $N$  of particles in the system, and then the result was extrapolated to infinitely large  $N$  [22].

The relationship between different approaches to the description of phase transitions has never before been investigated for one and the same microscopic model. This article purports to fill this gap.

We are going to consider a model of an adsorbed polymer chain in an external field, and obtain an exact analytical expression for its partition function. In the thermodynamic limit, the system under consideration exhibits one anisotropic

and two isotropic, ordered phases, characterized by two order parameters each. Phase transitions of the first and second order are possible between these phases, and there is a bicritical point.

We will obtain exact expressions for Landau’s free energy as a function of each of the order parameters. In the neighborhood of the bicritical point, it is possible to express the free energy as a function of two independent order parameters. We will also find an asymptotically exact analytical expression for the distribution of complex zeros of the partition function in the case of phase transitions of the first and second order. The exact analytical expression for the partition function of our model can be obtained not only in the thermodynamic limit  $N \rightarrow \infty$ , but also for finite values of  $N$ . This offers the opportunity of verifying the scaling assumptions concerning the functional dependence of the free energy and the locations of the complex zeros on the number of particles  $N$  in the system. In addition, it is possible to analytically trace the transition from ‘large’ systems to ‘small’ systems, and study the effects of the finiteness of the system in the case of phase transitions of the first and second order.

We believe that the main advantage of our model is not that it brings novel unexpected results in the physics of phase transitions — the model is too simple for that (the phase transitions of the second order in it prove to be of the mean-field type). Neither is the model good for drawing a comparison between theory and experiment; for polymer systems, such comparisons are made using much more realistic models [23]. The purpose of this paper is to prove the feasibility of an exact analytical description of phase transitions of the first and second order using different approaches and methods of the theory of critical phenomena. The possibility of analyzing the occurrence of phase transitions and studying the effects of the finiteness of the system, applying different methods of statistical physics to one and the same microscopic model, is also useful from the standpoint of teaching statistical physics, since phase transitions constitute one of the central and most fascinating chapters of this science.

## 2. Model. Partition function

The model is represented by an ideal Gaussian chain consisting of  $N$  segments, attached at one end to a flat surface, owing to which the translation entropy of the system as a whole is zero. The adsorption interaction between the segments of the chain and the surface is short-range. We are only interested in random walks in the direction of the normal, i.e., along the  $Z$  axis (walks in the  $X - Y$  plane are not restricted and are therefore described by conventional Gaussian functions). For a model of a continual Gaussian chain whose last  $N$ th segment is a distance  $z$  away from the surface, the partition function  $P(z|N)$  in the absence of external forces satisfies the differential equation [24]

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

with the initial condition  $P(z|0) = \delta(z)$ , which takes into account the fact that one end of the chain is attached to the plane  $z = 0$ . It is easy to see that Eqn (1) is the Schrödinger equation with  $\hbar = 1$ , and  $t = iN$  for the Green’s function that describes a quantum particle of mass  $3/l^2$  originally residing

in the plane. Further on, we assume that the segment length is equal to one ( $l = 1$ ) and express all energies in units of  $kT$ .

The short-range interaction between the segments of the chain and the surface is described by the boundary condition [25]

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

which is similar to that for the Schrödinger equation in the presence of a delta-shaped pseudopotential. From a mathematical standpoint, the adsorption of a macromolecule corresponds to the existence of the ground state in the corresponding quantum-mechanical problem. With  $c > 0$ , the macromolecule tends to lie flat on the plane; with  $c < 0$ , the macromolecule is desorbed; the case of  $c = 0$  corresponds to the so-called critical conditions of adsorption. The physical meaning of the parameter  $c$  is discussed in greater detail in Ref. [26].

Equations (1), (2) are also used for describing the diffusion of neutrons in the restricted half-space when particles are absorbed ( $c < 0$ ) or generated ( $c = 0$ ) on the boundary [27]. The critical condition ( $c = 0$ ) corresponds to the reflection of neutrons from the boundary.

The solution of equations (1), (2) was first obtained in Ref. [28] (see also Ref. [15]) and is expressed in terms of the dimensionless parameters  $\tilde{z} = z/(2R)$ ,  $\tilde{c} = cR$ , where  $R = (N/6)^{1/2}$  is the radius of inertia of the ideal polymer chain in free space:

$$P(\tilde{z}|\tilde{c}) = (\pi R^2)^{-1/2} \exp(-\tilde{z}^2) [1 + \pi^{1/2} \tilde{c} Y(\tilde{z} - \tilde{c})]. \quad (3)$$

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

### 3. Adsorption in the presence of an external force applied to the end of the chain

If a constant external force  $f$  is applied to the free end of the Gaussian chain, then the statistical weight of all paths ending at the same height  $z$  is  $P(\tilde{z}|\tilde{c}) \exp(fz)$ . The positive values of  $f$  correspond to forces that tend to tear the chain off the surface, and the negative values correspond to forces that tend to press the end of the chain down. Introducing a dimensionless variable  $\tilde{f} = fR$ , we obtain

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

After integration over all possible positions of the free end, we obtain the partition function for the adsorbed polymer chain in an external field [15]:

$$Q(\tilde{c}, \tilde{f}) = \frac{\tilde{c} Y(-\tilde{c}) - \tilde{f} Y(-\tilde{f})}{(\tilde{c} - \tilde{f})}. \quad (5)$$

### 4. Order parameters

In theories of adsorption, the role of the parameter of order is usually played by the mean fraction of the adsorbed segments  $\langle \theta \rangle = \langle m \rangle / N = -N^{-1} \partial \ln Q / \partial c$  [14, 15]. For the adsorbed chain, this fraction is finite and does not depend on  $N$ . For a chain that is desorbed or detached from the surface by an external force, we have  $\langle \theta \rangle \sim N^{-1}$ .

In the case of adsorption in an external field, it would be natural to define one more order parameter, namely, the mean stretching of the chain in the direction of the force (that is, in the direction normal to the plane)

$$\langle \zeta \rangle = \frac{\langle z \rangle}{N} = -N^{-1} \frac{\partial \ln Q}{\partial f}.$$

The stretching is negligibly small for an adsorbed chain and is on the order of unity for a detached chain.

Using Eqn (5), it is easy to obtain expressions for  $\langle m \rangle / R$  and  $\langle z \rangle / R$  that are directly related to the order parameters:

$$\frac{\langle m \rangle}{R} = \langle \theta \rangle \sqrt{6N} = \frac{(2\tilde{c}^2 + 1)Y(-\tilde{c}) + (2/\sqrt{\pi})\tilde{c}}{\tilde{c}Y(-\tilde{c}) - \tilde{f}Y(-\tilde{f})} - \frac{1}{\tilde{c} - \tilde{f}}, \quad (6)$$

$$\frac{\langle z \rangle}{R} = \langle \zeta \rangle \sqrt{6N} = \frac{(2\tilde{f}^2 + 1)Y(-\tilde{f}) + (2/\sqrt{\pi})\tilde{f}}{\tilde{f}Y(-\tilde{f}) - \tilde{c}Y(-\tilde{c})} - \frac{1}{\tilde{f} - \tilde{c}}. \quad (7)$$

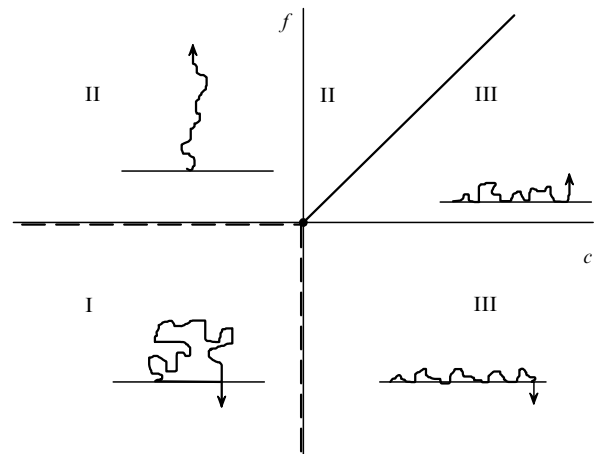
In the absence of an external force ( $f = 0$ ), equations (6), (7) reduce to the known expressions

$$\frac{\langle m \rangle}{R} = 2\tilde{c} + \frac{2}{\sqrt{\pi} Y(-\tilde{c})}, \quad (8)$$

$$\frac{\langle z \rangle}{R} = \frac{1}{\tilde{c}} - \frac{1}{\tilde{c} Y(-\tilde{c})}. \quad (9)$$

### 5. Phase diagram

In the case of an asymptotically long polymer chain ( $N \rightarrow \infty$ ), one may speak of its phase states. These states are conveniently represented on a phase diagram (Fig. 1). Movement upwards on the diagram corresponds to pulling the chain away; downward movement corresponds to pushing the end of the chain down onto the surface. The adsorption force increases to the right, and the repulsion between the segments of the chain and the surface increases to the left. The three separate regions on the diagram correspond to an ‘isotropic’ phase ( $\langle \theta \rangle = \langle \zeta \rangle = 0$ ), a ‘stretched’ phase ( $\langle \theta \rangle = 0$  and  $\langle \zeta \rangle > 0$ ), and an ‘adsorbed’ phase ( $\langle \theta \rangle > 0$  and  $\langle \zeta \rangle = 0$ ). Two dashed lines indicate phase transitions of the second order, the solid line denotes phase transitions of the first order; their intersection is the bicritical point  $c = f = 0$ .



**Figure 1.** Phase diagram of the system and typical conformations of the chain corresponding to each phase: I, ‘isotropic’ phase; II, ‘stretched’ phase; and III, ‘adsorbed’ phase.

Table 1.

	$\langle \theta \rangle$	$\langle \zeta \rangle$	
$f > 0$	$[N(f-c)]^{-1}$	$\frac{f}{3} \left[ 1 - \frac{3c}{N(f-c)f^2} \right]$ ,	$-c \gg 1$
	$\frac{f}{6} \left[ 1 + \frac{Nf(c-f)}{18} \right]$	$\frac{f}{6} \left[ 1 + \frac{Nf(f-c)}{18} \right]$ ,	$ c  \ll 1$
	$\frac{c}{3} \left[ 1 - \frac{3f}{N(c-f)c^2} \right]$	$[N(c-f)]^{-1}$ ,	$c \gg 1$
$f = 0$	$(Nc)^{-1}$	$\left( \frac{\pi}{6N} \right)^{1/2}$ ,	$-c \gg 1$
	$\left( \frac{2}{3\pi N} \right)^{1/2} \left[ 1 + (\pi-2)(6\pi)^{-1/2} N^{1/2} c \right]$	$\left( \frac{2}{3\pi N} \right)^{1/2} \left[ 1 + \frac{4-\pi}{2} (6\pi)^{-1/2} N^{1/2} c \right]$ ,	$ c  \ll 1$
	$\frac{c}{3}$	$(Nc)^{-1}$ ,	$c \gg 1$
$f < 0$	$(Nc)^{-1} \left[ 1 - \left( \frac{c}{f} \right)^2 \right]$	$2(N f )^{-1}$ ,	$-c \gg 1$
	$\left( \frac{\pi}{6N} \right)^{1/2} \left( 1 + \sqrt{\frac{\pi}{6}} N^{1/2} c \right)$	$(N f )^{-1}$ ,	$ c  \ll 1$
	$\frac{1}{3} c \left[ 1 + \frac{( f -c)}{N f c^2} \right]$	$[N(c+ f )]^{-1}$ ,	$c \gg 1$

Typical conformations of the chain are shown on each portion of the diagram.

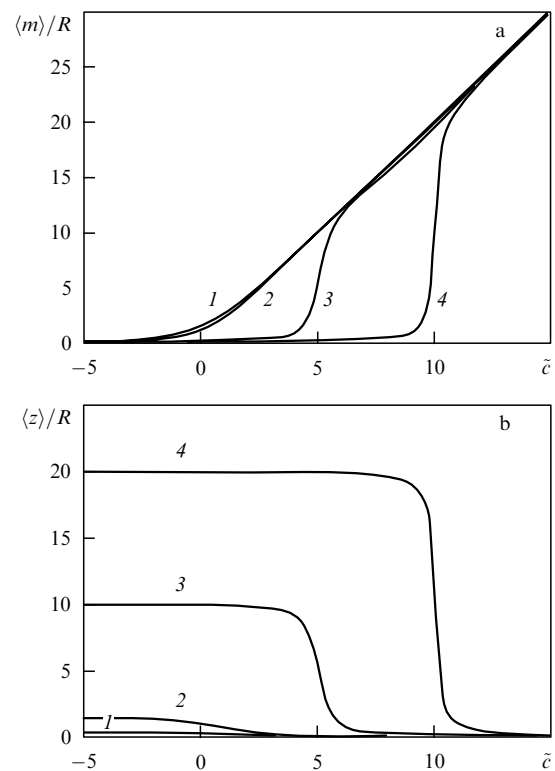
The approximate expressions for the order parameters for horizontal movement in different portions of the diagram are listed in Table 1.

The parameters  $\langle m \rangle / R$  and  $\langle z \rangle / R$  are plotted as functions of  $\tilde{c} = cR$  for several different values of  $\tilde{f}$  in Fig. 2a, b. Curves 1 correspond to the horizontal movement in the lower portion of the phase diagram (in the presence of a force pushing the free end of the chain toward the surface). Curves 2 describe the horizontal motion across the bicritical point (in the absence of an external force), and curves 3 and 4 correspond to horizontal movement in the upper portion of the diagram in the presence of a detaching force.

Figure 3a–d shows the mean order parameters — the fraction of the adsorbed segments of the chain  $\langle \theta \rangle$  and the stretching of the chain  $\langle \zeta \rangle$  — versus the magnitude of the adsorption interaction  $c$  for different values of  $N$ . Figure 3a, b corresponds to phase transitions of the second order, when the external force is zero ( $f = 0$ ) and the path on the diagram crosses the bicritical point. We see that as the number of segments  $N$  increases, the order parameter  $\langle \theta \rangle$  features a bend, which is typical of phase transitions of the second order. The second order parameter  $\langle \zeta \rangle$  is nonzero only for chains of finite length. Figure 3c, d corresponds to a phase transition of the first order, when there is a detaching force  $f = 0.2$ . In this case, both order parameters  $\langle \theta \rangle$  and  $\langle \zeta \rangle$  for the asymptotically long chain change abruptly at the point of transition  $c = f = 0.2$ .

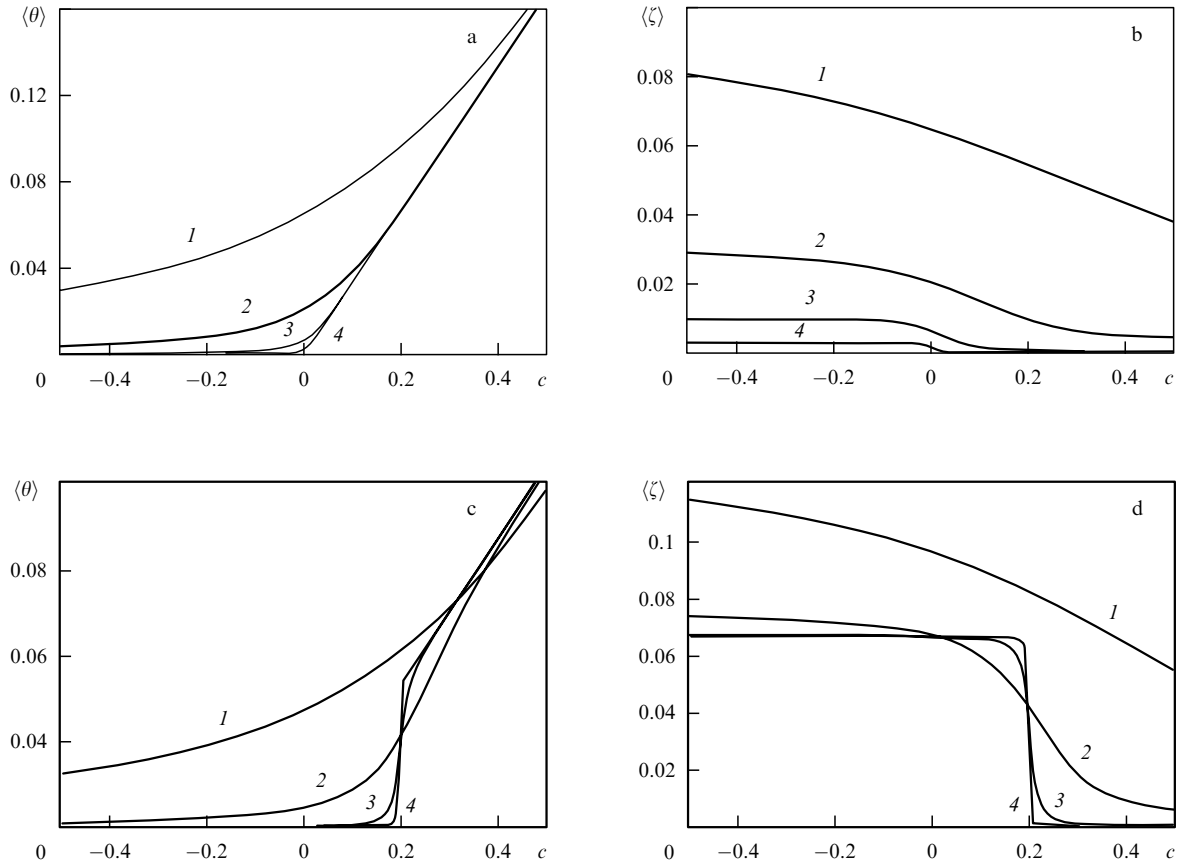
## 6. Symmetry properties

The partition function (5) is symmetrical with respect to the adsorption parameter  $\tilde{c}$  and the reduced external force  $\tilde{f}$ . One may say therefore that adsorption is in a sense equivalent to the action of an external force [16]. As follows from Eqns (6), (7), the mean number of adsorbed segments  $\langle m(c|f) \rangle$  is



**Figure 2.** (a) Reduced mean number of contacts  $\langle m \rangle / R = \langle m \rangle (N/6)^{-1/2}$  of the polymer chain with the plane and (b) the reduced mean height  $\langle z \rangle / R = \langle z \rangle (N/6)^{-1/2}$  of the free end of the chain vs. the reduced parameter of adsorption interactions  $\tilde{c} = cR$ . The magnitude of the reduced external force  $\tilde{f} = fR$  acting on the free end of the chain is  $-5$  (1), 0 (2), 5 (3), and 10 (4).

described by the same functional dependence as the mean height of the end of the chain  $\langle z(f|c) \rangle$ . It is easy to see that all the remaining moments of distributions with respect to the number of contacts  $m$  and the height of the end of the chain  $z$



**Figure 3.** Order parameters of the system, i.e., the mean fraction of contacts of the chain with the plane  $\langle \theta \rangle = \langle m \rangle / N$  (a, c) and the mean stretching of the chain  $\langle \zeta \rangle = \langle z \rangle / N$  (b, d), vs. the magnitude of the adsorption interactions  $c$  in second-order phase transitions (a, b), when the external force is absent ( $f = 0$ ), and in first-order phase transitions (c, d), when the detaching force is  $f = 0.2$ . The number of segments in the chain is  $N = 50$  (1),  $5 \times 10^2$  (2),  $5 \times 10^3$  (3), and  $5 \times 10^4$  (4).

also transform into one another when we make the substitution  $c \leftrightarrow f$ . The distributions themselves are similar as well. Because of this, a distribution with respect to the number of contacts  $c \leftrightarrow f$  can be derived from Eqn (4):

$$P(\tilde{m}|\tilde{c}, \tilde{f}) = (\pi R^2)^{-1/2} \exp[\tilde{c}^2 - (\tilde{m} - \tilde{c})^2] \times [1 + \pi^{1/2} \tilde{f} Y(\tilde{m} - \tilde{f})]. \quad (10)$$

As follows from the phase diagram, adsorption of the ideal chain on the plane in the absence of external forces ( $f = 0$ ) corresponds to motion along the line of phase transitions of the second order across the bicritical point and is similar to the detachment of the chain at the critical value of the energy of the adsorption interaction ( $c = 0$ ). Adsorption of the chain with the pressed end ( $f < 0$ ) is equivalent to stretching the chain attached to an inert or repulsive surface ( $c < 0$ ) and occurs as a phase transition of the second order. Adsorption of the chain in the presence of a continually acting detaching force ( $f > 0$ ) is equivalent to stretching the adsorbed chain ( $c > 0$ ).

## 7. Effects of the finiteness of the system

When analyzing the effects of the finiteness of the system, it is assumed [29] that the free energy of the system in the neighborhood of the phase transition depends on the size of the system  $L$  only in the combination  $L/\xi$  (where

$\xi \sim |T - T_c|^{-\nu}$  is the correlation length, and  $\nu$  is the corresponding correlation exponent), and the free energy is written in the form  $F = F(|T - T_c|L^{1/\nu})$ . If the system is characterized by the number of particles  $N$ , then we use the relation  $L \sim N^{1/d}$  and, assuming that  $d\nu = 2 - \alpha$ , obtain

$$F = F(|T - T_c|N^{1/(2-\alpha)}), \quad (11)$$

where  $\alpha$  is the critical exponent for the heat capacity.

In the vicinity of the critical point, the critical length  $\xi$  is much greater than the length of the element  $l$ , and then two characteristic regimes are observed: the scaling regime  $L/\xi \gg 1$ , in which  $F$  is a power function of its arguments, and the regime  $L/\xi \ll 1$ , in which  $F$  tends to a constant value. A smooth transition from one regime to the other occurs under the condition  $L/\xi \sim 1$ , that is, in a range

$$\Delta T \sim N^{-1/(2-\alpha)}. \quad (12)$$

Let us now compare Eqn (11), (12) with the results that follow from the exact partition function (5). As we go along the line of phase transitions of the second order  $f = 0$  on the phase diagram, the free energy varies as

$$F = \text{const} + \ln(Y(-\tilde{c})). \quad (13)$$

If we are moving in the lower portion of the phase diagram, where there is a permanent down-pressing force, and cross the

vertical line of phase transitions of the second order, then the free energy is

$$F \cong F_0 + \ln(\tilde{c}Y(-\tilde{c}) + \pi^{-1/2}), \quad (14)$$

where the regular part  $F_0$  contains the dependence on the down-pressing force  $-f$ .

In both cases, the free energy is a function of the scaling parameter  $\tilde{c} = c(N/6)^{1/2}$ . The value  $\tilde{c} \sim 1$  separates the characteristic regimes. Comparing Eqns (13), (14) with (11), (12), and taking into account the fact that  $|c|$  characterizes the deviation from the critical point, we see that the second-order transitions in our system are of a mean-field nature with a heat capacity exponent  $\alpha = 0$  and occur in a range of  $|c| \sim N^{-1/2}$  when crossing the vertical line of second-order phase transitions on the diagram (or in a range of  $|f| \sim N^{-1/2}$  when crossing the horizontal line). The width of the bicritical region is of the order of  $N^{-1/2}$  in both directions on the phase diagram.

Figure 4a shows the variation of the mean order parameter  $\langle\theta\rangle$  as a function of the inverse number of segments in the system ( $N^{-1}$ ) in the absence of an external force ( $f = 0$ ) for several values of  $c$ . Using the condition  $\tilde{c} \sim 1$ , it would be natural to define a characteristic chain length  $N^* \approx 6/c^2$  that separates ‘short’ and ‘long’ chains, that is, ‘small’ and ‘large’ systems. This characteristic value of  $N^*$

is indicated in Fig. 4a by arrows. As follows from the formulas listed in Table 1, for negative values of  $c$  the order parameter  $\langle\theta\rangle$  for ‘long’ chains tends to zero as  $N^{-1}$  as the chain becomes longer and remains constant ( $c/3$ ) when  $c$  is positive. On the other hand, for ‘short’ chains we have  $\langle\theta\rangle \sim N^{-1/2}$  irrespective of on which side of the transition point the system is. In the immediate neighborhood of the transition point  $c = 0$ , the value of  $N^*$  grows indefinitely, and so chains of almost any length behave as ‘short’ ones.

Let us now consider crossing the line of phase transitions of the first order when the adsorption forces of attraction to the plane increase and there is a constant detaching force  $f$ . If we are far enough from the bicritical point, and  $c \gg N^{-1/2}$ ,  $f \gg N^{-1/2}$ , then the free energy can be written as

$$\begin{aligned} F &= \ln\left\{2t \exp(t^2 + x^2) [x^{-1} \sinh(2tx) + t^{-1} \cosh(2tx)]\right\} \\ &= F_0 + \ln\left[\frac{\sinh(2tx)}{tx}\right], \end{aligned} \quad (15)$$

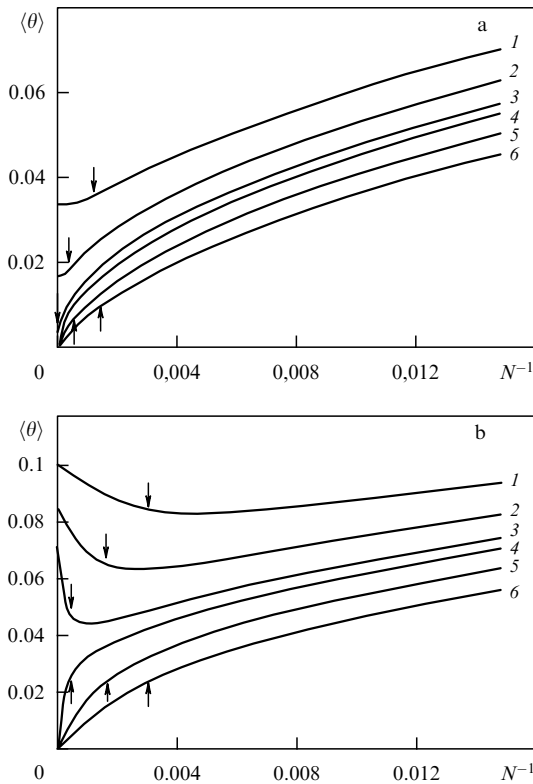
where  $t = (f + c)/2 \cong f$ ,  $x = (f - c)/2$ , and  $F_0$  is a function changing little in the neighborhood of the transition. We see that the free energy is determined by the combination  $tx \sim (Nf)\Delta c$ , where  $\Delta c$  is the deviation from the transition point  $c = f$ . Accordingly, the first-order phase transitions are characterized by the width  $\Delta c \sim (Nf)^{-1}$ , which decreases away from the critical point  $f = c = 0$ .

Since the critical exponent of heat capacity in the first-order phase transitions can formally be set equal to unity (see Section 10), this result agrees with the scaling assumption (12).

In the case of phase transitions of the first order, when the chain stretched by a constant force is adsorbed, the mean fraction of adsorbed segments  $\langle\theta\rangle$  in an asymptotically long macromolecule changes abruptly at the transition point  $c = f$  from zero to  $c/3$  (see Table 1). For finite values of  $N$ , the transition is smoothed out (Fig. 3c). One may define the characteristic size of the system  $N^* \approx 6(f\Delta c)^{-1}$  above which the polymer chain may be regarded as ‘large’; the polymer chain is considered ‘small’ when  $N < N^*$ . Figure 4b shows the order parameter  $\langle\theta\rangle$  versus  $N^{-1}$  for a constant stretching force  $f = 0.2$  and different deviations  $\Delta c = c - f$  from the point of phase transition. Arrows indicate the values of  $N^*$  which separate ‘large’ and ‘small’ systems. From Fig. 4b we see that if  $\Delta c < 0$ , then the limiting value is  $\langle\theta\rangle = 0$ . If  $\Delta c > 0$ , then the order parameter tends to a finite value of  $c/3$ . In ‘large’ systems, the order parameter approaches its limit linearly with respect to  $N^{-1}$ , and the slope of this function is determined by the magnitude and sign of  $(\Delta c)^{-1}$ , that is, by the distance from the transition point. At the same time, the order parameter for ‘small’ systems is always of the order of  $N^{-1/2}$ , irrespective of whether the system is above or below the transition point, as in the case of phase transitions of the second order. Making use of Eqn (6), for ‘small’ systems we can obtain the following expression:

$$\langle\theta\rangle \approx \left(3\sqrt{\frac{\pi N}{6}}\right)^{-1} \left[1 + \left(3 - \frac{8}{\pi}\right)6^{-1/2}N^{1/2}c\right]. \quad (16)$$

We see that linear extrapolation with respect to  $N^{-1}$  in the case of phase transitions of the first order is only allowable for ‘large’ systems with  $N \gg N^*$ , and the closer we are to the point of phase transition the greater is the critical value of  $N^*$ .



**Figure 4.** Mean parameter of order  $\langle\theta\rangle$  (the mean fraction of adsorbed segments) vs. the inverse size of the system  $N^{-1}$  (inverse number of segments in the chain) at phase transitions of the second order when the external force is absent (a), and at phase transitions of the first order (b) under a constant stretching force  $f = 0.2$ . Arrows indicate the characteristic size  $N^*$  separating ‘short’ and ‘long’ chains. The deviation from the transition point  $\Delta c = c - f$  is 0.1 (1); 0.05 (2); 0.01 (3);  $-0.01$  (4);  $-0.05$  (5), and  $-0.1$  (6).

## 8. Description based on Landau's theory

### 8.1 Phase transitions of the second order

The phenomenological theory of phase transitions proposed by L D Landau [17] is based on treating the free energy  $F$  of the system as a function of the order parameter  $\phi$ . Near the second-order phase transition, the free energy  $F$  is expanded in  $\phi$ ; the expansion in the case of the isotropic model is performed in even powers of  $\phi$ :

$$F(\phi) = F_0 + A(T - T_c)\phi^2 + B\phi^4 + \dots \quad (17)$$

The coefficients  $A$  and  $B$  are assumed to be positive and more or less constant in the neighborhood of the phase transition, and so the quadratic term changes its sign at  $T = T_c$ . Minimizing (17) in  $\phi$ , we obtain equilibrium values  $\phi_0 = 0$  at  $T > T_c$  and  $\phi_0 = [A|T - T_c|/2B]^{1/2}$  at  $T < T_c$ . The heat capacity exhibits a finite jump  $T_c A^2/2B$  at the point of transition.

For a Gaussian chain adsorbed on a plane, one may also consider the free energy per segment as a function of the fraction of adsorbed segments  $\theta = m/N$ , assuming that this order parameter may fluctuate and is not a mean value. The partition function of the chain  $P(\theta)$  in the absence of an external force ( $f = 0$ ) is expressed from Eqn (10):

$$P(\theta) = \left(\frac{\pi N}{6}\right)^{-1/2} \exp\left(-\frac{3}{2} N\theta^2 + Nc\theta\right). \quad (18)$$

Accordingly, the free energy  $F(\theta) = -N^{-1} \ln P(\theta)$  is

$$F(\theta) = F_0 - c\theta + \frac{3}{2} \theta^2. \quad (19)$$

Equation (19) has a physical meaning only when  $0 \leq \theta \leq 1$ , since the fraction of adsorbed segments cannot be negative. On the other hand, the free energy in Landau's

theory is invariant with respect to the substitution  $\phi \rightarrow -\phi$ , and is assumed to be analytical near  $f = 0$ . Introducing a new variable  $\phi$  defined by  $\theta = \phi^2$ , we obtain symmetrical behavior for the free energy over the interval  $[-1, 1]$ :

$$F(\phi) = F_0 - c\phi^2 + \frac{3}{2} \phi^4. \quad (20)$$

The free energy  $F$  versus  $\phi$  in this form is plotted in Fig. 5a for several values of  $c$  and is in perfect agreement with Eqn (17) of Landau's theory. Such curves can be found in almost any textbook on statistical physics; this time, however, they have been obtained from the exact partition function and hold not only in the thermodynamic limit, but also for systems of finite size.

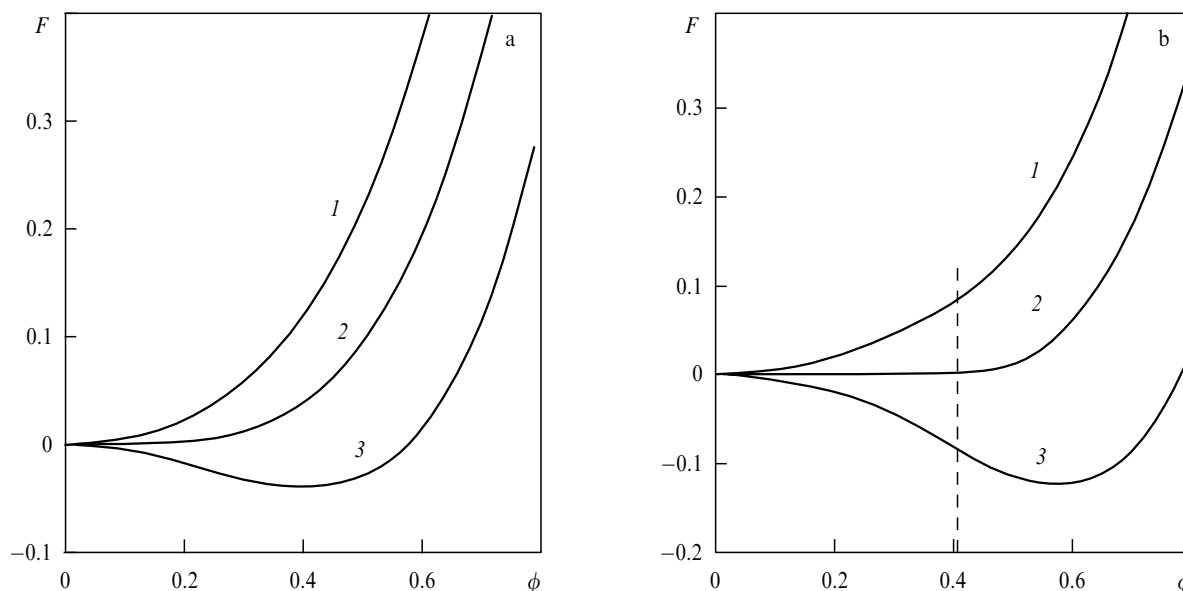
If the adsorbed system is under the action of a downpressing force ( $f < 0$ ), then, for not too weak forces  $|f| \gg N^{-1/2}$ , the free energy as a function of  $\phi$  is

$$F(\phi) = F_0 - c\phi^2 + \frac{3}{2} \phi^4 + \frac{1}{N} \log\left(1 + \frac{1}{3} |f| \phi^4\right), \quad (21)$$

which in the thermodynamic limit  $N \rightarrow \infty$  is equivalent to Eqn (20).

It is known that Landau's theory does not hold for low-molecular systems in the neighborhood of phase transition because of the strong correlations of fluctuations of the order parameter. For the polymer system under consideration, the order parameter is the fraction of adsorbed segments or the stretching of the chain. In either case the order parameter is not a local but rather a 'global' quantity that characterizes the macromolecule as a whole. Accordingly, there is no question of correlations of fluctuations of these order parameters, and the system always exhibits mean-field behavior.

The fact that Eqn (20) only involves two terms with  $\phi^2$  and  $\phi^4$  is explained by the elasticity of the Gaussian chain. If the finite stretchability of the polymer molecule is taken into account, the function  $F(\phi)$  will also involve higher-order terms.



**Figure 5.** Landau's free energy  $F$  vs. the parameter  $\phi$ , calculated for a polymer chain that undergoes (a) a phase transition of the second order (adsorption in the absence of an external force,  $f = 0$ ), and (b) a phase transition of the first order (adsorption with a detaching force,  $f = 0.5$ ). The dashed line indicates joining of the analytical branches of  $F(\phi)$ . The values of the parameters  $c - f$ , i.e., the deviation from the point of transition, is  $-0.5$  (1),  $0$  (2), and  $0.5$  (3).

## 8.2 Phase transitions of the first order

Let us consider the behavior of Landau's free energy in the case of phase transitions of the first order that occur upon crossing the line  $c = f$  on the phase diagram. According to Landau's theory, in this case the free energy  $F(\phi)$  in a certain range of external parameters must exhibit two minima. The deeper minimum corresponds to the equilibrium state of the system, while the other corresponds to a metastable state. As the controlling parameter is varied, the relative depth of these minima changes, and the point of phase transition corresponds to switching from one minimum to the other. In the case of phase transitions of the first order, the jump of the order parameter occurs abruptly and is not accompanied by the growth of fluctuations in the pretransition region.

In our polymer model, the first order phase transitions occur in a somewhat peculiar manner. Landau's free energy is expressed from the exact formula (10). In contrast to phase transitions of the second order, however, the function  $F(\phi)$  in the thermodynamic limit  $N \rightarrow \infty$  becomes nonanalytical at positive  $f$  and  $c$  and consists of two branches: a part of a parabola and a fourth-order curve, which are tangent at  $\phi^* = (f/3)^{1/2}$ :

$$F(\phi) - F_0 = \begin{cases} (f - c)\phi^2, & \phi \leq \phi^*, \\ \frac{1}{6}(f^2 - c^2) + \frac{3}{2}\left(\phi^2 - \frac{c}{3}\right)^2, & \phi \geq \phi^*. \end{cases} \quad (22)$$

At the point of tangency, the second derivatives of  $F(\phi)$  exhibit a break, but all singularities disappear when  $N$  is finite.

Figure 5b shows Landau's free energy versus  $\phi$  for a constant detaching force  $f = 0.5$  and several values of  $c$ . The dashed line indicates the value of  $\phi^*$ . At the transition point itself ( $c = f$ ), curve  $F(\phi)$  has a flat portion, which corresponds to a finite jump of the order parameter. The existence of this flat portion gives rise to anomalous fluctuations in the pretransition region.

Function  $F(\phi)$  always has only one minimum, and therefore there are no metastable states. The reason is as follows: each state at the point of transition consists of two parts (phases) — the stretched tail of the chain and the adsorbed part on the surface. All states, with arbitrary fraction of adsorbed segments, are equiprobable as indicated by the flat portion of the curve. On the other hand, the activation barrier, which separates the adsorbed and the stretched parts, is not present (the phase boundary is actually a single segment).

An analogy can be drawn with a liquid–gas mixture in a cylinder at a constant pressure equal to the saturated vapor pressure. The phase-separated states (gas and liquid) have the same free energy at any volume on the flat portion of the van der Waals curve. The total density of the system, which is the 'global' order parameter, will fluctuate between the densities of the liquid and the vapor. This phase-separated system corresponds to infinite compressibility (in the case of strictly equilibrium states).

## 9. Joint distribution with respect to two order parameters near the bicritical point

So far we have been discussing the behavior of the polymer system in terms of two order parameters  $\theta$  and  $\zeta$  (or  $\phi^2 = \theta$  and  $\psi^2 = \zeta$ ) taken separately. The height-of-the-free-end and the-number-of-contacts distributions are described by Eqns

(4) and (10), respectively. To better understand the cause for the appearance of the flat portion in the  $F(\phi)$  curve, it will be useful to consider Landau's free energy as a function of two independent variables, i.e.,  $F(\phi, \psi)$ . It can be demonstrated [30] that in the neighborhood of the bicritical point, where  $\phi \ll 1$  and  $\psi \ll 1$ , the joint distribution has the form

$$F(\phi, \psi) = -c\phi^2 - f\psi^2 + \frac{3}{2}\phi^4 + \frac{3}{2}\psi^4 + 3\phi^2\psi^2. \quad (23)$$

If we move along the line of first-order phase transitions ( $c = f$ ), crossing the phase diagram diagonally, then the Landau free energy will be a function of only one variable  $t^2 = \phi^2 + \psi^2 = \theta + \zeta$ :

$$F = -ct^2 + \frac{3}{2}t^4. \quad (24)$$

The mean value  $\langle \theta + \zeta \rangle$ , which is determined by the location of the minimum of function (23), behaves in the same way as in the mean-field theory of the second-order phase transitions:

$$\langle \theta + \zeta \rangle = \begin{cases} 0, & c < 0, \\ \frac{c}{3}, & c > 0. \end{cases} \quad (25)$$

On the line of the first-order phase transitions ( $c = f$ ,  $c, f > 0$ ), all states with the given mean value  $\langle \theta + \zeta \rangle = c/3$  exhibit anomalously large fluctuations with respect to each of the order parameters; for example, all states with any  $\theta$  in the range between 0 and  $c/3$  are equiprobable.

Note that in the analysis of critical behavior in a system of connected fields, the joint distribution of the Landau free energy with respect to two order parameters is specified from considerations of convenience and symmetry [18]. By contrast, the distribution  $F(\phi, \psi)$  in our polymer system is found from the exact partition function.

## 10. Complex zeros of the partition function

Thermodynamic functions display singularities at phase transitions; they themselves or their derivatives exhibit finite or infinite jumps. At the same time, the partition function, which is a sum of exponentials (a sum of the statistical weights of states), is positive and has no singularities. The only possibility for a singularity to arise is when the partition function vanishes (or tends to zero). This brought Yang and Lee [19] to the idea of considering the zeros of the partition function of the grand canonical ensemble in terms of complex numbers (as a function of a complex chemical potential). Later, Fisher [19] proposed studying the distribution of zeros of the partition function of the canonical ensemble in the complex plane of temperatures or  $\beta = 1/(kT)$ .

Yang and Lee demonstrated that, for finite values of  $N$ , the grand partition function only has complex-conjugate zeros, and has no zeros on the real axis. If a phase transition is possible in the system, then, as the number of particles increases, the complex zeros come closer to the real axis, and the gap between the zeros and the real axis vanishes in the limit  $N \rightarrow \infty$ . The Yang–Lee theorem states that in the complex plane of chemical potential these zeros lie on a circle of unit radius. For the distribution of zeros of the partition function of the canonical ensemble in the complex plane of temperatures it was empirically established that they normally lie on smooth curves and approach the real axis at a certain angle  $\omega$ .



Grossmann and Rosenhauer [20] gave a classification of phase transitions assuming that complex zeros occur on a certain line with a given linear density  $g(y)$ , where  $y$  is the coordinate along the imaginary axis. Their analysis is based on the formula for the internal energy of unit volume of the system for a given deviation from the critical temperature  $\Delta = \beta - \beta_c$ :

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

Assuming that the density of zeros is a power-law function  $g(y) \sim y^{1-\alpha}$ , they found that:

(1) If the density  $g(y)$  tends to a constant at small  $y$  ( $\alpha = 1$ ), then the zeros approach the real axis at right angles  $\omega = \pi/2$ , and the energy exhibits a finite jump  $2\pi g$  when crossing the point  $\beta = \beta_c$ . This obviously corresponds to a phase transition of the first order.

(2) If the density grows linearly with  $y$  ( $\alpha = 0$ ) and crosses the real axis at the angle  $\omega = \pi/4$ , then the energy varies smoothly, but the heat capacity exhibits a finite jump, which corresponds to a mean-field phase transition of the second order.

(3) If  $\alpha = 0$ , but  $\omega > \pi/4$ , or if  $0 < \alpha < 1$  with arbitrary  $\omega$ , then the heat capacity at the critical point will diverge logarithmically when  $\alpha = 0$ , or increase as  $c_v \sim |\Delta|^{-\alpha}$  for all  $\alpha$  other than zero. In both cases the value of angle  $\omega$  determines the magnitude of heat capacity on both sides of the transition. The vertical line  $\omega = \pi/2$  corresponds to the symmetrical transition.

This model of adsorbed polymer chain allows verification of the predictions of Grossmann and Rosenhauer. Moving over the phase diagram (Fig. 1), we can gradually go from phase transitions of the first order to phase transitions of the second order, which are of a mean-field nature. Accordingly, the complex zeros must first cross the real axis at right angles, and then approach it at an angle  $\pi/4$ . In the polymer model, the controlling parameter  $c$  (or  $f$ ) is similar to the inverse temperature  $\beta$ , and the number of adsorbed segments (or the height of the free end of the chain) is similar to the energy  $E$ . We will analyze the partition function  $Q(c, f_0)$  in the complex plane of the parameter  $c$  for a fixed value of the external force  $f = f_0$ , which may be positive or negative but always real.

Let us first consider the distribution of zeros when crossing the line of phase transitions of the first order ( $f_0 = \text{const} > 0$ ). These zeros are found from the equation

$$cY\left(-c\sqrt{\frac{N}{6}}\right) - f_0Y\left(-f_0\sqrt{\frac{N}{6}}\right) = 0, \quad c \neq f_0, \quad (27)$$

which, upon transition to the polar coordinates  $c = \rho \exp(i\chi)$  and using asymptotic expressions for  $Y(x)$ , can be reduced to the form

$$\rho^2 \cos 2\chi + \frac{6}{N} \log \frac{\rho}{f_0} - f_0^2 = 0, \quad (28)$$

$$\chi + \frac{1}{6} \rho^2 N \sin 2\chi = 2\pi k, \quad k = \pm 1, \pm 2, \dots \quad (29)$$

The line on which the zeros occur at  $N \rightarrow \infty$  is described in polar coordinates as

$$\rho^2 \cos 2\chi = f_0^2, \quad (30)$$

and in Cartesian coordinates  $x = \text{Re}(c)$ ,  $y = \text{Im}(c)$  as

$$x^2 - y^2 = f_0^2 \quad (31)$$

and is therefore a hyperbola which crosses the real axis at right angles at the point  $x = f_0$  and has two asymptotes directed at  $\omega = \pi/4$  to the real axis. From Eqns (29) and (30) we get the equation which defines the locations of zeros on the hyperbola:

$$\chi + \frac{1}{6} f_0^2 N \tan 2\chi = 2\pi k, \quad k = \pm 1, \pm 2, \dots \quad (32)$$

When  $\chi$  is small, that is, near the real axis, we have

$$\chi_k = \frac{6\pi k}{3 + Nf_0^2}. \quad (33)$$

The limit of the density of the zeros

$$g = \lim_{N \rightarrow \infty} \frac{1}{N} \frac{dk}{ds},$$

where  $ds = \sqrt{d\rho^2 + \rho^2 d\chi^2}$ , is calculated exactly from Eqns (29) and (32) and is

$$g(\rho) = (6\pi)^{-1} \rho. \quad (34)$$

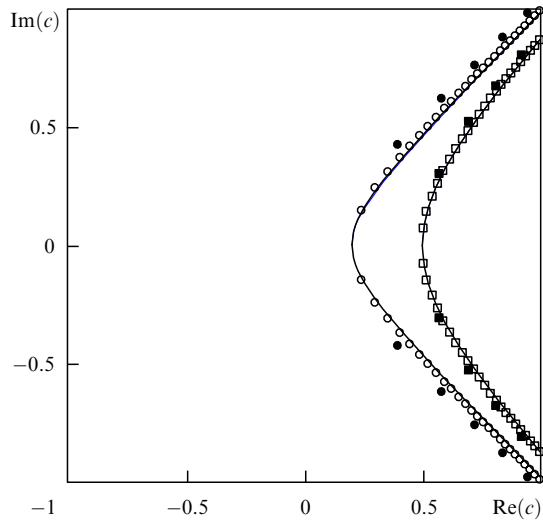
At the intersection with the real axis  $\rho = f_0$ ,  $\chi = 0$ , the density of zeros has a finite value of  $g_0 = f_0/(6\pi)$ , which in accordance with the above classification corresponds to a phase transition of the first order with a finite jump of the order parameter  $2\pi g_0 = f_0/3$  and is in agreement with the results of Table 1. Assuming that the distance  $s$  from the transition point along the curve on the asymptotic branches of the hyperbola is approximately equal to  $\rho$ , we find the location of the  $k$ th zero

$$\rho_k \cong \left( \frac{12\pi k}{N} \right)^{1/2}. \quad (35)$$

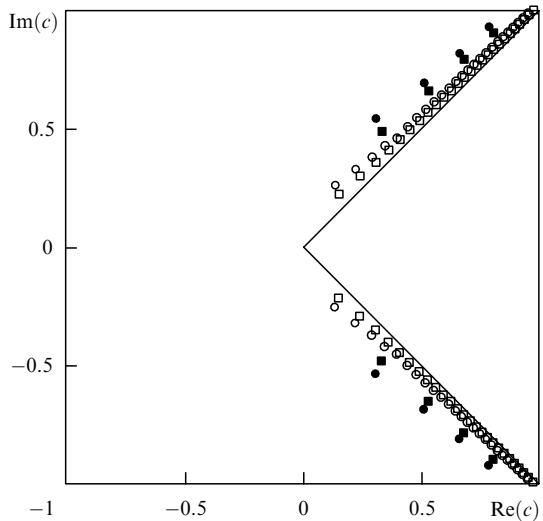
As we move on the diagram along the line of phase transitions of the first order toward the bicritical point, the focal length of the hyperbola  $f_0$  decreases and, accordingly, the density  $g_0$  decreases. At  $f_0 = 0$ , the hyperbola degenerates into two straight lines directed at the angle  $\omega = \pi/4$  to the real axis. The limiting density of zeros becomes  $g(|c|) = (6\pi)^{-1}|c|$ , which in accordance with the classification of Ref. [20] corresponds to a mean-field phase transition of the second order with a finite jump of the order parameter  $2\pi(6\pi)^{-1} = 1/3$ , where  $(6\pi)^{-1}$  is the coefficient in Eqn (34). The same result follows from straightforward differentiation of the free energy. As we recede from the bicritical point along the lines of phase transitions of the second order, neither the distribution of zeros nor their density exhibit any change:  $\omega = \pi/4$ ,  $g(\rho) = (6\pi)^{-1}\rho$ .

Figure 6 shows the arrangement of a few complex zeros of the partition function (5), calculated numerically for  $N = 100$  and  $N = 500$  in the case of phase transitions of the first order, when the polymer chain is adsorbed under a constant stretching force  $f = 0.2$  or  $f = 0.5$ . We see that the zeros occur on hyperbolas, and approach the real axis more closely, the greater the number of segments  $N$ .

The distribution of zeros in the case of phase transitions of the second order is shown in Fig. 7 for two cases: when the external force is absent ( $f = 0$ ), and when the external force



**Figure 6.** Distribution of zeros of the partition function in the complex plane of the parameter of adsorption interactions  $c$  for phase transitions of the first order (adsorption with a detaching force) at  $f = 0.2$  ( $\circ$ ,  $\bullet$ ) and  $f = 0.5$  ( $\square$ ,  $\blacksquare$ ). The solid symbols correspond to  $N = 100$ ; the open, to  $N = 500$ . The solid lines (hyperbolas) are calculated from Eqn (31).



**Figure 7.** Distribution of zeros of the partition function in the complex plane of the parameter of adsorption interactions  $c$  for phase transitions of the second order (adsorption with zero and a finite down-pressing force) at  $f = 0$  ( $\square$ ,  $\blacksquare$ ) and  $f = -0.2$  ( $\circ$ ,  $\bullet$ ). The solid symbols correspond to  $N = 100$ ; the open, to  $N = 500$ . The straight solid lines are directed at angles  $\omega = \pm\pi/4$  to the coordinate axes.

presses down the free end of the chain to the surface ( $f = -0.2$ ). As  $N$  increases, in both cases the zeros tend to occur on a straight lines at an angle  $\pi/4$  and approach the point  $c = 0$  on the real axis in accordance with the analytical results.

## 11. Scaling analysis of complex zeros of the partition function

According to Ref. [21], the distance from the  $k$ th zero to the real axis near the critical point obeys the scaling relation

$$y_k \sim L^{-1/\nu} k^{1/d\nu} \quad (36)$$

or, in terms of the number of particles  $N$ ,

$$y_k \sim \left(\frac{k}{N}\right)^{1/d\nu} \sim \left(\frac{k}{N}\right)^{1/(2-\alpha)}. \quad (37)$$

Setting  $\alpha = 0$  for phase transitions of the second order, we obtain the scaling prediction  $y_k \sim (k/N)^{1/2}$ , which agrees with the exact analytical result (35). On the other hand,  $\alpha = 1$  for phase transitions of the first order, and the scaling predictions also agree with the exact result  $y_k \approx f_0 \chi_k \approx (6\pi/f_0)(k/N)$  that follows from Eqn (29) and (33).

We found that the zero closest to the real axis in polar coordinates is

$$\chi_1 \approx \frac{6\pi}{3 + Nf_0^2}. \quad (38)$$

This relation can be used for evaluating the width of the bicritical region, assuming that this zero should occur not far from the asymptote  $\chi_1 \sim 1$ . Then  $Nf_0^2 \sim 1$  and  $f_0 \sim N^{-1/2}$  in accordance with the estimate made in Section 7.

In the lattice models, the partition function for finite systems is a polynomial and has a finite number of zeros. By contrast, the partition function in our polymer model has an infinite number of zeros for any  $N$ , since we have used the continual model with an infinite number of states.

## 12. Conclusion

We have considered a model of adsorption of a polymer chain in an external field, which admits exact analytical treatment in the calculation of the partition function. The model allows us to obtain exact expressions for the Landau free energy as a function of order parameters of the system in first-order and second-order phase transitions and in the neighborhood of the bicritical point. It is also possible to analytically study the distribution of complex zeros of the partition function. This rigorous treatment can be applied not only in the thermodynamic limit, but also to systems of finite size.

Now, there is a natural question: why such a treatment is possible, and what distinguishes this polymer model from the classical exactly solvable lattice low-molecular models.

We can point to at least three special features of our polymer model. First, the interactions between individual elements of the system (the monomer segments of the chain) are taken into account from the outset in writing the initial differential equation (1) for the random-walk chain. By assumption, each segment only interacts with its closest neighbors, while there are no bulk interactions between the segments that occasionally come close to each other. Second, both order parameters — the stretching of the chain and the fraction of segments in contact with the plane — are not local, but rather characterize the system as a whole. Because of this, there are no correlations of fluctuations of these order parameters. Third, the external field directed along the normal to the plane only acts on the free end of the chain and does not act either on kinks or on the adsorbed portions of the molecule. Given the Gaussian properties of the random walk, this makes the problem one-dimensional.

Owing to its simplicity, the behavior of our polymer model is of mean-field nature and, thus, to a certain extent trivial. On the other hand, by virtue of its being simple, the model can serve as a good example for discussing various methods and approaches in statistical physics and be a useful teaching aid.

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