Exactly solved polymer models with conformational escape transitions of a coil-to-flower type

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Abstract. – We analyze exact analytical partition functions for Gaussian chains near surfaces and interfaces. These partition functions contain the possibility of conformational first-order phase transitions. Such transitions occur when chains are tethered in space and exposed to a local perturbing field. Then the chain can partially escape from the field: the chain transforms from the confined coil to an inhomogeneous flower conformation. The flower consists of a strongly stretched stem and a very weakly deformed crown. A generic phase diagram including one binodal and two spinodal lines is found for three related systems. The height of the barrier between stable and metastable states as well as the dynamics of barrier crossings is discussed.

Introduction. – Phase transitions have always drawn much interest in (materials) science, and in polymer physics in particular. One of the most studied examples is the adsorption of a macromolecule onto solid surfaces [1–3]. Recently, escape transitions that occur upon squeezing a polymer chain by a cylinder (piston) received much attention [4–9]. Phase transitions in macromolecules near a liquid-liquid interface were also studied intensively in the past decade [10–12]. These transitions are of interest from a fundamental point of view because of the appearence of polymer flowers as an interesing new state of polymer matter. At the same time, the interest is motivated by a large number of practical applications. These include polymer chromatography, stabilization of colloids in suspensions, adhesion and lubrication, to mention just a few. Atomic force microscopy (AFM) offers unique possibilities to study the coil-to-flower transitions.

Much effort, typically from a theoretical point of view, has been put into studying conformational phase transitions in the various systems and geometries as mentioned above. In this letter we would like to show the connection between these problems and treat all of them on one and the same fundamental physical level. We introduce exactly solvable models pertaining to the escape transitions at liquid-liquid and liquid-solid interfaces, and demonstrate their equivalence.

Exactly solvable models provide an invaluable tool for a deeper understanding of the intricate physics of phase transitions. Their number is very limited in spite of enormous
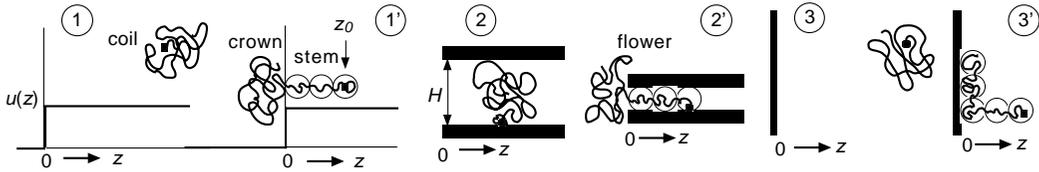
Fig. 1 – Schematic presentation of the three models used in this study. All three cases have a chain grafted at a (variable) position $z = z_0$ as indicated by the black dot. The chains on the left (labels 1, 2 and 3) are in the (perturbed) Gaussian conformation. The chains on the right (labels $1'$, $2'$ and $3'$) are in the flower (step + crown) conformation. Other details are in the text.

efforts in this field. In polymer physics, one could mention the Zwanzig-Lauritzen model of two-dimensional β-structure formation [13] and some closely related models of directed polymer adsorption [14, 15]. Another inherently related set consists of the DNA melting model [16, 17]. More relevant for the present paper is the model of adsorption of an ideal chain on surfaces of different geometry [18]. All of these models refer to phase transitions at a level of a single macromolecule where the number of monomeric units N of the chains is assumed to be very large. Earlier, we have shown that a model of adsorbing polymer chain with an external end-force applied to one of its ends admits an exact analytical analysis. This system has continuous and discontinuous phase transitions [19–21].

It is worth noting that even a closed expression for the partition function does not provide any clue to whether metastable states exist at all, and if so, what their properties are. To answer these questions, one has to choose an appropriate order parameter, s, and calculate the Landau free energy, $\Phi(s)$, so that the partition function can be represented as an integral over the states with different values of the order parameter: $Q = \int \mathrm{d}s \exp\left[-\beta N \Phi(s)\right]$, β being the inverse temperature. If the Landau free energy as a function of the order parameter has two minima, the lower minimum is associated with the thermodynamically stable state, while the other minimum corresponds to the metastable state. At the transition point, both minima are of equal depth. The lifetime of the metastable state is determined by the height of the barrier separating the local minimum from the global one.

The functional form of the Landau free energy has always been postulated on very general grounds as an expansion in powers of the order parameter [22]. The only example of an exact analytical calculation that we know of is the model of an adsorbing polymer chain to which an external end-force is applied to one of its ends [20]. This system exhibits a first-order phase transition. Nevertheless, to our surprise, metastable states are in this particular case absent. In this letter, we draw attention to three related models for which the exact solutions in terms of the Landau function are identified as well. For all present cases a first-order phase transitions will be shown. Associated with these first-order transitions there are well-defined metastable states. In fact, we demonstrate that all three models are mathematically equivalent. The models are presented in fig. 1 and are described as follows.

An isolated Gaussian polymer chain is fixed by one end at a distance z_0 from a liquid-liquid interface modeled as an external step potential with magnitude u. If the chain is fixed at a large distance from the interface, it exists in a coil conformation (cf. left side of fig. 1). However, if the distance z_0 is moderate, and the penalty implemented by the potential u is sufficiently large, the chain partially escapes into the other half space forming an inhomogeneous flower conformation with a stretched stem and a coiled crown.

An isolated Gaussian chain is compressed by a planar piston (cylinder) and tethered by one end to the surface a distance z_0 from the edge of the confinement. The separation between

the piston and the underlying planar surface is H. Here again two distinct states exist: a (compressed) coil (when H is sufficiently large) and a flower (at small H). The analogy between this model and the previous one was pointed out by Sevick and Williams [8].

An isolated Gaussian polymer chain is fixed by one end at a distance z_0 from an adsorbing solid surface characterized by the adsorption parameter c. Once again, the coil state is transformed into a flower with the crown now being adsorbed (into a pancake) onto the solid surface. Eisenriegler and coworkers already pointed to the existence of a first-order phase transition in this system but did not analyze this transition [2].

We obtain exact solutions for the characteristics of these models for the simple case of ideal Gaussian chains. In fact, situations for which a polymer chain undergoes an abrupt transition from a homogeneous conformation (be it a coil, a compact globule, or an adsorbed state) into an inhomogeneous flower state are more abundant. Not all of them are strictly equivalent to the three cases mentioned above. In particular, excluded-volume effects (especially important in compressed or globular states) shift the position of the transition point and some quantitative characteristics of each of the two states. However, all the main features of the escape transition can be investigated in the Gaussian approximation for related systems as well.

Landau free energy. –   In order to choose the appropriate order parameter it is instructive to visualize a continuous transformation from an initial coil (cf. left side of fig. 1) to the flower state (cf. right side of fig. 1). As a response to the presence of the external field (model 1), the confinement H (model 2) or the presence of an adsorbing surface (model 3), the ideal coil conformation is perturbed. Before the coil can escape from the unfavorable state, it must be stretched to reach the more favorable region. Then a seed crown is formed. This crown grows subsequently at the expense of the stem until the equilibrium flower state is reached. In this process, it is the chain stretching parameter that grows continuously. For the deformed coil, the parameter refers to the chain as a whole, while for the flower it refers only to the stem. Hence, the order parameter, s, is defined as follows:

$$
s = \begin{cases} (z_0 - z_N)/Na\,, & \text{for the coil state}\,, \\ z_0/na\,, & \text{for the flower state}\,, \end{cases} \tag{1}
$$

where a is the segment length, z_N is the coordinate of the free end, and n is the number of segments comprising the stem, *i.e.*, the number of segments between the grafting point and the first contact with the $z = 0$ boundary. This boundary is indicated in fig. 1; it is the position of the step in the segment potential (model 1), the edge of the confining cylinder (model 2), the position of the adsorbing surface (model 3).

With this choice, the Landau free energy of the deformed coil is obtained from the Green's function $G_{\mathrm{coil}} = \sqrt{3/(2\pi N)} \exp\left[-3(z_0 - z_N)^2/(2Na^2)\right]$ of a stretched Gaussian chain and expressed as a function of s:

$$
\Phi_{\mathrm{coil}}(s) = \frac{3}{2}s^2 - \frac{1}{2N}\ln\left(\frac{3}{2\pi N}\right) + \Delta\Phi\,, \tag{2}
$$

where $\Delta\Phi = u$, $\Delta\Phi = (\pi a/H)^2/8$ and $\Delta\Phi = 0$, for models 1, 2 and 3, respectively. The deformation-dependent contribution is the same for all three models. The parameter $\Delta\Phi$ reflects the effect of the external perturbation of the coil. This is given by the magnitude of the external potential (model 1), or by the compression ratio H/a as known for a Gaussian chain in a slit (model 2) or is identical to zero (model 3). The Landau function for the flower conformation is written as

$$
\Phi_{\mathrm{fl}} = -\frac{1}{N}\ln\left(G_{\mathrm{stem}}Q\right)\,, \tag{3}
$$

where Q is the partition function of the crown, and

$$G_{\text{stem}}(z_0, 0) = \frac{3}{\sqrt{6\pi}} \frac{z_0}{n^{3/2}a} \exp\left[-\frac{3z_0^2}{2na^2} + n\Delta\Phi\right] \tag{4}$$

is the Green's function of a subchain of n segments starting at z_0, ending at the $z = 0$ boundary, and making no other contacts with the outer region. The partition function of the crown needed for model 1 was calculated in [10] to be $Q_1 = \exp\left[-u(N-n)/2\right] I_0\left(u(N-n)/2\right)$, where I_0 is the modified Bessel function. In model 2, the crown is just an ideal coil anchored at an impenetrable surface, its partition function being $Q_2 = (6\pi(N-n))^{-1/2}$. Finally, in model 3, the crown is a subchain anchored at an adsorbing surface, so its partition function is given by $Q_3 = \exp\left[c^2a^2(N-n)/6\right] \text{erf}c\left(-ca\sqrt{(N-n)/6}\right)$.

Exact expressions for the Landau free energy as a function of the order parameter (and hence, the exact complete partition functions in integral form) are easily available. However, it is much more instructive to use asymptotic expressions of the partition functions for large values of N and discard the terms of the order $\frac{1}{N}\ln N$. Then, the Landau function simplifies to

$$\Phi_1(s, u) = \begin{cases} \frac{3}{2}s^2 + u\,, & s \leq \frac{z_0}{Na}\,, \\ \frac{3}{2}\frac{z_0}{Na}s + u\frac{z_0}{Nas}\,, & s \geq \frac{z_0}{Na}\,, \end{cases} \tag{5}$$

$$\Phi_2(s, H) = \begin{cases} \frac{3}{2}s^2 + \frac{\pi^2 a^2}{8H^2}\,, & s \leq \frac{z_0}{Na}\,, \\ \frac{3}{2}\frac{z_0}{Na}s + \frac{\pi^2 a^2}{8H^2}\frac{z_0}{Nas}\,, & s \geq \frac{z_0}{Na}\,, \end{cases} \tag{6}$$

$$\Phi_3(s, c) = \begin{cases} \frac{3}{2}s^2\,, & s \leq \frac{z_0}{Na}\,, \\ \frac{3}{2}\frac{z_0}{Na}s - \frac{c^2 a^2}{6} + \frac{c^2 a^2}{6}\frac{z_0}{Nas}\,, & s \geq \frac{z_0}{Na}\,, \end{cases} \tag{7}$$

for models 1, 2, and 3, respectively. The branch of the coil (cf. eq. (2)) and that of the flower (cf. eq (3)) meet at the point $s_0 = z_0/Na$.

The equivalence of the first two models is immediately obvious upon substituting $u \leftrightarrow (\pi^2 a^2)/(8H^2)$. The equivalence of models 1 and 3 is also clear upon substituting $u \leftrightarrow (c^2 a^2)/6$ and downshifting both branches of the Landau free energy of model 1 by the constant u.

From eqs. (5)-(7) it follows that the coil branch of the Landau function does not change by itself, but the position of the matching point of the two branches is a function of z_0/Na.

Phase diagram. – Taking model 1 as an example, it is clear that within a certain range of the two governing parameters z_0/Na and u there are two minima of the Landau function. The minimum at $s = 0$ corresponds to the coil state. The second minimum describing the flower state is found at $s_{\text{fl}} = \sqrt{2u/3}$. The binodal condition occurs when the two minima are equally deep. This leads to

$$\frac{z_0^*}{Na} = \sqrt{u^*/6}\,. \tag{8}$$

In the thermodynamic limit, $N \to \infty$, this defines the line of the first-order phase transitions. With an increase in the reduced grafting distance z_0/Na, or with the decrease in the potential magnitude u, the flower state becomes metastable. Once the position of the minimum of the flower state s_{fl} coincides with the barrier position z_0/Na, the metastable state disappears. This gives the equation of one of the spinodal line branches:

$$\frac{z_0^{**}}{Na} = \sqrt{\frac{2u^{**}}{3}} = 2\frac{z_0^*}{Na}\,. \tag{9}$$

To visualize metastable flower states more clearly it is instructive to find the number of segments belonging to the stem in the region between the binodal and the spinodal lines. From eqs. (1) and $s_{\rm fl} = \sqrt{2u/3}$ it follows that $n = z_0/(as_{\rm fl}) = (z_0/a)\sqrt{3/(2u)}$. Along the binodal line this gives $n^* = N/2$. Along the spinodal line it is found that $n^{**} = N$. This means that at the spinodal point the crown vanishes. We conclude that a metastable flower has more that one half of its segments in the stem, and the smaller the crown is, the closer we are to the spinodal.

The second spinodal branch describes the situation in which the coil state becomes unstable. The height of the barrier counted from the coil state minimum is just $(3/2)kTz_0^2/(a^2N)$. Equating this to kT, we find

$$z_0^{++} = \left(\frac{2}{3}N\right)^{1/2} a = 2R_{\rm g} \,, \tag{10}$$

where $R_{\rm g} = a\sqrt{(N/6)}$ is the gyration radius. The physical meaning of this spinodal branch is very transparent: the coil state becomes unstable once it can easily "touch" the energetically favorable region.

The phase diagram has in the $N \to \infty$ limit a very simple form once the coordinates $(z_0/Na, \sqrt{u})$ are used: it consists of two straight lines defined by eqs. (8), (9), while the spinodal branch of eq. (10) degenerates into $z_0^{**}/Na = 0$. Obviously, finite N effects are very important in view of practical applications. The coordinates that are more convenient to account for the finite size of a macromolecule turn out to be $\left(z_0/R_{\rm g}, \sqrt{uN}\right)$. The binodal line equation with finite-size corrections has the form $z_0^*/R_{\rm g} = \sqrt{u^*N} + \ln 2/\sqrt{u^*N}$. The two branches of the spinodal are $z_0^{**}/R_{\rm g} = 2\sqrt{u^{**}N}$ and $z_0^{++}/R_{\rm g} = 2$. Due to finite N effects each of these lines is broadened: for the binodal line, the thickness is $\sim (uN)^{-1/2}$, while for the spinodal lines, the thickness is of order unity. For the escape transition of a compressed chain, the coordinates would be $(z_0/R_{\rm g}, a\sqrt{N}/H)$, while for the adsorption problem these are $(z_0/R_{\rm g}, ca\sqrt{N})$.

Barrier heights separating stable and metastable states. – The analytical expressions for the Landau function allow us to describe the free-energy barrier separating the two minima. The barrier height counted from the coil state minimum is simply

$$\Delta_{\rm coil} = \frac{3}{2}\frac{z_0^2}{Na^2} = \left(\frac{z_0}{2R_{\rm g}}\right)^2 = F_{\rm str} \,. \tag{11}$$

The barrier height counted from the flower state minimum, when $\sqrt{\frac{2u}{3}} \geq \frac{z_0}{Na}$, is given by

$$\Delta_{\rm fl} = \frac{3}{2}N \left(\sqrt{\frac{2u}{3}} - \frac{z_0}{Na}\right)^2 = \left(\sqrt{F_{\rm str}} - \sqrt{F_{\rm conf}}\right)^2 \,, \tag{12}$$

where $F_{\rm conf} = uN$. The barrier height as counted from the metastable (upper) minimum controls the lifetime of the metastable state. It follows from eq. (11) that the metastablity of the coil state is, *e.g.*, in model 2, not affected by H, as long as one does not cross the binodal line (this is valid only for Gaussian chains). The decay rate of the metastable flower is determined by the difference $\exp\left[-\left[\pi\sqrt{3}R_{\rm g}/2H - z_0/2R_{\rm g}\right]^2\right]$ and increases with separation H, while the decay rate of the metastable coil is associated with $\exp\left[-[z_0/2R_{\rm g}]^2\right]$.

A more accurate estimate for the characteristic decay time of the metastable states can be obtained from the Fokker-Plank equation formalism. Assuming that the slowest mode is associated with the relaxation of the order parameter and all the other degrees of freedom equilibrate quickly, we write a 1-dimensional Fokker-Plank equation for the probability density $P(s,t)$ with $N\Phi(s)$ the Landau function playing the role of the effective potential:

$$\frac{\partial}{\partial t}P(s,t) = \frac{\partial}{\partial s}D(s)\left[\frac{\partial P(s,t)}{\partial s} + P(s,t)N\frac{\partial \Phi(s)}{\partial s}\right] . \tag{13}$$

Here $D(s)$ is the diffusion coefficient along the configuration space path described by the order parameter s. The conventional diffusion coefficient D_z associated with the change in the end-to-end distance of a free-draining chain is $D_z = kT(N\zeta)^{-1}$, where ζ is the friction coefficient per segment. Since the time required for a certain displacement is invariant with respect to changing the dynamic variable, $(\mathrm{d}s)^2/D(s) = (\mathrm{d}z)^2/D_z$ which leads to $D(s) = kTN^{-3}\zeta^{-1}$. The two branches of the Landau function $\Phi(s)$ are given by eqs. (2) and (3).

As follows from the standard analysis of the Fokker-Plank equation [23,24], the mean first passage time τ_{coil} required by the chain initially in the coil state to go to the top of the barrier is

$$\tau_{\mathrm{coil}} = \frac{N^3\zeta}{kT}\int\limits_{0}^{z_0/Na}\mathrm{d}s\,\exp\left[N\Phi_{\mathrm{coil}}(s)\right]\int\limits_{-\infty}^{s}\mathrm{d}q\,\exp\left[-N\Phi_{\mathrm{coil}}(s)\right] . \tag{14}$$

Using the standard approximation of the internal integral by the coil partition function we obtain the final result as: $\tau_{\mathrm{coil}} = \frac{\pi}{3}\tau_{\mathrm{Rouse}}erf(z_0/(2R_{\mathrm{g}}))\mathrm{erf}i(z_0/(2R_{\mathrm{g}}))$, where $\tau_{\mathrm{Rouse}} = N^2a^2\zeta/kT$ is the Rouse fundamental relaxation time, and erf$i$ is the error function on the imaginary axis. For $z_0 \gg R_{\mathrm{g}}$ one obtains

$$\tau_{\mathrm{coil}} \cong \frac{2\sqrt{\pi}R_{\mathrm{g}}}{3z_0}\tau_{\mathrm{Rouse}}\exp\left[\Delta_{\mathrm{coil}}\right] . \tag{15}$$

The spinodal region corresponds to $z_0 \sim R_{\mathrm{g}}$, with τ_{coil} on the order of the Rouse fundamental relaxation time. Similarly, one obtains the mean first passage time for the chain initially in the flower state τ_{fl}. Apart from a near vicinity of the spinodal, the expression reduces to

$$\tau_{\mathrm{fl}} \cong \sqrt{\frac{8\pi}{3}}\frac{z_0\tau_{\mathrm{Rouse}}}{N^2a}\frac{1}{u^2 - \frac{3}{2}\left(\frac{z_0}{Na}\right)^2}\exp\left[\Delta_{\mathrm{fl}}\right] . \tag{16}$$

Near the spinodal line the lifetime vanishes as $\tau_{\mathrm{fl}} \cong 2\sqrt{\pi N}/3\tau_{\mathrm{Rouse}}\left(\sqrt{u} - \sqrt{u^{**}}\right)$.

Experimental investigations of conformational transitions on surfaces (model 2 and 3) are in principle feasible by Atomic Force Microscopy (AFM) measurements. It is well documented that such apparatus is sensitive enough to register stretching forces of individual polymer chains [25–27]. Moreover, in such apparatus the time by which the chain is confined can be varied. This gives interesting possibilities to measure barrier crossings events implying the occurrence of hysteresis effects. The experiments will not be easy. For example, it is important to work with energetically homogeneous surfaces, *i.e.* in model 3 [28], or with well-defined geometries (model 2) [29].

Conclusions. – Conformational transitions of single macromolecules near interfaces are of interest for tuning material properties. They can, at least in principle, be investigated by AFM experiments. Results of such experiments will give a deep understanding in phase transitions in finite-size systems. Indeed, the polymer system may be a very interesting

model to investigate finite-size effects in phase transitions in general. We have shown that it is possible to give a unified picture of a number of systems in which conformational phase transitions occur. The point which makes this possible is the strong analogy between the structure of not only the partition function but also the Landau free energy as a function of the order parameter. The identification of the stretching function as the order parameter in the systems is the key that allows us to accurately analyse the lifetime of metastable states and gives an insight into the existence of hysteresis effects.

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