Analytical theory of finite-size effects in mechanical desorption of a polymer chain

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We discuss a unique system that allows exact analytical investigation of first- and second-order transitions with finite-size effects: mechanical desorption of an ideal lattice polymer chain grafted with one end to a solid substrate with a pulling force applied to the other end. We exploit the analogy with a continuum model and use accurate mapping between the parameters in continuum and lattice descriptions, which leads to a fully analytical partition function as a function of chain length, temperature (or adsorption strength), and pulling force. The adsorption-desorption phase diagram, which gives the critical force as a function of temperature, is nonmonotonic and gives rise to re-entrance. We analyze the chain length dependence of several chain properties (bound fraction, chain extension, and heat capacity) for different cross sections of the phase diagram. Close to the transition a single parameter (the product of the chain length N and the deviation from the transition point) describes all thermodynamic properties. We discuss finite-size effects at the second-order transition (adsorption without force) and at the first-order transition (mechanical desorption). The first-order transition has some unusual features: The heat capacity in the transition region increases anomalously with temperature as a power law, metastable states are completely absent, and instead of a bimodal distribution there is a flat region that becomes more pronounced with increasing chain length. The reason for this anomaly is the absence of an excess surface energy for the boundary between adsorbed and stretched coexisting phases (this boundary is one segment only): The two states strongly fluctuate in the transition point. The relation between mechanical desorption and mechanical unzipping of DNA is discussed. © 2010 American Institute of Physics.

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I. INTRODUCTION

Manipulation of individual macromolecules is an important tool for understanding their mechanical properties. Much interest in static and dynamic properties of a polymer chain at a surface has been evoked by experiments with atomic force microscopy (AFM), optical/magnetic tweezers, photon microscopy, etc.1–5 The force needed to detach a chain from an adsorbing surface was measured both with uncharged polymers and with polyelectrolytes.6–9 For different types of substrates, this force is in the range of 50–80 pN.

Several theoretical studies10–23 have provided insight into the equilibrium behavior and the mechanism of polymer detachment from an adsorbing surface. The first analytical theory10 for mechanical desorption of a chain grafted with one end to a surface by an external force applied to the other end was constructed a long time ago using a lattice model in the limit of infinite chain length. Later, theories for a finite Gaussian continuum chain were proposed.11–14 These were used to interpret AFM experiments.15 The response of an adsorbed polymer chain to a pulling force with a lateral component was also analyzed.15 Recently a theory for mechanical desorption of an infinitely long self-avoiding polymer chain was developed and verified by Monte Carlo (MC) simulations with a coarse-grained off-lattice bead-spring model.17,18 Computer simulations of mechanical desorption of self-avoiding walks on simple square and cubic lattices have also been reported.19–22

There is a close analogy between mechanical desorption of a polymer chain and mechanical unzipping of double-stranded DNA. Mechanical unzipping of DNA and the critical untwisting force as a function of temperature were studied analytically by a directed walk model.22,23

The lattice theory of mechanical desorption10 is formulated in terms of two dimensionless parameters: an adsorption parameter \(\chi = \epsilon/kT\) and a force parameter \(\varphi = f\ell/kT\). Here \(\epsilon\) is the adsorption energy or the depth of the square-well potential for an adsorbed segment; the width of the well is the step length \(\ell\). The parameter \(f\) is the external force exerted on the free end of the chain. For simplicity, we omit the Boltzmann constant \(k\) so the symbol \(T\) stands for the thermal energy. We also omit \(\ell\) so all lengths are in units of the step length. Moreover, we keep \(\epsilon\) constant and express all energies in units \(\epsilon\). Hence, we write simply \(\chi = 1/T\) and \(\varphi = f/T\), where the thermal energy \(T\) is in units \(\epsilon\) and the force \(f\) in units \(\epsilon/\ell\). Mathematically, this is equivalent to setting \(k\), \(\ell\), and \(\epsilon\) unity.

Although the temperature is included in both parameters...
$\chi$ and $\varphi$, the temperature dependence was not discussed in the original model.\(^{10}\) In a recent paper,\(^{16}\) we presented analytical theory for the temperature phase diagram (detachment force versus $T$) and discussed the properties of an infinitely long lattice chain subject to mechanical desorption.

Analytical solutions for finite chain lengths in a lattice model do not exist so far. However, analytical theory for a continuum model with finite chain length $N$ is available.\(^{11-13}\) In this continuum model two other parameters occur: The adsorption strength is described by a parameter $c$ and the pulling force enters the partition function as a dimensionless combination $u = f d b / k T$, where $b$ is the Kuhn segment length. We distinguish between the force parameters $f d b$ in the continuum model and $f$ in a lattice for reasons that will be explained later. The adsorption parameter $c$ does not contain the temperature explicitly. This continuum model describes finite-size effects but suffers from unphysical behavior for strong adsorption and strong extension: The adsorbed fraction may exceed unity and the chain may be extended beyond the contour length $N b$.

In this paper we present an analytical theory for mechanical desorption of lattice chains that contains the temperature $T$ and the chain length $N$ as explicit parameters. The theory incorporates the finite-size effects of the continuum theory into the lattice model and eliminates the unphysical behavior. This is accomplished by a realistic mapping between the adsorption parameters $c$ and $\chi$, and between the force parameters $u$ and $\varphi$. In the present paper we restrict ourselves to a flexible chain on a six-choice lattice so the step length $\ell$ equals the Kuhn length $b$.

Adsorption of ideal chains is not just an academic exercise. It is becoming increasingly clear that adsorption of a real chain with excluded-volume interactions is qualitatively very close to that of an ideal chain, which provides a motivation for further studies on ideal chains, for which analytical solutions are possible. We return to this issue in Sec. VI.

This paper is organized as follows. In Sec. II we give a qualitative picture of mechanical desorption and we make a comparison with a simple plaster (zipper) model,\(^{13}\) which captures the essential features for long chains at the transition. In Sec. III we discuss the continuum and lattice models for adsorption, for stretching, and for mechanical desorption, and we describe the mapping procedure between the lattice and continuum parameters, which enables a lattice theory for finite chain lengths. In Sec. IV we first present some results for the adsorption of finite chains in the absence of a force and then discuss the force-temperature phase diagram for mechanical desorption. We cross this phase diagram by varying the temperature at constant force and show how the bound fraction, stretching, energy, and heat capacity vary around the first-order transition. We also cross the phase diagram at constant temperature and varying force, which is the situation realized most easily in AFM experiments. In Sec. V we focus on some unusual features of the first-order transition. In Sec. VI we summarize the main results, point out the analogy between the continuum model and general scaling theory of phase transitions, and discuss the analogy of mechanical desorption and force-induced unzipping of DNA.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{skvortsov.png}
\caption{Schematic picture of chain conformations of an end-grafted chain when the force parameter $u$ is increased at a constant value of the adsorption parameter $c$. When $u < c$ [diagram (a)] the force has little effect, when $u \geq c$ [diagram (b)] an adsorbed part coexists with a stretched part: Both parts are on average of the same size, but the fluctuations are very strong. Diagram (d) is a simplification at the transition according to the so-called plaster model (Ref. 11).}
\end{figure}

II. QUALITATIVE PICTURE OF MECHANICAL DESORPTION

Mechanical desorption occurs when the pulling force exerted on one end of an adsorbing chain grafted with the other end to a surface is high enough to counteract the adsorption energy. We thus need two parameters to characterize this mechanical desorption. In a lattice model these are $\chi = e / k T$ (which we write as $\chi = 1 / T$) for the adsorption strength and $\varphi = f / k T$ (which we write as $\varphi = \beta / T$) for the force. In fact, $\chi$ plays the same role as $\beta = 1 / k T$ as often used in statistical physics and $\varphi = \beta f$. In the continuum model we have $c$ as the adsorption parameter and $u$ as the force parameter. In this section we use the continuum parameters because as we shall see in the following sections, the (first-order) transition between an adsorbed and detached chain occurs exactly at $u = c$.

Figure 1 shows a qualitative picture. In diagram (a) ($u < c$) we have an adsorbed chain where the stretching parameter $\zeta = \langle z \rangle / N$ is close to zero; here $\langle z \rangle$ is the average position of the free end. Diagram (c) shows the opposite case $u \geq c$: now $\zeta$ is close to unity. Diagram (b) is for $u = c$, which is around the transition where an adsorbed sequence coexists with a stretched part. At this point $\zeta$ is on average around 0.5, but both parts of the chain strongly fluctuate.

We shall analyze the dependence of the bound fraction $\theta$, the stretching parameter $\zeta$, and their fluctuations (related to the heat capacity) as a function of $u$ and $c$, and pay special attention to the transition. It turns out that close to this transition point a simplified plaster model\(^{13}\) [diagram (d)], in which the entropic contributions due to loops and in the tail are neglected, describes the essential features of the transition for long chains. We return to this point in the last part of Sec. III A.

III. THEORY

In Sec. III A we first consider the continuum model for an end-grafted chain on an adsorbing surface without force,
and then we apply a force as well; we present the phase
diagram in terms of the parameters \( u \) (force) and \( c \) (adsorption
strength) and study the first-order transition around \( u = c \) in some
detail. In Sec. III B we summarize some classical
lattice results for ideal chains of infinite length. In Sec. III C
we discuss the mapping of the continuum and lattice parameters
for the adsorption strength and the force; for the adsorption
strength this is done in terms of asymptotes for the adsor-
ption and desorption branches. This mapping eliminates
the divergences for strong adsorption and high extension in
the continuum model, but is not accurate around the critical
adsorption-desorption transition in the absence of a force. We
improve on this point in Sec. III D and we present the ana-
lytical partition function for finite lattice chains, from which
all the thermodynamic properties follow.

A. Continuum model

An exactly solved model that includes \( N \) explicitly is the
adsorption of a continuum Gaussian chain. Chain configura-
tions are described as Brownian trajectories starting from
the surface; the interaction with the surface is described by pa-
rameter \( c \). We first consider the situation in the absence of a
force.

1. Adsorbed chain without force

The statistical weight \( P(z,N,c) \) for a walk of \( N \) steps
starting at \( z = 0 \) and ending at position \( z \) satisfies the Edwards
diffusion equation \(^{25,26} \)

\[
\partial P/\partial N = (1/6) \partial^2 P/\partial z^2.
\]  

(1)

This differential equation is the continuum analog of the dis-
crete lattice recurrence relation.\(^{27-29} \) The starting condition
for Eq. (1) is \( P(z,0) = \delta(z) \), which is the Dirac delta function.
The boundary condition at the surface is \(^{26} \)

\[
P^{-1} \partial P/\partial z|_{z=0} = -c.
\]  

(2)

So a given slope at the surface as defined by the extrapola-
tion length \( 1/c \) is imposed: The initial tangent of \( P(z) \) extrap-
olates to \( z=1/c \) on the abscissa axis. The critical point
corresponds to \( c = 0 \), adsorbed states to \( c > 0 \), and then \( 1/c \) is
proportional to the average thickness of the adsorbed chain.
The solution of Eqs. (1) plus (2) is well known \(^{30,31} \) and may be
written as

\[
P(z,N,c) = \frac{1}{R} e^{-z^2/4R^2} \left[ \pi^{1/2} + cRY(z/2R - cR) \right],
\]  

(3)

where \( R = \sqrt{N/6} \) is the radius of gyration and the function \( Y \)
is defined as \( Y(x) = e^{x^2} \text{erfc}(x) \).

Integrating \( P(z,N,c) \) over the position \( z \) of the free end
gives the partition function \( Q(N,c) \) in the absence of a force

\[
Q(N,c) = Y(-c R) \approx \begin{cases} 
2e^{Nz/6}, & cR \gg 1 \\
1 + 2c \sqrt{6/N}, & |cR| \ll 1 \\
1/(c \sqrt{\pi N/6}), & -cR \gg 1.
\end{cases}
\]  

(4)

The average fraction of surface contacts is \( \theta = N^{-1} \partial \ln Q/\partial c \).
A full analytical expression for \( \theta(N,c) \) is
available (see Ref. 32) but we only give here the asymptotes,
which follow directly from Eq. (4),

\[
\theta(N,c) \approx \begin{cases} 
\frac{c/3}{2/\sqrt{6\pi N}}, & c \gg 1 \\
0, & c = 0 \\
|c|^N, & -c \gg 1.
\end{cases}
\]  

(5)

In the strong adsorption region \( \theta \) increases linearly with \( c \)
and may exceed unity.

2. Stretching an adsorbed chain

In the presence of an external force acting in the
\( z \)-direction the statistical weight \( P(z,N,c,u) \) has to be multi-
plied by \( e^{uc} \), where \( u = f_{\text{ext}}/T \), with \( f_{\text{ext}} \) is the force as it appears
in the continuum partition function

\[
P(z,N,c,u) = P(z,N,c)e^{uc}.
\]  

(6)

Integration of \( P(z,N,c,u) \) over \( z \) gives the partition function
\( Q(N,c,u) \) of an adsorbed chain in the presence of a
force,\(^{11,12} \)

\[
Q(N,c,u) = uY(-u R) - cY(-c R)/u - c.
\]  

(7)

Equation (7) reduces to \( Q = Y(-c R) \) [Eq. (4)] for \( u = 0 \) and to
\( Q = Y(-u R) \) for \( c = 0 \). In the latter case we have

\[
Q(N,u) = Y(-u R) \approx \begin{cases} 
2e^{Nu z/6}, & uR \gg 1 \\
1 + 2u \sqrt{6/N}, & |uR| \ll 1 \\
1/(|u| \sqrt{\pi N/6}), & -uR \gg 1,
\end{cases}
\]  

(8)

which is Eq. (4) with \( c \) replaced by \( u \).

The average stretching degree \( \zeta = \langle z \rangle / N \) is found from
\( \zeta = N^{-1} \partial \ln Q/\partial u \).\(^{11,12} \)

\[
\zeta(N,u) \approx \begin{cases} 
\frac{u/3}{2\sqrt{6\pi N}}, & u \gg 1 \\
0, & u = 0 \\
|u|^N, & -u \gg 1,
\end{cases}
\]  

(9)

which is Eq. (5) with \( c \) replaced by \( u \).

For strong stretching \( \zeta \) is proportional to the force and
may exceed unity: The end-to-end distance can become
longer than the contour length. Equations (8) and (9)
(stretching without adsorption) are the same as Eqs. (4) and
(5) (adsorption without force), provided we interchange \( u \) and \( c \). This is because of the symmetry of the partition func-
tion with respect to the parameters \( c \) and \( u \).

When we have both adsorption energy and a force we find the bound fraction \( \theta(N,c,u) \) and stretching parameter
\( \zeta(N,c,u) \) from differentiating \( \ln Q \) with respect to \( c \) and \( u \),
respectively, using the full form of Eq. (7).

3. Phase diagram, bound fraction \( \theta \), and stretching parameter \( \zeta \)

The phase diagram in terms of the parameters \( u \) and \( c \) is
shown in Fig. 2(a); it contains a first-order transition (solid
line) between adsorbed \( (u < c) \) and stretched \( (u > c) \) states
for positive \( u \) and \( c \), and two second-order transitions
(dashed lines). According to a standard classification the in-
tersection of the dashed lines corresponds to a bicritical point, which is shown as the dot in Fig. 2(a). For \( u < 0 \) and \( c < 0 \) the average position \( \langle z \rangle \) of the free end is \( 1/|u| \), independent of the chain length. Middle segments are much further away (order \( \sqrt{N} \)) because they are repelled by the surface. Hence, the chain conformation is essentially one big loop, with the grafting segment on the surface and the other end close to it. In the remainder of this work we focus on the first-order transition for positive \( u \) and \( c \).

Starting from the adsorbed phase we may cross the phase line by increasing \( u \) at constant \( c \) [arrow 1 in Fig. 2(a)] or by decreasing \( c \) at constant \( u \) (arrow 2). In the former case we reach the transition point at \( u_t = c \), in the latter at \( c_t = u \). Close to the transition point, the chain properties change strongly. Figures 2(b) and 2(c) show how \( \theta \) and \( \zeta \) vary as a function of \( u \) upon crossing the phase line vertically, for two values of \( c \) (0.6 and 1.5) and three chain lengths \( N \) (150, 500, and 1500). For high \( N \), \( \theta = c/3 \) is constant and \( \zeta \) is zero before the transition, and \( \theta \) is zero and \( \zeta = u/3 \) after it; both quantities show a jump at the transition. For shorter chains the behavior is more gradual.

### 4. The transition around \( u = c \)

We consider an arbitrary point \((a, a)\) on the phase line of Fig. 2(a), and values of \( u \) and \( c \) very close to \( a \). Then the difference \( u - c \) is very small. For high \( cR \) and \( uR \) the partition function of Eq. (7) may now be approximated (for details, see Ref. 32) as

\[
\frac{Q}{Q_{tr}} = \frac{1}{t(\coth t - 1)}, \quad t = aR^2(u - c),
\]

where \( Q_{tr} \) is the value at the transition point, which is a constant for given \( a \) and \( R \). The parameter \( t \) is proportional to the product of the chain length \( N \) and the difference \( u - c \), and is negative at the adsorption side and positive at the stretched side. For a vertical crossing \((a = c = u_a)\) it equals \( t = (N(u_a)/6)(u - u_a) \) for a horizontal crossing \( t = (N(c_t)/6)(c_t - c) \). The form given in Eq. (10) allows variation of both \( u \) and \( c \).

Differentiation of Eq. (10) gives an extremely simple result,

\[
\frac{\theta}{\theta_{tr}} = 1 - L(t), \quad \frac{\zeta}{\zeta_{tr}} = 1 + L(t),
\]

where \( \theta_{tr} \) and \( \zeta_{tr} \) are the values at the transition and \( L(t) \) is the Langevin function,

\[
L(t) = \coth t - 1 \sim \begin{cases} 
-1 + 1/|t|, & -t > 3 \\
1/3, & |t| < 0.5 \\
1 - 1/|t|, & t > 3.
\end{cases}
\]

The important implication of Eq. (11) is that around the transition the relative bound fraction \( \theta/\theta_{tr} \) and the relative stretching parameter \( \zeta/\zeta_{tr} \) are a universal function of one parameter \( t \sim N\Delta u \) (constant \( c \)) or \( t \sim N\Delta c \) (constant \( u \)). For long chains \( \theta_{tr} = c/6 \) (half the value for adsorption without force) and \( \zeta_{tr} = u/6 \) (half the value for stretching without adsorption), and for shorter chains there are minor 1/N corrections: \( \theta_{tr} = \zeta_{tr} = (1 + (\pi^2 - 2)/a^2)/6 \).

Plots of the relative quantities \( \theta/\theta_{tr} \) and \( \zeta/\zeta_{tr} \) at constant \( c \) as a function of \( t = cR^2\Delta u \) are given in Fig. 3, for the same set of parameters as in Figs. 2(b) and 2(c). Symbols are the full calculations, the solid curves are the “master curves” 1 - \( L(t) \) and 1 + \( L(t) \), the dashed curves are the asymptotes 2 - 1/|t|, 1 - 1/3, and 1/|t| for \( \theta \) and 1/|t|, 1 + 1/3, and 2 - 1/|t| for \( \zeta \). For the bound fraction the agreement is excellent, although for short chains and weak adsorption, some minor deviations occur at the adsorption side. For the stretching parameter the agreement is perfect for \( t < 1 \), but at the stretched side we see deviations that are stronger for shorter chains and weak adsorption. These are caused by the fact that our simple approximation \( \zeta/\zeta_{tr} = 1 + L(t) \) does not capture the linear increase \( \zeta = u/3 \) beyond the transition. Much better agreement at the stretched side is obtained in the form \( \zeta/(u/6) = 1 + L(t) \) (not shown).

Since parameter \( t \) is proportional to \( N\Delta u \) and \( \theta \) and \( \zeta \) are universal functions of \( t \), the width of the transition zone in terms of \( \theta(u) \) and \( \zeta(u) \) is proportional to 1/N, as shown in Figs. 2(a) and 2(b). The closer the system is to the bicritical point, the narrower is the region where the bound fraction and stretching parameter can be described by Eqs. (11) and (12) with \( t \sim N\Delta u \). Close to the bicritical point the control parameter is expected to be \( N^{1/2}\Delta u \).

Also the fluctuations \( \delta \theta^2 = \langle \theta^2 \rangle - \langle \theta \rangle^2 \) in the bound frac-
tion and $\delta^2 = (\zeta^2) - (\zeta)^2$ in the stretching can be expressed in only one parameter $t$, by differentiating Eq. (11) with respect to $t$,

$$\frac{\delta^2}{\delta^2 t} = \frac{\delta^2}{\delta^2 t} = 3 \left( \frac{1}{t^2} - \frac{1}{\sinh^2 t} \right) = \begin{cases} 1 - \frac{t^2}{2}, & |t| < 0.5 \\ 3t^2, & |t| > 3. \end{cases}$$

(13)

The transition values for long chains are $\delta^2 = \delta^2 = a^2/108$, for shorter chains there are again $1/N$ corrections: $\delta^2 = \delta^2 = (1 + 4a^2 - 2)\alpha/a^2/108$. We do not show a plot of the relative fluctuations for the continuum model; later (Fig. 13) we will do that for the relative heat capacity (directly related to these fluctuations) for the generalized lattice model.

It is instructive to compare the above results with the simplified plaster model [see Fig. 1(d)], for which an exact partition function is available. The stretched part of the plaster has a length $z$ and an energy $-\varphi z$ (in units $T'$), the adsorbed part has a length $N-z$ and an energy $-\chi(N-z)$. Here the force parameter $\varphi$ and the adsorption parameter $\chi$ have the same meaning as in the lattice model. The partition function for this plaster model is $Q = e^{\chi} \int_0^\infty e^{(\varphi-\chi)z} dz = (e^{\chi} - e^{\chi})/\chi$. For small $\varphi-\chi$ and high $\varphi N$ and $\chi N$ the relative partition function $Q / Q$ may be written in exactly the same form as Eq. (10), with now $t = N(\varphi-\chi)/2$. In the plaster model the transition values are $\theta = \theta = \varphi / 2$. Although the force and adsorption parameters are different in the plaster model and in the continuum model, in both cases the parameter $t$ is proportional to $N$ times the deviation from the transition point.

B. Lattice model

Lattice models include the temperature explicitly and the finite monomer size leads to proper saturation of the adsorption order parameter ($\theta = 1$) at $\chi = 1/T \gg 1$. A lattice model also describes stretching effects correctly: The chain can never be extended more than the contour length. Unfortunately, an analytical description of the adsorption curve $\theta(\chi)$ exists (so far) only for infinite chain length. In this section we briefly summarize some classical lattice results.

1. Adsorbed chain without force

Rubin calculated the exact partition function for an ideal walk on a lattice for a whole class of regular lattices. For a six-choice lattice the free energy $F$ per step is given by

$$F(\chi) = \ln \left[ \frac{6}{p} \right]$$

$$= \begin{cases} -\chi + \ln(6/4), & \chi \gg \chi_c \\ -(25/6)(\chi-\chi_c)^2, & \chi \approx \chi_c, \end{cases}$$

(14)

where $p = 1/(1 - e^{-\chi})$. Equation (14) is valid for $\chi \gg \chi_c$, where the critical value is $\chi_c = \ln(6/5)$ corresponding to $T_c = 1/\chi_c = 5.485$. The quadratic dependence around the critical point implies a second-order transition. For infinite chain length, $F(\chi) = 0$ for $\chi \ll \chi_c$.

The bound fraction $\theta$ is found by differentiating Eq. (14) with respect to $\chi$,

$$\theta(\chi) = \frac{1 - p + p}{\sqrt{3} + p}$$

(15)

In the lattice model the bound fraction saturates at $\theta = 1$ for high $\chi$. Close to the critical point $\theta$ is linear in $\chi - \chi_c$, in agreement with general theoretical results for mean-field systems.

The energy of the adsorbed chain is simply $E = -\varphi$ (in units $e$). Differentiating with respect to $T$ gives the heat capacity

$$C(\chi) = \frac{1}{2} \varphi^2 (p-1) \left[ 1 - \frac{6 + p}{3 + p} \right]$$

(16)

The heat capacity increases with decreasing $\chi$ (increasing $T$) up to the value $(25/3)\chi_c^2 = 0.277$ at the critical point $T_c$. For $T > T_c$, the energy and heat capacity are zero so $C$ displays a finite jump at the critical point, which is fully consistent with mean-field theory of the second-order transition.

2. Stretching a free chain

The stretching free energy per step of a free chain fixed at one end on a six-choice lattice in the presence of a force $f$ applied to the other end is given by

$$F(\varphi) = \ln \left[ \frac{3}{2 + \cosh \varphi} \right]$$

(17)

where $\varphi = f/T$. Differentiating with respect to $f$ gives the stretching parameter

$$\zeta(\varphi) = \frac{\sin \varphi}{2 + \cosh \varphi}$$

(18)

We see that $\zeta = 1$ for strong stretching: In the lattice model $\zeta$ does not diverge.

The energy $E$ of the stretched coil is $E = -f\zeta$. Differentiating with respect to $T$ gives the heat capacity $C$,

$$C(\varphi) = \varphi^2 \frac{1 + 2 \cosh \varphi}{(2 + \cosh \varphi)^2}$$

(19)

C. Mapping of continuum and lattice parameters

The main idea of this paper is to combine the positive features of the continuum and lattice models. This is achieved by using the analytical continuum partition function with the parameters $c$ and $u$ appropriately modified to include the temperature explicitly and to reproduce the correct thermodynamics of the lattice model. In its simplest form, the mapping is found by considering two limiting cases where the full partition function is reduced to simpler expressions: adsorption without force at $u = 0$ and the force effect without adsorption at $c = 0$. In the former case the partition function depends only on $c$ and $N$: $Q(N, c) = Y(-cR)$; in the latter it is only a function of $u$ and $N$: $Q(N, u) = Y(-uR)$.
1. Mapping of the adsorption parameters \( c \) (continuum) and \( \chi \) (lattice)

In the absence of a force the free energy per step \( F=-N^{-1}T \ln Q \) for the adsorption and desorption branches in the continuum model is given by Eq. (4),

\[
\frac{F(c)}{T} = \begin{cases} 
-1/6 & c \geq 0 \\
-1/6 \ln(-c\sqrt{\pi N/6}) & c \leq 0
\end{cases} \tag{20}
\]

where \( c \) does not contain the temperature explicitly.

In the lattice model we have

\[
\frac{F(T)}{T} = \frac{6}{N} \ln \left( \frac{3+p-2}{\sqrt{3+1/(1-e^{-T})}} \right), \quad T \leq T_c \tag{21}
\]

where \( p=1/(1-e^{-T}) \) is a function of temperature. The adsorption branch is the Rubin result for infinite chain length [Eq. (14)], the desorption branch for finite \( N \) was also obtained by Rubin.\(^{24}\)

Following Ref. 35 we demand that the asymptotic behavior of the free energy far from the critical point in both models is the same. This gives two branches of the mapping function \( c(T) \),

\[
\begin{align*}
\frac{c^2}{6} = & \ln \left[ 6(1-e^{-x})(\sqrt{3+1/(1-e^{-x})} - 2) \right], \quad c \geq 0 \\
& -6(e^{-x} - e^{-x_i}), \quad c \leq 0
\end{align*} \tag{22}
\]

We see that \( c \) is now a function of temperature. For strong adsorption \( c^2/6 = 1/T + \ln(2/3) \). Close to the critical point \( c = 5/(1-T - 1/T) \). For \( T \to \infty \) the lower limit for \( c \) is \(-1\).

The \( N \)-dependent partition function \( Q(N,T) = Y(-c(T)\sqrt{N/6}) \) combines the correct lattice description of the strong adsorption-desorption limits with the proper crossover in a closed analytical form, and includes explicit temperature effects as well. The unphysical behavior in the continuum model (unlimited growth of the adsorbed fraction) is automatically removed. This is because we redefined the continuum parameter \( c \) in such a way that the continuum equation for adsorbing chains reduces to that of the lattice, where proper saturation of the bound fraction occurs.

Another way of explaining how the divergence disappears is the following. The bound fraction is found from \( d \ln Q/\ln Q = (dc/\ln Q)dc \ln Q/dc \). The new feature is the factor \( dc/\ln Q \), which for strong adsorption equals \( 3/c \), which precisely compensates \( \theta = c/3 \) as obtained from the continuum model.

2. Mapping of the force parameters \( u \) (continuum) and \( \varphi = f/T \) (lattice)

In view of the symmetry of the full partition function as a function of the two parameters \( c \) and \( u \), the elastic free energy in the continuum model should have two branches corresponding to positive (stretching) and negative (compressing) forces. Unlike in the adsorption problem, no general solution for the grafted lattice chain partition function valid for both positive and negative forces is known. However, since the stretching free energy contains no effect of the grafting surface and is just that of a Gaussian coil subject to a stretching force, it is sufficient to consider only positive \( u \). From Eq. (8),

\[
F(u)/T = -u^2/6. \tag{23}
\]

For the stretching free energy in the lattice model we rewrite Eq. (17),

\[
\frac{F(T,f)}{T} = -\ln \left( \frac{2}{3} + \frac{1}{3} \cosh \frac{f}{T} \right). \tag{24}
\]

Equating Eqs. (23) and (24) we obtain the mapping between \( u \) in the continuum model and \( \varphi \) in the lattice model,

\[
u = \sqrt{6 \ln \left( \frac{2}{3} + \frac{1}{3} \cosh \frac{f}{T} \right)} \tag{25}
\]

For weak stretching \((f/T < 2.5)\) Eq. (25) reduces to the simple form \( u = \varphi \) or \( f_c = f \); then the forces in both models are the same. For strong stretching \((f/T > 10) u = \sqrt{6} \varphi \) or \( f_c/T = \sqrt{6}/T \). To analyze the effect of a stretching force \( f \) and the temperature \( T \) on a lattice chain, we substitute this \( u(T,f) \) into the continuum expression for \( Q(N,u) \). This solves the extensibility problem in the continuum model since \( \xi \) follows from \( d \ln Q/\ln \varphi = (du/\ln \varphi) d \ln Q/du \). The factor \( du/\ln \varphi = 3/u \) for strong stretching compensates the increasing \( \xi = u/3 \) in the continuum model.

D. Refinement for \( c(\chi) \) around the critical point

The \( c(\chi) \) mapping of Eq. (22) gives a problem around \( c=0 \) since there, the mapping function is nonanalytic. The function \( c(\chi) \) itself and its first derivative \( dc/d\chi \) are continuous at \( c=0 \) but the second derivative \( dc^2/d\chi^2 \) is discontinuous. For finite chain lengths we should remove this discontinuity. This is especially important for calculating the heat capacity, which jumps for infinite chain length but not for finite \( N \). Using Eq. (22) gives the unphysical result that there is a jump for finite \( N \).

In the continuum model the heat capacity \( C_\alpha \) is calculated as \( C_\alpha = -d\theta_c/dT = -(d\theta_c/dc)(dc/dT) \), where \( dc/dT \) is defined because after mapping \( c \) is a function of \( T \). However, we need \( \theta = \theta_c(dc/d\chi) \). Differentiation with respect to \( T \) gives

\[
C = C_\alpha dc + \theta_c \chi^2 d^2 c/d\chi^2 \tag{26}
\]

and we see that we need a more accurate (nondiscontinuous) expression for the second derivative.

Such an approach was developed by Fleer et al.\(^{36}\) and by Gorbonov et al.\(^{37}\) These authors substituted the continuum expression for \( P(z,N,c) \) [Eq. (3)] into the lattice recurrence relation, which is the discrete analog of Eq. (1). This recurrence relation reads \( G(0,N+1) = e^4 G(0,N) + G(1,N)/6 \) (Refs. 27–29) for the layer next to the surface; here \( G(z,N) \) is the statistical weight that segment \( N \) ends up in layer \( z \), given that the previous segment \( N-1 \) can only be at \( z-1 \), at \( z \), or at \( z+1 \). For a segment ending at \( z=0 \), the only previous positions are \( z=0 \) or \( z=1 \). This leads to
subject to a pulling force. Obtaining the bound fraction, stretching, and heat capacity in a closed analytical form is a purely mathematical problem; details can be found in Ref. 32.

IV. RESULTS

In Sec. IV A we first discuss the temperature dependence of the bound fraction $\theta$, the heat capacity $C \equiv -d\theta/dT$, and the average extension $\langle z \rangle$ in the absence of a force. Next, in Sec. IV B we consider the phase diagram that describes the force needed to detach a chain as a function of temperature. In Sec. IV C we analyze the effect of crossing the phase diagram by varying the temperature at a constant force, both for constant chain length $N$ (and several force levels) and for constant force (and several chain lengths), and we discuss the chain length dependence around the transition. Finally, in Sec. IV D we cross the phase diagram by changing the force at constant temperature.

A. Adsorption of finite lattice chains without force

Figure 5 shows how the bound fraction $\theta$, the heat capacity $C$, and the average extension $\langle z \rangle$ (normalized on the radius of gyration) for finite lattice chains in the absence of a force depend on temperature. The solid curves give our analytical results for $N=30, 100, 300,$ and $3000$; the dotted (discontinuous) curves are for infinite chain length [Eq. (15) for $\theta$ and Eq. (16) for $C$].

The curve for $N=3000$ in Fig. 4(a) is close to the discontinuous Rubin result ($\theta=0$ for $T>T_c$). For smaller chain lengths we see a smooth gradual change. For $T>T_c$ the bound fraction reaches a final level $\theta=6/N$. At the critical temperature its value is $\theta=(50/3\pi N)^{1/2}$ [Eq. (5) multiplied with $dc/d\chi=5$]. The symbols in Fig. 5 are exact numerical calculations according to the matrix method. The agreement with the analytical results is excellent not only for the bound fraction but also for the heat capacity and the stretching. This demonstrates the validity of the analytical approach.

In Fig. 5(b) for $C$ the dotted curve is the infinite-$N$ result [Eq. (16) with $C=0$ for $T>T_c$]; at the critical point $C$ jumps from 0.277 to zero. For finite chains, $C$ changes gradually with a very smooth behavior for low $N$. For small $N$ the position of the maximum of the heat capacity deviates considerably from the transition point.

It was recognized long ago that the localization of the transition point from numerical simulations with finite chains

\[ e^{-x} = \frac{4P(0,N,c) + P(1,N,c)}{6P(0,N+1,c)}, \]  

which gives a direct mapping of the $c$ and $\chi$ parameters for any chain length $N$.

The limiting form of Eq. (27) for $N \to \infty$ is

\[ \chi = \begin{cases} \frac{c^2}{6} - \ln \frac{4 + e^{-c}}{6}, & c \geq 0 \\ -\frac{5-c}{6}, & c \leq 0, \end{cases} \]  

which may be compared to Eq. (22). The desorption branches are identical. The adsorption branches are mathematically different but numerically virtually (within 0.1%) the same. For finite chain lengths Eq. (27) gives a continuous second derivative and a smooth heat capacity unlike Eq. (22).

Figure 4 shows $c$ and the derivatives $dc/d\chi$ and $dc^2/d\chi^2$ as a function of temperature for several chain lengths. The function $c(T)$ is smooth: There is hardly any chain length dependence at the adsorption side and only a weak dependence in the desorption branch. The first derivative $dc/d\chi$ is smooth for finite $N$ but shows a kink at the critical point for $N \to \infty$; at this point $dc/d\chi=5$ for long chains. The second derivative $dc^2/d\chi^2$ is continuous (although nonmonotonic) for finite chain lengths; exactly at the critical point the slope of the curve (i.e., the third derivative) is proportional to $R$. For $N \to \infty$ this third derivative becomes infinite, which gives the jump in $dc^2/d\chi^2$.

The refinement in mapping [Eq. (27)] is only important for a correct description of the bound fraction and the heat capacity for short chains and weak forces in the vicinity of the bicritical point. For most figures in this paper simple mapping [Eq. (22)] is adequate; only in Fig. 5 (no force) full $N$-dependent mapping is required.

E. The partition function for finite lattice chains

Mapping allows us to incorporate explicitly finite-size effects for all thermodynamic quantities. Since we now have the precise relation between $c$ and $\chi = 1/T$ and between $u$ and $\varphi = f/T$, we can rewrite the partition function $Q_N(N,c,u)$ in the continuum model as $Q(N,c(T),u(f,T))$ and use it as the partition function $Q(N,T,f)$ in the lattice model to find all thermodynamic properties of an adsorbed finite lattice chain subject to a pulling force. Obtaining the bound fraction,
is a difficult computational problem. A popular recipe is to associate the transition point with the position of the heat capacity maximum.\(^3^9\) The curves \(C(T)\) in Fig. 5(b) do not suggest this procedure for determining this point: The maximum cannot be far from \(T_c\) and extrapolation to infinite chain length is definitely required. A more accurate estimate for \(T_c\) is obtained from the intersection of the \(C(T)\) curves for different chain lengths.

Figure 4(c) shows the average extension \(\langle z\rangle\), normalized on the radius of gyration \(R\). In the limit of infinite \(N\) the behavior is discontinuous: In the desorption regime \(\langle z\rangle/R = \sqrt{\pi}\) and in the adsorption regime \(\langle z\rangle/R\) is zero for \(N \to \infty\). For finite \(N\) we see a gradual transition between these limits. All the curves for different \(N\) intersect at the same point \(\langle z\rangle/R = 2/\sqrt{\pi}\) at \(T = T_c\). This common intersection could provide a good estimate of the critical point in numerical calculations. We stress that the calculations for finite chains in Fig. 5 are neither possible in the original continuum model (since it does not contain the temperature) nor in Rubin’s lattice model (which does not contain the variable \(N\)).

In Fig. 5 it is clearly visible how the second-order adsorption transition develops when the chain length is varied. In the thermodynamic limit the heat capacity shows a finite jump at the transition, which is in contrast with the diverging behavior seen in most second-order transitions for low-molar-mass systems.\(^4^0\) A finite heat capacity jump is predicted by the Landau mean-field theory,\(^4^0\) and adsorption of a polymer chain is one of the few examples (along with the transition to a superconducting state\(^3^3\)), which is perfectly consistent with this framework.

B. Phase diagram of a lattice chain in the presence of a force

At the transition the elastic free energy \(F(f_u, T)\) [Eq. (24)] equals the adsorption free energy \(F(T)\) [Eq. (21)]. Hence, the transition force is given by\(^1^6\)

\[
f_u = T \ln(\sqrt{3} + (1 - e^{-1/T}))^{-1/2} - 2, \quad T \approx T_c.
\]

The phase diagram \(f_u(T)\) is shown in Fig. 6; it may be compared to the \(u(c)\) phase diagram in Fig. 2(a) for the continuum model. The difference is in the detachment curve corresponding to the first-order transition between adsorbed and stretched states, which is a straight line \(u(c)\) in Fig. 2(a) but a nonmonotonic \(f_u(T)\) in Fig. 6. The second-order transitions in Fig. 6 are analogous to those in Fig. 2(a). As in Fig. 2(a), the bicritical point is indicated by the dot.

The detachment curve has a maximum at \(f^* = 2.098\) and \(T^*/T_c = 0.308\). For low \(T\) (strong adsorption) Eq. (27) reduces to \(f_u = 1 + T / \ln 4\). This relation follows from an expansion for low \(T\) but also from equating the free energy \(Nf_u\) of a fully stretched chain with the free energy \(N(1 + \ln 4)\) of a fully adsorbed chain; the \(\ln 4\) represents the entropy difference between these two states. Recall that all energies are in units \(\varepsilon\). For \(T\) close to \(T_c\), Eq. (29) simplifies to \(f_u = 5(1 - T/T_c)\).

A horizontal line for a constant force \(f > f^*\) does not intersect the detachment curve: The chain is always desorbed. For \(0 < f < 1\) the detachment curve is crossed only once. For a force between \(f = 1\) and \(f^*\), there are two intersections and now there is an adsorption window at intermediate \(T\), whereas the chain is stretched outside this window. Hence, the stretched state does not only exist at high temperature, but it is re-entered at low \(T\).

The phase diagram of Fig. 6 provides the guideline for Secs. IV C and IV D. In Sec. IV C we consider horizontal crossings (changing temperature at constant force), and in Sec. IV D we discuss a vertical crossing (varying the force at constant temperature). As a first example we show in Fig. 7 the bound fraction \(\theta(T)\) and stretching parameter \(\zeta(T)\) upon crossing the phase diagram horizontally at several force levels and for a high chain length \(N = 3 \times 10^4\). These curves are very close to those for infinite chain length as discussed before.\(^1^6\) For \(f = 2.05\) or below, \(\theta\) within the adsorption window is given by the Rubin equation [Eq. (15), dotted curve in Fig. 7(a)] and \(\zeta\) is nearly zero. For \(f\) close to \(f^*\) the adsorption window narrows quickly and \(\theta\) drops to half the Rubin value, while \(\zeta\) approaches half the value given by Eq. (18). The curves for \(f = f^*\) are analyzed in more detail in Fig. 10.

In Sec. IV C we consider finite-size effects. We stress that all the results for finite lattice chains are obtained analytically and have been verified numerically.

C. Finite-size effects when crossing the phase diagram at constant force

1. One crossing

Figure 8 gives a cross section at constant force \(f = 0.8\) for different \(N\). At this force the transition occurs at \(T_u / T_c = 0.827\). The figure shows the bound fraction \(\theta\) (a), the stretching parameter \(\zeta\) (b), the energy \(E = -\theta - f_u \zeta\) (in units \(\varepsilon\))
This maximum becomes lower with decreasing temperature and for short chains it is hardly visible. The agreement is excellent. Only for \( N = 30 \) do some minor deviations occur at relatively high \( T \).

For a long chain (\( N = 10^4 \)) \( \theta \), \( \zeta \), and \( E \) show a jump at the transition. For smaller \( N \) the transition becomes more gradual and for short chains it is hardly visible.

The heat capacity \( C(T) \) shows a maximum for any \( N \). This maximum becomes lower (and wider) and shifts to lower temperature with decreasing \( N \). Around the transition point the heat capacity resembles a \( \delta \) peak for long chains, but in fact \( C(T) \) follows a power law \( C \sim N(T-T_\theta)^{-2} \), as will be discussed in more detail in Sec. V (Fig. 13).

### 2. Two crossings

Figure 9 shows the analogous situation for a constant force \( f = 2.05 \), which is just below \( f^* \) in Fig. 6. Now there are two crossings: One occurs at \( T_u / T_c = 0.23 \) and the other at \( T_u / T_c = 0.40 \). Inside this window the bound fraction \( \theta(T) \) for infinite chain length is nonzero and is given by Eq. (15); the stretching parameter \( \zeta(T) \) inside this window is zero. Outside the window the stretching parameter \( \zeta \) is nonzero and follows Eq. (18), and \( \theta(T) = 0 \). For large \( N (= 10^4) \) the results in Figs. 9(a) and 9(b) are close to those for infinite \( N \).

The energy [Fig. 9(c)] starts at \( E = -f = 2.05 \) for \( T = 0 \) and shows jumps at both transitions. The heat capacity \( C(T) \) [Fig. 9(d)] shows two sharp peaks for high \( N \), resembling the \( \delta \) peaks for infinite \( N \). In between the peaks \( C(T) \) is given by Eq. (16) while outside the adsorption window, it is given by Eq. (19). For smaller \( N \) there is no longer a distinct adsorption window and all the curves become much smoother. For \( N = 30 \) hardly any transition can be seen.

Typically for first-order transitions in finite systems, the \( \theta \) and \( \zeta \) curves for different \( N \) intersect almost in a single point, which could be used for localizing the transition in numerical simulations. The transitions at low \( T \) are much sharper than those at high \( T \); this is due to the fact that the relevant Gibbs weights (free energies in units \( kT \)) are much larger at low \( T \).

### 3. Crossing at the maximum \( f \) of the phase diagram

An intriguing situation occurs when the phase diagram of Fig. 6 is crossed exactly at its top at \( f^* \). Figure 10 shows the bound fraction \( \theta \) and stretching parameter \( \zeta \) as a function of temperature for \( N = 30, 300, 3000, \) and 30 000. The dotted curve in Fig. 10(a) is the Rubink equation (no force) that in Fig. 10(b) is \( \zeta = 0 \); these curves are shown for orientation.

For nearly all chain lengths the peak value of \( \theta(T) \), exactly at the transition point, is half the value in the absence of a force, and the value at the dip in \( \zeta(T) \) is half that of a free coil, as is also the case in the continuum model [Eq. (11)]. Only for small \( N (= 30) \) do we see a slight deviation due to \( 1/N \) corrections. The width of the peak in \( \theta \) and that of the dip in \( \zeta \) increases with decreasing chain length.

Thus, the naive picture of a window of vanishing width and full height has to be modified by stating that the window has only half the limiting height. Finite-size effects broaden the window but its height is retained. The effect is extremely sensitive to the precise value of the external force: Very accurate information about the phase diagram around the top is necessary for demonstrating it.
D. Crossing the phase diagram at constant temperature

In Sec. IV C we considered horizontal crossings of the phase diagram, keeping the force constant and varying the temperature. From an experimental point of view (e.g., in AFM experiments) it is easier to keep the temperature constant and vary the force. That corresponds to a vertical crossing of the phase diagram.

In Fig. 11 we show the bound fraction \(\theta(f)\) and \(\zeta(f)\) at two temperatures \(T/T_c=0.541\) (\(f_u=1.781\)) and \(T/T_c=0.251\) (\(f_u=2.073\)), for three values of the chain length \(N=150, 500,\) and 1500. The discontinuous curves in Fig. 11 are for infinite chain length, where \(\theta\) jumps from the Rubin value to zero and \(\zeta\) from zero to the limiting behavior \(\zeta=1/3T\). For finite \(N\) we see the expected gradual transition, which is sharp at high \(N\) and very smooth for short chains. For \(N=150\) hardly any transition can be seen.

All data for \(\theta(f)\) and \(\zeta(f)\) in Fig. 11 could be presented as a master curve \(\theta/\theta_u\) and \(\zeta/\zeta_u\) as a function of a single parameter \(t\), just as in Fig. 3 for the continuum model. We may translate the continuum version \(t=AN(u-u_c)\) with \(A=u_u/6\) [see below Eq. (10)] to the lattice version by substituting \(u=\theta/f\), which gives \(t=AN(f-f_u)\) with \(A=f_u/(6T_c)^2\). We do not give such a plot as it is nearly identical to Fig. 3.

1. The chain length dependence close to the transition

According to Eq. (11) applied to the lattice model, the relative bound fraction around the first-order transition may be approximated as \(\theta/\theta_u=1-L(t)\), with \(t=AN\Delta f\) as shown above. In this section we keep \(\Delta f=\) constant and focus on the \(N\)-dependence. For positive \(\Delta f\) we may define \(t=N/N^*\), where \(N^*=\Delta f^{-1}\) is a crossover chain length. The closer to the transition point, the higher is the crossover value \(N^*\). Equation (11) at the stretching side transforms into

\[
\frac{\theta}{\theta_u} \approx 1 - L(N/N^*) \approx \begin{cases} 
1 - N/3N^*, & N < 0.5N^* \\
N/N^*, & N > 3N^*.
\end{cases}
\]

At the adsorption side we find analogously \(\theta/\theta_u=1 + L(N/N^*)\).

Figure 12 shows \(\theta/\theta_u\) as a function of \(1/N\) for \(T/T_c=0.541, f_u=1.781\) and \(T/T_c=0.251, f_u=2.073\) and three values of \(\Delta f=0.01\) (adsorption side, \(\theta<\theta_u\)), 0 (transition point), and 0.01 (stretched side, \(\theta<\theta_u\)).

In the transition point \(N^*\) is infinite and \(\theta/\theta_u=1\) for any chain length \(N\); this is the horizontal line in Fig. 12. For \(\Delta f=0.01\) and \(\Delta f=0.01\) we have \(N^*=2950\) (\(T/T_c=0.541\)) and \(N^*=550\) (\(T/T_c=0.251\)). The higher the temperature, the higher is the value of \(N^*/N^*\sim1-A/T^2\). For long chains \((N \approx 3N^*) \theta/\theta_u\) decreases as a straight line \(2-N^*/N\) at the adsorption side, and it increases as \(N^*/N\) at the stretched side; these straight lines extrapolate to \(N=N^*\) at \(\theta=\theta_u\). For shorter chains \((N<0.5N^*)\) the adsorbed fraction gradually approaches \(\theta_u\). Short chains do not feel the difference between the two phases and distribute more or less equally; long chains do feel the difference and distribute preferentially in one of the phases, approaching the transition value as \(1/N\).

A general scaling picture of the transition for excluded-volume chains, which is to be discussed in more detail in Sec. VI A, predicts also \(\theta \sim 1/N\) for long chains at the desorption side [see Eq. (34)]. As far as we know, there is no scaling theory for the short-chain regime. Our analytical mean-field theory describes both regimes, as well as the transition region, in a simple and transparent way.

V. UNUSUAL FEATURES OF THE PHASE TRANSITION IN MECHANICAL DESORPTION

A. Divergence of the heat capacity

The detachment curve in the phase diagram of Fig. 6 separates adsorbed and desorbed states of the polymer chain. There is a first-order phase transition when we cross this curve. For long chains, the average order parameter (bound fraction \(\theta\)) as well as other characteristics display a jump at the transition point and the heat capacity shows a peak, as usual for first-order transitions. At the same time there are some unusual features in this transition.

Figure 13(a) presents the heat capacity \(C(T)\) for a cross section of the phase diagram at a constant force \(f=0.8\), for temperatures very close to transition point \(T_u/T_c=0.8274\) and for several long chains (in the range of \(4 \times 10^4\) to \(10^5\)). The heat capacity increases to a maximum value \(C_{tr}\) in the transition point. This maximum is approximately proportional to \(N\). An accurate analysis (see Ref. 32 for details) gives
Cmated as = 0.8 for five high values of N: N/10^3 = 100, 85, 70, 55, and 40 (a). The normalized value C/\( C_T \) as a function of the parameter \( t = aN\Delta T \) for N/10^3 = 100 (squares), 10 (circles), and 3 (diamonds) (b). The solid curve in (b) is the limiting behavior at large N and the dotted curves are its asymptotes (see text).

\[
\left( \frac{C_u}{N} \right) \approx \frac{1}{1047} \left( \frac{T}{T_c} \right)^2 \left( f - \frac{T_u}{T_c} - B \right)^2,
\]

where \( A = (65/3)/T_c = 3.95 \) and \( B = 5 - A = 1.05 \). A plot of \( C_u/N \) as a function of 1/N (not shown) is fully consistent with Eq. (31).

The heat capacity close to the transition can be approximated as 
\[
C/C_T = 3(1/\sqrt{1 - \sin^2 t})
\]
[see Eq. (13)], where in this case (constant f) \( t = aN\Delta T \), with \( \Delta T = T - T_c \) and \( a = (f/T_u)^3/6 \). Figure 13(b) shows this master curve (solid curve) and compares it with the numerical data for three chain lengths: N=3000, 10^4, and 10^5. The dotted sections are the asymptotes \( C/C_u = 1 - t^2/5 \) (low \( |t| \)) and \( C/C_u = 3/t^2 \) (high \( |t| \)).

For a long chain (N=10^5) the numerical data are symmetric around the transition and coincide with the universal curve. Around the top a parabolic function is appropriate and beyond we have a power law \( r^{-2} \). For shorter chains the curves are asymmetric at the adsorption side (\( t < 0 \)). An interesting feature is that the half width of the peak is a constant in terms of \( t (t = \sqrt{6}) \) at \( C/C_u = 1/2 \). This implies that \( N(\Delta T)^{1/2} \) is constant: The width of the peak \( C(T) \) is proportional to \( 1/N \), whereas its height is proportional to \( N \). Hence, it approaches a \( \delta \)-peak for \( N \rightarrow \infty \).

A very important point is that just outside the transition the heat capacity decays as a power law \( C \sim (T - T_c)^{-2} \). An increase in \( C(T) \) as a power law upon approaching the transition point is a well-known feature for second-order transitions.\(^{33,40}\) Here we see that such a power law does also apply to a first-order transition: There is a common feature for both second- and first-order transitions in mechanical desorption.

### B. Unimodal distribution

In low-molar-mass systems two phases coexist in the transition point at the first-order transition. For those systems the distribution functions for the energy and for the order parameter have a bimodal form close to transition point. The highest maximum of the distribution functions for the energy corresponds to the stable state, the lowest to a metastable state. For a polymer chain that is mechanically desorbed there are also two phases (or states): adsorbed and stretched. These phases coexist in the region close to the transition point in the same chain. However unlike in low-molar-mass systems the distributions of a polymer chain in the transition region have a unimodal form.

As an example we show in Fig. 14 the distribution of the end point for a long chain (N=10^4) at a constant force \( f = 0.8 \) near the transition point \( T_c/T_u = 0.8274 \); this distribution is given by Eq. (6) with \( c = c(T) \) and \( u = u(T, f) \) according to our mapping procedure. Exactly at the transition point there is a wide flat region instead of a bimodal distribution and there are no metastable states as typical for first-order transitions. For a temperature slightly below \( T_u \) the chain is in the adsorbed state with a monotonically (exponentially) decreasing distribution function. For a temperature slightly above \( T_u \) there is a stretched phase with a peak located close to \( z/2R = 7 \).

We note that a unimodal distribution is also predicted by the plaster model. In this model the distribution is a simple exponential \( P(z) \sim e^{-z^2/\chi^2} \). Hence, at the transition (\( \varphi = \chi \)) it is a constant, like in Fig. 14 for \( z/2R < 7 \). For \( \varphi < \chi \) (stretching side) there is an exponential increase, at the adsorption side an exponential decrease, as in the left part of Fig. 14.

The reason for this unusual behavior lies in the specifics of the system: Two coexisting phases (adsorbed and stretched) are separated by one segment only. As a result there is no loss of surface energy: The creation of a new phase does not need any nucleation.

### VI. DISCUSSION

We discuss three issues. In Sec. VI A we demonstrate that the main results of our paper, in particular, finite-size effects for mechanical desorption based on the model of an ideal chain, are qualitatively very close to those for a real chain with excluded-volume interactions. We present some reflections about the relation between the continuum model for polymer adsorption and more realistic models. We look at the continuum model from the point of view of scaling theory of phase transitions and show that all the strong and weak points of the continuum model are similar to those in the scaling approach. We review the available literature on the value of the critical index \( \phi \), which characterizes the
behavior of a polymer chain close to adsorption point for excluded-volume chains, and we will see that \( \phi \) is close to the ideal-chain value 0.5 so that our analytical results for ideal chains might be relevant for real chains as well.

In Sec. VI B we compare mechanical desorption of a polymer chain from a solid surface with mechanical unzipping of a polymer-polymer complex like DNA. Finally, in Sec. VI C we summarize our main results and discuss the question why the phase transitions in our system have unusual features.

A. Continuum model and general scaling theory of phase transitions

The canonical partition function of an excluded-volume chain in the absence of a force has the following form:41,42

\[
Q(N, \tau) = Q_c(N) \Psi(x), \quad x = N^{\phi},
\]

where \( Q_c(N) \) is the partition function at the critical point. The crossover scaling function \( \Psi(x) \) depends only on a scaling parameter \( x = N^{\phi} \), where \( \tau = 1 - \chi / \chi_c \) is the deviation from the critical point, with \( e^x \) as the statistical weight of a single contact with the surface and \( e^{\chi_c} \) as its value in the critical point, and \( \phi \) is the crossover index. We discuss the value of \( \phi \) at the end of this section. The parameter \( \tau \) is defined such that it is negative at the adsorption side of the transition and positive at the desorption side.

The asymptotic behavior of \( \Psi(x) \) can be deduced on very general grounds.43 The asymptote for \(-x \gg 1\) is exponential because for strong adsorption the free energy \( F \sim -\ln \Psi \) has to be proportional to \( N: \ln \Psi \sim |x|^{1/\phi} \sim N |x|^{1/\phi} \). In the desorption regime the free energy \( \ln \Psi \sim \ln x \) is a logarithmic function of \( N \).43 At the critical point \( \Psi \) is a constant and for small deviations \( \ln \Psi \) should be linear in \( x \): We write simply \( \ln \Psi \sim -1 - x \) because any constant can be absorbed into \( Q_c \). The asymptotic behavior of \( \Psi(x) \) is thus

\[
\ln \Psi(x) \sim \begin{cases} 
|1|^{1/\phi}, & -x \gg 1 \\
1 - x, & |x| \ll 1 \\
\text{in } x, & x \gg 1.
\end{cases}
\]

The average bound fraction \( \theta \), which is the adsorption order parameter, is found from \( N^{-1} \partial \ln Q/\partial \tau \),

\[
\theta \sim \begin{cases} 
|1|^{1/\phi}, & -\tau \gg 0 \\
N^{\phi}, & \tau = 0 \\
N^{1-\phi}, & \tau \gg 0
\end{cases}
\]

We compare the general scaling relations [Eqs. (33) and (34)] for an excluded-volume chain with the ideal-chain model, as given in Eqs. (4) and (5). For ideal chains \( \phi = \frac{1}{2} \) and the scaling parameter \( x \sim N^{1/2} \) is then nothing else than the argument \(-x = -cR \) in the partition function \( Y(x) \) of Eq. (4): \( Y(x) \) has exactly the same scaling as \( \Psi(x) \) in Eq. (33). Also the order parameter \( \theta \) in Eq. (5) scales the same as in Eq. (34) (with \( \phi = \frac{1}{2} \)). Hence, for ideal chains we may identify the crossover scaling function \( Y \) with the function:

\[
\Psi(x) = Y(-cR).
\]

This is a rare example of a crossover scaling function which is exactly known in a closed analytical form.

All the strong and weak points of the continuum model stem from this fact. In particular, the adsorption curve \( \theta(c) \) grows linearly with \( c \) without saturation, which is consistent with \( c \rightarrow |1|^{1/\phi} \) [Eq. (34)] as implied by the general crossover form of the partition function \( |1|^{1/\phi} \) in Eq. (33). Any improvements in the strong adsorption regime necessarily involve corrections to the crossover scaling. We introduced such corrections by redefining the continuum parameters such that the partition function reduces to that of the lattice, where proper saturation of \( \theta \) occurs.

B. The crossover index \( \phi \)

De Gennes44 proposed \( \phi = 1 - \nu \), where \( \nu = 0.588 \) is the Flory exponent in \( R \sim N^\nu \), which would give \( \phi = 0.41 \). This was based on the assumption that the density profile of a critically adsorbed chain is essentially the profile of an unperturbed coil cut in the middle by a fictitious plane, as is the case for ideal-chain adsorption. It was soon recognized45 that this picture is not valid for an excluded-volume chain.

The mean-field value \( \phi = \frac{1}{2} \) applies to higher-dimensional space with \( d \approx 4 \), where excluded-volume effects are negligible. A conformal-invariance approach46 in \( d=2 \) also gives, rather unexpectedly, \( \phi = \frac{1}{2} \). It was also found that \( \phi = \frac{1}{2} \) applies rigorously to adsorption of randomly branched self-avoiding polymers on a lattice.47,48 This prompted a tempting suggestion that \( \phi = \frac{1}{2} \) is a superuniversal index. However, field-theoretical calculations49 based on two different methods (\( \varepsilon \)-expansion with the Padé–Borel summation and massive statistics versus the finite-size scaling parameter \( N \)) seemed to contradict the superuniversality hypothesis; the results are \( \phi = 0.483 \) and 0.52, respectively. In any case, field-theoretical considerations suggest that \( \phi \) is close to 1/2.

Numerical studies using different MC algorithms were employed to attack the problem of adsorption (Ref. 50 and references therein). A traditional way of evaluating \( \phi \) from simulations involves plotting various scaled chain characteristics versus the finite-size scaling parameter \( N^{\phi} \) in the hope of obtaining data collapse on two universal curves corresponding to the adsorption and desorption regimes. In this method, \( \chi_c \) and \( \phi \) must be adjusted simultaneously until the best collapse is achieved. Earlier studies produced estimates \( \phi = 0.588 \pm 0.03 \) (Ref. 31) and \( \phi = 0.53 \pm 0.007 \).51 The latter value was supported recently: \( \phi = 0.54 \pm 0.01 \). It was shown, however, that a slight change in the estimated \( \chi_c \) leads to large effect on the estimate for \( \phi \). Descas et al.52 demonstrated that parameter pairs \( \phi = 0.59 \), \( \chi_c = 1.01 \), and \( \phi = 0.50 \), \( \chi_c = 0.98 \) in the bond-fluctuation model give almost the same overall quality of the data collapse.

A more refined analysis was suggested by van Rensburg and Rechnitzer41 who studied adsorption of self-avoiding walks (SAW) in two-dimensional (2D) and 3D and obtained extremely accurate data for \( N \) up to 300. These authors demonstrated that analysis of heat capacity data has many pitfalls. A more robust procedure is based on studying the energy ratios \( E_{N+1}/E_N \) for walks of different lengths. The values reported were \( \phi = 0.501 \pm 0.015 \) (in accordance with
the exact theoretical value 1/2) and $\chi_c=0.565 \pm 0.010$ for the square lattice, and $\phi=0.5005 \pm 0.0036$ and $\chi_c =0.288 \pm 0.020$ for the cubic lattice.

Explicit corrections were introduced by Grassberger et al.\cite{42,43} in their analysis of extensive numerical data obtained by a chain-growth MC algorithm (pruned-enriched Rosenbluth method for SAWs on a simple cubic lattice with an adsorbing surface). An earlier estimate for $N \leq 2000$ gave $\phi=0.496 \pm 0.004$ and $\chi_c=0.286 \pm 0.003$.\cite{42} In the next paper\cite{43} for $N$ up to 8000 it was shown that corrections to scaling persist even for very large $N$ (beyond 1000), masking the true value of $\phi$, which is now actually somewhat below 1/2: $\phi=0.484 \pm 0.002$ and $\chi_c=0.2857 \pm 0.0001$.

There are also some results for off-lattice models. MC simulation of off-lattice chains with $N$ up to 512 demonstrated that the heat capacity extrapolated to $N \rightarrow \infty$ experiences a finite jump, which is consistent with the mean-field value $\varphi=0.5$.\cite{10} Simulations with a bead-spring model gave $\phi=0.5 \pm 0.02$.\cite{33}

We conclude that the crossover exponent $\phi$, which defines not only the near-critical behavior but also the adsorption of asymptotically long chains further from the critical point, is close to $\phi=0.5$ for real chains. This means that the thermodynamics of real self-avoiding polymers is to a large extent described by ideal-chain models. Quantitatively, excluded-volume effects lead to a shift in the transition point and to a change in the numerical values of the entropy of a strongly adsorbed state, etc., but these effects are of the same nature as the difference between various lattice models. This is in contrast with geometrical characteristics (chain size in lateral and normal directions), which are governed by the Flory indices $\nu$ for 2D and 3D spaces, which are quite different for ideal and real chains. Because $\nu=0.5$ the finite-size results for ideal chains are probably relevant for real chains as well.

C. Analogy between mechanical desorption and unzipping of DNA

Finally, we consider the analogy between mechanical desorption of a polymer chain from a solid surface and mechanical unzipping of two complementary polymer chains. In a simple model due to Causo et al.\cite{54} the two strands of DNA are considered as two self-avoiding polymer chains on a simple cubic lattice. Each monomer on one strand has its complementary monomer at the same contour position in the other strand. Two complementary monomers are favored to be in contact with a binding energy $\varepsilon$. Causo et al. studied the unzipping of this polymer-polymer complex (as a model for DNA) for varying $\varepsilon$ without external force. For ideal lattice chains they found that the phase transition from double strand to molten state is of second order, but for chains with excluded-volume interactions it transforms unexpectedly into a first-order transition, with some unconventional characteristics very similar to the mechanical desorption transition of an ideal chain under external force as considered in this paper. In particular, the contact number distribution is flat in the transition point (like the end-point distribution in Fig. 14) and the heat capacity at the transition is proportional to $N$ and has a form similar to Fig. 13(a) (probably, it could be described as a power law). The interpretation in Ref. 54 of this anomalous behavior is the same as ours: the absence of a substantial surface energy between the two phases.

In a later paper this model was extended by Orlandini et al.,\cite{55} who applied a pulling force to the two ends of strands, see the inset of Fig. 15. Their results for the end-to-end separation in the force direction (comparable to our stretching parameter $\xi$) versus temperature for $2N=150$ and $\varepsilon=1$ are reproduced in Fig. 15. The analogy with our Figs. 7(b) and 9(b) is striking.

The temperature $T$ in Fig. 15 is normalized on the denaturation temperature $T_d=0.58 \pm 0.02$, obtained from unzipping the polymer-polymer complex in the absence of a force. We may compare this with an estimate for a lattice model. The entropy of two denatured chains on a five-choice lattice is $2 \ln 5$, whereas the entropy of a double chain (both chains parallel) is $\ln 3$. Hence, for ideal chains the denaturation temperature (in units $\varepsilon$) is $T_d=1/\ln(25/3)=0.472$, which is rather close to the simulation value.

Although Causo et al.\cite{54} and Orlandini et al.\cite{55} presented their model as thermal or mechanical denaturation (unzipping) of the two strands of DNA, it is clear that their model does not take into account three important features of DNA: the rigidity of the native unzipped parts of DNA, the cooperative character of unzipping two-strand helical rigid sections, and the heterogeneity of DNA. We believe that their model is better described as a mechanical unzipping of a polymer-polymer complex, where both polymers are flexible. Comparison of the temperature dependence of the stretching degree for unzipping of a (homo-) polymer-(homo-) polymer complex (Fig. 15) and the similar dependence for mechanical desorption of a single polymer chain from a solid surface [Figs. 7(b) and 9(b)] demonstrates the close analogy between these systems. There are addition analogies: (i) The phase diagram for unzipping a polymer-polymer complex is similar to Fig. 6, with re-entrance,\cite{25} (ii) the bound fraction exhibits a power law divergence near the unzipping transition $\theta-\left(f-f_0\right)^{-1}$ (Ref. 56) similar to Figs. 3 and 12, and (iii) the end-point distribution near the unzipping transition is given by

![FIG. 15. Square end-to-end separation (normalized to $N^2$) in the force direction as a function of temperature (normalized to the denaturation temperature $T_d=0.58 \pm 0.02$) for mechanical unzipping of DNA, for $\varepsilon=1$, and force levels as indicated. This figure is reproduced from Ref. 55; we corrected the misprint in Fig. 14.](http://jcp.aip.org/about/rights_and_permissions)
\[ P(z) \sim \exp\left(\frac{f}{T} - \sqrt{\mu_{\text{ads}}} z\right), \] which is in agreement with Eq. (3); in the transition point both distributions are flat (see Fig. 14). Therefore unzipping of a polymer-polymer complex has the same unusual features as mechanical desorption of a single chain. We can speculate that unzipping of this complex occurs without metastable states, and is characterized by a power law dependence of the heat capacity: 

\[ C \sim (T - T_u)^{-2}. \]

### D. Main results and conclusions

We summarize the main results of our paper.

1. We introduced the temperature in the continuum model and eliminated the defects of this model by mapping on a lattice model. In fact we transformed the continuum theory into a standard lattice model for adsorption and stretching of a single polymer chain of any length. This enables a full analytical description for the temperature dependence at the second-order (adsorption/desorption) and first-order (mechanical desorption) phase transitions of polymer chains of finite length.

2. The full phase diagram, which gives the dependence of the detachment force on temperature, contains two lines for second-order transitions, a curve for the first-order transition, and a bicritical point. The first-order curve is nonmonotonic and gives rise to the re-entrance effect.

3. The first-order transition for mechanical desorption has some unusual features. There are no metastable states, there is no bimodal distribution in the transition region, and the fluctuations (and the heat capacity) increase anomalously as a power law \((T - T_u)^{-2}\).

4. The unusual features of the first-order transitions are not an artifact of the ideal-chain model used in this paper. The force-induced desorption of an adsorbed polymer chain with excluded-volume interactions was recently analyzed analytically and by computer simulation using a coarse-grained off-lattice bead-spring model.\(^ {18}\) The critical detachment force \(f^*\) was obtained as a function of \(\varepsilon/T\), where \(\varepsilon\) was taken as constant. The interval of observed \(\varepsilon/T\) values in the computer simulations does not allow to draw conclusions about the re-entrance effect. However, it was demonstrated that although the phase transition of chain detachment is clearly of first order, no trace of a bimodal distribution in the vicinity of the transition can be detected.

We briefly discuss the specific features of this unusual behavior. The above authors\(^ {18}\) saw an analogy between the detachment transition and the so-called escape transition.\(^ {57}\) In the escape transition an end-grafted chain is compressed by a piston. Beyond a critical compression the conformation of the confined chain changes abruptly from a compressed coil to an escaped state. The latter consists of a stretched tether from the grafting site to the piston border and an expelled fraction of the coil outside the piston. It is clear that these two states cannot exist simultaneously: The polymer coil as a whole has to reorganize toward the escaped state. Hence, there is no phase coexistence. Bhattacharya et al.\(^ {18}\) stated that in mechanical desorption “the states on both sides of the phase diagram cannot coexist simultaneously,” and as a result there is a “dichotomic transition.”

In our opinion there is no analogy between mechanical desorption and the escape transition. The polymer chain in the escape transition exists either in a compressed or in an escaped state. There is no coexistence between these two states. In contrast to the escape transition, the typical conformation in the detachment transition is a combination of an adsorbed part and a stretched part of the same polymer chain, see Fig. 1. Adsorbed and stretched phases coexist at the same time in the same macromolecule. These two phases fluctuate and in the transition point the fluctuations are very large. In the transition point all conformations with a different number of adsorbed units have the same statistical weight. The unimodal form of the distributions and the absence of metastable states are caused by the fact that there is no free energy loss at the border between adsorbed and stretched phases: This border extends only over one segment length. The unusual features of the first-order detachment transition are due to very strongly fluctuating coexisting phases that have the same energy.

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