On the Escape Transition of a Tethered Gaussian Chain; Exact Results in Two Conjugate Ensembles

Alexander M. Skvortsov,[1] *Leonid I. Klushin,*[2] *Frans A. M. Leermakers**[3]

Summary: Upon compression between two pistons an end-tethered polymer chain undergoes an abrupt transition from a confined coil state to an inhomogeneous flower-like conformation that is partially escaped from the gap. In the thermodynamic limit the system demonstrates a first-order phase transition. A rigorous analytical theory of this phenomenon for a Gaussian chain is presented in two ensembles: a) the H-ensemble, in which the distance H between pistons plays the role of the control parameter, and b) the conjugate f-ensemble in which the external compression force f is the independent parameter. A loop region for $\langle f(H) \rangle$ with negative compressibility exists in the H-ensemble, while in the f-ensemble $\langle H(f) \rangle$ is strictly monotonic. The average lateral forces taken as functions of H (or $\langle H \rangle$, respectively) have distinctly different behavior in the two ensembles. This result is a clear counterexample of the main principles of statistical mechanics stating that all ensembles are equivalent in the thermodynamic limit. Another theorem states that the thermodynamic potential as a function of volume must be concave everywhere. We demonstrated that the exact free energy in the H-ensemble contradicts this statement. Inapplicability of these fundamental theorems to a macromolecule undergoing the escape transition is clearly related to the fact that phase coexistence in the present system is strictly impossible. This is a direct consequence of the tethering and the absence of global translational degrees of freedom of the polymer chain.

Keywords: atomic force microscopy; macromolecules; phase transition; statistical theory

Introduction

One of the most inspiring research areas in modern soft condensed matter physics over the past decade has been the manipulations of individual polymer chains by atomic force microscopy, magnetic levitation force microscopy, photonic force microscopy, by optical tweezers and by using the surface force apparatus [1]–[6]. These methods have made it possible to measure the elasticity of materials at the molecular level and led to a new expanding field of nanomechanics. In a typical force spectroscopy experiment a single polymer chain with contour length of ~100–200 nm is tethered to an inert, nonadsorbing surface and compressed or stretched by some probe tip with a radius of curvature of ~20–50 nm. The radius of curvature is larger than the radius of gyration of the isolated chain R_g ~10–15 nm.

A theoretical description capturing the essential features of this setup is based on a model of an end-fixed polymer chain of contour length Na compressed between two cylindrical pistons of radius L, see Fig. 1. Experimentally, preparing pistons with flat parallel surfaces turns out to be quite difficult, but the basic model with cylind-

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[1] Chemical-Pharmaceutical Academy, Prof. Popova 14, 197022 St. Petersburg, Russia
[2] American University of Beirut, Department of Physics, Beirut, Lebanon
[3] Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands
Fax: (+31) 317 48 37 77
E-mail: Frans.Leermakers@wur.nl

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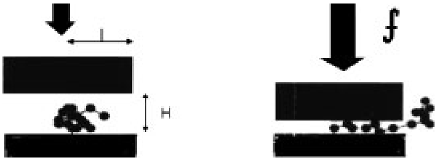

Figure 1.
Schematic representation of the coil-to-flower transition probed in the atomic force microscope setting: a polymer chain is grafted on the lower substrate and is compressed by the top piston. On the left the chain is in the coil state and on the right it has a flower conformation. The piston size *L*, confinement distance *H* and the compression force *f* are indicated.

rical geometry contains all the essential physics.

At weak compressions, the chain is deformed uniformly to make a relatively thick pancake; the resistance force due to the compressed chain increases monotonously as the distance 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, and the remainder of the segments forms a coiled crown outside the pistons, thus escaping from the confinement set by the pistons. The resistance force decreases abruptly, indicating a first-order-like transition. This phenomenon was named the escape transition and was studied by numerical calculations, computer modeling [7]–[12], and by using the scaling approach [13]. A rigorous analytical theory for the equilibrium and kinetic aspects of the escape transition for a Gaussian chain was constructed recently in [14]–[15].

The escape transition was mostly analyzed in the ensemble where the distance H between the two pistons serves as an independent control parameter (analogous to the canonical NVT ensemble). The scaling approach describing the escape transition in f-ensemble, where the independent parameter is the conjugate force, was developed in [12] and numerical calculations for short polymer chains are available in [10]. In this paper we present an analytical theory of the escape transition for Gaussian chains in the H- and f-ensembles. We demonstrate that there exists qualitative differences in the behavior of thermodynamic properties of the system in the two ensembles and discuss the origin of this nonequivalence.

Phase transitions in macromolecular systems can be fundamentally divided into two types. The first type occurs in condensed bulk matter, involves a macroscopically large number of molecules, and is basically similar to that in ordinary fluids or solids. The size of a single molecule plays only a minor role in the equilibrium features of these transitions. Crystallization, segregation of incompatible liquids, and liquid-crystalline ordering can serve as examples [16]–[17]. The size of a single molecule plays only a minor role in the equilibrium features of these transitions. The second type of phase transitions belongs exclusively to the realm of polymers since it is realized at the level of a single macromolecule. That is what we are dealing with here, and this notion requires a conceptually clear understanding. A single macromolecule always consists of a finite, albeit a very large number of segments, while a rigorous definition of phase transitions involve taking the thermodynamic limit. Since the number of segments in a real macromolecule is typically 10^2–10^4, finite-size effects in the single-molecule phase transitions may be significant and have to be addressed. The best-known examples are the coil-globule [18] transition, as well as adsorption at a solid-liquid interface [19]–[21] to which the escape transition was shown to be closely related [14].

The Partition Functions and Free Energies in *H*- and *f*-Ensembles

The full partition function in H-ensemble was obtained in [15] and has the following form:

$$\begin{aligned} Q(H,N) &= Q_{coil} + Q_{fl} \\ &= \operatorname{erf}\left(\frac{L}{2R_g}\right)\exp\left[-\left(\frac{\pi R_g}{H}\right)^2\right] \\ &\quad + \exp\left(-\frac{\pi L}{H}\right)\left[1-\operatorname{erf}\left(\frac{L}{2R_g}-\frac{\pi R_g}{H}\right)\right] \end{aligned} \tag{1}$$

The first term takes into account all coil configurations, when the chain is confined in the inter-piston volume; the second describes escaped configurations consisting of a confined and stretched stem and an unconfined crown.

The two asymptotic branches of the free energy $F(H, L, N) = -\ln Q(H, L, N)$ are (up to the main terms):

$$F(H, L, N) \approx \begin{cases} \left(\frac{\pi L}{H}\right) - \ln 2, & H < H_{tr} \\ \frac{\pi^2 Na^2}{6H^2}, & H > H_{tr} \end{cases} \qquad (2)$$

This defines the equilibrium transition line in the *H*-*L* plane

$$H_{tr} = \frac{\pi Na^2}{6L} \qquad (3)$$

The free energy at the transition point is equal to $F(H_{tr}, L, N) = 6(L/Na)^2$. We have used k_BT as the energy unit and will omit it in the following.

In the conjugate ensemble where the external compression force *f* plays the role of the independent variable instead of the piston separation *H*, the partition function *Q*(*f*,*L*,*N*) can be obtained by the Laplace transform of eqn. (1):

$$Q(f, L, N) = \int_0^\infty Q(H, L, N) \mathrm{e}^{-fH} \mathrm{d}H \qquad (4)$$

Up to the main terms, the partition function is given by:

$$Q(f, L, N) \approx \frac{L^{1/4}}{2^{1/2}} \left(\frac{\pi}{f}\right)^{3/4} \exp(-2(\pi f L)^{1/2}) + (Na^2)^{1/6} \frac{\pi^{3/2}}{(3f)^{2/3}} \exp\left(-\frac{(Na^2)^{1/3}}{2}(3\pi f)^{2/3}\right) \qquad (5)$$

Two asymptotic branches of the free energy $F(f,L,N) = -lnQ(f,L,N)$ are:

$$F(f, L, N) \approx \begin{cases} 2(\pi L f)^{1/2}, & f < f_{tr} \\ 2^{-1}(Na^2)^{1/3}(3\pi f)^{2/3}, & f > f_{tr} \end{cases} \qquad (6)$$

The transition point in the force ensemble is $f_{tr} = \frac{16}{\pi}\left(\frac{4}{3}\right)^4 \frac{L^3}{N^2 a^4}$, and the free energy in the transition point is $F(f_{tr}, L, N) = 8(4/3)^2 (L/Na)^2$.

The Average Lateral Force in the Two Ensembles

The average lateral force $\langle f_L \rangle$ can be obtained in both ensembles by differentiating the free energies *F*(*H*,*N*,*L*) or *F*(*f*,*N*,*L*) with respect to piston size *L*. The corresponding curves of $\langle f_L \rangle$ vs. *H* (in the H-ensemble) and vs. *f* (in the *f*-ensemble) are presented in Fig. 2a,b for the following values of *L* and *N* parameters: (*L*/*a*;*N*) = 40;400, 80;800 and 160;1600. In *H*-ensemble the lateral force drops at $H = H_{tr}$ from $\pi/H_{tr} = 6L/Na^2$ to zero, whereas in *f*-ensemble it jumps at $f = f_{tr}$ from zero to (9/64)(Na/L^2). For comparison, we also present the lateral force $\langle f_L \rangle$ as a function of *H* or $\langle H \rangle$ (in the *H* and *f*-ensembles, correspondingly) in Fig. 2c for (*L*/*a*;*N*) = 160;1600. A difference between the ensembles clearly exists in a certain region around the transition point: in contrast to a jump-wise drop in the *H*-ensemble, the decrease in $\langle f_L \rangle$ as a function of $\langle H \rangle$ in the *f*-ensemble is quite smooth.

Compression Force-Separation Curves in Two Ensembles: $\langle f \rangle$ vs. *H* and $\langle H \rangle$ vs. *f*

The average compression force $\langle f \rangle$ in *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:

$$\langle f \rangle \approx \begin{cases} \frac{\pi L}{H^2}, & H < H_{tr} \\ \frac{\pi^2 Na^2}{3H^3}, & H > H_{tr} \end{cases} \qquad (7)$$

With the increase in *H*, the average force $\langle f \rangle$ jumps from $6^2 L^3/\pi N^2 a^2$ to twice this value at the transition point.

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

$$\langle H \rangle \approx \begin{cases} \left(\frac{\pi^2 Na^2}{3f}\right)^{1/3}, & f < f_{tr} \\ (\pi L/f)^{1/2}, & f > f_{tr} \end{cases} \qquad (8)$$

As *f* is increased, $\langle H \rangle$ drops from $3\pi Na^2/4^2 L$ to 3/4 of this value at the transition point.

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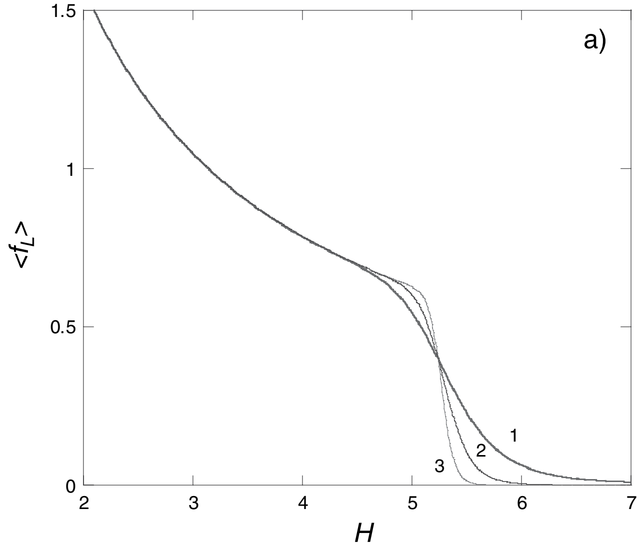
In Figure 3a the curves of the average compression force $\langle f \rangle$ vs. H in the H-ensemble are presented for three sets of the parameters values $(L/a;N) = (40;400)$; (80;800) and (160;1600) at fixed ratio $L/Na = 0.1$. For larger values of N, an upward jump in the average compression force develops near the transition value $H_{tr.}$, and as a result there appears a region of negative compressibility. This region narrows down and eventually shrinks to a point as the thermodynamic limit is approached. The jump magnitude in $\langle f \rangle$ for relatively short polymer chain can be considerably smaller than the limiting value cited above.



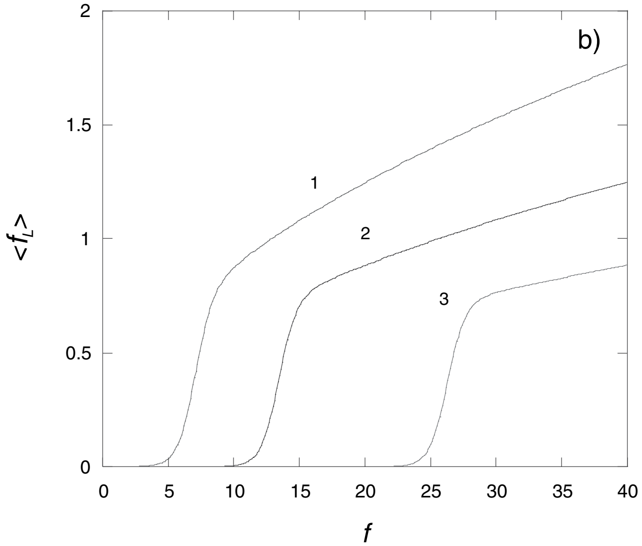


Figure 2.

Average lateral force $\langle f_L \rangle$ as a function of H in the H-ensemble (a) , as a function of f in f-ensemble (b), and as a function of H (solid line) and of $\langle H \rangle$ (dashed line) in both ensembles (c). $(L/a;N) = 40;400$ (1), 80;800 (2) and 160;1600 (3) in (a)–(b). $(L/a;N) = 160;1600$ in (c).

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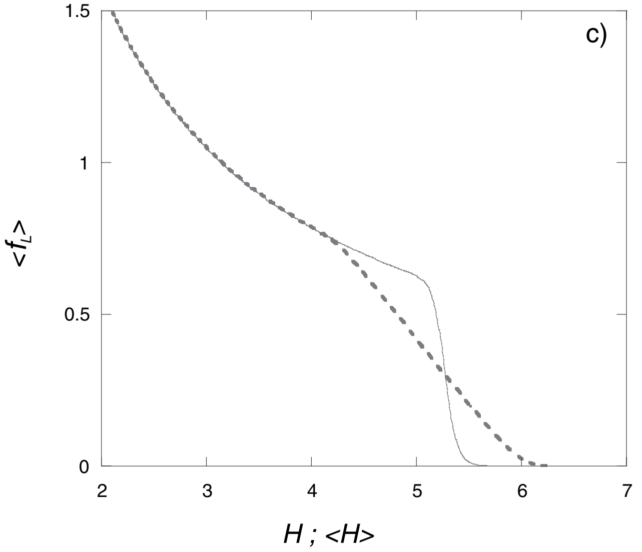

Figure 2. Continued.

Figure 3b shows the inverse curve: $\langle H\rangle$ as a function of the compression force, f, in the force ensemble. The region of negative compressibility is clearly absent.

For comparison, the average compression force $\langle f\rangle$ as a function of the compression distance H in H-ensemble is presented in Fig. 3c together with the compression force f as a function of the average compression distance $\langle H\rangle$ in the f-ensemble at $(L/a;N) = (160;1600)$. The curves of Fig. 3c demonstrate nonequivalence of the two ensembles in the same region that appeared above in the discussion of the lateral force (Fig. 2c).

Convex Region in the Free Energy as a Function of Compression Distance

To understand more clearly the situation of non-equivalence of the two ensembles, we present the Helmholtz free energy in the H-ensemble $F(H,L,N) = -\ln Q(H,L,N)$ as a function of H in Fig. 4.

It is easy to show that the curve $F(H)$ is convex in the range of $(3^3/2^5)H_{tr} < H < (3^2/2^3)H_{tr}$. For $L/Na = 0.1$ ($H_{tr} = 5.236$) this region is equal to $4.42 < H < 5.89$ in agreement with Figs. 2c, 3c. A general theorem of statistical mechanics states that a convex region of the free energy signalizes some sort of phase segregation of the system in this region and the standard double-tangent construction should be applied (it leads to a lower free energy). However, in our case simultaneous coexistence of the two phases is impossible due to the global nature of the phases: at the transition point, the system simply fluctuates as a whole between the two equally probable states (phases). This behavior is not common to low-molecular-mass systems. A unique feature of a macromolecule undergoing the escape transition is the absence of global translational degrees of freedom due to chain tethering. As a result, the convex region of the free energy in the H-ensemble corresponds to true equilibrium. In the f-ensemble, however, such a region is automatically eliminated by the Laplace transform (4).

It is important to note that the results discussed are not the artifacts of the simple Gaussian model employed: introducing the excluded volume interactions does not affect the qualitative features of the transition [12]. Nor do they depend on many other details such as the exact position of the grafting point, the geometry and the

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precise alignment of the pistons (within certain limits). One should be able to observe the unusual behavior described above experimentally since the current state of the AFM spectroscopy has the phenomenon within its reach.

Conclusions

One of the main principles of statistical mechanics states that all ensembles are equivalent in the thermodynamic limit [22]. The results presented above demonstrate a

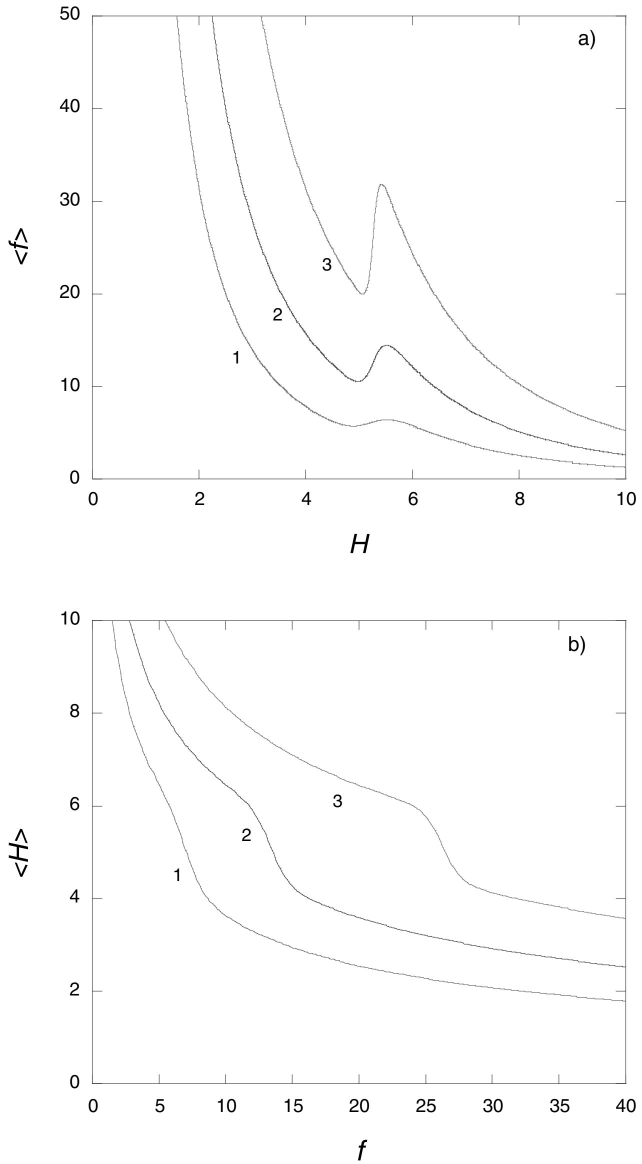

Figure 3.
Average compression force $\langle f\rangle$ as a function of H in the H-ensemble (a), and the average compression distance $\langle H\rangle$ as a function of f in the f-ensemble (b) for $(L/a;N) = 40;400$ (1), $80;800$ (2), and $160;1600$ (3). Comparison the $\langle f\rangle$ vs. H (solid line) and f vs. $\langle H\rangle$ (dashed line) curves in both ensembles at $(L/a;N) = 160;1600$ (c).

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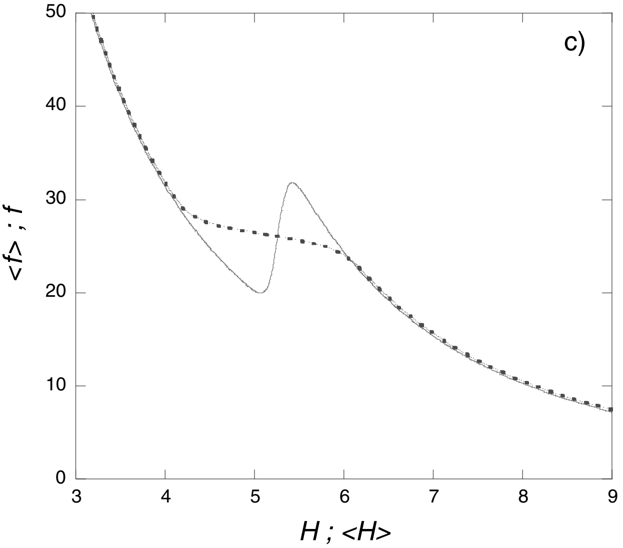

Figure 3. Continued.

clear counterexample of this principle. 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. We have also shown that the negative compressibility in the *H*-ensemble is a strictly equilibrium result that follows from the exact partition function and is not

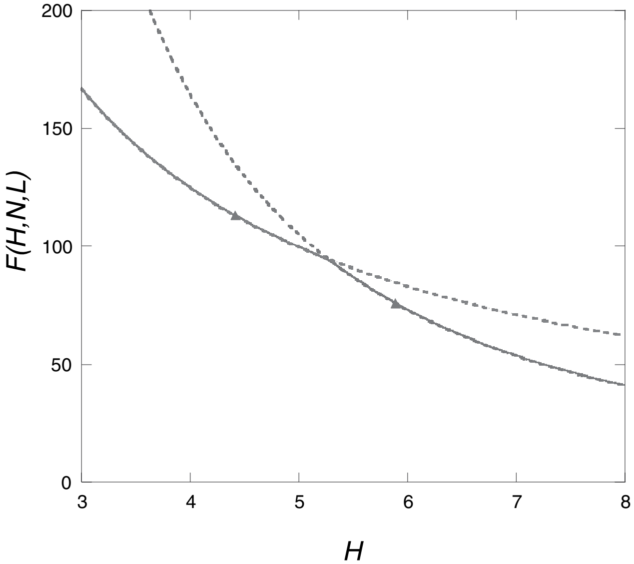

Figure 4.
Helmholtz free energy *F*(*H*,*N*,*L*) in the *H*-ensemble as a function of the separation distance *H* for ($L/a;N$) = 160; 1600. The limits of the convex region are shown by triangles. Two branches of the free energy are shown by dashed lines.

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related to unstable states. These results are in obvious contradiction with a theorem of statistical mechanics stating that the pressure must be a monotonic function of volume [23]. Another theorem states that the thermodynamic potential as a function of volume must be concave everywhere [22]–[23]. We have seen that the exact free energy in the *H*-ensemble contradicts this statement. The theorems of statistical mechanics concerning the monotonic decrease of pressure and the concavity of the thermodynamic potential as functions of volume are based on a general assumption about homogeneity of the system in question. Inapplicability of these fundamental theorems to a macromolecule undergoing the escape transition is clearly related to the fact that phase coexistence in the coil-to-flower problem is strictly impossible. This is a direct consequence of the absence of global translational degrees of freedom due to tethering.

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