

Negative compressibility and nonequivalence of two statistical ensembles in the escape transition of a polymer chain

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An end-tethered polymer chain compressed between two pistons undergoes an abrupt transition from a confined coil state to an inhomogeneous flowerlike conformation partially escaped from the gap. This phase transition is first order in the thermodynamic limit of infinitely long chains. A rigorous analytical theory is presented for a Gaussian chain in two ensembles: (a) the H -ensemble, in which the distance H between the pistons plays the role of the independent control parameter, and (b) the conjugate f -ensemble, in which the external compression force f is the independent parameter. Details about the metastable chain configurations are analyzed by introducing the Landau free energy as a function of the chain stretching order parameter. The binodal and spinodal lines, as well as the barrier heights between the stable and metastable states in the free energy landscape, are presented in both ensembles. In the loop region for the average force with dependence on the distance H (i.e., in the H -ensemble) a negative compressibility exists, whereas in the f -ensemble the average distance as a function of the force is strictly monotonic. The average fraction of imprisoned segments and the lateral force, taken as functions of the distance H or the average H , respectively, have different behaviors in the two ensembles. These results demonstrate a clear counterexample of a main principle of statistical mechanics, stating that all ensembles are equivalent in the thermodynamic limit. The authors show that the negative compressibility in the escape transition is a purely equilibrium result and analyze in detail the origin of the nonequivalence of the ensembles. It is argued that it should be possible to employ the escape transition and its anomalous behavior in macroscopically homogeneous, but microscopically inhomogeneous, materials. © 2007 American Institute of Physics. [DOI: [10.1063/1.2406075](https://doi.org/10.1063/1.2406075)]

INTRODUCTION

When an isotropic pressure is applied to some material, it is expected that it reduces the material dimensions. This behavior corresponds to a positive compressibility. Although this response is found for simple systems, such as a gas, some crystalline materials exhibit a negative compressibility in one or more dimensions.¹ Also in soft-condensed matter this behavior may be found, e.g., the bilayer membrane is known to expand its thickness upon an increase of the pressure.² Materials with a negative linear (or surface) compressibility may have interesting applications and therefore this effect enjoys considerable interest.^{1,3,4} It is believed that a specific set of conditions should be met before it is possible to find this unexpected behavior: confinement, dilatation, and spatial anisotropy.³ In this paper we consider a system which meets these requirements and report on the possibility that there exists a sudden and pronounced negative compressibility, in particular, when the system suffers a phase transition. Our system features a polymer chain which, due to the many segments along the chain, can be seen as a thermodynamic system in itself. This polymer chain is grafted with one of its

ends onto a surface and compressed by a piston. Upon compression it suffers an escape transition, wherein its conformations change abruptly from a confined coil to a partially escaped flower. We study this transition in two conjugate ensembles, namely, the constant confinement and the constant force ensembles.

According to statistical mechanics there is an equivalence of different statistical ensembles in the appropriate thermodynamic limit, including the special regions at or near a phase transition in the phase diagram.⁵ Another general theorem of statistical mechanics states that the equilibrium pressure is a monotonic nonincreasing function of the volume, which means that the compressibility cannot be negative.⁶ Note that the above mentioned systems with negative linear (or surface) compressibility should have a positive compressibility in the other dimension(s) such that overall the system obeys the compressibility theorem. We show in this paper, however, that the escape transition does not obey the compressibility theorem and gives different results for the two complementary ensembles. As we solve the partition function exactly, it is possible to elaborate on the origin of these anomalies.

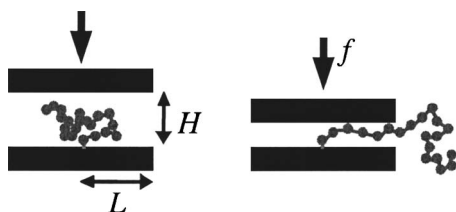


FIG. 1. The simplest model describing the situation in the atomic force microscopy: a grafted polymer chain compressed between two pistons. The radius of the piston L , the distance between the two surfaces H , and the compression force f are indicated. On the left, the chain is only weakly compressed. On the right, the chain has a flower conformation.

One may argue that our system (a single chain in a confined environment) is exotic. However, one of the emerging research areas in soft-condensed matter physics is the manipulation of individual polymer chains by atomic force microscopy, magnetic levitation force microscopy, photonic force microscopy, and by using optical tweezers and the surface force apparatus.^{7–12} Using these methods it is possible to measure the elasticity of materials at the molecular level. This exciting possibility gives an impulse to the new and expanding field of nanomechanics. Thus far, most of the work has been conducted on biopolymers such as polymerase, xantan, proteoglycans, and others.^{13–16} Fascinating examples of the single-chain manipulations are the twisting of DNA molecules by applying an external torque, and the separation of double stranded DNA into two single strands.¹⁷ Similar research for synthetic polymers is just beginning.^{18–21}

We can thus envision a force spectroscopy experiment, wherein a single polymer chain, with contour length of ~ 100 – 200 nm, is tethered to an inert, nonadsorbing, surface and compressed by the probe tip with a radius of curvature of ~ 20 – 50 nm. In this example it is relevant that the radius of curvature is larger than the radius of gyration of the isolated chain $R_g \sim 10$ – 15 nm. As we will see, this is a prerequisite to find a well-defined conformational transition upon confinement. A theoretical description capturing the essential features of this setup may start with a model wherein an end-fixed polymer chain, with contour length Na , is compressed between two cylindrical pistons of radius L , see Fig. 1.

If the parameters satisfy the conditions $Na > L > R_g$, a phenomenon that was named the escape transition can occur upon progressive squeezing of the polymer between the pistons. At weak deformations the chain is compressed uniformly into a relatively thick pancake (left side of Fig. 1). The resistance force increases monotonously as the distance H between two pistons decreases. Beyond a certain critical compression, the chain conformation changes abruptly. One part of the chain forms a stem stretching from the anchoring point to the piston edge, whereas the remainder of the segments forms a coiled crown outside the pistons, thus escaping from underneath the piston (right side of Fig. 1). The resistance force decreases abruptly, indicating a first-order transition. The escape transition was studied rather extensively both by analytical^{22–26} and numerical^{27–36} methods.

A Monte Carlo simulation by Milchev *et al.*³² of the escape transition for an off-lattice bead-spring model demon-

strated that the density profile at the transition point is, indeed, bimodal as expected for a first-order transition. The force-deformation curve was found to be nonmonotonic, resembling the van der Waals loop and implying a negative compressibility within a certain deformation range. A general theorem of statistical mechanics, however, states that the equilibrium pressure has to be a monotonic nonincreasing function of the volume and the compressibility cannot be negative.^{5,6} A loop in the pressure-volume curve (corresponding to a concave region in the thermodynamic potential) indicates that the homogeneous state is unstable and the true equilibrium is achieved as a phase-segregated state. The properties of the pure phases and their relative volumes are obtained by the well-known Maxwell construction for the pressure-volume isotherm or by the double tangent construction for the thermodynamic potential.⁵ The pressure in the phase-segregated state is independent of the volume, thus eliminating the loop and the region of negative compressibility.

Following this general recipe Milchev *et al.*³² “corrected” their force-deformation curves by applying a Maxwell construction. As a result, they had to conclude that a relatively wide transition region should be present instead of a well-defined transition point, in contradiction with their own data. Sevick and Williams³⁰ pointed out that the construction must be misleading since the loop in the force-deformation curves was obtained also from exact numerical calculations³¹ of the partition function for short chains.

A rigorous analytical theory for the equilibrium and kinetic aspects of the escape transition for a Gaussian chain was constructed recently in Ref. 25. The effects of metastability were analyzed by introducing the Landau free energy as a function a suitable order parameter. It was demonstrated that the loop in the force-deformation curves corresponds to the true equilibrium in the system and is not related the metastable states. Consequently, no spurious Maxwell construction is needed.

The escape transition was mostly analyzed in the ensemble where the distance H between two pistons serves as an independent parameter (analogous to the canonical NVT ensemble). A scaling approach, describing the escape transition in f -ensemble, where the independent parameter is the conjugate force, was developed recently³² and also numerical calculations for short polymer chain are available.³⁰ In contrast to the H -ensemble, there is no negative compressibility loop; instead, the force-deformation curve is monotonic, with a flat portion, resembling the normal gas-liquid coexistence. Although this seems to be in line with the standard thermodynamic expectations, there appears a new problem: the two conjugate ensembles produce different results. This is in conflict with yet another general theorem of statistical mechanics stating the equivalence of various statistical ensembles (including the phase coexistence regions in the phase diagram) in the appropriate thermodynamic limit.⁵

In previous work^{25,26} we have mainly concentrated on results for the escape transition in the H -ensemble. In this paper we aim to bring together results for the escape transition for Gaussian chains in both the H - and f -ensembles. We prove the qualitative *differences* in the behavior of thermo-

dynamic properties of the system in the two ensembles and we discuss the origin of this nonequivalence. Some preliminary discussion on this topic can be found elsewhere.²⁶ We visualize the metastable and the coexisting states in the escape transition and analyze the origin of the negative compressibility region as obtained from the equilibrium canonical partition function.

ESCAPE TRANSITION IN THE H -ENSEMBLE

General equations

We consider an ideal Gaussian chain consisting of N segments, attached on one end at the center between two pistons of radius L (cf. Fig. 1). Clearly only the radial direction is of interest here. A short-range repulsive force exists between the chain segments and the surfaces of the pistons. It was shown^{25,30} that the confinement effect of the pistons is equivalent to an effective potential per segment in $k_B T$ units $u = \frac{1}{6}(\pi a/H)^2$. The nature of this effective potential is purely entropic (u is the loss of entropy per polymer segment in slit).

In the continuum limit, the statistical weight $G(N, r)$ of a chain with the N th segment at radial distance r from the symmetry axis satisfies the Schrödinger-type equation in cylindrical coordinates:

$$\frac{\partial}{\partial N} G(N, r) - \frac{a^2}{6} \frac{\partial^2}{\partial r^2} G(N, r) - \frac{a^2}{r} \frac{\partial}{\partial r} G(N, r) + U(r)G(N, r) = 0, \quad (1)$$

where the potential field takes the simple form of $U(r) = u$ for $r < L$ and zero otherwise. The appropriate initial condition $G(0, 0) = \delta(0)$ describes the fact that one end of the chain is attached at $r = 0$. It is convenient to present $G(N, r)$ as a sum of two terms: G_{coil} for the imprisoned coil conformations (that is, the part of the chain that is within the gap between the two surfaces) and G_{flower} for the partially escaped flower conformations. For the imprisoned coil, the solution of Eq. (1) can be found using the standard reflection method. The result can be written as

$$G_{\text{coil}}(N, r) = \frac{3r}{a} \exp\left(-\frac{3r^2}{2Na^2} - Nu\right) \times \left\{ 1 - \left(1 - \frac{L}{Na}\right) \exp\left(-6\frac{L}{Na} \left(\frac{L-r}{Na}\right)\right) \right\}. \quad (2)$$

Here it was assumed that the “reflected” part of the solution is, in all cases, a very small correction since $L \gg R_g$, and therefore, the cylindrical boundary can be treated as planar.

The Green’s function of the stem having n units is known.³⁶ The result for the case of cylindrical geometry of the space between two pistons has the form

$$G_{\text{stem}}(n, L) = \frac{3L^2}{na^2} \exp\left(-un - \frac{3L^2}{2na^2}\right). \quad (3)$$

The partition function of an $(N-n)$ -segment crown end fixed at the point where the potential u drops to zero, was calculated exactly in Ref. 36 and is given by

$$\begin{aligned} Q_{\text{crown}}(N-n, u) &= \exp\left(-\frac{u(N-n)}{2}\right) I_0\left(\frac{u(N-n)}{2}\right) \\ &\approx 1 - u(N-n)/2 \quad \text{for } u(N-n) \ll 1 \\ &\approx (\pi u(N-n))^{-1/2} \quad \text{for } u(N-n) \gg 1, \end{aligned} \quad (4)$$

where I_0 is the modified Bessel’s function.

Order parameter and Landau function

It was suggested in Refs. 23 and 25 that the parameter that characterizes the chain stretching can serve as the order parameter of the escape transition. For the imprisoned coil states, this parameter refers to the chain as a whole, $s = r/Na$, and the Landau free energy is given by $\Phi_{\text{coil}}(s) = -N^{-1} \ln G_{\text{coil}}(N, r)$ with $r = sNa$. Again, the thermal energy $k_B T$ is omitted. For the partially escaped states, only the stem is stretched and the order parameter is defined as $s = L/na$. The stem is the subchain composed of n imprisoned segments, starting from the fixed chain end and ending with the first segment that reaches the edge of the pistons. The two definitions of the order parameter match smoothly at $r = L$ when $n = N$. The other branch of the Landau function, which describes the partially escaped flower states, is written as $\Phi_{\text{fl}}(s) = -N^{-1} \ln(G_{\text{stem}}(n, L) Q_{\text{crown}}(N-n, u))$ with $n = L/as$. Expressing the restricted partition functions $\Phi_{\text{coil}}(s)$ and $\Phi_{\text{fl}}(s)$ in terms of the order parameter s and neglecting the terms of order $N-1$, one arrives at the following simple analytical expressions for the two branches of the Landau free energy:

$$\Phi(s, H) \approx \begin{cases} \frac{3}{2}s^2 + \frac{1}{6}\left(\frac{\pi a}{H}\right)^2 & \text{for } s \leq \frac{L}{Na} \\ \frac{3L}{2Na}s + \frac{L}{6Na}\left(\frac{\pi a}{H}\right)^2 \frac{1}{s} & \text{for } s \geq \frac{L}{Na}. \end{cases} \quad (5)$$

The minima of the Landau function define the average value of the order parameter in the stable or metastable states. The binodal condition is found when the two minima of the Landau function are of equal depth. Then, the two states coexist and the radial density and the free end distribution have a bimodal character.²⁵

The compressed coil minimum is located at $s_{\text{coil}} = 0$ and its depth is given by $\Phi(s_{\text{coil}}) = N^{-1}(\pi R_g/H)^2$. The minimum, corresponding to the escaped flower state, is found at $s_{\text{esc}} = \pi a/3H$, and this minimum is $\Phi(s_{\text{esc}}) = \pi L/NH$. This defines the equilibrium transition line in the H - L plane,

$$H_{\text{tr}} = \frac{\pi R_g^2}{L} = \frac{\pi Na^2}{6L}. \quad (6)$$

If the confinement width H is slightly above H_{tr} , the escaped flower state becomes metastable. With further increase in H , the height of the barrier separating the metastable minimum from the global one decreases and, eventually, metastability is lost. This happens in the spinodal point, when the position of the escaped state minimum, s_{esc} , coincides with the position of the barrier $s_0 = L/Na$. Thus, the spinodal condition is given by

$$H^* = \frac{2\pi R_g^2}{L} \left(1 + \frac{R}{L}\right)^{-1} \approx \frac{2\pi R_g^2}{L} = \frac{\pi N a^2}{3L}, \quad (7)$$

that is, metastability is lost completely when the confinement width is twice as large as that at the equilibrium transition point.

The analytical expressions for the Landau free energy allow us to compute the height of the barrier separating the coil and the escaped-flower minima. The barrier height counted from the coil state minimum, in scaling variables, is simply given by

$$\Delta_{\text{coil}} = \frac{L^2}{4R_g^2} \quad (8)$$

and is interpreted as the elastic free energy of stretching of the chain to the edge of the piston. The barrier height counted from the flower state minimum depends on the proximity to the spinodal and equals

$$\Delta_{\text{fl}} = \frac{L^2}{4R_g^2} \left(\frac{H^*}{H} - 1\right)^2. \quad (9)$$

We have illustrated the Landau function of the coil and flower states as a function of the order parameter graphically in a previous publication²⁵ and we refer to this work for more details.

The partition function and free energy

The full partition function can be obtained by integrating over the order parameter s :

$$Q(H, N) = \exp(-F) = \int ds \exp(-N\Phi(s)). \quad (10)$$

Apart from the preexponential term (which can be neglected as demonstrated by numerical estimates), the result has the following form:

$$Q(H, N) = Q_{\text{coil}} + Q_{\text{fl}} = \text{erf}\left(\frac{L}{2R_g}\right) \exp\left[-\left(\frac{\pi R_g}{H}\right)^2\right] + \exp\left(-\frac{\pi L}{H}\right) \left[1 - \text{erf}\left(\frac{L}{2R_g} - \frac{\pi R_g}{H}\right)\right]. \quad (11)$$

Two asymptotic branches of the free energy $F(H, L, N) = -\ln Q(H, L, N)$ are

$$F(H, L, N) \approx \begin{cases} \left(\frac{\pi L}{H}\right) - \ln 2 & \text{for } H < H_{\text{tr}} \\ \frac{\pi^2 R_g^2}{H^2} & \text{for } H > H_{\text{tr}}. \end{cases} \quad (12)$$

One branch of the free energy can be continued in the metastable region and stops in spinodal point $H=H^*$ at $F(H^*) = (3/2)(L^2/Na^2)$; the other metastable branch formally continues to $H=0$. In the transition point the free energy is equal to $F(H_{\text{tr}}) = 6L^2/Na^2$.

The curve $F(H)$ is not concave within the range of $(3^3/2^5) < H/H_{\text{tr}} < (3^2/2^3)$. However, the standard double-tangent construction cannot be applied, since a simultaneous coexistence of the two phases is impossible due to the very

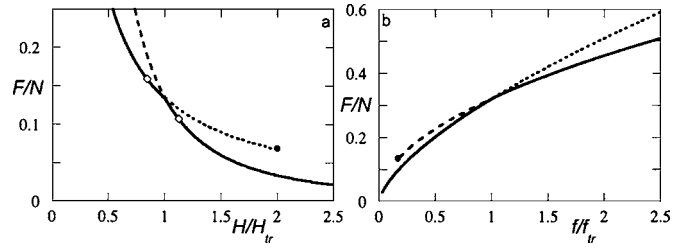


FIG. 2. (a) The Helmholtz energy per segment $F(H, N, L)/N$ as a function of normalized separation distance H/H_{tr} in H -ensemble. (b) $F(f, N, L)/N$ as a function of the normalized compression force f/f_{tr} in the f -ensemble, for $L/a=90$; $N=600$. The equilibrium branches are shown by solid lines; the metastable branches by dashed and dotted lines. The equilibrium branches cross at binodal points $H/H_{\text{tr}}=1$ and $f/f_{\text{tr}}=1$. The spinodal points are at $H^*/H_{\text{tr}}=2$, and $f^*/f_{\text{tr}}=(3/4)$ (Ref. 6) are shown by the solid points. The borders of the concave region of F/N in the H -ensemble are shown by a pair of \diamond .

nature of the phases (see Discussion). The Helmholtz energy per segment F/N as a function of H/H_{tr} is presented in Fig. 2(a) for $L/a=90$ and $N=600$. The equilibrium branches are shown by solid lines and the metastable branches by a dashed and dotted line. The spinodal point is shown by a solid dot. The borders of the region where $F(H)/N$ is not concave are shown by diamonds.

THE ESCAPE TRANSITION IN THE f -ENSEMBLE

Landau function and partition function in force ensemble

Conjugate to the H -ensemble is the ensemble wherein the external compression force f plays the role of the independent variable. The Landau function in the (f, L, N) -ensemble is given by the Laplace transform: $\exp(-N\Phi(s, f)) = \int_0^\infty \exp(-N\Phi(s, H)) e^{-fH} dH$. Using the asymptotes given in Eq. (5) for the Landau function $\Phi(s, H)$, we obtain

$$\Phi(s, f) \approx \begin{cases} \frac{3}{2}s^2 + \frac{1}{2} \left(\frac{3\pi fa}{N}\right)^{2/3} & \text{for } s \leq \frac{L}{Na} \\ \frac{3L}{2Na}s + \frac{(3\pi f)^{2/3}}{2N} \left(\frac{La}{s}\right)^{1/3} & \text{for } s \geq \frac{L}{Na}, \end{cases} \quad (13)$$

with minima at $\Phi_{\text{coil}}(0) = \frac{1}{2}(3\pi fa/N)^{2/3}$ and $\Phi_{\text{fl}}((\pi f/L)^{1/2}a/3) = (2/N)(\pi fL)^{1/2}$ for the coil and flower states, respectively. The binodal and spinodal conditions are

$$f_{\text{tr}} = \frac{4^6}{3^4} \frac{L^3}{\pi N^2 a^4}, \quad (14)$$

$$f^* = \frac{9L^3}{\pi N^2 a^4},$$

and $f_{\text{tr}}/f^* = (4/3)^6 \approx 17$.

The barrier heights for the coil state in the f -ensemble are the same as in the H -ensemble, and are given by $\Delta_{\text{coil}} = 3L^2/2Na$. The barrier height for the flower state is

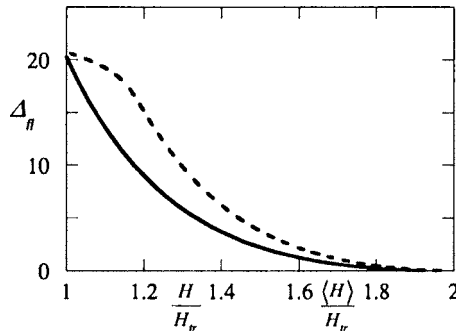


FIG. 3. The barrier heights for the metastable flower state in H - and f -ensembles as a function of normalized compression distance H/H_{tr} (solid line) and as a function of average normalized compression distance $\langle H \rangle/H_{tr}$ (dashed line). Parameters are $L/a=90$ and $N=600$.

$$\begin{aligned} \Delta_{\#} &= \frac{3L^2}{2Na^2} + \frac{(Na^2)^{1/3}}{2} (3\pi f)^{2/3} - 2(\pi fL)^{1/2} \\ &= \left(\frac{L}{2R}\right)^2 + \frac{6^{1/3}}{2} (3\pi fR)^{2/3} - 2(\pi fL)^{1/2}. \end{aligned} \quad (15)$$

The barrier heights for metastable flower state, as a function of compression distance H , and $\langle H \rangle$ in H - and f -ensembles are presented in Fig. 3 for $L/a=90$ and $N=600$. As we can see these two dependencies are similar to each other. Close to binodal points the barriers in the two ensembles have the same heights and decrease to zero at the spinodal points.

The partition function $Q(f, L, N)$ in the f -ensemble can be obtained after integration of $\Phi(s, f)$ on s or as a Laplace transform of Eq. (11). The main terms of the partition functions are

$$\begin{aligned} Q(f, L, N) &\approx \frac{L^{1/4}}{2^{1/2}} \left(\frac{\pi}{f}\right)^{3/4} \exp(-2(\pi fL)^{1/2}) \\ &\quad + (Na^2)^{1/6} \frac{\pi^{3/2}}{(3f)^{2/3}} \exp\left(-\frac{(Na^2)^{1/3}}{2} (3\pi f)^{2/3}\right). \end{aligned} \quad (16)$$

The two asymptotic branches of the free energy $F(f, L, N)$ are

$$F(f, L, N) \approx \begin{cases} 2(\pi Lf)^{1/2} & \text{for } f < f_{tr} \\ 2^{-1}(Na^2)^{1/3}(3\pi f)^{2/3} & \text{for } f > f_{tr}. \end{cases} \quad (17)$$

The free energy $F(f, L, N)$ in the f -ensemble is presented in Fig. 2(b) as a function of the external compression force. One branch of the free energy can be continued in the metastable region and stops in the spinodal point $f=f^*$ at $F(f^*, L, N)/N=6L^2/Na^2$; the other metastable branch formally continues to infinite force.

THE AVERAGE CHARACTERISTICS

The force-distance relations

The average compression force $\langle f \rangle$ in the H -ensemble can be obtained by differentiating the free energy $F(H, L, N)$ with respect to H . The two asymptotic branches are given by

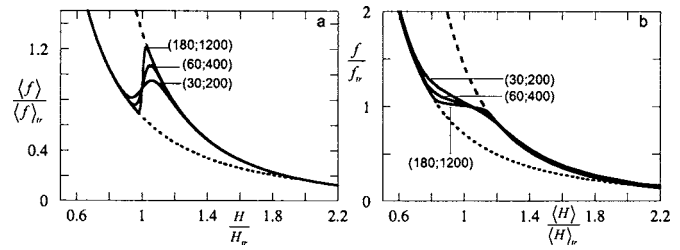


FIG. 4. (a) The average normalized compression force $\langle f \rangle/\langle f \rangle_{tr}$ as a function of the relative compression distance H/H_{tr} in the H -ensemble. (b) The average compression distance $\langle H \rangle/\langle H \rangle_{tr}$ (plotted on the x axis) as a function of the normalized applied compression force f/f_{tr} (plotted on the y axis) in the f -ensemble. Metastable regions are shown by dotted and dashed lines. Parameters are $(L/a; N)=(30; 200)$, $(60; 400)$, and $(180; 1200)$.

$$\langle f \rangle \approx \begin{cases} \frac{\pi L}{H^2} & \text{for } H < H_{tr} \\ \frac{2\pi^2 R_g^2}{H^3} & \text{for } H > H_{tr}. \end{cases} \quad (18)$$

At the transition point, $\langle f \rangle$ jumps from $2L^3/\pi R_g^4$ to one-half of this value as H is decreased.

In Fig. 4(a) the average compression force in the H -ensemble is given for three sets of parameters $(L/a; N)=(30; 200)$, $(60; 400)$, and $(180; 1200)$ at fixed ratio $L/Na=0.15$. The force is normalized by its average value at the equilibrium transition point taken as $\langle f \rangle_{tr} = \frac{1}{2}((\pi L/H_{tr}^2) + (2\pi^2 R_g^2/H_{tr}^3)) = 54L^3/\pi N^2 a^4$. The dotted and dashed lines are the metastable continuations of the equilibrium lines. The lower branch of metastability runs up to the spinodal point $H^*/H_{tr}=2$.

As expected there is a loop exactly at the region where the Helmholtz energy is concave [see Fig. 2(a)]. For finite systems, the actual magnitude of the jump in the average force ensemble is smaller than the limiting value cited above. At the fixed L/Na ratio the transition becomes sharper with increasing chain length. The region of negative compressibility narrows down and eventually shrinks to a point as the thermodynamic limit is approached. In this limit, the local convexity condition, $\partial^2 F/\partial H^2 > 0$, is satisfied almost everywhere. However, the free energy remains globally concave within a finite range of H due to a kink that develops in the $F(H)$ curve at the transition point.

The average compression distance $\langle H \rangle$ in the f -ensemble is obtained by differentiating the free energy $F(f, L, N)$ with respect to f . The asymptotic branches are

$$\langle H \rangle \approx \begin{cases} (\pi L/f)^{1/2} & \text{for } f < f_{tr} \\ (\pi^2 Na^2/3f)^{1/3} & \text{for } f > f_{tr}. \end{cases} \quad (19)$$

It is easy to show that, at the force corresponding to spinodal conditions, $\langle H(f^*) \rangle = H^*$. Therefore in the spinodal point $\langle H(f^*) \rangle/H_{tr}=2$. Figure 4(b) shows $\langle H \rangle$ as a function of the compression force [for comparison with Fig. 4(a), where we presented the normalized force f/f_{tr} as a function of $\langle H \rangle$]. The region of negative compressibility is absent (as well as the concave region in free energy) in the force ensemble. The monotonic behavior of free energy $F(f, L, N)$ is obvious from the equation for Laplace transform (we will return to this

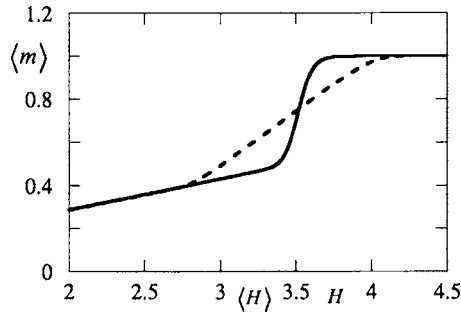


FIG. 5. The fraction of imprisoned segments $\langle m \rangle$ as a function of compression distance H in the H -ensemble (solid line) and as a function of the average compression distance $\langle H \rangle$ in the f -ensemble (dashed line). Parameters are $L/a=60$ and $N=400$.

below). Figures 4(a) and 4(b) show a possible hysteresis loop in a closed compression-decompression cycle. Observing such a loop requires relatively large, but finite, waiting times comparable to the lifetimes of the metastable states discussed above. Note that the hysteresis loop in the f -ensemble is realized by a jump from the metastable to the stable branches at a fixed force (parallel to the x axis), which differs in shape from that in the H -ensemble, where it forms by a jump at fixed H (parallel to the y axis).

As it is easily seen, these ensembles are not equivalent in the region $(3^3/2^5) < H/H_{tr} < (3^2/2^3)$, where the free energy $F(H)$ is not concave [see Fig. 2(a)].

The lateral force

The average lateral force $\langle f_L \rangle$ can be obtained in both ensembles by differentiating the free energies $F(H, N, L)$ and $F(f, N, L)$ with respect to the piston size L . In the H -ensemble the lateral force drops at $H=H_{tr}$ from $\pi/H_{tr} = 6L/Na^2$ to zero, whereas in the f -ensemble it has no drop. The difference between the ensembles exists in the same region as the difference for the compression force.

The average fraction of imprisoned segments

The area under the coil and stem profiles gives us the average number of imprisoned segments which may also be computed by $\langle M \rangle = \partial F / \partial u$. The exact relation between $\langle M(H) \rangle$ and the average compression force $\langle f(H) \rangle$ for a Gaussian chain was obtained in Ref. 25 and has the form

$$\frac{\langle M(H) \rangle}{\langle f(H) \rangle} = \frac{3H^3}{\pi^2 a^2}. \quad (20)$$

Here we present two asymptotic branches for the reduced average fraction of imprisoned segments $\langle m \rangle = \langle M(H) \rangle / N$:

$$\langle m(H) \rangle \approx \begin{cases} 1 & \text{for } H > H_{tr} \\ \frac{3LH}{\pi a^2 N} & \text{for } H < H_{tr}. \end{cases} \quad (21)$$

The difference of the fraction of imprisoned segments $\langle m \rangle$ for the two ensembles is presented in Fig. 5. In the H -ensemble $\langle m \rangle$ is presented as a function of compression distance H . It has a sigmoid form and in the appropriate limit has a jump in H_{tr} as we discussed before. In f -ensemble we

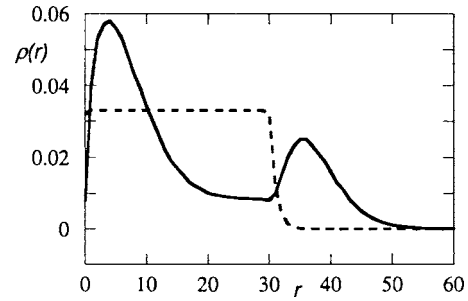


FIG. 6. Radial density profiles for an ideal polymer chain that suffers an escape transition at the binodal (solid line) and spinodal (dashed line) conditions. Piston radius is $L/a=30$ and the number of repeat units is $N=200$.

calculated $\langle m \rangle$ and $\langle H \rangle$ as a function of compression force f , and then plotted $\langle m \rangle$ from the average compression distance $\langle H \rangle$. The values L and N were the same in both ensembles. As we can see in the force ensemble $\langle m \rangle$ increases gradually with increasing $\langle H \rangle$. With increasing N and L , the curve did not become more abrupt. This result resembles the (classical) condensation of a saturated gas upon a decrease of the volume.

Density profile in the escape transition

When we assume that the effect of the boundary is negligible (this is true for $L \gg 2R_g$), the density profile along the radial coordinate (integrated over the vertical z coordinate) in the coil state is given by

$$\rho_{\text{coil}}(\mathbf{r}, N) = N^{-1} \int_1^N \frac{3r}{na^2} e^{-3r^2/2na^2} dn. \quad (22)$$

The volume fraction profile of the flower conformations is the sum of the density profiles of the stem and the crown $\rho_{\text{fl}} = \rho_{\text{stem}} + \rho_{\text{crown}}$. Provided that the crown is large enough to be at least metastable, $R_g^c \gg H$, it does not penetrate back into the interpiston slit. Then the expression for the density profile simplifies to

$$\rho_{\text{crown}}(r) = \frac{1}{2\pi^{1/2} r R_g^c} \left(\text{erfc} \left(\frac{r-L}{2R_g^c} \right) - \text{erfc} \left(\frac{r-L}{R_g^c} \right) \right). \quad (23)$$

The radial density due to the stem can be written rigorously in terms of Green's functions; its asymptotic form is, however, very simple

$$\rho_{\text{stem}}(r) = \frac{3H}{\pi a^2} \quad (24)$$

as it is just the inverse of the local stem stretching (which remains constant throughout the stem). The normalized density profiles for a Gaussian chain in the coil and flower conformations for $N=200$ and $L/a=30$ are shown in Fig. 6. The radial density profile for flower conformations was calculated at the transition point where the number of segments in the stem is equal to $N/2$. The full density profile close to the transition point has a binodal form. Similar results were obtained in Ref. 32 by Monte Carlo simulations. At the spinodal point $H=H^*$, the density profile of flower conformations has no crown part and is almost constant. In Fig. 6 we show a typical result for $L/a=30$ and $N=200$.

Spinodal state and mechanism of nucleation

In the classical theory of nucleation for low-molecular compounds the formation of a new phase is realized through critical nucleation cores. The rate J of formation of such clusters is determined by the work of critical cluster formation $J \sim \exp(-\Delta/RT)$ and depends on the lowest value of the barrier height Δ for a cluster.

In the escape transition the new (escaped) phase emerges via a single nucleus when the free end of the chain reaches the piston edge and forms a seed crown of one or just a few segments; its appearance involves a global change in the chain conformation. This nucleus is at the top of the nucleation barrier, and therefore we have to associate it with the critical nucleus. Contrary to the standard picture of nucleation in classical systems, the critical nucleus in escape transition remains the same irrespective of the external parameters (or the position in the phase diagram), as long as the metastable state does exist. The nucleation barrier height for the metastable coil $\Delta = \Delta_{\text{coil}} = 3L^2/2Na^2$ is determined by the stretching free energy. The picture of the critical nucleus remains exactly the same in other coil-to-flower transitions induced by a stepwise external potential or an adsorbing surface.²³

It is well known that the classical spinodal decomposition occurs via growth of long-wave fluctuations of the order parameter. In contrast to this, the escape transition is adequately described in terms of a single global order parameter. This allows one to construct a simple theory for both equilibrium and kinetic aspects of this phenomenon. The nature of the order parameter also dictates the basic mechanism leading to a decay of an unstable state.

Note that not all single-chain phase transitions are naturally described in terms of a single global order parameter. For instance, in the coil-globule transition the order parameter is the local monomer density. Correspondingly, the kinetics of the coil collapse is governed by the growth and coalescence of multiple nucleation centers, although its initial stage does not necessarily involve any change in the large-scale coil conformation.

DISCUSSION

We have demonstrated that the behavior of a squeezed tethered polymer chain undergoing the escape transition is notably different in two experimental settings, corresponding to two conjugate statistical ensembles.

At this point it is worth mentioning that the nonequivalence between the various statistical ensembles for finite systems (finite chain length N) is standard. The specific property of the escape transition, however, is the nonequivalence of two conjugate ensembles in the thermodynamic limit where both the number of monomer units N and the radius of the piston L tend to infinity, while the ratio L/N remains constant. For finite L and infinite N there is no transition (as well as for finite N and infinite L), because the transition point is proportional to N/L f.c. Eq. (6).

We have further shown that a negative compressibility in the H -ensemble is strictly an equilibrium result that follows from the exact partition function and is not related to un-

stable states. There are several nontrivial issues here which should be addressed. (1) Our results are in obvious contradiction with a theorem of statistical mechanics stating that the pressure must be a monotonic function of volume. (2) Another theorem states that the thermodynamic potential as a function of volume must be convex everywhere. We have seen that the exact free energy in the H -ensemble contradicts this statement. Moreover, in contrast to the region of negative compressibility that shrinks to a single point in the $N \rightarrow \infty$ limit, the region where $F(H)$ is globally concave remains always finite. (3) One of the main principles of statistical mechanics states that all ensembles are equivalent in the thermodynamic limit. The results presented above demonstrate a clear counterexample. (4) The escape transition generated by squeezing a chain between two pistons is fundamentally similar to the behavior of a chain in a step potential or near an adsorbing chain. The equivalence of these three models was demonstrated before and exploited in the present paper. However, no abnormal response functions similar to negative compressibility were found in the other systems.

The theorems of statistical mechanics concerning the monotonic decrease of the pressure and the convexity of the thermodynamic potential as functions of volume are based on a general assumption about the homogeneity of the system in question. The inapplicability of these fundamental theorems to one macromolecule undergoing the escape transition is clearly related to the fact that this system is not homogeneous. The inhomogeneity is a direct consequence of the tethering: since the global translational degrees of freedom are absent, the region near the anchoring point always has a finite monomer concentration, while some volume well outside the pistons is never visited by the chain.

To clarify the other questions, we have to analyze the general properties of conjugate statistical ensembles. In a pair of conjugate ensembles we define a “primary” and “secondary” one in the sense that the partition function of the secondary ensemble is the direct Laplace transform of the partition function in the primary one. In this terminology, for example, the microcanonical ensemble is primary with respect to the canonical ensemble, being conjugate to the total energy; similarly, the NVT ensemble is primary with respect to the NPT ensemble, and the H -ensemble in the escape transition is primary with respect to the f -ensemble.

In the normal standard case, the primary free energy $F(x)$ is convex down with respect to the primary control parameter, x . The equivalence of the two ensembles in the thermodynamic limit follows from the fact that the secondary partition function is dominated by the maximum of the exponent, and therefore, the secondary free energy is given by the Legendre transform

$$\Omega(p) = -\ln \int_0^\infty e^{-F(x)-px} dx = F(x_0) - px_0, \quad (25)$$

where $p = -\partial F(x)/\partial x$ is the conjugate parameter. The convexity condition ensures that the extremum at x_0 is a maximum. The convexity also means that $\partial F(x)/\partial x$ is a monotonically growing function of x and the Legendre transform is uniquely defined.

In the case when the primary free energy is not convex everywhere, the exponent, $-F(x)-px$, may have two maxima. Since in the thermodynamic limit, only one global maximum contributes, the secondary free energy turns out to be the Legendre transform of the convex envelope of $F(x)$ rather than of the primary free energy itself.

For a van-der-Waals fluid in the NVT ensemble, the same convex envelope is created by accounting for phase-segregated states with simultaneously coexisting phases (the double-tangent construction). In our case, simultaneous phase coexistence of a coil and a flower is impossible, $F(H)$ is different from its convex envelope, and this automatically implies the nonequivalence of the two ensembles. The region of negative compressibility corresponds to a small region of H near the transition point where the $F(H)$ curve is locally concave, while the two ensembles are nonequivalent wherever the free energy differs from its convex envelope, see Fig. 2(a).

The whole argument concerning the convex envelope applies only to the primary free energy. The secondary free energy is always a concave function of its variable p , which follows directly from the integral representation for the secondary partition function. Anomalous response functions (similar to negative compressibility) are strictly impossible in the secondary ensemble, irrespective of whether the thermodynamic limit was achieved or not.

We now address the contrast between anomalies observed in the escape transition and the much more standard transitions for a chain in a step potential or near the adsorbing plane, keeping in mind that all three systems were proved to be equivalent. The partition function of the chain in a step potential is defined as

$$Q(u) = \sum_c e^{-m_c u}, \quad (26)$$

where the summation runs over all possible walks (conformations) of the chains, and m_c is the number of segments in the negative half-plane for this conformation. It is clear that we are dealing with the secondary ensemble. As stated before, nothing peculiar happens in the secondary ensemble because its equation of state $m(u)$ is always monotonic.

It is important to note that the unusual results discussed above are not artifacts of the simple Gaussian model employed. Introducing excluded-volume interactions does not affect the qualitative features of the transition. The transition also does not depend on many other details such as the exact position of the grafting point, the geometry and the precise alignment of the pistons (within certain limits), etc. Indeed, the situations when the two conjugate ensembles are nonequivalent are not as exotic as it seems at first glance. As a result, one should be able to observe this unusual behavior in experiments, since the current state of the atomic force microscope spectroscopy has the phenomenon within its reach.

We further can imagine that it is possible to fabricate materials with a macroscopic negative compressibility based on confined polymers. At this stage it is reasonable to formulate some requirements for such materials. Of course, these systems should be microscopically inhomogeneous. Chains with radius R_g should be grafted sparsely onto surfaces that

are a few times larger than R_g (e.g., chains may be grafted onto the faces of clay platelets). Then these surfaces should be stacked such that the chains are trapped, and these stacks must be dispersed in a relatively soft gel swollen by a low molecular weight good solvent. The external deformation will squeeze surfaces closer to each other and, as some critical force, induce the coil-to-flower phase transitions, wherein the chains partially escape to the resin phase. In this transition region the compressibility may be negative and the effects should be much more pronounced than in low molecular weight systems.^{1,3}

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