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Mechanical desorption of a single chain: Unusual aspects of phase coexistence at a first-order transition

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The phase transition occurring when a single polymer chain adsorbed at a planar solid surface is mechanically desorbed is analyzed in two statistical ensembles. In the force ensemble, a constant force applied to the nongrafted end of the chain (that is grafted at its other end) is used as a given external control variable. In the z-ensemble, the displacement z of this nongrafted end from the surface is taken as the externally controlled variable. Basic thermodynamic parameters, such as the adsorption energy, exhibit a very different behavior as a function of these control parameters. In the thermodynamic limit of infinite chain length the desorption transition with the force as a control parameter clearly is discontinuous, while in the z-ensemble continuous variations are found. However, one should not be misled by a too-naive application of the Ehrenfest criterion to consider the transition as a continuous transition: rather, one traverses a two-phase coexistence region, where part of the chain is still adsorbed and the other part desorbed and stretched. Similarities with and differences from two-phase coexistence at vapor-liquid transitions are pointed out. The rounding of the singularities due to finite chain length is illustrated by exact calculations for the nonreversal random walk model on the simple cubic lattice. A new concept of local order parameter profiles for the description of the mechanical desorption of adsorbed polymers is suggested. This concept give evidence for both the existence of two-phase coexistence within single polymer chains for this transition and the anomalous character of this two-phase coexistence. Consequences for the proper interpretation of experiments performed in different ensembles are briefly mentioned.

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I. INTRODUCTION AND OVERVIEW

Understanding the cooperative effects in single polymer chains has recently become a subject of very intense research. These effects include protein folding, unzipping of DNA, translocation of biomolecules through pores, and adsorption and desorption of polymers on fluid membranes or on solid substrates. (See. e.g., [1] for a recent review and [2–6] for some further references.) Particularly useful is the experimental study of conformational changes of polymers under the action of pulling forces [6–9].

Polymers at interfaces [10–12] may show a complex phase behavior already in the absence of a pulling force, for instance, because of the interplay of the attractive potential due to the surface and the solvent quality (with poor solvents giving rise to an effective attraction between the monomers of the chain in the solution). In poor solvents, adsorption may compete with the collapse transition into compact globules, in the bulk as well as adsorbed to the surface, or even crystalline states [13–17]. Here we shall only be concerned with the adsorption transition of an end-grafted flexible polymer (which takes a "mushroom configuration" under good solvent conditions) to a quasi-two dimensional "pancake" [18,19]. Despite long-standing efforts [20–28], even this generic problem is still under discussion [29]. In the presence of an external pulling force, the number of phases increases due to the appearance of the stretched chain state, and numerous phase transitions can occur.

While the basic aspects of phase transitions in bulk condensed matter are well understood [30], phase transitions in a single macromolecule have some unusual features, which sometimes hamper their understanding. These unusual properties start already on the most basic level, the distinction of the different phases of a system in terms of the order parameter, as introduced in the Landau theory of phase transitions [31,32]. In standard condensed matter, the order parameter is an extensive thermodynamic variable, such as, e.g., the magnetization in a ferromagnetic, or the particle number density, in the case of the vapor-liquid phase transition. The latter case is a generic example for a phase transition of first order, where, according to the classical Ehrenfest classification, first derivatives of the thermodynamic potential with respect to intensive thermodynamic variables have a jump. For example, by taking in a fluid the pressure p as a control variable, the partial derivative of the Gibbs free energy

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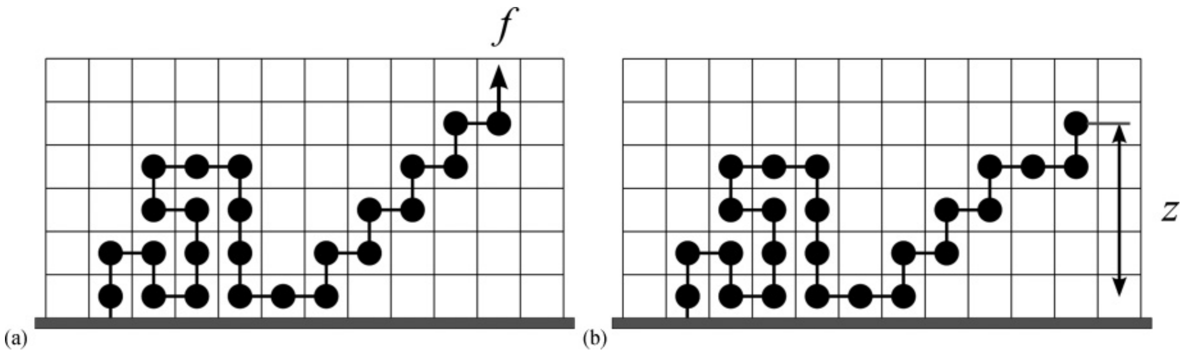

FIG. 1. End-grafted adsorbed polymer chain pulled from the surface in the force ensemble (with fixed given force f) (a) and the z-ensemble (for fixed distance of the free chain end above the substrate) (b).

with respect to pressure at constant temperature, the volume, jumps from a small value of the bulk liquid to a larger value of the vapor when the liquid evaporates.

In contrast, the order parameter characterizing the phase transition of a single macromolecule is often chosen as a global parameter describing the conformation of the chain as a whole. In the coil-stretch transition in a macromolecule subjected to a pulling force, the order parameter is the end-to-end distance of the polymer (possibly normalized by the contour length of the linear macromolecule). In the so-called escape transition, whereby a polymer coil grafted at one end on a substrate (a "polymer mushroom") is compressed by a piston, which can lead to an abrupt change of conformation from a deformed coil to an inhomogeneous "flower state," the order parameter is the degree of stretching of the whole chain [33,34]. In the adsorption of a single chain onto a planar solid or liquid substrate the fraction of monomers in contact with the substrate is commonly taken as the order parameter [11,12,18–29].

A difference between phase transitions of bulk matter and single macromolecules arises, however, when we consider the transition as a function of an extensive variable as a control parameter. For example, if the volume of a fluid at constant temperature is varied, the liquid-vapor transition shows up as a strictly horizontal part on the P-V diagram at the transition pressure (where, in the thermodynamic limit, particle number $N \to \infty$). The interpretation of this horizontal piece (volume V in the region $V_\ell < V < V_g$) is that phase coexistence occurs, whereby two macroscopic regions of volume fractions x of gas and $1 - x$ of liquid occur, with $x = (V - V_\ell)/(V_g - V_\ell)$ (the "lever rule"). These coexisting phases are separated by an interface which also has a macroscopic area (of order $V^{(d-1)/d}$ in d dimensions). Apart from interfacial effects, considering the NVT ensemble rather than the NPT ensemble gives nothing new (since both ensembles are simply related via a Legendre transformation).

For phase transitions of single chains, in some cases phase coexistence simply is impossible. As an example, a compressed polymer mushroom underneath a piston may be either "imprisoned" or "escaped," but it would not make sense to consider a state which is a mixture of both pure phases. Phase coexistence in this case is impossible, and in the transition region the equivalence between the different statistical ensembles ("force ensemble," in which the force on the piston is the control variable, and "height ensemble," in which the height of the piston above the surface is controlled) fails [33,34].

In the present paper, we shall focus on a conceptually much simpler problem, the transition where an adsorbed chain is pulled off a solid surface by force f [35–49] (Fig. 1). Again, two conjugate ensembles are conceivable, the force ensemble (fixed given force) and the z-ensemble (fixed distance of the free chain end above the substrate), and these are experimentally realizable and relevant [7–9]. In this case "phase coexistence" analogous to the liquid-vapor transition between part of the chain that is still adsorbed and the nonadsorbed, stretched part of the chains is possible (Fig. 1), as will be analyzed in detail in the present paper. Of course, it is well known that fluctuations differ in the various ensembles of statistical mechanics [31], and hence also finite-size effects differ in these two ensembles [50,51]. However, as we shall see, in the thermodynamic limit the f-ensemble and the z-ensemble yield strictly equivalent results (which are again related by Legendre transformations).

Nevertheless, there is one important difference from the liquid-vapor case: while in the latter the two pure phases are separated in the "free energy landscape" by a barrier (due to the need to create an interface of area proportional to $V^{(d-1)/d}$ to move from one state to the other, when they coexist), there is no such barrier for the transition from the adsorbed coil to the stretched chain: the analog of a macroscopic interface between coexisting states does not exist; at the "interface" there is just a single effective monomer (or a few of them, if we consider an extended finite range of the adsorption potential and/or semiflexible polymers, etc.).

This lack of interfacial contributions to the thermodynamic potential in the regime of phase coexistence also has important consequences for the finite-size effects that lead to a rounding of the transition for finite-chain length. While for phase transitions in bulk condensed matter physics finite-size effects are quite negligible (with the notable exception of phase transitions in small clusters or nanoparticles), for phase transitions in simple macromolecules N usually is only the order 10^2 to 10^4 (while for DNA up to $N = 10^{10}$ is possible). Although the thermodynamic limit for single chains is in principle accessible to experimental studies since many polymers can be synthesized with their molecular weight being varied over several decades without changing the intrachain interactions, the influence of finite-size effects is completely different from that in bulk matter: the finite-size effects for a liquid droplet are dominated by the surface contributions to the free energy, while a polymer in a good solvent taking a typical coil conformation does not have a well-defined surface at all. Therefore we shall discuss finite-size effects for our problem in detail.

In the present paper, we shall compare the phase transition and the associated finite-size effects at the mechanical desorption of an adsorbed chain in the f-ensemble and in the z-ensemble, using a simple lattice model ignoring the excluded volume interactions. Although this neglect has the consequence that some physical properties of the chain are not correctly described (e.g., the lateral dimension of adsorbed chains scales like $N^{1/2}$ rather than $N^{3/4}$ [11]), it is useful for elucidating the physical nature of the desorption transition in the two conjugate ensembles. We choose this simple model intentionally, since it is exactly solvable in the thermodynamic limit $N \to \infty$, while for finite N all the equilibrium properties are calculated numerically. In this way we can show that the underlying phenomenon is the same first-order transition in the thermodynamic limit $N \to \infty$, although its manifestations in various quantities in the two conjugate ensembles are dramatically different.

Finally, we would like to explain the motivation of this work. Mechanical desorption is very closely related to the problem of DNA unzipping, which has generated an extensive body of experimental, analytical, and numerical studies (see the review [1]). The most direct analogy appears when a real double-stranded DNA is replaced by a complex of two homopolymers [49,52]. It was in the context of this simple model that mechanical unzipping was classified as a standard first-order transition and the equivalence of the f- and z- ensembles was noted [5]. On the other hand, detailed computer simulations of mechanical desorption in the z-ensemble [46] revealed unexpected continuous change of the adsorption order parameter with temperature, which the authors referred to as characteristic of second-order transitions. Comparison with the jumpwise behavior of the adsorption order parameter in the f-ensemble [44,45] prompted some doubt as to whether the ensemble equivalence is applicable in this case. A straightforward reference to a fundamental theorem on the equivalence of conjugate ensembles [53] is not entirely convincing since phase transitions in single macromolecules are known to demonstrate notable exceptions to this theorem. One example, namely the escape transition, was mentioned above, and the other refers to the homo-DNA unzipping when the force is applied to interior (rather than to end) monomers [54]. The background reason underlying the possibility of ensemble nonequivalence is related to the abnormal nature of the covalent potentials preserving the linear structure of a chain. As long as these bonds do not break at room temperature, the corresponding potential is presented as a function increasing with distance indefinitely, which excludes it from the class of potentials to which the theorem applies.

The other aspect of mechanical desorption that caused some confusion was the question of whether the notion of phase coexistence is applicable to this case. In Ref. [44] mechanical desorption in f-ensembles was considered as a dichotomic transition without phase coexistence. Indeed, first-order transitions in a single chain without phase coexistence are known, as mentioned above for the escape transition. Other examples for the first-order phase transitions without phase coexistence within a single chain include polymer chains tethered near an adsorbing solid surface and near a step potential, as has been discussed in a recent review [55]. It can be inferred from [54] that homo-DNA unzipping by a force applied to an interior monomer may also belong to this class. In the present paper we demonstrate that chain desorption by the end force is rather an exception where the notion of phase coexistence is particularly productive and perfectly applicable at the critical detachment value of the force.

The main focus of this paper is therefore to study phase coexistence within a single macromolecule and to identify its peculiar features as compared to the phase coexistence in other condensed matter analogies. These analogies prompted us to revise the traditional way of defining the adsorption order parameter and to suggest a local version of it, which turns out to be perfectly suited for such a study. It allows an unequivocal demonstration of the ensemble equivalence in the case of end desorption and may be useful for clarifying more complicated situations where inhomogeneous chain configurations arise.

II. MODEL AND METHOD

A. Model

We consider a single flexible polymer chain consisting of N monomer units grafted by one chain end onto a solid planar substrate (Fig. 1). We use a lattice model where chain conformations are represented as walks on the simple 5-choice cubic lattice (with no immediate reversals; this model is also known as the nonreversal random walk (NRRW) model [56]). Excluded volume interactions are ignored. A lattice step represents the repeat unit of the polymer chain, and its length ℓ (the lattice spacing) henceforth is taken as the unit of length. The interaction of the chain with the infinite planar surface at $z = 0$, to which the chain is grafted, occurs only in the lattice plane $z = 1$ adjacent to the surface. Each contact of a repeat unit with the surface leads to an energy gain ε. In real systems, ε has the meaning of an exchange free energy upon replacing a solvent molecule in contact with the surface by the chain repeat unit and hence can be temperature dependent, but this complication will be disregarded here.

We consider the effect of a force f applied to the other end of the chain in the $+z$ direction normal to the surface. Such a force gives rise to a stretching energy $f\ell$ per step in the direction of the force. By choosing units such that $\varepsilon = 1$, $k_B = 1$, and $\ell = 1$, the parameters are the force f and the temperature T. We use the reduced parameter $\tau = T_c/T$, where $T_c = 1/\ln(5/4)$ is the critical temperature (in units of ε/k_B) of the adsorption transition in the absence of the force.

B. Numerical approach

The present treatment is based on a Green's function formalism as used by Rubin [21] for ordinary random walks on the simple cubic lattice and later generalized to the NRRW model [49]. The central quantities are the statistical weights $G(z;n)$ of all conformations of tethered chain parts of length n with one free end in the layer z. In order to take into account that immediate reversals are forbidden, the Green's function must be represented as a sum of three components with respect to the direction of the last monomer-monomer link: $G(z;n) = G^{\uparrow}(z;n) + G^{\leftrightarrow}(z;n) + G^{\downarrow}(z;n)$, where the upper index shows the direction with respect to the adsorbing surface: away from it (↑), parallel to it (↔), or toward the surface (↓).

The components of these Green's functions satisfy the following recursion relations:

$$\begin{aligned} G^{\uparrow}(z;n+1) &= G^{\uparrow}(z-1;n) + G^{\leftrightarrow}(z-1;n), \\ G^{\leftrightarrow}(z;n+1) &= 4G^{\uparrow}(z;n) + 3G^{\leftrightarrow}(z;n) + 4G^{\downarrow}(z;n), \\ G^{\downarrow}(z;n+1) &= G^{\leftrightarrow}(z+1;n) + G^{\downarrow}(z+1;n), \end{aligned} \tag{1}$$

at $z > 0$. At the surface, however, we have

$$\begin{aligned} G^{\uparrow}(0,n+1) &= 0, \\ G^{\leftrightarrow}(0,n+1) &= [3G^{\leftrightarrow}(0,n) + 4G^{\downarrow}(0,n)]\exp(1/T), \\ G^{\downarrow}(0,n+1) &= [G^{\leftrightarrow}(1,n) + G^{\downarrow}(1,n)]\exp(1/T). \end{aligned} \tag{2}$$

The first of these relations simply expresses the fact that the surface is impenetrable for the monomers. The starting point for the recursion is the distribution of dimers ($n = 2$),

$$\begin{aligned} G^{\uparrow}(0;2) &= 0, \quad G^{\uparrow}(1;2) = \exp(1/T), \\ G^{\uparrow}(z>1;2) &= 0, \quad G^{\leftrightarrow}(0;2) = 4\exp(2/T), \\ G^{\leftrightarrow}(1;2) &= 0, \quad G^{\leftrightarrow}(z>1;2) = 0, \\ G^{\downarrow}(0;2) &= 0, \quad G^{\downarrow}(1;2) = 0, \quad G^{\downarrow}(z>1;2) = 0. \end{aligned} \tag{3}$$

Recursively applying Eqs. (1)–(3), one can easily calculate $G(z;n)$ for every chain length n. The partition function of tethered chains is then obtained by summing over all positions of the free chain end,

$$Z(N) = \sum_{z=0}^{N\ell} G(z;N). \tag{4}$$

From $Z(N)$ and the Green's functions one can calculate various observables. For example, the probability that monomer n is adsorbed on the surface can be written as

$$p(n) = G(0;n)Z(N-n)\exp(-1/T)/Z(N), \tag{5}$$

and the average fraction of adsorbed monomers θ becomes

$$\theta = (1/N)\sum_{n=1}^{N} p(n) = \langle m\rangle/N, \tag{6}$$

where m is the number of polymer surface contacts.

III. TREATMENT OF THE MECHANICAL DESORPTION TRANSITION

A. The average fraction of adsorbed monomers at the mechanical desorption, as described in the two conjugate ensembles

From Eq. (4) it is obvious that $G(z;N)$ is nothing but the constrained partition function that the end of the chain is at the distance z above the surface, and hence it is straightforward to compute all thermodynamics quantities of interest in the z-ensemble from this constrained partition function, according to the standard rules of statistical thermodynamics. On the other hand, the partition function in the f-ensemble simply is obtained from $Z(N,z) = G(z;N)$ as [31]

$$Z(N,f) = \sum_{z} Z(N,z)\exp(fz/T). \tag{7}$$

Equation (7) just expresses the standard rule of statistical mechanics to transform from one statistical ensemble to the thermodynamically conjugate ensemble; note that Eq. (7) holds also for finite N and not only in the thermodynamic limit (where Eq. (7) reduces to a simple Legendre transformation between the corresponding thermodynamic potentials [31]). [Note also that the average restoring force is $f = T(\partial \ln Z(N,z)/\partial z)$.]

Here we are particularly interested in the average fraction of adsorbed monomers, θ, as defined in Eq. (6), which traditionally is taken as the order parameter in the adsorption transition. Figures 2(a) and 2(b) display the curves of θ versus the external pulling force f and θ versus the reduced height z/N of the chain end, for two values of $\tau(=T/T_c)$, namely $\tau = 1.5$ and $\tau = 5$.

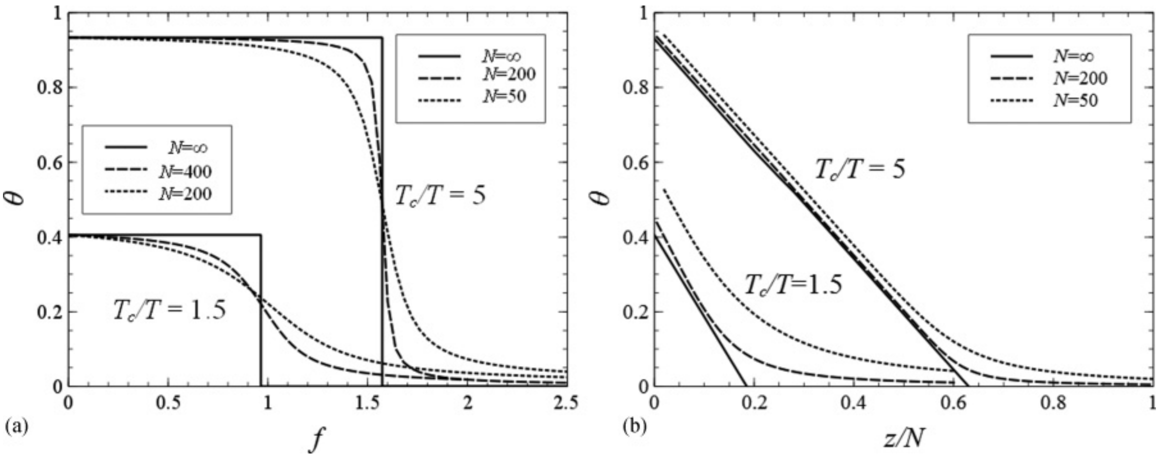

FIG. 2. Fraction of adsorbed monomer units for nonreversal random walk chains on the simple cubic lattice as a function of the external pulling force acting at the free chain end (a) and as a function of fixed (reduced) height of the chain end, z/N (b). The values of $\tau = T_c/T$ and the chain lengths N are indicated.

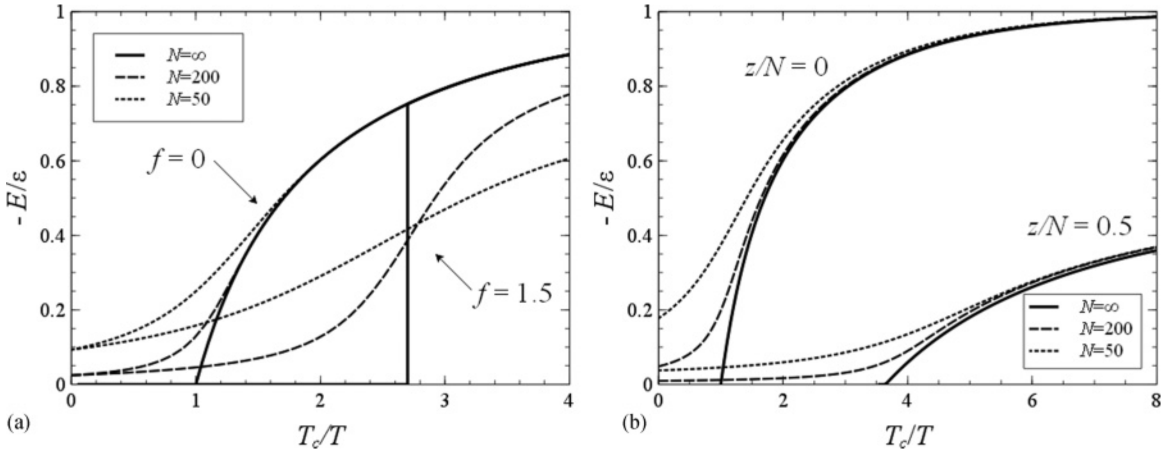

FIG. 3. Average adsorption energy $-E/\varepsilon = \theta$ as a function of reduced inverse temperature (T/T_c) in the constant f-ensemble (a) and in the constant z-ensemble (b). Three chain lengths $N = 50$, $N = 200$, and $N = \infty$ are shown in both cases. Panel (a) includes the cases $f = 0$ and $f = 1.5$, while panel (b) includes the cases $z/N = 0$ and $z/N = 0.5$.

Clearly, there is a big difference between Figs. 2(a) and 2(b). In the thermodynamic limit, $N \to \infty$, the curves of θ versus f exhibit a jump in the order parameter at a well-defined transition force f_{tr}, which is a clear signal of a first-order transition.

In contrast, the dependence of the order parameter θ on z/N shows a continuous change, with only a discontinuity of slope occurring at a particular transition point $(z/N)_{\mathrm{tr}}$, in the limit $N \to \infty$. For finite N, these discontinuities in both ensembles get progressively rounded as the chains become shorter.

If one had only the information shown in Fig. 2(b), one might be misled to conclude from the fact that the order parameter is a continuous function of the control variable that the transition at $(z/N)_{\mathrm{tr}}$ is a continuous phase transition. The same misleading conclusion would result from a consideration of the specific heat, which traditionally is considered by the "Ehrenfest criterion" [31] to distinguish the order of phase transitions: according to this criterion, the specific heat exhibits a delta-function singularity at a first-order transition (reflecting the latent heat of the latter), while there is a weaker singularity of the specific heat (finite jump or power-law divergence [30]) at a continuous (second-order) phase transition.

In our model, the average energy of the adsorbed chain per monomer is simply related to the order parameter as $E = -\varepsilon\theta$. The heat capacities in the two ensembles then become $C = dE/dT$ (z-ensemble) and $C = dE/dT - f d\langle z\rangle/dT$ (f-ensemble). [Note that a change of temperature in the f-ensemble changes also the mechanical part of the energy $f\langle z\rangle$ which is present in this ensemble.]

Figures 3 and 4 show both the energy and the specific heat as a function of temperature in both ensembles. We have included here the case of no force ($f = 0$) in the f-ensemble and $z/N = 0$ in the z-ensemble: this case is nothing but the ordinary adsorption transition in an end-grafted chain with a free end ($f = 0$) or in a loop ($z/N = 0$) having both ends pinned at the surface, which is known to have the character of a continuous transition [11,18–29]. Indeed, one finds in this case the expected behavior: the energy (Fig. 3) vanishes smoothly (for $N \to \infty$) as $T_c/T \to 1$ from above. For finite N, the transition is rounded, and the curves for the same value

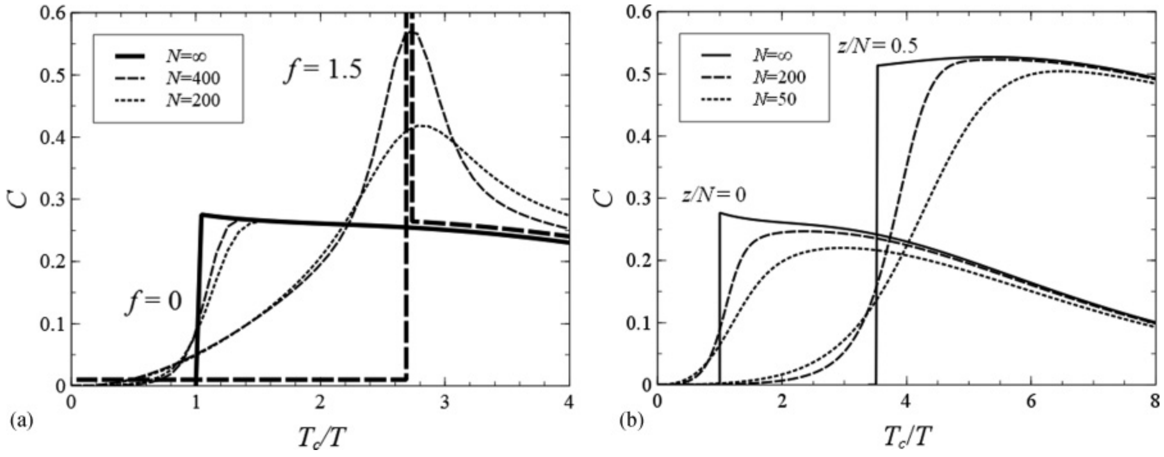

FIG. 4. Specific heat of the lattice chain as a function of $\tau = T_c/T$ in the f-ensemble, at two values of the pulling force (a) and in the z-ensemble, for two choices of the reduced height z/N (b). The chain lengths are $N = 50$ (dotted lines), 200 (dashed lines), and ∞ (solid lines). Note that the case $f = 0$ corresponds to a second-order transition, in the f-ensemble, and thus for $N \to \infty$ a finite jump develops, while for $f = 1.5$ the first-order transition shows up via a δ peak.

of N differ somewhat in the two ensembles, while the curves $-E/\varepsilon$ versus T_c/T become identical for $N \to \infty$ at $f = 0$ and $z/N = 0$ [but note that the range of T_c/T shown in Fig. 3(b) is twice that in Fig. 3(a)]. With respect to the specific heat, there are larger differences, particularly with respect to finite-size effects. We note, of course, that the specific heat is a second derivative of the thermodynamic potential, and such quantities generally differ in conjugate statistical ensembles (since there is a difference between the specific heats at constant pressure or constant volume in fluids and solids).

Now the energy (or order parameter) for $f = 1.5$ develops a jump as $N \to \infty$, and the specific heat develops a delta-function singularity; these are clear signals of the first-order character of the transition. In contrast, in the z-ensemble the energy (or the order parameter) varies smoothly, similar to the case $z/N = 0$, and the specific heat develops a jump. Qualitatively, in the z-ensemble the behavior at $z/N > 0$ is always rather similar to the case $z/N = 0$, where we know that the transition is second order. Should we then conclude that this problem leads to another case of statistical ensemble inequivalence (as is known to occur for the polymer escape transition [33,34])?

Of course, as we shall see below, the answer to this question is no. The flaw in the consideration of Figs. 2–4 in terms of Ehrenfest criteria is that the latter require the use of statistical ensembles with a single extensive variable (such as the f-ensemble, with only N as an extensive variable) rather than two of them (with the variable z here playing also the role of an extensive variable, which may not be obvious at first sight). Before we expand on this issue, we turn to a particularly puzzling feature of this problem, the so-called detachment line in the infinite chain limit.

B. Analytical theory for detachment lines at different modes of mechanical desorption: infinite chain limit

The transition line in the constant-force ensemble can be defined by the position of the jump in the order parameter: the transition occurs when the chemical potential $\mu_{\text{ads}}(\epsilon/T)$ of the adsorbed polymer chain becomes equal to the chemical potential $\mu_{\text{str}}(f/T)$ of the stretched chain. For a NRRW model on a simple cubic lattice there exists an explicit analytical form expressing ϵ/T in terms of μ_{ads}, i.e., the inverse of the $\mu_{\text{ads}}(\epsilon/T)$ function [48]:

$$\epsilon/T = \log\frac{2}{3x} - \log\left[1+\sqrt{1+\frac{2}{(3x)^2}\left(1-3x-x^2-5x^3-\sqrt{(1-3x-x^2-5x^3)^2-64x^4}\right)}\right], \tag{8}$$

where $x = \exp[\mu_{\text{ads}}/T]$ is the inverse partition function per step. The chemical potential of the stretched chain as a function of force is also available [48]:

$$\exp\left[\frac{-\mu_{\text{str}}}{T}\right] = 2+\cosh(f/T) + \sqrt{\cosh^2(f/T)+4\cosh(f/T)-1}. \tag{9}$$

The detachment line in terms f_{tr} versus T/T_c for the present model on a cubic lattice was obtained earlier in Ref. [48]. It is derived by combining Eqs. (9) and (8) with the equilibrium condition

$$\mu_{\text{ads}}(\epsilon/T) = \mu_{\text{str}}(f/T) \tag{10}$$

and is shown in Fig. 5(a). Upon crossing the detachment line (except at the critical adsorption point) the chemical potential has a slope discontinuity, indicating that this is a line of first-order phase transitions, ending at the abscissa in a critical point.

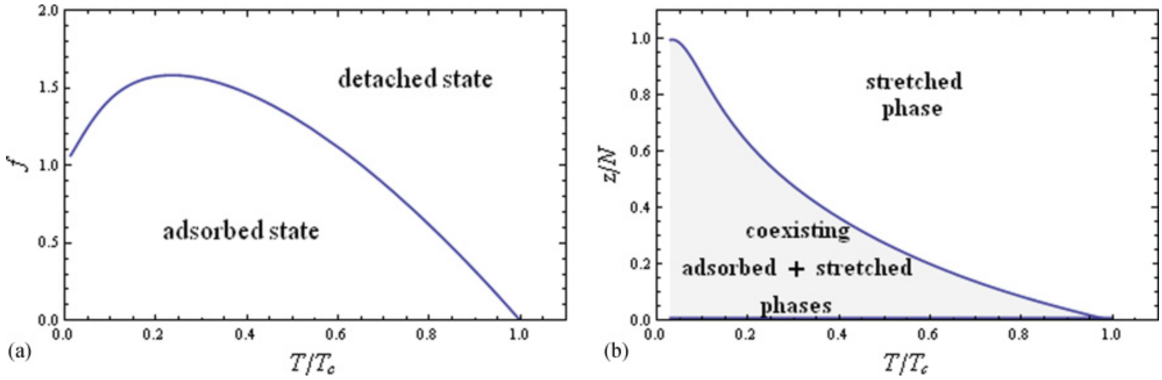

FIG. 5. (Color online) Phase diagram for mechanical desorption of adsorbed polymers in the infinite chain limit, as obtained in the f-ensemble (a) and the z-ensemble (b). The curve (a) showing f_{tr} as a function of the normalized temperature T/T_c displays a maximum. This implies that at some given force the chain is adsorbed in a certain temperature window and desorbed outside it: the stretched state is re-entered at low temperature. The transition at $f = 0$ is the second-order adsorption transition, while the transition at $f > 0$ is the first-order transition. The phase diagram (b) in the z-ensemble is the labeling region in between the abscissa and the detachment line $(z/N)_{\text{tr}}$ vs T/T_c. The labeling region must be interpreted as a two-phase coexistence between a stretched part and an adsorbed part of the chain.

The asymptotic form of this line in case of strong adsorption(at $\tau \gg 1$) is given by

$$f_{\rm tr} \simeq \varepsilon + T \ln 3, \tag{11}$$

while in the opposite limit of weak adsorption close to the critical point (at $\tau - 1 \ll 1$) it has the form

$$f_{\rm tr} \simeq \frac{10\sqrt{2}\ln(5/4)}{3}\sqrt{\frac{T}{T_c}}\,(T_c - T)\,. \tag{12}$$

We now construct the detachment line as defined in Ref. [46] for the adsorbed chain torn off the plane by gradually increasing its end height z/N. The free energy of an ideal adsorbed chain with one end at the distance z can be written as a sum of the free energies of the adsorbed and stretched parts of the chain:

$$F = (N - n)\mu_{\rm ads}\,(\epsilon/T) + n\mu_{\rm str}(\xi). \tag{13}$$

Here the first term is the adsorption free energy, which is linear in the number of monomers in the adsorbed pancake, $(N - n)$, and depends on adsorption interaction parameter ϵ/T through the monomer chemical potential in the unperturbed adsorbed chain $\mu_{\rm ads} < 0$ calculated with respect to the reference coil state. The second term is the free energy of the stem consisting of n monomers; $\xi = z/n$ is the strain (the degree of stretching) of the stem.

The equilibrium distribution of monomers between the stem and the adsorbed part is obtained by minimizing Eq. (13) with respect to n, which leads to

$$\mu_{\rm ads}(\epsilon/T) = \left(\frac{\partial F_{\rm str}}{\partial n}\right)_z = \mu_{\rm str}\,(\xi)\,. \tag{14}$$

Equations (14), (9), and (8) define together the equilibrium strain of the stem, ξ, as a function of the adsorption strength, ϵ/T, and therefore provide the number of monomers in the stem,

$$n_{\rm eq} = \frac{z}{\xi(\epsilon/T)}, \tag{15}$$

and finally the equilibrium Helmholtz free energy $F_{\rm eq}(N,z,\epsilon/T)$.

The fraction of adsorbed units is calculated as

$$\theta_z = \frac{1}{N}\frac{\partial F_{\rm eq}}{\partial \epsilon} = \theta_0\left(1 - \frac{z}{N\xi(\epsilon/T)}\right), \tag{16}$$

where $\theta_0 = \partial\mu_{\rm ads}/\partial\epsilon$ is the fraction of adsorbed units in a chain with the free end at the surface. One can see that θ_z decreases linearly with z/N until it vanishes. There is a slope discontinuity in θ_z at the transition point defined by $\theta_z = 0$:

$$\left(\frac{z}{N}\right)_{\rm tr} = \xi(\epsilon/T). \tag{17}$$

The dependence of the strain on ϵ/T can be found by using the equation of state $\xi(f/T)$ determined from Eq. (9), and the relation between the force and ϵ/T follows from Eq. (10). This case is presented on Fig. 5(b) in terms of the parameters $(z/N)_{\rm tr}$ versus T/T_c.

The numerical results that we have presented (Figs. 2–5) show that the phase transition effected by the mechanical desorption of an adsorbed chains has a rather different character, depending on the considered ensemble: if the desorption occurs by varying the external pulling force we encounter a first-order phase transition from zero relative extension $\langle z\rangle/N$ (as $N \to \infty$) and nonzero adsorption order parameter θ to the stretched state with nonzero $\langle z\rangle/N$ and $\theta = 0$. In contrast, if z/N is taken as the external control variable, the variation of θ is continuous, and so the "transition" at the detachment line, where θ vanishes, could be mistaken as a second-order transition, if one would apply standard Ehrenfest criteria naively and without reflection.

The fact that such a naive interpretation actually is in error should be obvious from the observation that all the results presented in Figs. 2–5 are deduced from the same statistical weight $G(z;n)$ which we can use to compute the partition function in both the z-ensemble $Z(N,z)$ and in the f-ensemble, $Z(N,f)$, and these partition functions are conjugate to each other [Eq. (7)] and indeed are equivalent in the thermodynamic limit. The apparent differences between the behavior of the f-ensemble and the z-ensemble can be readily understood in terms of the consequences of phase coexistence. Phase coexistence at first-order phase transitions is a well-known concept for bulk matter, but it is less so for transitions of single polymer chains. Therefore we discuss this interpretation in some detail in the next section.

IV. PHYSICAL PICTURE OF A FIRST-ORDER TRANSITION IN CONJUGATE ENSEMBLES

A. van der Waals fluid

A classical example of a first-order phase transition is the vapor-liquid transition of fluids [30,31]. We recall the textbook description of this transition in two conjugate ensembles: the constant-pressure (N,P,T) ensemble, which has only the particle number N as a single extensive thermodynamic variable, and the constant-volume (N,V,T) ensemble, with two extensive variables. In both cases we only address the behavior in the thermodynamic limit, $N \to \infty$.

In the (N,P,T) ensemble the two intensive variables pressure P and temperature T define uniquely the phase of the system in thermal equilibrium. Phase coexistence of vapor and liquid occurs only along a line $P_{\rm coex}(T)$ in the (P,T) diagram. This line in van der Waals theory starts at $P = 0, T = 0$ and ends with a second-order transition at the critical point $P(T_c)$, T_c [see Fig. 6(a); in real systems the line starts at the triple point where also the solid phase comes into play]. Each point on this coexistence line $P_{\rm coex}(T < T_c)$ corresponds to two-phase equilibria, the volume fractions x and $1 - x$ of the two phases are not fixed.

When one crosses the coexistence line, extensive thermodynamic variables such as volume V, entropy S, and average internal energy E change discontinuously. As an example, Fig. 6(b) shows the first-order phase transition at constant T, plotting V as a function of P to show the abrupt change of V at $P = P_{\rm coex}(T)$, using the van der Waals mean-field equation of state, defined by the equation [30,31]

$$[P/P_c + 3(V_c/V)^2](3V/V_c - 1) = 8T/T_c \tag{18}$$

together with the Maxwell construction. Of course, we do not imply that Eq. (18) is accurate for any real fluid; but the general

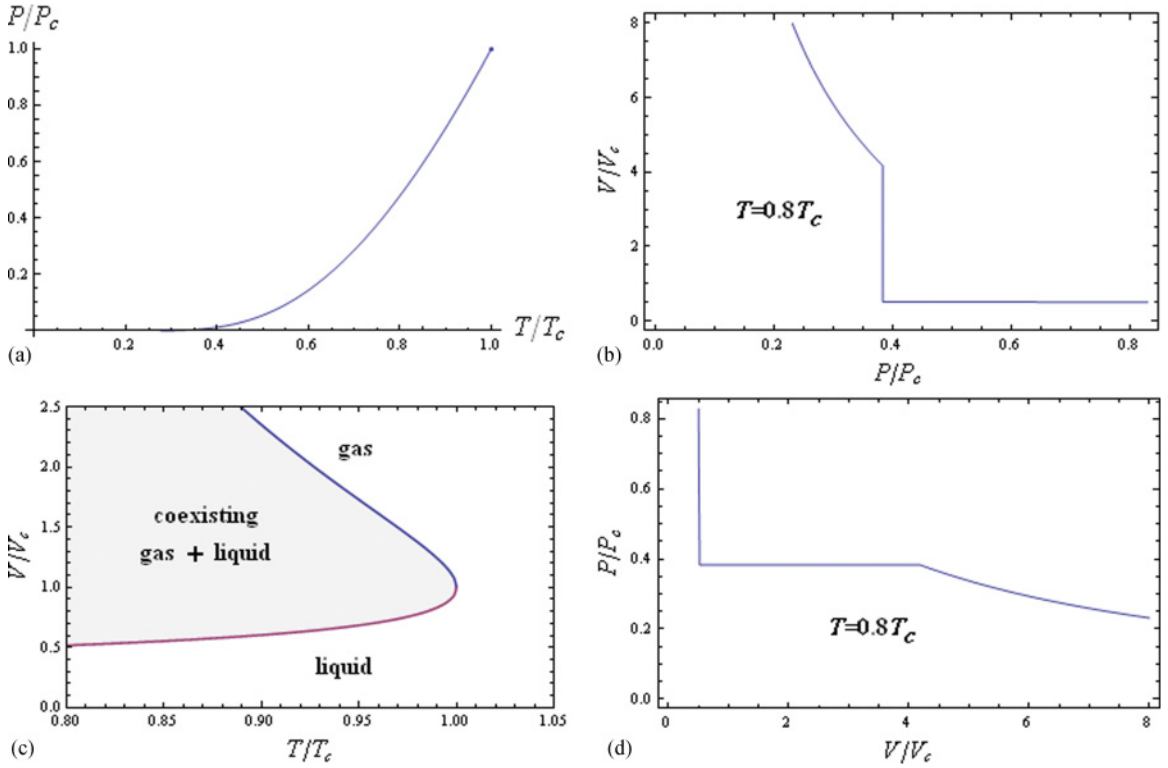

FIG. 6. (Color online) (a) Phase diagram of the van der Waals fluid in the plane of variables of reduced pressure (P/P_c) vs reduced temperature (T/T_c), P_c and T_c being pressure and temperature, respectively, at the critical point terminating the coexistence line. (b) Vapor-liquid transition along the isotherm at $T = 0.8T_c$, showing V/V_c as a function of P/P_c. At $P = P_{\text{coex}}$ there is an abrupt decrease of V, signalling the first-order transition. (c) Phase diagram of the van der Waals fluid in the plane of variables (V/V_c, T/T_c). The coexistence curve separates the pure vapor and liquid phases from the two-phase coexistence region. (d) Vapor-liquid transition P/P_c as a function of V/V_c along the isotherm at $T = 0.8T_c$, exhibiting a flat region that signals the coexisting gas and liquid phases.

features of phase coexistence that we wish to emphasize can already be nicely illustrated with this simple example. By using standard thermodynamic relations, also energy E and entropy S can be worked out, and their jumps at $P = P_{\text{coex}}(T)$ can be easily constructed. Note that one can consider also the transition at fixed pressure P by varying the temperature T, which then occurs at $T = T_{\text{coex}}(P)$, with $T_{\text{coex}}(P)$ simply being the inverse function of $P_{\text{coex}}(T)$.

We now consider the phase diagram in the NVT ensemble [Fig. 6(c)]. In the plane of variables (V,T), phase coexistence now occurs everywhere in the two-phase coexistence region, to the left of the vapor-liquid coexistence curve in Fig. 6(c). While the van der Waals theory is inaccurate with respect to some quantitative aspects—e.g., it predicts the parabolic variation of the coexistence curve $V_{\text{gas}}(T) - V_\ell(T) \propto (1 - T/T_c)^\beta$ with $\beta = 1/2$ rather than the correct critical exponent β, which is close to $\beta \approx 1/3$ in $d = 3$ dimensions [30]—it correctly accounts for the qualitative aspects of gas-liquid phase coexistence.

Following an isotherm along the V axis, one passes from the homogeneous liquid at $V = V_\ell(T)$ into the region with constant pressure P, where liquid and saturated vapor coexist in equilibrium, with volume fractions $x = [V - V_{\text{gas}}(T)]/[V_\ell(T) - V_{\text{gas}}(T)]$, $1 - x$, until at $V = V_{\text{gas}}(T)$ the liquid fraction has disappeared [Fig. 6(d)]. Thus, the pressure P as a function of V at fixed T is a continuous function; only its slope changes discontinuously at $V_\ell(T)$ and $V_{\text{gas}}(T)$, the end points of the horizontal part at $P = P_{\text{coex}}$ in the isotherm [Fig. 6(d)]. Of course, the isotherms in the NVT ensemble [Fig. 6(d)] and NPT ensemble [Fig. 6(c)] are strictly equivalent: in the limit $N \to \infty$, the two ensembles are related via a Legendre transformation between the Gibbs $\{G(T,P,N)\}$ and Helmholtz $\{F(T,V,N)\}$ free energies, with G/N being the chemical potential $\mu(T,P)$,

$$G(T,P,N) = N\mu(T,P) = F(T,V,N) + PV. \tag{19}$$

With respect to the corresponding isotherms [Figs. 6(b) and 6(d)], the Legendre transformation simply means an interchange of variables taken for the ordinate and abscissa in the (P,V) plane.

B. Analogy between vapor-liquid transitions and the mechanical desorption of a single chain

The picture of the mechanical desorption of adsorbed polymers in the limit where their chain length N has been taken to infinity (Fig. 5) bears a striking resemblance to the vapor-liquid transition, if we compare the f-ensemble of the polymer to the NPT ensemble and the z-ensemble of the polymer to the NVT ensemble of the fluid: Fig. 6(a) should be compared to Figs. 5(a) and 6(b) should be compared to Fig. 5(b); the vapor (states with large V) correspond to the detached states, (z/N) for $N \to \infty$ being nonzero; the liquid (states with small V) correspond to the adsorbed states $(z/N) = 0$ for $N \to \infty$.

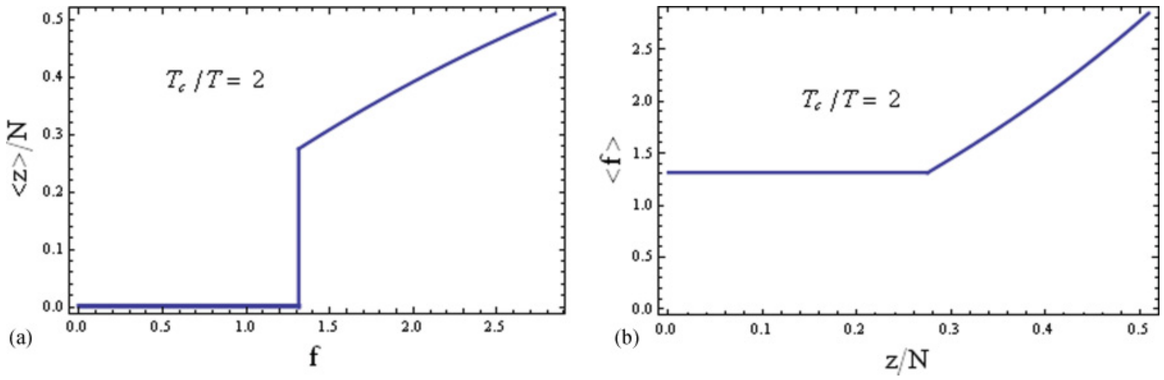

FIG. 7. (Color online) Isotherms for mechanical desorption (in the limit $N \to \infty$) in different ensembles, for $T_c/T = 2$, where T_c is the temperature of the critical adsorption transition without applied forces. (a) In the f-ensemble ($\langle z\rangle/N$ vs f) the first-order transition from adsorbed to stretched states of the chain appears as a discontinuous jump. (b) In the z-ensemble ($\langle f\rangle$ vs z/N) the transition shows up as a horizontal straight line, at $\langle z\rangle = f_{\text{tr}}$, indicating phase coexistence in between $z = 0$ and $z = (\langle z\rangle/N)_{\text{tr}}$.

Of course, the character of the critical point in the polymer problem (adsorption transition of the end-grafted polymer chain) is not of the simple (Ising-model type) criticality that vapor-liquid critical points of actual real fluids display [30], but we do not at all wish to dwell on critical phenomena here, but rather we are concerned with the general analogy of phase diagrams, and the consequences of phase coexistence. Thus, we emphasize again that all states in between the abscissa in Fig. 5(b) and the detachment line in this diagram correspond to phase coexistence between fluid [with small volume $V_\ell(T)$] and vapor [with large volume $V_{\text{gas}}(T)$]: as long as (z/N) is below the detachment line, there is still a fraction of $1 - x$ of the chain adsorbed and a fraction x detached, and $x \to 1$ only when the detachment line in Fig. 5(b) is reached.

These considerations are corroborated by isotherms $\langle z\rangle/N$ versus f in the f-ensemble for $T < T_c$ [Fig. 7(a)] or $\langle f\rangle$ versus z/N in the z-ensemble [Fig. 7(b)]: The first-order transition between pure phases (completely adsorbed, $\langle z\rangle/N = 0$) and nonadsorbed and stretched ($\langle z\rangle/N > 0$) occurs discontinuously at a transition value f_{tr} of the force, from $z = 0$ up to $(\langle z\rangle/N)_{\text{tr}}$. In the conjugate z-ensemble, the first-order transition shows up as a horizontal two-phase coexistence region. Again we emphasize that the curves in Figs. 7(a) and 7(b) are completely equivalent—one function is just the inverse function of the other one; the diagram in Fig. 7(a) turns into that in Fig. 7(b) by interchanging which variable is used as abscissa or as ordinate, i.e., via a Legendre transformation.

The analogy between the mechanical desorption of macromolecules and standard first-order transitions in condensed matter systems can be further elucidated by considering the variation of the energy and specific heat at these transitions. Figures 8(a) and 8(b) show the average potential energy per particle in the NVT ensemble as a function of volume (a) and of temperature (b). [Note that the kinetic energy ($3k_BT/2$) is not included, for the sake of comparison with the polymer system, where kinetic energy has been disregarded from the start.] The average potential energy per particle in a particular phase depends on the local density and has to be calculated separately for the two phases. When one traverses the two-phase coexistence region, the fraction of particles belonging to the liquid phase changes linearly as a function of volume (lever rule); since the global average of the energy is found by weighting the energies of the coexisting phase according to their weights, a linear variation of the potential energy in the two phase-coexistence region results [Fig. 8(a)]. When we instead consider a variation of the potential energy as a function of T/T_c at fixed off-critical volume, such as $V = 3V_c$ [Fig. 8(b)], a smooth but nonlinear curve results. (The lever rule also applies in this case, but the volume fraction x of the liquid phase, which comes into play when the coexistence curve is crossed, has a nonlinear dependence on T, as is obvious from the shape of the coexistence curve.) Similarly, the specific heat shows a jump, when the coexistence curve is crossed, due to the gradual onset [proportional to the volume fraction $x(T)$ of the contribution due to the liquid phase to the specific heat]. Obviously, it would be completely wrong from a naive consideration of Fig. 8 to conclude that the continuous variation of the quantities shown implies that continuous (second-order) phase transitions occur: it is simply misleading to think in terms of Ehrenfest criteria, when one studies a system in a statistical ensemble with more than one extensive variable; only when the NPT ensemble is used is the Ehrenfest criterion useful for the discussion of the liquid-vapor transition.

In Fig. 8(b), the curve for $V = V_c$ actually passes right through the critical point, and hence this curve does correspond to a second-order transition. But as a caveat, we mention that in a real fluid the non-mean-field character of critical phenomena would imply a somewhat different behavior; namely the energy at $V = V_c$, $T = T_c$ for real fluids does not have a kink, but rather near T_c a singularity proportional to $|T - T_c|^{1-\alpha}$ occurs, with $\alpha \approx 0.1$ as the critical exponent of the specific heat [30]. Thus, in reality, there occur small qualitative differences in behavior, when one crosses the coexistence curve through the critical point, rather than away from it. Nevertheless, it remains generally true (beyond the mean-field level of the van der Waals fluid) that the potential energy (and the specific heat) exhibit kink singularities when one enters the two-phase coexistence region with $V \neq V_c$.

Returning to the polymer desorption problem, by studying the total potential energy E as a function of z/N, we see a linear variation [Fig. 8(c)], in full analogy with Fig. 8(a). Note that the only anomalous feature is that one branch of the coexistence

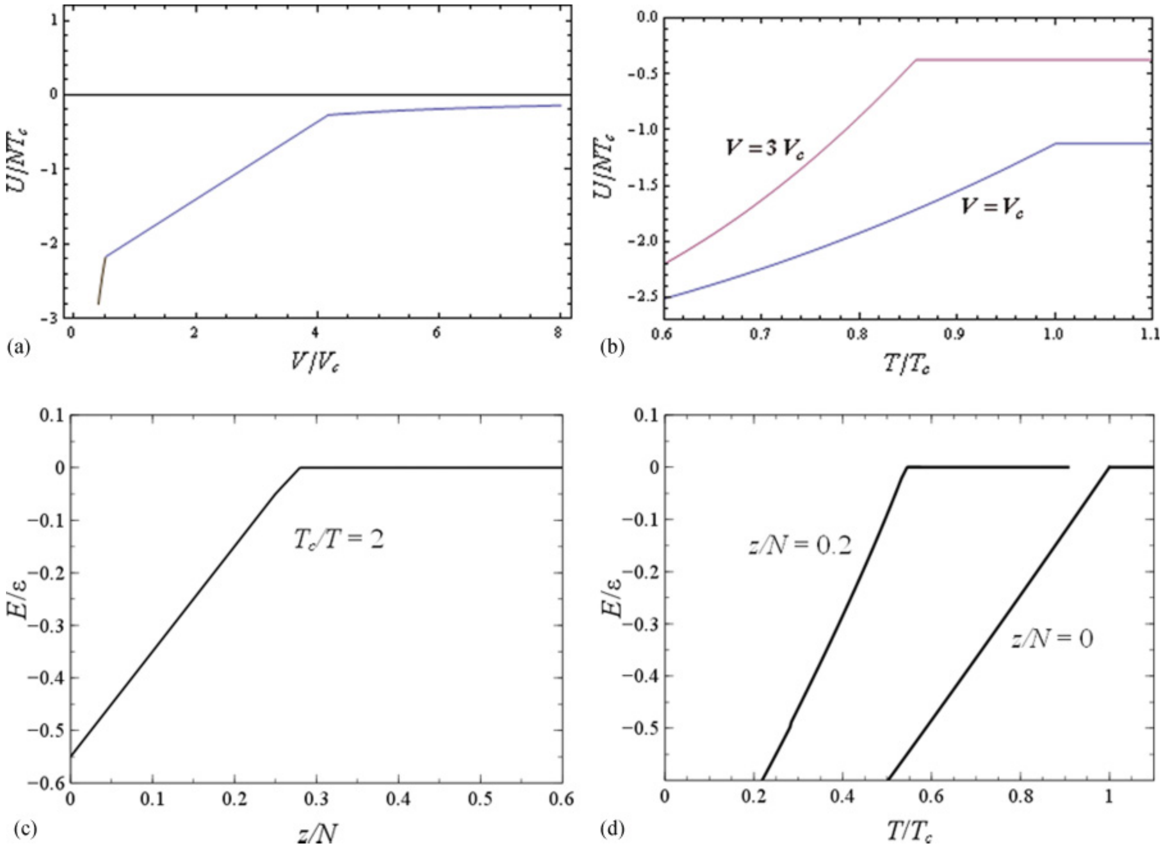

FIG. 8. (Color online) Average potential energy per particle, in units of T_c, of the van der Waals fluid in the (NVT) ensemble (a) plotted at fixed temperature $T/T_c = 0.8$ vs reduced volume V/V_c and (b) plotted at fixed values of V/V_c (as indicated in the figure) vs T/T_c. Note that in (a) the linear part of the curve in between the two kinks shows the variation inside the two-phase coexistence region, while in (b) the (nonlinear) parts of the curves on the left side of the kinks are due to two-phase coexistence, and the kink positions again signify that the coexistence curve is crossed. Only for $V = V_c$ is this a second-order transition. Panels (c) and (d) show the analogous variation of the average energy per monomer (in units of ε) at the mechanical desorption of the chain in the z-ensemble as function of z/N for $T_c/T = 2$ and as function of T/T_c for two values of z/N. While for $z/N = 0.2$ the kink at $E/\varepsilon = 0$ reflects the crossing of the coexistence curve where one leaves the two-phase coexistence region (because then no part of the chain is any longer adsorbed), the kink for $z/N = 0$ at $T = T_c$ shows the location of the second-order transition for the present NRRW model.

curve is at $z/N = 0$, and hence any small nonzero value of z/N already is inside the two-phase coexistence region. Also the plots of E versus T [Fig. 8(d)] look very similar to their liquid-vapor counterparts [Fig. 8(b)]. We note that for a polymer chain with excluded volume effects in the true second-order case ($z/N = 0$) the kink at $T = T_c$ is replaced by a (weakly) singular vanishing as $(1 - T/T_c)^{-1+1/\phi}$, where ϕ is the crossover index, which is close to 0.5 [11,22,26–28].

C. Local order parameter

The notion that a phase transition is of first order may at first sight seem puzzling when the order parameter varies as smoothly as exemplified in Figs. 2(b) and 3(b). This dilemma is avoided by complementing the previous definition of the order parameter θ, which did refer to the chain as a whole, and hence was unsuitable for detecting phase coexistence, by a more appropriate local order parameter, which can reflect the inhomogeneous structure of the partially desorbed chain. A suitable definition of local order parameter that is applied in the adsorbed part of the chain only should then yield a result that is independent of the given (normalized) position of the chain end, z/N.

This concept is again easily illustrated in a qualitative manner by the analogy with the liquid-vapor transition (Fig. 9). In the fluid, the control variable is the volume (which is varied via the height of the piston in the left half of Fig. 9), while for polymer desorption, it is z/N. In both cases there is an interval of values where two phases coexist. Of course, in the liquid the two phases are separated by an interface which is also macroscopic, which is not the case in the polymer problem. Coexistence of the adsorbed and stretched parts of the chain, which are referred to as “phases” within the same macromolecule, may seem quite peculiar, due to the absence of a macroscopic “surface” at the boundary between these phases. There is no analog of a surface free energy (associated with the vapor-liquid interface) for the polymer problem!

In the fluid, a local order parameter may be defined as the average volume per molecule in a small subsystem (which is still large enough to contain many molecules but negligibly small on the macroscopic scales of Fig. 9). Studying this local volume per particle $\upsilon(z)$ as a function of the position z of the subsystem over the bottom of the container in Fig. 9,

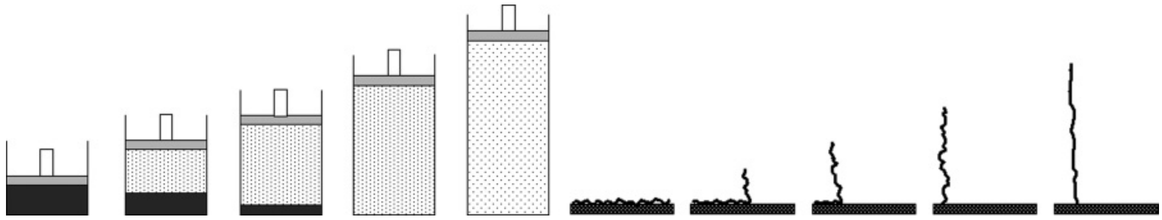

FIG. 9. Qualitative analogy between vapor-liquid systems (left) and the mechanical desorption of an adsorbed polymer chain (right) to illustrate phase coexistence. In the fluid, phase coexistence is controlled by the height of the piston: in the left-most sketch we have only fluid; the two following graphs show two-phase coexistence (with fluid on the bottom separated by a meniscus from the vapor on top); the last two sketches refer to single-phase vapor at two different volumes. For the polymer, phase coexistence is controlled by the height of the free chain end: the left-most sketch ($z > 0$) refers to the (single-phase) adsorbed chain, in the next two graphs part of the chain is still adsorbed, and the last two graphs on the right are in the single-phase region of desorbed chains with different degree of stretching.

we see that $\upsilon(z)$ has a small constant value [characteristic of bulk fluid right at the coexistence curve in Fig. 6(c)] and then it increases to a much larger value when one crosses the meniscus, staying again constant [at the value of bulk vapor right at the coexistence curve in Fig. 6(d)] for still larger choices of z.

Guided by this analogy, we introduce a local order parameter for a polymer chain at mechanical desorption, defining θ_k as the average probability of finding the kth monomeric unit in contact with the surface. The global order parameter profile along the chain contour is then

$$\theta = \frac{1}{N}\sum_{k=1}^{N}\theta_k. \tag{20}$$

We first analyze the behavior of θ_k in the f-ensemble [Fig. 10(a)]. Recall from Fig. 2(a) that for $T_c/T = 5$ and $N = 200$ the global order parameter is almost constant and

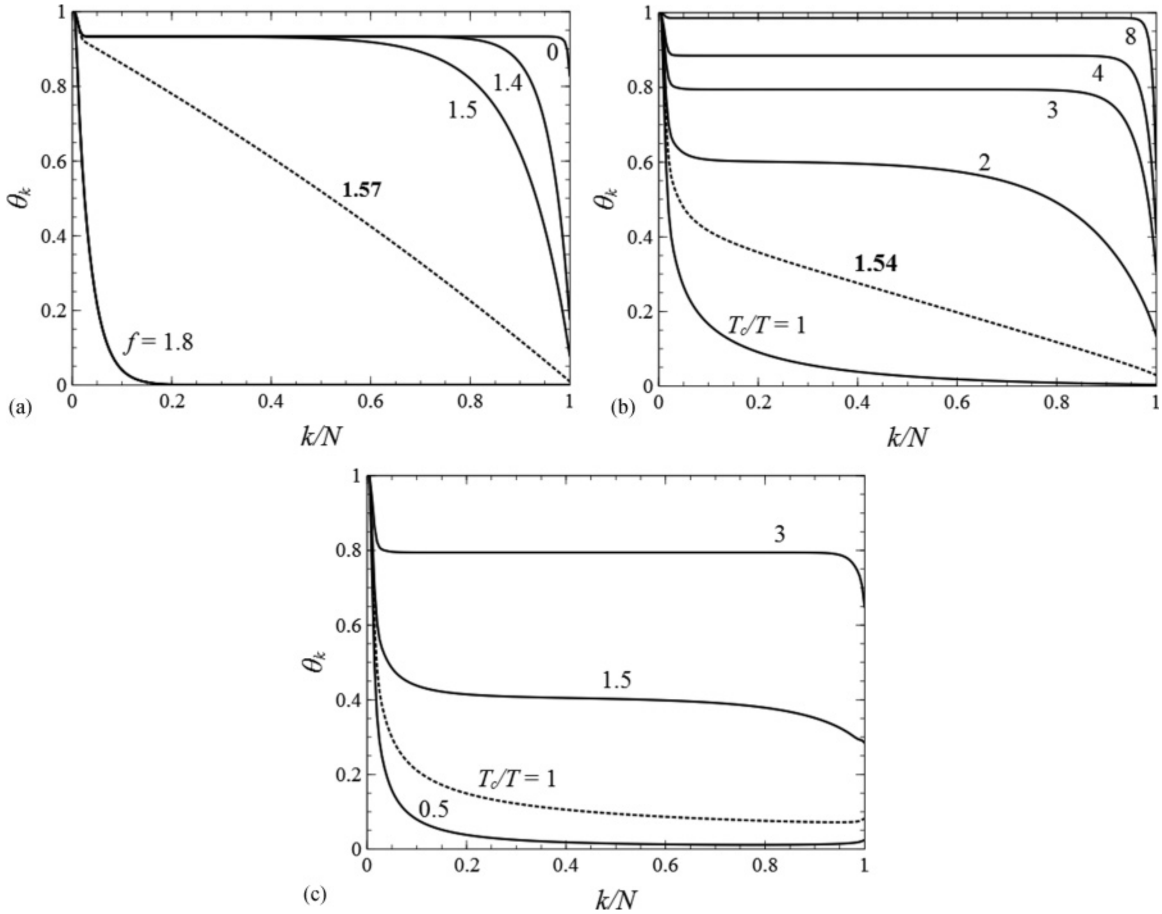

FIG. 10. The local order parameter profile θ_k plotted vs the scaled monomer position k/N in the f-ensemble, for $N = 200$ and varying f at $T_c/T = 5$ (a) or varying T_c/T at fixed $f = 1$(b). For $N \to \infty$, the first-order transition (where θ jumps from a nontrivial value to zero) occurs at $f = 1.57$ in case (a) and at $T_c/T = 1.54$ in case (b). Case (c) shows the analogous behavior for the second-order transition when $f = 0$.

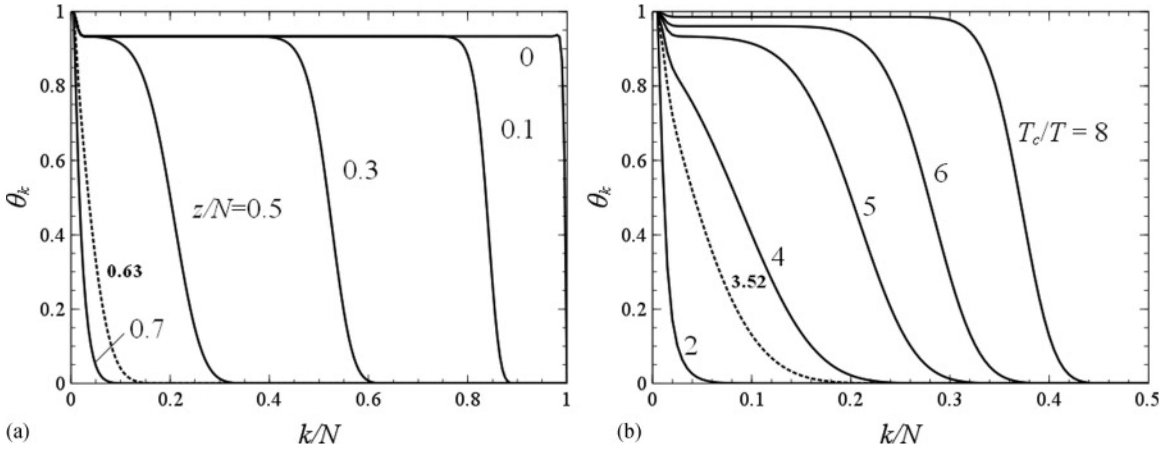

FIG. 11. The local order parameter θ_k plotted vs the scaled monomer position k/N along the chain, for the z-ensemble at $T_c/T = 5$ and several choices of z/N (a) and for fixed height $z/N = 0.5$ and several choices of T_c/T (b). The profiles corresponding to the crossing of the coexistence curve [where the adsorbed phase completely disappears in the limit $N \to \infty$; Fig. 5(b)] are shown by dotted lines. The coexistence curve is crossed at $z/N = 0.63$ in (a) and $T_c/T = 3.52$ in (b). Note the strong finite-size effects.

nonzero for $f \leqslant 1.5$ and almost equal to zero for $f \geqslant 1.6$, i.e., the typical picture of a first-order transition that is weakly rounded because of the finite length N of the chain. The local order parameter for $f < 1.5$ is also almost constant as a function of k/N, except for a few monomeric units close to the free chain end (which occurs at $k = N$). At the transition point (f_{tr}), the local order parameter decreases almost linearly with z/N.

This behavior reflects large fluctuations due to the zipping-unzipping mechanism of mechanical desorption at f_{tr}: all phase-separated states with different lengths of the torn-off tail have the same statistical weight [35,49]. We note that in bulk condensed matter at a first-order transition such large fluctuations are suppressed, of course, due to the hysteresis of the free energy barrier between the pure coexisting phases (caused by the need to form a macroscopic interface); in simulations of small finite systems, however, where this interfacial barrier may be of the order of a few $k_B T$ only, these large fluctuations between the coexisting phase are relevant [57]. Beyond the transition point, the local order parameter decays quickly to zero for all monomers except those near the grafting point (and, of course, this finite-size effect plays no role in the limit $N \to \infty$). For θ_k with k away from the chain ends, the local order parameter thus changes discontinuously (or almost so for finite N) when f exceeds f_{tr}.

By varying T_c/T at fixed force the situation is similar [compare Figs. 10(b) to 3(a) but note that $f = 1.5$ rather than $f = 1$ is shown in Fig. 3(a)]. Again, θ_k is constant along the chain, apart from the regions near the chain ends; this constant plateau value decreases with T/T_c, until at the transition point of the first-order transition again a region of linear decrease of θ_k with k is found, while, beyond the transition point, θ_k is close to zero. This behavior is different from the case of the second-order transition occurring for $f = 0$, however, where the plateau value of θ_k gradually decreases to almost zero at $T_c/T = 1$ [Fig. 10(c)] and never shows the remarkable linear behavior which is a hallmark of the first-order transition [Figs. 10(a) and 10(b)]. At the first-order transition, both local and global order parameters behave similarly and exhibit the discontinuous change that develops for $N \to \infty$ when one crosses the transition line in the (f,τ) plane [Fig. 5(a)].

In contrast, by varying z/N in the z-ensemble at fixed T [Fig. 11(a)] the local order parameter profiles clearly demonstrate that the local properties of the coexisting phases remain the same, and only the position of the "interface" is moved when z/N varies. The direct analogy to the vapor-liquid case (Fig. 9) should be evident. The linear drop in the global order parameter θ in Fig. 2(b) clearly does not reflect any change in the properties of the adsorbed phase but just reflects the shift in the position of the "interface" in Fig. 11(a), thus confirming that the simple interpretation of Fig. 2(b) in terms of the lever rule for coexisting phases is inevitable. The interpretation of Fig. 11(b) is similar: with the increase in temperature the adsorbed phase gradually "evaporates," and since the interfacial region broadens with increasing temperature, very strong finite-size effects occur, and thus for finite N the z-ensemble clearly is much less suitable for estimating the location of the coexistence curve [Fig. 5(b)] that emerges in the thermodynamic limit.

D. An extension: negative forces and loop adsorption

There is one aspect of the polymer problem, however, for which the vapor-liquid transition has no counterpart: in the (P,T) plane, the first-order transition line ends in a standard critical point at T_c, $P_{\text{coex}}(T_c) = P_c$ [30,31]. However, the critical point in the phase diagram in the (f,T) plane in Fig. 5, occurring at the axis $f = 0$, has a very different character from this critical point. This fact is realized when one considers the generalization of the problem to the case of negative forces $f < 0$ at the free chain end, which drive the chain end toward the grafting surface. In the limit of $N \to \infty$, the chain becomes in many respects equivalent to a "loop" (i.e., a chain with both ends grafted to the surface, but without fixing the lateral distance of chain ends at the surface).

Figure 12(a) shows the variation of the global order parameter with inverse temperature for a typical example, and Fig. 12(b) shows the corresponding behavior of the local order

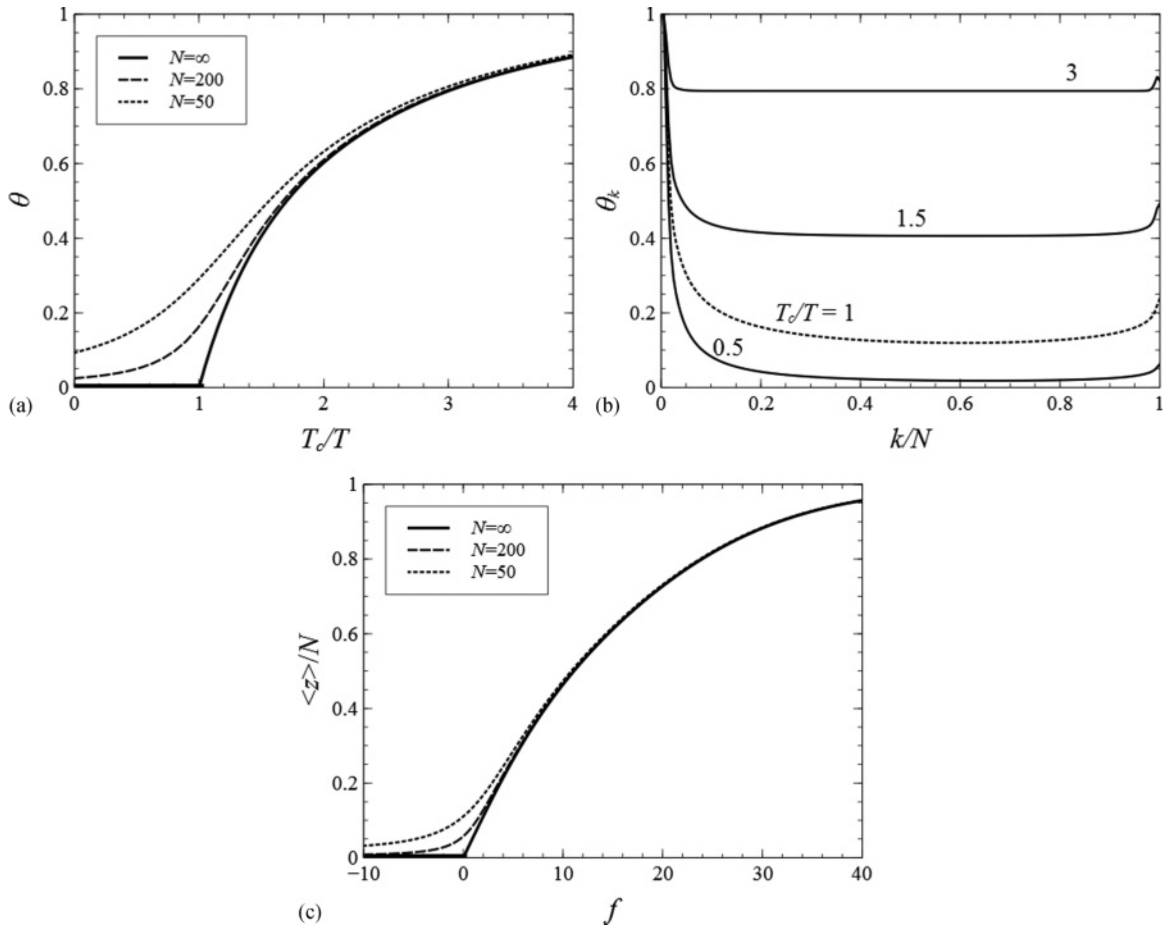

FIG. 12. (a) Global order parameter θ plotted vs T_c/T in the f-ensemble at a force $f = -1$ driving the free chain end toward the substrate surface. Three chain lengths $N = 50$, 200, and ∞ are shown, as indicated. (b) Local order parameter θ_k plotted vs the scaled monomer position k/N along the chain in the f-ensemble, for $N = 200$ and $f = -1$, at four choices of T_c/T as indicated. (c) Extension $\langle z\rangle/N$ of the polymer chain for a chain attached to a nonadsorbing surface at $T/T_c = 2.0$, plotted vs force. Three chain lengths $N = 50$, 200, and $N = \infty$ are included, as indicated.

parameter θ_k as introduced in the previous section. It is seen that the behavior of the global order parameter as a function of T_c/T for $f = -1$ is very similar to that for $f = 0$ [compare to the data for $f = 0$ in Fig. 3(a)]. And Fig. 12(b) differs from its counterpart for $f = 0$ [Fig. 10(c)] only near the end where the force acts: the local order for k/N near unity is now enhanced rather than reduced, although the enhancement is not as large as near the grafted end. Since this negative force has only local effects, it also does not lead to a shift of the adsorption transition temperature, $T_c(f < 0) = T_c(0)$. Physically, this means that adsorption of a polymer chain in a loop conformation occurs summarily to that of a grafted chain with the free end. When one includes the region $f < 0$ in the phase diagram [Fig. 5(a)], the isolated critical point at ($T = T_c$, $f = 0$) becomes part of a (vertical) critical line (Fig. 13)!

An interesting behavior, however, is also detected when one considers the region $T > T_c$ and studies the variation of the chain extension $\langle z\rangle/N$ with f, changing f from negative to positive values [Fig. 12(c)]. For $f < 0$ one finds that $\langle z\rangle/N \to 0$ as $N \to \infty$; since the chain monomers cannot take any positions with $z < 0$, the chain cannot get stretched to values $\langle z\rangle/N < 0$ like an unconstrained chain (with one end fixed at $z = 0$ but otherwise free). For such a free chain with one end fixed at $z = 0$, and the other end under the action of the force f, we would have simply the symmetry relation $\langle z\rangle|_{-f} = -\langle z\rangle|_f$, and clearly the variation of $\langle z\rangle$ with f does not involve any phase transition; the problem is fully analogous to the magnetization process of bulk paramagnetic matter (including ferromagnetic materials at temperatures above the Curie temperature) induced by an external magnetic field. Now the part of the $\langle z\rangle/N$ versus f curve for $f > 0$ and $N \to \infty$ is essentially equivalent to the extension versus force of such a free chain. Thus crossing the line $f = 0$, $T > T_c$ in the (f,T) phase diagram of a chain grafted to a surface clearly is not a phase transition in the standard sense, but nevertheless it is a dividing line between different states of the chain (Fig. 13). For $T > T_c$ and $f > 0$ the chain is stretched, i.e., $\langle z\rangle/N$ is nonzero, as expected since the coil configuration must respond to the force. For $f = 0$ and $T > T_c$ we have a desorbed "polymer mushroom"; the average value of $\langle z\rangle$ is of order $N^{1/2}$ for our NRRW model with Gaussian statistics (but if excluded volume interactions are included, we rather would have $\langle z\rangle \propto N^{\nu}$, where ν is the "Flory exponent," with $\nu = 3/4$ in $d = 2$ dimensions and $\nu = 0.588 \approx 3/5$ in $d = 3$ dimensions [58,59]). For $f < 0$ and $T < T_c$, the value of $\langle z\rangle$

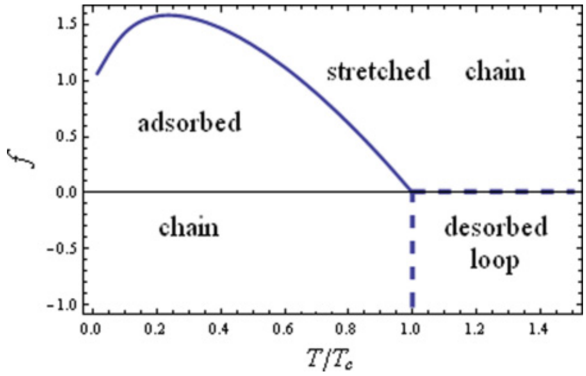

FIG. 13. (Color online) Phase diagram of a single chain (in the limit $N \to \infty$), end-grafted with one end at an impenetrable surface at $z = 0$ which is attractive to the surface, while on the free chain end a mechanical force f in the z direction perpendicular to the surface acts. For $T/T_c < 1$ and $f < 0$ the chain is adsorbed in a quasi-two-dimensional configuration. At $T = T_c$ for $f < 0$ a continuous transition to a desorbed state of the chain occurs (desorbed loops). For $f > 0$ and $T/T_c < 1$ a first-order phase transition occurs from the adsorbed state of the chain to a stretched state (with $\langle z\rangle/N > 0$). This transition is shown by the full line, which ends at a (multi)critical point at $T = T_c$, $f = 0$. For $T/T_c > 1$ and $f = 0$ (broken line) the state of the chain changes from a desorbed state (for $f \leqslant 0$) to a stretched state (with $\langle z\rangle/N > 0$). Note that crossing the line $f = 0$, $T/T_c < 1$, does not involve any transition.

will be only of order unity (at least for large enough values of $|f|$), but the gyration radius component $\langle R_{gz}^2\rangle^{1/2}$ in the z direction perpendicular to the surface will be of the order of N^ν still: this is what we mean by a "desorbed loop" in Fig. 13. At this point, we mention that the excluded volume actually presents a further complication for the region $T > T_c$ and $f > 0$ as well: in the limit $N \to \infty$, the extension versus force for $f \to 0$ becomes singular, $\langle z\rangle/N \propto f^{1/\nu-1}$ [60], while for Gaussian chains ($\nu = 1/2$) it is linear. Of course, for finite N this singularity is rounded off for small enough $\langle z\rangle$ [$\langle z\rangle$ not much larger than $\langle R_{gz}^2\rangle^{1/2}$], so for real polymers the actual behavior may be more complicated than shown in Fig. 12(c). However, such excluded volume effects on extension versus force curves [61] are beyond our focus here.

V. DISCUSSION

In this paper we have presented an analysis of the states of end-grafted macromolecules at attractive surfaces under the action of a mechanical force f acting on the free end of the chains. Particular attention was paid to the proper interpretation of the phase transitions that occur in the thermodynamic limit of infinite chain length, $N \to \infty$. By numerical solutions of the NRRW model on a simple cubic lattice we have also illustrated the extent of rounding of these transitions as a function of the chain length.

A key result of our findings is that a proper interpretation of the phase behavior is easily found when one chooses a statistical ensemble with two intensive variables (temperature T and force f), the chain length N being the only extensive variable. Then it is readily recognized that for $f > 0$ there always occurs a first-order transition from the adsorbed to the stretched state of the chain (while for $f < 0$ a second-order transition from the adsorbed chains to desorbed loops occurs, similar to the second-order adsorption-desorption transition of end-grafted chains in the absence of a force).

When one instead works in the conjugate statistical ensemble, where temperature and (relative) extension z/N of the free chain end are used as control variables, one observes a continuous variation of the order parameter and other variables, with kink singularities when the so-called detachment line in the $(z/N,T)$ plane is crossed. However, the proper interpretation of this detachment line is a boundary ("coexistence curve") of a two-phase coexistence region (the other boundary being the abscissa axis, $z/N = 0$). Thus, the kink singularity simply signifies that one leaves the regime where the behavior of the system is controlled purely by one phase and enters the regime where the familiar lever rule of phase coexistence controls the system's properties. Since the interpretation of a partially desorbed state of a single chain (n monomers still adsorbed and $N - n$ monomers desorbed) as two-phase coexistence inside a single chain clearly is somewhat less intuitive and not yet commonly accepted, we have tried to present a detailed pedagogic analogy with two-phase coexistence at the vapor-liquid transition of a simple fluid. We expect that our detailed discussion will settle this issue, of the proper interpretation of the "detachment line" in the $(z/N,T)$ plane, about which rather confusing discussions can be found in the literature. We emphasize thus that despite the continuous variation of properties when this line is crossed it does not signify a continuous phase transition (or second-order transition) in the sense of the Ehrenfest classification; a too-naive application of this criterion simply leads to wrong results; one must not apply it when one uses a statistical ensemble with more than one extensive variable, but one can use it only in statistical ensembles with a single extensive variable (and, for phase transitions involving single polymer chains, the chain length N is a natural choice of this extensive variable, of course). This fact may seem almost obvious for ordinary phase transitions of bulk matter, and hence it is hardly discussed much in textbooks; for single chain transitions often the choice of global or (if possible) also local order parameters is not at all obvious, and two-phase coexistence in a single chain, if it is possible, can have very anomalous properties [such as the macroscopically large fluctuations at the first-order transition, which have been detected via the linear profiles of the local order parameters (Fig. 11) and which are due to the lack of interfacial free energy barriers between the coexisting phases].

A new concept for the description of the mechanical desorption of adsorbed polymers that we have emphasized here is the use of local order parameter profiles, as exemplified in Figs. 10–12. Such data give evidence for both the existence of two-phase coexistence within single polymer chains for this transition and the anomalous character of this two-phase coexistence.

We have tried here to discuss the global picture of the behavior associated with the mechanical desorption of single adsorbed chains in the most simple terms, and we have disregarded complications that aspects such as excluded volume forces, chain stiffness, or more complicated chemical architecture (random copolymers or branched polymers such as star polymer, comb polymers, etc.) can provide. These aspects are left to future study.

Finally, we mention that considerations about the proper interpretation of results due to the use of a statistical ensemble where one crosses a coexistence curve not in a critical point are needed in many physical contexts. For example, consider the problem of adsorption of molecular monolayers at surfaces in ultrahigh vacuum: At submonolayer coverage one commonly observes "island formation." When such a island is heated up, one may observe that it gradually shrinks to zero. Simulation attempts to describe this "island evaporation" in terms of a critical exponent [62,63] are clearly misleading; at off-critical conditions one has a continuous island vanishing again simply as a consequence of the lever rule. However, since here interfacial effects matter, the details of this behavior are somewhat different from the single chain problem studied here.

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[1] S. Kumar and M.-S. Li, Phys. Rep. **486**, 1 (2010).

[2] D. K. Klimov and D. Thirumalai, Proc. Natl. Acad. Sci. USA **96**, G166 (1999).

[3] D. Marenduzzo, A. Trovato, and A. Maritan, Phys. Rev. E **64**, 031901 (2001).

[4] J. J. Kasianowicz, E. Brandin, D. Branton, and D. Deamer, Proc. Natl. Acad. Sci. USA **93**, 13770 (1996).

[5] D. K. Lubensky and D. R. Nelson, Phys. Rev. Lett. **85**, 1572 (2000).

[6] R. Lavery, A. Lebrun, J.-F. Allemand, D. Bensimon, and V. Croquette, J. Phys. Condens. Matter **14**, R383 (2002).

[7] S. B. Smith, L. Finzi, and C. Bustamante, Science **25**, 1122 (1992).

[8] T. Hugel and M. Seitz, Macromol. Rapid Commun. **22**, 989 (2001).

[9] T. Hugel, M. Rief, M. Seitz, H. E. Gaub, and R. R. Netz, Phys. Rev. Lett. **94**, 048301 (2005).

[10] G. J. Fleer, M. A. Cohen-Stuart, J. M. H. H. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Chapman & Hall, London, 1993).

[11] E. Eisenriegler, *Polymers Near Surfaces* (World Scientific, Singapore, 1993).

[12] R. R. Netz and D. Andelman, Phys. Rep. **380**, 1 (2003).

[13] R. Rajesh, D. Dhar, D. Giri, S. Kumar, and Y. Singh, Phys. Rev. E **65**, 056124 (2002).

[14] S. Metzger, M. Müller, K. Binder, and J. Baschnagel, J. Chem. Phys. **118**, 8489 (2003).

[15] J. Krawczyk, A. Owczarek, T. Prellberg, and A. Rechnitzer, Europhys. Lett. **70**, 726 (2005).

[16] J. Luettmer-Strathmann, F. Rampf, W. Paul, and K. Binder, J. Chem. Phys. **128**, 064903 (2008).

[17] M. Moddel, W. Janke, and M. Bachmann, Phys. Chem. Chem. Phys. **12**, 11548 (2010).

[18] P. G. de Gennes, J. Phys. (France) **37**, 1445 (1976).

[19] P. G. de Gennes, Macromolecules **13**, 1069 (1980).

[20] H. L. Frisch, R. Simha, and F. R. Eirich, J. Chem. Phys. **21**, 363 (1953).

[21] R. J. Rubin, J. Chem. Phys. **43**, 2992 (1965).

[22] E. Eisenriegler, K. Kremer, and K. Binder, J. Chem. Phys. **77**, 6296 (1982).

[23] H. Meirowitch and S. Livne, J. Chem. Phys. **88**, 4507 (1988).

[24] P.-Y. Lai, Phys. Rev. E **49**, 5420 (1994).

[25] R. Hegger and P. Grassberger, J. Phys. A: Math. Gen. **27**, 4069 (1994).

[26] H. Diehl and M. Shpot, Nucl. Phys. B **528**, 595 (1998).

[27] S. Metzger, M. Müller, K. Binder, and J. Baschnagel, Macromol. Theory Simul. **11**, 985 (2002).

[28] R. Descas, J.-U. Sommer, and A. Blumen, J. Chem. Phys. **120**, 8831 (2004).

[29] K. Binder, W. Paul, T. Strauch, F. Rampf, V. Ivanov, and J. Luettmer-Strathmann, J. Phys. Condens. Matter **20**, 49215 (2008).

[30] H. E. Stanley, *An Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).

[31] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Butterworth-Heinemann, London, 1980), 3rd ed.

[32] P. M. Chaikin and T. Lubensky, *Principles of Condensed Matter Physic*s (Cambridge University Press, Cambridge, 1995).

[33] L. I. Klushin, A. M. Skvortsov, and F. A. M. Leermakers, Phys. Rev. E **69**, 061101 (2004).

[34] D. I. Dimitrov, L. I. Klushin, A. Skvortsov, A. Milchev, and K. Binder, Eur. Phys. J. E **29**, 9 (2009).

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

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

[37] L. I. Klushin, A. M. Skvortsov, and A. A. Gorbunov, Phys. Rev. E **56**, 1511 (1997).

[38] X. Chatellier and J.-F. Joanny, Phys. Rev. E **57**, 6923 (1998).

[39] B. J. Haupt, J. Ennis, and E. M. Sevick, Langmuir **15**, 3886 (1999).

[40] F. Celestini, T. Frisch, and X. Oyharcabal, Phys. Rev. E **70**, 012801 (2004).

[41] P. K. Mishra, S. Kumar, and Y. Singh, Europhys. Lett. **69**, 102 (2005).

[42] J. Krawczyk, A. Owczarek, T. Prellberg, and A. Rechnitzer, J. Stat. Mech. (2005) P05008.

[43] S. Bhattacharya, H.-P. Hsu, A. Milchev, V. G. Rostiashvili, and T. A. Vilgis, Macromolecules **41**, 2920 (2008).

[44] S. Bhattacharya, A. Milchev, V. G. Rostiashvili, A. Milchev, and T. A. Vilgis, Phys. Rev. E **79**, 030802 (2009).

[45] S. Bhattacharya, V. G. Rostiashvili, A. Milchev, and T. A. Vilgis, Macromolecules **42**, 2236 (2009).

[46] S. Bhattacharya, A. Milchev, V. G. Rostiashvili, and T. A. Vilgis, Eur. Phys. J. E **29**, 285 (2009).

[47] A. M. Skvortsov, L. I. Klushin, and T. M. Birshtein, Polym. Sci. Ser. A (Russia) **51**, 469 (2009).

[48] A. M. Skvortsov, L. I. Klushin, G. J. Fleer, and F. A. Leermakers, J. Chem. Phys. **130**, 174704 (2009).

[49] A. M. Skvortsov, K. I. Klushin, G. J. Fleer, and F. A. Leermakers, J. Chem. Phys. **132**, 064110 (2010).

[50] T. L. Hill, *Thermodynamics of Small Systems* (Benjamin, New York, 1963).

[51] J. T. Titantah, C. Pierleoni, and J.-P. Ryckaert, Phys. Rev. E **60**, 7010 (1999).

[52] E. Orlandini, S. M. Bhattacharjee, D. Marenduzzo, A. Maritan, and F. Seno, J. Phys. A: Math. Gen. **34**, L751 (2001).

[53] D. Ruelle, *Statistical Mechanics: Rigorous Results* (Benjamin, New York, 1969).

[54] R. Kapri, S. M. Bhattacharjee, and F. Seno, Phys. Rev. Lett. **93**, 248102 (2004).

[55] L. I. Klushin and A. M. Skvortsov, J. Phys. A: Math. Theor. **44**, 473001 (2011).

[56] K. Kremer and K. Binder, Comput. Phys. Rep. **7**, 289 (1988).

[57] K. Binder and D. P. Landau, Phys. Rev. B **30**, 1477 (1984).

[58] P. G. de Gennes, *Scaling Concepts in Polmyer Physics* (Cornwell University Press, Ithaca, NY, 1979).

[59] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980).

[60] P. Pincus, Macromolecules **9**, 386 (1976).

[61] H.-P. Hsu, W. Paul, and K. Binder, Europhys. Lett. **95**, 68004 (2011).

[62] T. Müller and W. Selke, Eur. Phys. J. B **10**, 549 (1999).

[63] M. Pleimling and W. Selke, J. Phys. A **33**, L199 (2000).