

The rolling transition of a Gaussian chain end-grafted at a penetrable surface

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(Received 13 October 1999; accepted 2 February 2000)

A Gaussian chain at a liquid–liquid interface is considered. The solvents are represented by an external potential field u that has a constant value in one half-space and is zero elsewhere. One end of the chain is fixed at the boundary where the external potential field changes its value. For this model the exact partition function is available. The system features a first-order phase transition for which the external potential is the control parameter; the chain rolls from one half-space to the other upon changing the sign of the external potential. The chain distributes its N segments over both regions when the external potential difference between the two regions $|u| \ll 1/N$, otherwise the chain puts virtually all its segments in the region with the lowest potential. The relation between the problem of a Gaussian chain at a solid/liquid boundary and that of a chain at a liquid/liquid interface, is illustrated. Applications of the model are discussed. © 2000 American Institute of Physics. [S0021-9606(00)50616-3]

I. INTRODUCTION

Macromolecules constitute an interesting state of matter from many points of view.¹ Any attempt to make a complete list of examples to illustrate this statement is bound to fail as so many disciplines make use of these materials. Similarly, the more restricted topic of macromolecules at interfaces has attracted huge attention from the experimental as well as from the theoretical side.² In the field of life sciences one may, e.g., be interested in the interaction of naturally occurring macromolecules with lipid bilayers. In colloid science applications, one is usually using polymers to modify the interfacial characteristics and study the influence of polymers on the colloidal stability. These fundamental properties have an impact in many applications ranging from food processing, the formulation of paints and pharmaceutical products, the production of, e.g., magnetic tapes, and their use as adhesives and lubrication agents.

The first theoretical investigation of polymers at interfaces dates back to Simha and co-workers.³ Nowadays many kinds of techniques are being used to unravel the important and fundamental features of these systems. Most of the attention has been devoted to polymers adsorbing from a liquid solution onto a solid substrate. This special case has recently been reviewed in depth.²

Historically, lattice models have played an important role in the theory of polymer adsorption. From this it is well-known that the adsorption of macromolecules at the solid

substrate has a highly cooperative nature. There exists a critical adsorption energy below which most of the polymer segments avoid the surface, whereas above this adsorption energy the chain has many contacts with the substrate. This critical adsorption energy can be interpreted as the energy needed on a segment level to compensate for the conformational entropy loss of a chain when it is at the substrate. The point of critical adsorption is known to be a bicritical point and the adsorption transition is of a second-order type.⁴

The continuum model employing the Gaussian chain model is a valuable standard model for theoretical investigations. The theory of adsorption of the Gaussian chain end-grafted to a solid surface was formulated by Lepine and Gaille⁵ and by Eisenriegler^{6,7} for a continuum model, in particular for the case that the segments interact with the substrate through short-range forces. The distribution function of the free end position is expressed in terms of two dimensionless parameters: the dimensionless distance $\tilde{z} = z/2R_g$ and a dimensionless adsorption parameter $\tilde{c} = cR_g$, where the radius of gyration is related to the length of the chain N by the well-known formula, $R_g = l\sqrt{N}/6$ (l is a segment length). It is given by

$$P_{\text{ads}}(\tilde{z}, \tilde{c}) = \frac{1}{R_g \sqrt{\pi}} \exp(-\tilde{z}^2) [1 + \tilde{c} \sqrt{\pi} \cdot Y(\tilde{z} - \tilde{c})], \quad (1)$$

where $Y(t) = \exp(t^2) \text{erfc}(t)$, and in turn erfc is the complementary error function. Equation (1) is an exact result for the end-grafted Gaussian chain. Integration of Eq. (1) leads to the exact partition function for this system. The properties of this system have been examined in large detail.

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The adsorption energy per segment as used in the lattice models is both experimentally accessible and relatively easy to work with. However, the adsorption parameter, c (with dimension inverse length) as used in Eq. (1), is more fundamental. The effect of the critical adsorption energy is incorporated in c such that when $c > 0$ the chain is adsorbing, whereas when $c < 0$ the chain avoids the surface. Physically c determines the thickness of the polymer layer (c is the inverse size of the adsorption blob). At the critical point of adsorption $c = 0$ and when $c \gg 1/R_g$, the chain is at the surface.

Much less frequently studied is the behavior of macromolecules at penetrable interfaces. Examples of penetrable surfaces are the liquid/liquid interface between two demixed solvents, the boundary between a polymeric gel and a solution, the interface between a polymer brush and the solution, etc. We mention the work of Stratouras and Kosmas who studied polymers that are interacting with a penetrable surface by using diffusionlike equations.^{8,9} Besides of the interacting surface the remaining volume was a good solvent in either side of the penetrable surface. Semiflexible chains adsorbing on an (also) energetically symmetrical liquid–liquid interface were considered by van Eijk and co-workers¹⁰ using numerical self-consistent field calculations. The wetting behavior of polymers at a liquid–liquid interface^{11,12} has recently also been studied.

In this paper the behavior of an isolated Gaussian chain which is grafted with one of its ends to the boundary of a penetrable interface is studied. We will defer from the problem how to create such a grafting condition. If in addition the molecular nature of the molecular components that are responsible for the presence of the interface is ignored, and replaced by an artificial external potential field felt by the polymer units, one arrives at a model which is in fact quite general. In the following it is not necessary to specify whether the step in the external potential has an entropic origin (e.g., when the interface is the boundary between two polymer gels which differ only in polymer density and not in chemical composition) or is enthalpic in nature (e.g., in a liquid/liquid interface). The central idea is thus to consider the chain to feel an external potential which behaves as a Heaviside step function (see Fig. 1). The external potential assumes the value u for negative coordinates and 0 for positive ones. It will be shown that there is an analytical partition function for this system. Moreover it will be discussed that upon changing the sign of the external potential the chain will roll over to the phase of the lowest external potential. The rolling transition is, in the limit of infinite chain length, a first-order phase transition. With the exact partition function available it is possible to fully analyze this phase transition. Of course the partition function that is discussed is of a mean-field character, as the Gaussian chain is used in the model. Nevertheless, the situation remains rather special; in the whole field of statistical physics there are only a few models available which allow the investigation of a phase transition exactly. The analysis of the partition function from the phase transition point of view will be published somewhere else,¹³ here we will focus on what we can learn from it from a polymer perspective. At this point we like to stress

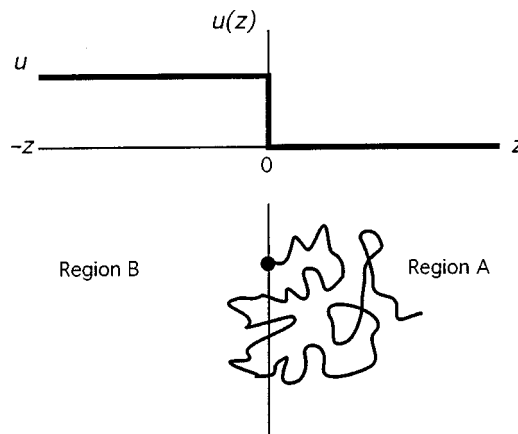


FIG. 1. Schematic representation of the system under investigation. Region A is the region with positive z -coordinates. Region B is the other half-space. The stepwise character of the external potential is indicated. The coil is sitting with most of its segments in the region where the potential is most favorable. It does not leave the interface as it is grafted with one of its ends to the boundary as indicated by the black dot. The potential u in region B can take positive or negative coordinates and the potential in region A is the reference and thus equal to zero.

that we are not doing the dynamics of the rolling transition, it is only the statistics of the chain conformations we are interested in.

The remainder of this paper is as follows. First we will present a derivation of the known partition function of this system (most of the details are deferred to Appendix A). Next, some properties of the grafted chain in the stepwise external potential are discussed. The end-point distribution of the unrestricted end and the thermodynamic characteristics are placed central. In Appendix B we briefly collect the results of a similar problem where the second end of the Gaussian chain is also restricted to be at the interface. This results in looplike conformations. Also for this system exact results are obtained. Finally, a discussion of the results is presented and possible applications of the present model are pointed out.

II. MATHEMATICAL FORMULATION OF THE MODEL AND THE EXACT SOLUTION FOR THE PARTITION FUNCTION

The aim of this section is to present a rigorous theory that describes an ideal Gaussian chain of N segments grafted with one of its ends to the coordinate where the applied external potential changes its value. As mentioned above, let this be at $z = 0$. We denote to the negative coordinates as region B and to the region with positive coordinates, including $z = 0$, as region A. The dimensionless external potentials in both regions are $u_B = u$ and $u_A = 0$, respectively (see Fig. 1). In this problem only the z -coordinate is of interest and the chain properties in the x - y directions may be given by a simple Gaussian function.

It is well-known that the exact partition function for a Gaussian chain is found by solving Edwards diffusion equation¹⁴ for a randomly growing chain in an external potential. The equation features an end-point distribution

$P(z, N)$, which is the statistical weight of finding the end of the chain with length N at coordinate z . There are two diffusion equations applicable in the two regions,

$$\frac{l^2}{6} \frac{\partial^2 P(z, N)}{\partial z^2} - uP(z, N) = \frac{\partial P(z, N)}{\partial N} \quad z \leq 0, \quad (2a)$$

$$\frac{l^2}{6} \frac{\partial^2 P(z, N)}{\partial z^2} = \frac{\partial P(z, N)}{\partial N} \quad z \geq 0. \quad (2b)$$

Implicit in Eq. (2) is that the Gaussian chain is chosen as the reference state. We will consider in the following positive values of u in the negative half-space. The other case, i.e., $u < 0$, follows from a trivial reflection principle; it is then possible to choose the reference of the potential on the negative side of the system and have a positive potential in the positive half-space; a return to the present case is possible when subsequently the direction of the coordinate system is reversed. The system is thus symmetric as to the sign of the external potential u . [The suggested procedure is completely equivalent to keeping the reference of the external potential in the positive half-space. Then the potential may be positive or (of course) negative in the negative half-space. In some of the equations given below one can not simply insert negative values of the potential. It is then necessary to introduce an extra negative sign (equivalent with working with the absolute value); see the reflection principle. We trust that this will be straightforward for the reader. Below we will occasionally remind the reader about this issue.] We continue without loss of generality.

The initial conditions for Eq. (2) specify that the chain is grafted with the first segment to $z=0$. This is dealt with by a delta function, i.e., $P(z, 0) = \delta(z)$. Of course for $z = \pm\infty$ the end-point distributions must vanish and thus we impose $P(-\infty, N) = P(\infty, N) = 0$.

Let the Laplace transform with respect to the contour length of the chain be given by $g(z, p)$. As worked out in Appendix A, the Laplace transformed end-point distributions in the two regions A and B are

$$g(z, q) = \frac{\exp(z\sqrt{q+v})}{\sqrt{q} + \sqrt{q+v}} \quad z \leq 0, \quad (3a)$$

$$g(z, q) = \frac{\exp(-z\sqrt{q})}{\sqrt{q} + \sqrt{q+v}} \quad z \geq 0, \quad (3b)$$

where we have introduced $q = 6p/l^2$ as the conjugate of the square of the radius of gyration and $v = 6u/l^2$. Physically, $v^{-1/2}$ represents the length scale related to the external field parameter u . Direct inverse Laplace transformation of the end-point distribution can only be done in special limits. We will do this below. Integrating $g(z, q)$ over the space coordinate and applying the inverse Laplace transformation gives the exact partition function

$$Q(u, N) = Q(U) = \exp(-U/2) I_0(U/2), \quad (4)$$

where $I_n(x)$ is a modified Bessel function and

$$U = v \frac{6}{l^2} \cdot R_g^2 = uN.$$

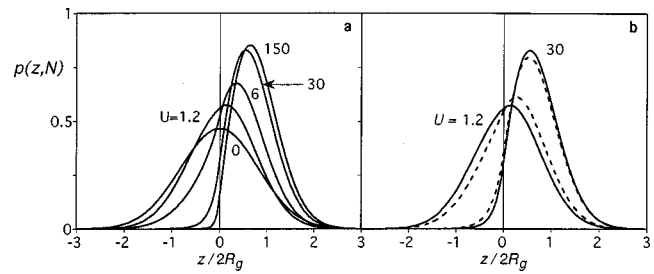


FIG. 2. The normalized end-point distribution as a function $p(z, N)$ of the normalized distance from the step in the potential profile, $z/2R_g$. The values of the external potentials, $U = uN$, for the negative coordinates are indicated (the potential for positive coordinates is zero). (a) Numerical evaluation of end-point distribution. (b) Comparison of numerical evaluation of the end-point distribution (solid line) with the analytical approximation (dashed line).

When $U \gg 1$, the partition function takes the limiting form $Q(U) = (\pi U)^{-1/2}$. In the other limit where $U \ll 1$ we find $Q(U) = 1 - U/2$. The partition function Eq. (4) was obtained before by Chatellier in his Ph.D. thesis.¹⁵ An equation similar to Eq. (4) was obtained by Wang, Nemirovsky, and Freed¹⁶ using a slightly different model. A detailed analysis of the partition function such as presented below, is not found in the literature.

III. ANALYSIS OF THE PARTITION FUNCTION OF THE PINNED GAUSSIAN CHAIN IN THE STEP POTENTIAL

The analysis of the partition function for the Gaussian chain pinned at a step profile of the external potential may conveniently be split up into two aspects. First, we will analyze the structure of the chain by way of the end-point distribution as a function of the external potential, then the thermodynamic properties will be discussed. From both aspects the nature of the phase transition in the system becomes apparent.

A. End-point distributions

In Eqs. (3a) and (3b) we have presented the end-point distributions in the q -space. The inverse Laplace transformation to the usual N -coordinate is not feasible. For this reason there is no closed expression for the end-point distribution and we have to resort to either numerical evaluation of this distribution or to analytical approximations. We will follow both routes.

In Fig. 2(a) we present the result of the numerical inverse Laplace transformation of the normalized with $Q(U)$ end-point distribution function for various values of the external field U . Only the results for positive values of the external potential are shown. The larger the U value the more the segments are pushed towards the positive z -coordinates. When $U=0$ there is a simple Gaussian distribution. The first and most important conclusion from Fig. 2(a) is that the distribution function remains a smooth function with a single maximum for all values of the external potential. The maximum of the end-point distribution for $U=0$ is naturally at $z=0$, and for larger values of U this maximum shifts to higher z -values. At the same time the maximum of the end-

point distribution increases in size with increasing value of the external potential. From the seemingly unimportant changes in the distribution of free ends we propose a simplistic view of the events that occur near $U=0$. Upon the sign change of the external potential the chain rolls with its segments from the positive to the negative coordinates, i.e., towards the low potential side. The grafting point is the pivoting point of this rolling motion. Whether the reported changes in the end-point distribution are significant or not, will be discussed below in more detail.

In an attempt to find an analytical approximation for the end-point distribution, we consider Eq. (3a) in the limit of $u \gg q$. In real space this condition is equivalent with $u \gg 1/N$; the potential field strongly repels the segments towards the positive half-space. We obtain

$$g(z, q) = \frac{\exp(-z\sqrt{q})}{\sqrt{q} + \sqrt{v}} \quad z \geq 0. \tag{5}$$

It is possible to inverse Laplace transform this result. After normalization the end-probability we obtain is

$$P(z, N) = P_{\text{ads}}(\tilde{z}, \sqrt{U}) = \frac{1}{R_g \sqrt{\pi}} \exp(-\tilde{z}^2) [1 - \sqrt{\pi U} \cdot Y(\tilde{z} + \sqrt{U})] \quad z \geq 0, \tag{6}$$

where we have recovered the Eisenriegler result for a chain end-grafted to a solid–liquid boundary [cf. Eq. (1)], where the identification $\tilde{z} \leftrightarrow -\sqrt{U}$, or $cl \leftrightarrow -\sqrt{6u}$ connects both problems. In other words, a very negative c parameter in the solid–liquid system (no adsorption) corresponds to an unfavorable potential in region B. It is as if the chain in region A is feeling a very repulsive impenetrable barrier at $z=0$, albeit, in principle, penetrable of course.

Inspection of Fig. 2(a) suggests that, for relatively high values of the external potential U , the distribution function for $z < 0$ is exponentially decaying away from the interface. This part of the chain thus behaves as if the chain is adsorbed at an interface with a positive c parameter (an adsorbing surface). This suggests that we can approximate $P(z, N)$ for the negative part of the distribution function with $P_{\text{ads}}(\tilde{z}, -\sqrt{U})$. As c^{-1} is the layer thickness (adsorption blob) in the solid–liquid case, $l/\sqrt{6u}$ may be called the penetration depth of the chain in the unfavorable region of the liquid–liquid interface.

The next problem is to match both branches for the end-point distribution at $z=0$. Introducing the ratio $R = P_{\text{ads}}(0, \sqrt{U})/P_{\text{ads}}(0, -\sqrt{U})$ which reduces to

$$R = \frac{1 - \sqrt{\pi U} \cdot Y(\sqrt{U})}{1 + \sqrt{\pi U} \cdot Y(-\sqrt{U})}, \tag{7}$$

it becomes possible to collect the contributions and obtain the unnormalized end-point distribution,

$$P(\tilde{z}, \sqrt{U}) \approx (1 - \theta(z)) P_{\text{ads}}(\tilde{z}, \sqrt{U}) + R \theta(z) P_{\text{ads}}(\tilde{z}, -\sqrt{U}), \tag{8}$$

where $\theta(z)$ is the Heaviside function which assumes zero for $z < 0$ and unity otherwise. Finally, the distribution function, Eq. (8), needs to be normalized to unity which results in $p(\tilde{z}, \sqrt{U})$. It is easily checked that for $U=0$ the distribution function goes to the correct result; it becomes a Gaussian,

$$p(\tilde{z}, 0) = \frac{1}{R_g \sqrt{\pi}} \exp(-\tilde{z}^2). \tag{9}$$

In the limit of very large external potential, it must be the case that the liquid–liquid interface becomes essentially impenetrable for the polymer and the problem reduces exactly to the solid–liquid result with a large negative adsorption parameter. In this case the end-point distribution is given by

$$p(\tilde{z}, \infty) = \tilde{z} \exp(-\tilde{z}^2) \tag{10}$$

and Eq. (8) is exact in this limit as well. In the intermediate region it is expected that Eq. (8) is an approximation.

In Fig. 2(b) we compare a few examples of the distribution as predicted by Eq. (8) with exact ones. In this graph the dashed lines represent the prediction of Eq. (8), whereas the continuous lines are the exact numerical results as found by inverse Laplace transformation of the end-point distribution of Eq. (3). The examples shown are the worst cases. We thus conclude that Eq. (8) is in fact a very good description of the distribution function for the present system.

Let us go on by analyzing the end-point distribution function in some more detail. For this we return to the exact end-point distribution in Laplace space. It is possible to integrate the appropriate moments over the end-point distribution in q -space and take the inverse Laplace transform of the result of that. The end-point distribution is known both in regions A and B. It is therefore possible to subdivide the partition function into one applying only to the A and one applying only to the B region, respectively. It then proves feasible to analyze various moments over the end-point distribution specified to the region the end is in, and obtain information on the fluctuations of the end-point specified to the region in which the end is found. We will not go into this level of detail here. Instead we will discuss the overall results, i.e., the average over both regions A and B. The goal is thus to obtain information about the overall end-point fluctuations. To this end we need the first and second moment over the end-point distribution. Using the mentioned route by integration in Laplace space and subsequent inverse Laplace transformation, the average distance of the end-point is found to be

$$\langle z \rangle = R_g \frac{\exp\left(\frac{U}{2}\right) \text{erf} \sqrt{U} + i \exp\left(-\frac{U}{2}\right) \text{erf}(i\sqrt{U})}{\sqrt{6U} I_0\left(\frac{U}{2}\right)} \approx \begin{cases} \frac{2}{3\sqrt{\pi}} UR_g & U \ll 1 \\ R_g \sqrt{\pi} - \frac{l}{\sqrt{6}} & U \gg 1 \end{cases}. \tag{11}$$

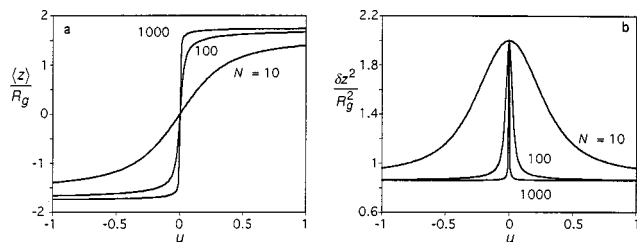


FIG. 3. (a) First moment over the end-point distribution [cf. Eq. (11)] as a function of the external potential u . (b) Fluctuations of the end-points as a function of the value of the external potential u . The values of the degree of polymerization are indicated.

Note that with the limiting condition $U \ll 1$ used in Eq. (11) and below, it is implicitly assumed that $U \geq 0$; the negative potential case follows from application of the reflection principle; for $U < 0$ the average position is negative. For small values of the external potential $\langle z \rangle \rightarrow 0$ as expected. The limit of the first moment over the end-point distribution for high values of the external potentials $\langle z \rangle = \sqrt{\pi} R_g$, is known from the Gaussian chain end-grafted on a nonadsorbing surface,^{6,7} cf. Eq. (10).

The second moment over the end-point distribution is found to be

$$\langle z^2 \rangle = 4R_g^2 \left(1 - \frac{\sinh\left(\frac{U}{2}\right)}{U \cdot I_0\left(\frac{U}{2}\right)} \right) \approx \begin{cases} 2R_g^2 \left(1 + \left(\frac{U}{4}\right)^2 \right) & U \ll 1 \\ 4R_g^2 \left(1 - \frac{\sqrt{\pi U}}{2U} \right) & U \gg 1 \end{cases} \quad (12)$$

Here the asymptote for high potentials is known from the end grafted chain at a nonadsorbing surface. Also the value $\langle z^2 \rangle \approx 2R_g^2$ at $u=0$ is well-known from the Gaussian chain, and the result $\langle z^2 \rangle = 4R_g^2$ for large potentials follows from Eq. (10). From Eq. (14) it is seen that the average square of the end-point displacement from the border at $z=0$ is largest when the value of the external potential is large and that it goes through a minimum at $u=0$. At this point the chain is not disturbed and can probe both positive and negative coordinates. The factor of 2 between the high and low potential limits is easily explained. When $u=0$ effectively $N/2$ segments will be on one side of the system and the remaining segments are on the other side, whereas for large U effectively all segments are on one side of the system. Thus for large fields the square of the distance can take twice the value of the zero-field value.

In Fig. 3 we present the average position of the free end and the fluctuations of it. The average position of the free end is negative for negative potentials (here we applied the reflection principle discussed above) and is positive for positive values of the external potential in region B. The limits specified in Eq. (11) can be retrieved from this graph. Of interest is to notice that the transition of the end-point from the negative to the positive coordinates, is more abrupt with

increasing chain lengths. The fluctuations of the end-points, $\delta z^2 = \langle z^2 \rangle - \langle z \rangle^2$, go through a sharp maximum for $u=0$, with a magnitude of $\delta z^2 = R_g^2(\pi - 2)$ as is shown in Fig. 3(b). It is of interest to mention that the fluctuations for very large potentials do not vanish. The reason for this is that the chain, although it has all its segments on one side of the system, still is able to fluctuate. The limiting value for high potentials is given by $\delta z^2 = (4 - \pi)R_g^2$. In the limit of large N the relative fluctuations do not vanish. The fluctuations behave, in the thermodynamic limit, similar to a delta-function.

Although the end-point distribution remains single peaked, we clearly find well-defined changes in the various moments of the end-point distribution, as well as a pronounced maximum in the end-point fluctuations. These observations indicate that the rolling motion that occurs around zero field is a phase transition.

B. Thermodynamics

From the structural characteristics of the Gaussian chain in the stepwise external potential there were some findings pointing to a phase transition near $u=0$ where the chain rolls from one region to the other. To fully characterize these findings, it is necessary to consider the thermodynamic characteristics of the system. With the partition function given by Eq. (4) we may obtain all thermodynamic characteristics of the Gaussian chain in the stepwise external potential field. The variables in the model are the chain length N and the value of the external potential u which combine into a single parameter $U = uN$. The free energy, which is normalized with respect to the contributions of an unrestricted Gaussian chain, is given by

$$F(U) = -\ln Q(U) = \frac{U}{2} - \ln \left(I_0 \left(\frac{U}{2} \right) \right) \approx \begin{cases} \frac{U}{2} \left(1 - \frac{U}{8} + \left(\frac{U}{8} \right)^3 \right) & U \ll 1 \\ \frac{1}{2} \left(\ln(\pi U) - \frac{1}{2U} - \frac{1}{2U^2} \right) & U \gg 1 \end{cases} \quad (13)$$

From Eq. (13) it seems odd that the free energy only grows logarithmically with N for large U . However, one should keep in mind that Eq. (13) is only the correction of the free energy on the reference, which is the Gaussian chain. Of course the free energy of the Gaussian chain is proportional with N . The free energy as given in Eq. (13) is symmetric, i.e., $F(U) = F(-U)$, which follows from the reflection principle discussed above [cf. Eq. (2)]. The limiting behavior $F(U)/N \approx u/2$ is found only in a very small u range, especially for large N . The free energy near $U=0$ is excellently represented by two straight lines. The free energy is continuous in $U=0$, but the derivative with respect to u is not. From Eq. (13) it is easily seen that $(dF/dU)_{U \uparrow 0} = -1/2$ (note the reflection principle), whereas $(dF/dU)_{U \downarrow 0} = 1/2$. According to the classification of Ehrenfest this discontinuity indicates that the system passes a first-order phase transition at $U=0$. For very high fields the free energy grows only logarithmically

mically with the field and as a consequence the free energy per segment decreases with increasing length of the chain. This is expected, because the chain does not need to react too much upon changing the field if all the segments are already transferred to the region where the potential is zero.

The average energy in the system is given by $E = -U[\partial \ln Q(U)/\partial U]$. To evaluate E it is more convenient to consider the average fraction of segments that is in the region with negative z -coordinates (i.e., phase B). When the potential in this phase is positive the fraction s will naturally tend to zero, whereas if the potential is negative s will tend to unity. Let us denote the average fraction by $\langle s \rangle$,

$$\begin{aligned} \langle s \rangle &= -\frac{\partial \ln Q(U)}{\partial U} \\ &= \frac{1}{2} \left(1 - \frac{I_1(U/2)}{I_0(U/2)} \right) \\ &\approx \begin{cases} \frac{1}{2} \left(1 - \frac{U}{4} + 4 \left(\frac{U}{8} \right)^3 \right) & U \ll 1 \\ \frac{1}{2U} \left(1 + \frac{1}{2U} + \frac{1}{U^2} \right) & U \gg 1 \end{cases} \end{aligned} \tag{14}$$

This equation is correct also if $U < 0$. The limiting values for large values of the external field correspond to the case where the chain is almost completely restricted to one region of space. When the potential is positive $\langle s \rangle$ approaches zero, whereas when it is negative $\langle s \rangle$ goes to unity. It changes stepwise from 1 to 0 in the limit of $N \rightarrow \infty$.

The consequence for the average energy E is found from the fraction $\langle s \rangle$,

$$E(U) = \langle s \rangle U \approx \begin{cases} \frac{U}{2} \left(1 - \frac{U}{4} + 4 \left(\frac{U}{8} \right)^3 \right) & U \ll 1 \\ \frac{1}{2} \left(1 + \frac{1}{2U} + \frac{1}{U^2} \right) & U \gg 1 \end{cases} \tag{15}$$

The value of E is necessarily zero for $U = 0$ and becomes $1/2$ for very large values of the external potential. Note that this limiting value of the interaction energy of 0.5 kT per chain is independent of the chain length. In passing we note that when the potential is $U < 0$, it is easy to see that it is necessary to use $E(U) = (1 - \langle s \rangle)U$. It is of interest to point to the fact that the energy passes through a maximum. This is necessary as the limiting value for the energy for high potentials is reached from above. The maximum is found to be for a potential near $u_{\max} \approx 3.4/N$ and takes a value $E(u_{\max}) \approx 0.6$.

The energy is continuous at $u = 0$, but similarly to the free energy, the first derivative of the energy jumps from $-1/2$ to $1/2$. This last jump indicates that the rolling transition has also features of a second-order phase transition.

The fluctuations in the average fraction of segments is given by

$$\begin{aligned} \delta s^2 &= \langle s^2 \rangle - \langle s \rangle^2 \\ &= \frac{1}{4} \left(1 - \left(\frac{I_1(U/2)}{I_0(U/2)} \right)^2 - \frac{2I_1(U/2)}{I_0(U/2)U} \right) \\ &\approx \begin{cases} \frac{1}{8} \left(1 - \frac{3}{4} \left(\frac{U}{4} \right)^2 \right) & U \ll 1 \\ \frac{1}{2U^2} \left(1 + \frac{1}{U} \right) & U \gg 1 \end{cases} \end{aligned} \tag{16}$$

From the expansions of Eq. (16) as well as from symmetry considerations we see that the fluctuations do not depend on the sign of the external potential but only on the value. For high values of the external potential the fluctuations are damped and $\delta s^2 \sim (U)^{-2}$. Near the transition point $U = 0$ the fluctuations have a parabolic form $\delta s^2 \sim -U^2$. The smaller is the chain length, the broader is its parabola. The fluctuations approach a delta-functionlike behavior for infinite chain length. The width of the transition can also be estimated from Eq. (16) and is of the order of $\Delta u N \approx 1$, i.e., it decreases proportional with $1/N$.

Finally, the dimensionless entropy given by $S(U) = E(U) - F(U)$ also changes abruptly near the transition point,

$$\begin{aligned} S(U) &= -\frac{U}{2} \frac{I_1(U/2)}{I_0(U/2)} + \ln \left(I_0 \left(\frac{U}{2} \right) \right) \\ &\approx \begin{cases} -\left(\frac{U}{4} \right)^2 + \frac{3}{4} \left(\frac{U}{4} \right)^4 & U \ll 1 \\ -\frac{1}{2} \ln \left(\frac{\pi U}{e} \right) + \frac{1}{2U} + \frac{3}{4U^2} & U \gg 1 \end{cases} \end{aligned} \tag{17}$$

of course $S(u, N) = S(-u, N)$. From Eq. (17) we learn that the entropy is negative for a polymer chain as a whole (remember the Gaussian chain is the reference) and that it jumps to zero near the transition point. The increase in the entropy reflects the fact that the unperturbed Gaussian chain has the optimum conformational degeneracy. In the limit of large N , $S(U)$ becomes similar to a delta function near $u = 0$.

Similarly as the energy, the entropy is also continuous at $u = 0$. In contradistinction with the energy however, the first derivative of the entropy remains continuous at the transition point. Also higher derivatives have no singular behavior. So from the point of view of the entropy the rolling event is not special.

For convenience of the reader we have plotted in Fig. (4) the thermodynamic quantities of the system of interest. We not only present the full free energy, entropy, and energy but the quantities normalized to the contribution per segment as well. In these figures one can graphically check the limiting behavior. The average fraction of segments in contact with region B and on the fluctuations in this quantity, as discussed above, are illustrated in Fig. 5.

Let us summarize our findings. From the analysis of the end-point distribution it was concluded that the rolling tran-

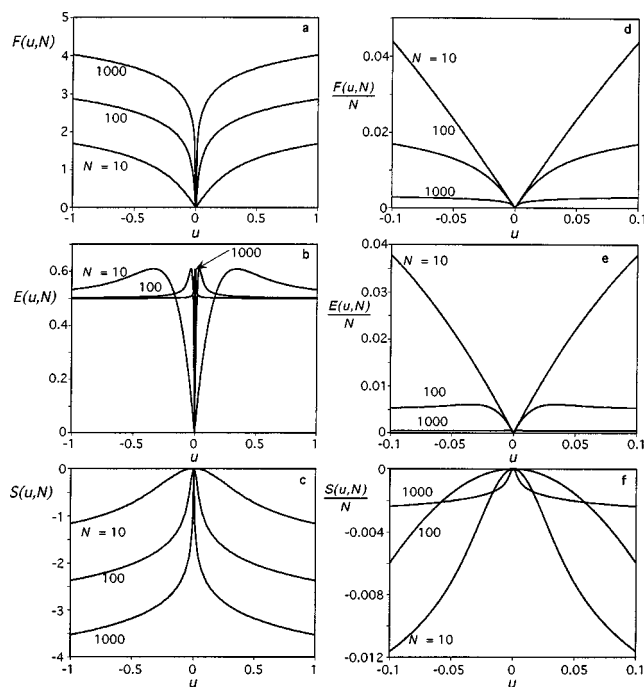


FIG. 4. (a) Free energy, $F(u, N)$, (b) the energy $E(u, N)$, and (c) the entropy $S(u, N)$ for the system as a whole, and these corresponding quantities per segment are given in graphs d, e, f, respectively. The thermodynamic quantities are given as a function of the external potential u for various values of the molecular weight N of the polymer as indicated.

sition is a phase transition. From the analysis of the free energy it was determined that the transition is of the first-order type. The energy, however, remains continuous at the transition, but its first derivative jumps. This is indicative of a second-order phase transition. Finally, the entropy in the system, and its derivatives, remain continuous at $u=0$. Similar anomalous phase transitions take place in other polymer systems. Known examples are (i) the adsorption transition of an end-grafted chain onto a solid interface to which an external force is applied to the free end,¹⁷ (ii) the coil-globule transition upon the decrease of solvent quality.^{18,19}

It is of interest to mention that in the Figs. 2–5 the effects of increasing chain lengths are systematically illustrated. By increasing the chain length one moves towards the thermodynamic limit of this system, and thus it is easily checked how the system evolves towards a first-order phase transition when the thermodynamic limit is taken.

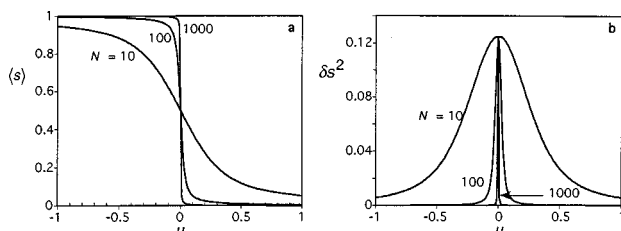


FIG. 5. (a) Average fraction of segments $\langle s \rangle$ in the negative half-space, (b) the fluctuations in the fraction of segments in the negative half-space, as a function of the external potential u . The degree of polymerization is indicated.

IV. DISCUSSION

In this paper an exactly solvable model has been discussed. The model comprises a Gaussian chain restricted by one of its ends at the boundary of a penetrable surface. Due to the mathematical simplicity a detailed analysis was possible. Of course the Gaussian chain model is not the rigorous solution of the real polymer system. For this reason the partition function discussed above is necessary of a mean-field-type. Nevertheless we believe that the results are of significant interest, partly from a polymer theoretical point of view, partly from a statistical mechanical point of view and also from an application point of view.

From the perspective of polymer modelling the system discussed in this paper is rather special. It features a first-order phase transition, but the end-point distribution remains single peaked. Usually phase transitions in inhomogeneous polymer systems are characterized by a binodal distribution of this function. The analysis discussed above clearly showed that hidden in the end-point distribution there are features of the phase transition which only appeared after taking moments over the end-point distribution. There is one more case known to us with similar features. For the adsorption of a Gaussian chain on a solid interface with an external force on one of its ends, the end-point distribution of the unconstrained end remains unimodal, despite the fact that there is a first-order phase transition.^{4,17} From this, and from the present example, one should therefore be cautious when definite conclusions are drawn based upon the binodal shape of the end-point distribution in relation to the existence of phase transitions.

From a statistical mechanical point of view the present model is of significant interest as it is a model which allows a full analysis of a phase transition. Not only the thermodynamic limit is available analytically, but also the finite size effects are analyzed straightforwardly. In this paper we showed the peculiarities of the chain conformations near the phase transition, as well as the corresponding thermodynamics. Following Ehrenfest's classification, the rolling transition is clearly first-order. It is also possible to analyze for this system the Landau function which is a free energy as a function of an order parameter in this system. The full analysis of this will be the topic of a forthcoming paper. It is finally possible to analyze the complex zeros of this partition function analytically. These complex zeros are consistent with predictions in the literature,^{20,21} as we showed elsewhere.¹³

From an application point of view the present system is significant. There is a number of systems that may benefit from the analysis given above. In fact the model that we analyzed above was defined in an attempt to make a predictive model for the first-order adsorption to flower transition in a polymer brush.²² In this problem there are long minority chains end-grafted into a brush composed of shorter ones. The minority chains can, in contrast to the brush chains adsorb onto the solid substrate. If they do so, they are in the adsorbed state, but otherwise they assume a flowerlike conformation. Such a flower is composed of a stem, with a similar structure as the chains in the brush, and a crown floating above the brush where the remainder of the segments is situated. The analogy between the adsorption to flower transition

and the rolling transition becomes clear if one models the brush as a step-profile in external potential and allowing the end of the chain not grafted at the brush–solution interface (as in the present model) but some distance away in the brush region, i.e., at the solid boundary. The rolling transition corresponds in this case to the interpenetration of the crown into the brush. We thus believe that the present model is significant in solving some of the issues related to the adsorption to flower transition in brushes. Problems similar to the rolling transition may be found when chains are end-grafted on the edge of a polymer gel, or between two gels put next to each other. In this case the external potential can also take the shape of a Heaviside step-function. Interestingly, the origin of this potential field is, especially when the two gels only differ in polymer concentration, predominantly entropic in nature. The chain can remain in solution or in one half-space, or “roll” into the (other) gel upon changing the conditions. The model may also be of help in considering the adsorption of polymers at a liquid/liquid interface (here the origin of the potential jump is essentially energetic in nature). In this case, the finite surface tension of the liquid/liquid interface, and the corresponding adsorption of the chains at the boundary, should be incorporated in the model, similarly as, e.g., in Refs. 8 and 9.

A related problem of a Gaussian chain, which has both its ends at the boundary where the external potential changes, can also be solved exactly. Again, the rolling transition is first-order. In Appendix B we collect a few central results for this problem, but we defer from the full analysis here.

V. CONCLUSIONS

The model of a Gaussian chain is a useful tool to investigate polymer problems in inhomogeneous systems. In this paper we proved that when a penetrable interface is modeled as a step function in the external potential, and when the Gaussian chain is end-grafted to the boundary of this step in the potential, there exists a close expression for the partition function. The model features a first-order phase transition, which we named the rolling transition. Upon changing the sign of the external potential in each half-space, the chain rolls from one side to the other. Only in the absence of the external potential the chain is unperturbed and probes both the positive and negative coordinates. In the presence of the field, the chain is thus confined to one half-space and loses some entropy due to this. As a consequence both the free energy and the energy have a discontinuity in their first derivative at the transition point. The end-point distribution however remains single peaked; the distribution only changes its shape. In the thermodynamic limit this change is significant as it causes the fluctuations of the end-point to peak at the transition. The model is mathematically very transparent, which suggests that the model may be instructive for people interested in learning about phase transitions in general.

ACKNOWLEDGMENTS

This work was partially supported by NWO Dutch–Russian program for Agricultural and Food Research. J.vM. was supported by the Dutch organization of scientific research. The authors thank A. A. Gorbunov for many useful discussions and the help in calculating (properties of) the end-point distributions. A.M.S. acknowledges support from Russian Fund of Fundamental Investigations (RFFI) Grant No. 9903-33385a.

APPENDIX A: THE DERIVATION OF THE PARTITION FUNCTION

The start is the Edwards diffusion equation which has been introduced above,

$$\begin{aligned} \frac{l^2}{6} \frac{\partial^2 P(z, N)}{\partial z^2} - uP(z, N) &= \frac{\partial P(z, N)}{\partial N} \quad z \leq 0, \\ \frac{l^2}{6} \frac{\partial^2 P(z, N)}{\partial z^2} &= \frac{\partial P(z, N)}{\partial N} \quad z \geq 0, \end{aligned} \quad (\text{A1})$$

where we kept the segment length in the problem for sake of completeness.

The Laplace transform of the end-point distribution with respect to the contour length $g(z, p)$ is used to write the Laplace transform of the diffusion Eqs. (2a) and (2b),

$$\frac{l^2}{6} \frac{\partial^2 g(z, p)}{\partial z^2} = (p + u)g(z, p) \quad z \leq 0, \quad (\text{A2a})$$

$$\frac{l^2}{6} \frac{\partial^2 g(z, p)}{\partial z^2} = pg(z, p) - \delta(z) \quad z \geq 0. \quad (\text{A2b})$$

Introducing $q = 6p/l^2$ (the conjugate parameter for the square of the radius of gyration) and $v = 6u/l^2$ leads to

$$\frac{\partial^2 g(z, q)}{\partial z^2} = (q + v)g(z, q) \quad z \leq 0, \quad (\text{A3a})$$

$$\frac{\partial^2 g(z, q)}{\partial z^2} = qg(z, q) - \frac{6}{l^2} \delta(z) \quad z \geq 0. \quad (\text{A3b})$$

Let us next use the Laplace transform with respect to the spatial coordinate as $f(t, q)$, to write the diffusion equation in the (t, q) coordinates,

$$f(t, q) = \frac{\frac{\partial g(0, q)}{\partial z}}{t^2 - (\sqrt{q+v})^2} + \frac{g(0, q)t}{t^2 - (\sqrt{q+v})^2} \quad z \leq 0, \quad (\text{A4a})$$

$$f(t, q) = \frac{-\frac{6}{l^2} + \frac{\partial g(0, q)}{\partial z}}{t^2 - (\sqrt{q^2})} + \frac{g(0, q)t}{t^2 - (\sqrt{q^2})} \quad z \geq 0. \quad (\text{A4b})$$

It is possible to transform Eqs. (A4a) and (A4b) back to z -space. The result is

$$g(z, q) = g(0, q) \cosh(z\sqrt{q+v}) + \frac{\partial g(0, q) \sinh(z\sqrt{q+v})}{\sqrt{q+v}} \quad z \leq 0, \quad (\text{A5a})$$

$$g(z, q) = g(0, q) \cosh(z\sqrt{q}) + \left[\frac{\partial g(0, q)}{\partial z} - \frac{6}{l^2} \right] \frac{\sinh(z\sqrt{q})}{\sqrt{q}} \quad z \geq 0. \quad (\text{A5b})$$

Using the condition that the end-point distribution vanishes at plus and minus infinite we arrive at

$$\frac{\partial g(0, q)}{\partial z} = g(0, p) \sqrt{q+v} \quad z \leq 0, \quad (\text{A6a})$$

$$\frac{\partial g(0, q)}{\partial z} = \frac{6}{l^2} - g(0, p) \sqrt{q} \quad z \geq 0. \quad (\text{A6b})$$

Matching both equations leads to $g(0, q) = 6[l^2(\sqrt{q} + \sqrt{q+v})]$. Combining this result with Eqs. (A5) and (A6) leads to

$$g(z, q) = \frac{\exp(z\sqrt{q+v})}{\sqrt{q} + \sqrt{q+v}} \quad z \geq 0, \quad (\text{A7a})$$

$$g(z, q) = \frac{\exp(-z\sqrt{q})}{\sqrt{q} + \sqrt{q+v}} \quad z \geq 0, \quad (\text{A7b})$$

where an unimportant constant $6/l^2$ is dropped. To calculate the partition function we need to integrate the end-point distribution function over whole space. The integration is split obviously into two. From minus infinite to zero we use Eq. (A7a), whereas for the positive coordinates Eq. (A7b) is used,

$$\int_{-\infty}^{\infty} g(z, q) dz = \frac{1}{\sqrt{q}\sqrt{q+v}}. \quad (\text{A8})$$

After inverse Laplace transformation to N -space we find

$$Q(u, N) = \exp\left(-\frac{u}{2}N\right) I_0\left(\frac{u}{2}N\right), \quad (\text{A9})$$

where $I_0(x)$ is a modified Bessel function.

APPENDIX B: THE GAUSSIAN CHAIN WITH BOTH ENDS AT THE BORDER OF A LIQUID-LIQUID INTERFACE

In this Appendix we collect a few results of a Gaussian chain which has both ends fixed at $z=0$. This means that the end-point distribution of Eq. (2) [cf. Eqs. (A7a) and (A7b)]

needs to be applied for the case that $z=0: g(0, p) = (\sqrt{q} + \sqrt{q+v})^{-1}$. Inverse Laplace transformation gives the partition function for the looplike conformations,

$$Q_{\text{loop}}(u, N) = \frac{1 - \exp(-uN)}{2\sqrt{\pi N}(uN)}. \quad (\text{B1})$$

This partition function was also found in the thesis of Chatellier.¹⁵

Of course the analysis of the end-point is impossible in this case. Thus only the route of the thermodynamics is open to analyze the rolling transition of the loop conformation. The free energy is given by

$$F_{\text{loop}}(u, N) = -\ln(1 - \exp(-U)) + \ln(2\sqrt{\pi N}U) \approx \begin{cases} \ln(2\sqrt{\pi N}) + \frac{U}{2} & U \ll 1 \\ \ln(2\sqrt{\pi N}) + \ln U & U \gg 1, \end{cases} \quad (\text{B2})$$

from which we see that at $u=0$ a phase transition of the first-order occurs, $(dF/dU)_{U \downarrow 0} = -(dF/dU)_{U \uparrow 0} = 1/2$. Other thermodynamic quantities follow similarly as given above.

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