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Critical Conditions of Polymer Chromatography

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Abstract

Polymer adsorption is a ubiquitous phenomenon with numerous technological and healthcare applications. The mechanisms of polymer adsorption on surfaces and in pores are complex owing to a competition between various entropic and enthalpic factors. Due to adsorption of monomers to the surface, the chain gains in enthalpy yet loses in entropy because of confining effects. This competition leads to the existence of critical conditions of adsorption when enthalpy gain and entropy loss are in balance. The critical conditions are controlled by the confining geometry and effective adsorption energy, which depends on the solvent composition and temperature. This phenomenon has important implications in polymer chromatography, since the retention at the critical point of adsorption (CPA) is chain length independent. However, the mechanisms of polymer adsorption in pores are poorly understood and there is an ongoing discussion in the theoretical literature about the very existence of CPA for polymer adsorption on porous substrates.

In this work, we examine the mechanisms of chain adsorption on a model porous substrate using Monte Carlo (MC) simulations. We distinguish three adsorption mechanisms depending on the chain location: on external surface, completely confined in pores, and also partially confined in pores in so-called “flower” conformations. The free energies of different conformations of adsorbed chains are calculated by the incremental gauge cell MC method that allows one to determine the partition coefficient as a function of the adsorption potential, pore size, and chain length. We confirm the existence of the CPA for chain length independent separation on porous substrates, which is explained by the dominant contributions of the chain adsorption at the external surface, in particular in flower conformations. Moreover, we show that the critical conditions for porous and nonporous substrates are identical and depend only on the surface chemistry. The theoretical results are confirmed by comparison with experimental data on chromatographic separation of a series of linear polystyrenes.

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1. Introduction

Adsorption of polymer chains on porous substrates is a complex physico-chemical phenomenon relevant to a broad range of applications such as drug delivery, filtration, and adhesion, as well as various separation methods including liquid chromatography of macromolecules. Adsorption of polymeric chains is governed by the competing mechanisms of enthalpic attraction and entropic repulsion¹. At strong adsorption conditions, the enthalpy gained due to adsorption interaction exceeds the entropy loss due to restrictions imposed by confining pore geometry on chain conformations, and chains are predominantly adsorbed. The free energy of adsorbed chains decreases with the chain length and the partition coefficient that determines the concentration of adsorbed chains increases. At weak adsorption conditions, the entropy penalty is prohibitive and chains are effectively repelled from pores. The free energy of adsorbed chains increases with the chain length and the partition coefficient decreases. The transition between strong and weak adsorption is quite sharp, and following the seminal work of de Gennes² and others³⁻⁵ who studied *chain adsorption on plain surfaces*, it is treated as a critical phenomenon, occurring at what is termed the critical point of adsorption (CPA). Skvortsov and Gorbunov (S-G)⁶ demonstrated the CPA conditions during adsorption in pores using the *ideal chain* model without the effect of excluded volume. However, the subsequent molecular simulation studies with more elaborate models of *real chains with excluded volume*⁷⁻⁸ questioned the existence of CPA for polymer adsorption on porous substrates despite the fact that the experimental manifestation of this phenomenon is widespread in polymer chromatography^{1, 9-11}. Here, we investigate this controversy by using Monte Carlo simulations and posit that the critical conditions in polymer chromatography are related to the specific mechanism of partial confinement of chains in so-called flower conformations¹², when only a part of the chain is located inside the pore.

As noted above, the phenomenon of critical adsorption is widely exploited in polymer chromatography. Separation of macromolecules is typically performed on porous substrates. When adsorption is weak (ideally, negligibly small), steric (size exclusion) interactions between the polymer chains and porous substrate provides separation by molecular size. This separation regime is known as size exclusion chromatography (SEC) that is widely used to measure molar mass distribution of polymers. In SEC mode, larger chains are excluded from the

pore volume and elute earlier than their smaller counterparts. When adsorption is strong, in the regime of liquid adsorption chromatography (LAC), adsorption prevails and retention increases with the molecular weight; the order of elution is opposite to that in SEC with larger chains retained more strongly than shorter chains. The intermediate regime of mutual compensation between the attractive adsorption and repulsive steric interactions is called liquid chromatography at critical conditions (LCCC)⁹⁻¹⁰. In LCCC, elution of polymer chains is molecular weight-independent, enabling the separation of polymer fractions by other structural and/or chemical factors, e.g. by the type and number of various functional groups in telechelic polymers¹³. The respective experimental conditions that correspond to the CPA for a given class of polymers can be achieved by variation of either solvent composition or temperature of the polymer solution¹⁴. Although LCCC is widely used for separation of complex polymers and biopolymers by difference in chemical structure, and the critical adsorption conditions are well documented for many systems, the mechanisms of chain adsorption on porous substrates are still poorly understood and the conclusions derived from different theoretical models are controversial.

Detailed analyses of critical adsorption on non-porous surfaces were performed by using various theoretical and computational models^{3-6, 12, 15-20}. The underlying theory of LCCC on porous substrates was suggested by Skvortsov and Gorbunov (S-G)⁶, who considered adsorption of *ideal* chains confined in slit-shaped pores. In modeling studies, the adsorption strength is controlled by the magnitude of the effective interaction energy, U . S-G defined the CPA as the value of $U = U_C$, at which the difference in free energies between adsorbed and unconfined chains vanishes. This condition was interpreted as a complete mutual compensation of the effects of enthalpic and entropic interactions so that the concentration of chains confined in pores equals to the concentration of unconfined chains in bulk solution. They showed that the CPA exists for ideal chains and corresponds to the conditions of molecular weight-independent elution in LCCC.

However, further modeling studies showed that the existence of CPA for chains adsorbed in pores is limited to the ideal chains. In Monte Carlo simulations of real chains with excluded volume, Cifra & Bleha⁷ and Gong & Wang⁸ found that the equilibrium partition between the free unconfined chains in the solution and chains confined within pore channels of several shapes always depends on the chain length regardless of the adsorption potential. These authors suggested to redefine the CPA as the magnitude of adsorption potential, U

$= U_C$, at which the partition coefficient varies the least with the chain length. This definition may explain the apparent observation of critical conditions in chromatographic experiments, assuming that the deviations in the partition coefficient are smaller than the limits of experimental accuracy. This conclusion was confirmed by Yang and Neimark¹² who used self-consistent field theory (SCFT) to simulate adsorption of real chains inside spherical cavities.

Another mechanism that may explain the experimental evidence of critical conditions for chain adsorption on porous substrates is the presence of partially confined or ‘flower’ chain conformations^{12, 21-22}. Specifically, it has been shown¹² that when the characteristic chain size exceeds the pore size, the portion of chains completely confined within pores diminishes, as the adsorption potential reduces to its critical value ($U \rightarrow U_C$), and the flower conformations outweigh completely confined states. This effect is accompanied by the adsorption of chains on the external surface of the substrate²⁰, where the chain entropy is significantly increased relative to the pore²³.

In our previous work, the critical conditions of chain adsorption were studied with a MC simulation model of real (excluded volume) chains interacting with non-porous substrates, in particular, in chromatographic columns packed with non-porous particles^{20, 24}. In that case, adsorption occurs *exclusively* on the particle external surface. In this work, we re-examine the phenomenon of polymer adsorption on porous substrates and its application to polymer chromatography using the same MC simulation model that was used. We explore the chain adsorption taking into account three general mechanisms¹²: adsorption on the external surface, complete adsorption inside pores, and partial adsorption in pores in flower conformations, see Fig. 1. We determine the critical conditions for this model and show that while the CPA does not exist for completely confined chains, it does exist for the chains which are allowed to be adsorbed partially within the pores and on the external surface. Moreover, in the vicinity of CPA, these two adsorption mechanisms (external adsorption and partial confinement) dominate and the fraction of completely confined chains diminishes.

The remainder of this paper is structured as follows. In Section 2, we re-visit the thermodynamic definition of the critical condition of adsorption and show that the CPA implies the equality of the incremental chemical potentials of adsorbed and free chains, rather than the equality of the respective free energies as was

assumed in earlier literature. Section 3 details our MC simulation set-up employed for modeling adsorption of real chains. In Section 4, we study chain adsorption at the plain surface, and show the existence of CPA at a certain value of the effective adsorption potential $U = U_C$. This value is then used as a benchmark to probe the existence of critical conditions for chains completely confined to pores in Section 5. It is shown that, in contrast to ideal chains, the CPA does not exist for real chains completely confined to pores and the partition coefficient of completely confined chains progressively decreases with the chain length. In Section 6, we study the mechanism of partial confinement in flower conformations and calculate the respective partition coefficient, which turns out to be chain length independent at the same critical adsorption potential $U = U_C$, as determined for the external surface. In Section 7, these partition coefficients are combined into an apparent partition coefficient, which is calculated and used to predict the retention volumes of chain molecules on porous adsorbents. Using a simplistic model of a surface corrugated with an array of ink-bottle spherical pores, we calculate the retention volumes for a series of linear polystyrenes separated on a chromatographic column packed with porous particles. The model involves two column parameters, the packing porosity and surface area, which are adjusted to get a quantitative agreement with the experiment. The relative weights of different mechanisms of adsorption are discussed, and it is shown that adsorption on the external surface and in flower conformations are dominant. As the magnitude of the adsorption potential increases to its critical value, the chains are expelled from the pores to the external surface, helping to explain the existence of the CPA for porous substrates. The results are summarized in Section 8.

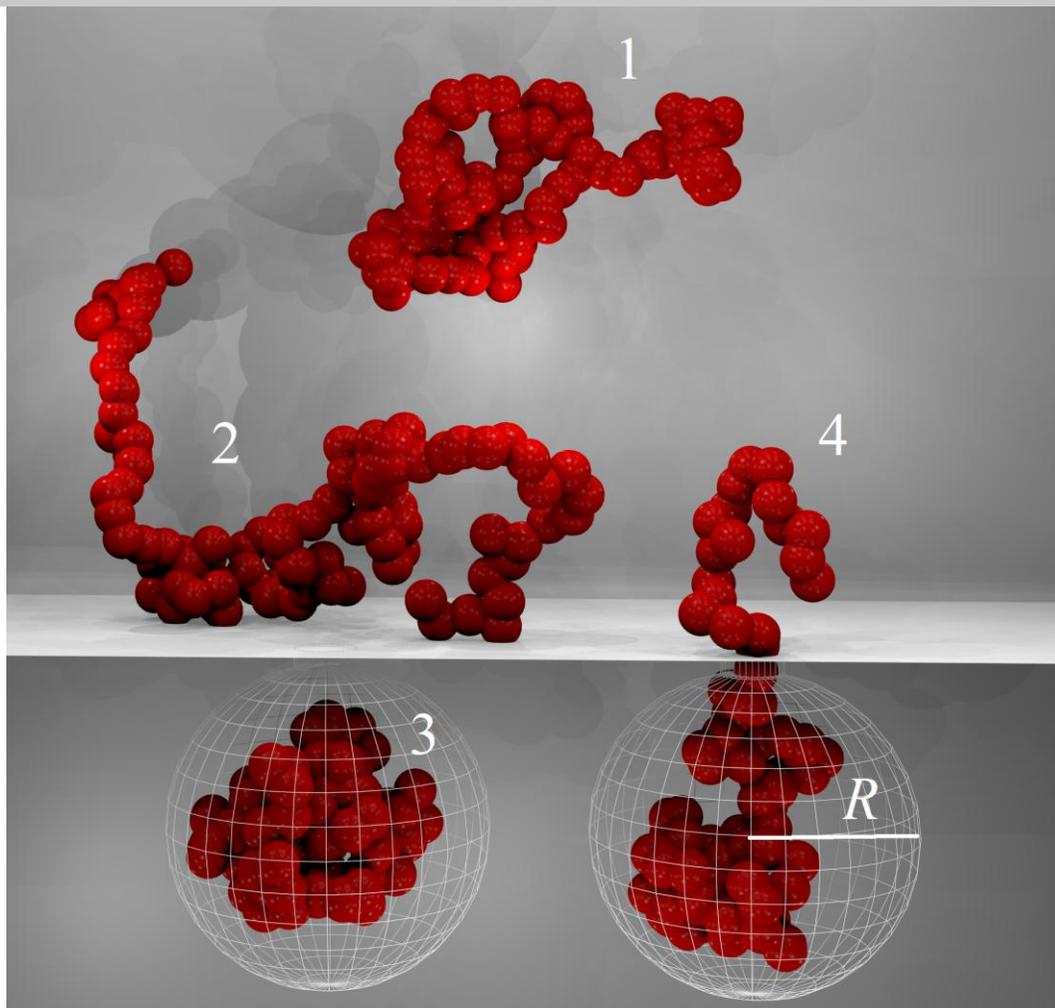


Figure 1. Characteristic conformations of polymer chain interacting with nanoporous substrate: 1 –unconfined chain in bulk solution, 2 – chain adsorbed at the external surface, 3 – chain completely confined within the pore, 4 – partially confined flower conformation.

2. Critical conditions of polymer adsorption

There are several definitions for the critical conditions of adsorption for polymer chains based on various chain properties, i.e. number of adsorbed monomers³, radius of gyration⁴, and chain free energy⁶. The latter definition implies the equality of the excess free energies of adsorbed and free chains, $F(N) = F^0(N)$. This condition is correct for the models of ideal chains, however, for real chains with excluded volume, it holds only in the limit of infinitely long chains. As shown in^{12, 24} in the general case of real chains with exclusion volume, the CPA condition of chain length independent separation requires the equality of the incremental chemical potentials of adsorbed and free chains:

$$\mu_{incr}(N) = \mu_{incr}^0 \quad \text{at CPA for } N > N^* \quad (1)$$

This condition is held provided that the chain length N is sufficiently long, $N > N^*$, (N^* is a certain small number (~ 10) of chain segments²⁵).

The incremental chemical potential defined as the difference between free energies of chains of length $N+1$ and N , $\mu_{incr}(N) = F(N+1) - F(N)$, is a measure of the work necessary to add or remove a segment at the end of a chain²⁶. As such, the free energy of a chain is the sum of the incremental chemical potentials of its constituent segments $F(N) = \sum_{i=0}^{N-1} \mu_{incr}(i)$. For a free unconfined chain, it has been shown previously that the free energy F^0 is a linear function of the incremental chemical potential: $F^0(N) = \sum_{i=0}^{N-1} \mu_{incr}^0(i) + (i - N^*)\mu_{incr}^0$ ²⁶. Similar linear dependence holds also for the chains tethered or adsorbed to a nonporous surface^{12,24}.

The CPA condition (1) follows from the fact that the chain partition coefficient depends on the difference of the excess free energies of adsorbed and free chains, $F(N) - F^0(N) = \Delta F(N)$, which must be chain length independent, but not necessarily null, at the CPA. The latter implies that

$$d \Delta F(N)/dN = 0 \text{ at CPA} \quad (2)$$

and therefore, $\mu_{incr} = \frac{dF(N)}{dN} = \mu_{incr}^0 = \frac{dF^0(N)}{dN}$, confirming Eq. (1). A general derivation of the critical condition (1) is given the *Supporting Information*.

In order to demonstrate the existence of critical conditions on porous substrates, MC simulations were undertaken to calculate the incremental chemical potential of chains of different length at various adsorption states shown in Fig. 1. The incremental chemical potentials were summed to calculate the chain free energies, which were utilized to determine the respective partition coefficients for the three different mechanisms of chain adsorption. The details of the simulation procedure are outlined below.

3. Chain model and simulation methodology

Chain and Adsorbent Models

The polymer molecules are modeled as freely jointed chains of spherical beads of diameter b . Adjacent beads are connected by a harmonic potential $U_b = k(r_{12} - b)^2$ where k is the harmonic spring constant, equal to 50

$k_B T/b^2$ and r_{12} is the center-center distance between the beads. In this model, there is no stiffness or limitation on bond angles or torsions and non-neighbor beads interact via the standard Lennard Jones potential $U_{LJ} = \varepsilon((b/r_{12})^{12} - (b/r_{12})^6)$, where ε is the bead-bead interaction energy, equal to $0.125k_B T$. The number of beads in the chain varies from $N = 1$ to $N = 200$ as in our previous studies^{20, 24}. These chains have corresponding gyration radii of $R_G = 1$ to $10b$ in free solution, calculated during simulation by ensemble average. The free chains approach thermodynamically good solvent conditions, i.e. random-coil conformation with excluded volume interaction, by setting reduced temperature $T^* = k_B T/\varepsilon = 8$, near the athermal limit²⁷. The adsorption interaction between the beads and the surface is modeled by a square-well potential of width b . The same adsorption potential is applied to both the plain surface and the spherical pore walls. The magnitude of the adsorption potential, U , is varied from 0 to $-1k_B T$ to capture the full range of adsorption and exclusion conditions²⁰. All energies mentioned below are in $k_B T$ units.

Simulation Methodology

The chains were equilibrated by a series of 400 million MC displacement, insertion, removal, and configurational bias regrowth²⁸ moves using the standard Metropolis algorithm. The incremental chemical potential of the chains was determined via the incremental gauge cell method²⁵ and averaged over 500 million MC production moves. Free chain radii of gyration were likewise averaged over 500 million MC production moves, after equilibration. Simulation details and the method for determining the critical conditions for different adsorption mechanisms (external surface, complete confinement, and partial confinement) are given below.

4. Determination of the critical point of adsorption on a nonporous surface

The simulation method for determining the CPA follows the procedure outlined in our previous paper²⁰. Chains are anchored by their terminal monomers at distance $z = 0 \dots L$ from the surface of the planar adsorbent measured in b units, where L is sufficiently far from the surface to approximate a free chain. For every z , the incremental chemical potential is measured for each chain length $N = 1-200$ (corresponding to gyration radii $R_G \sim 1 \dots 10b$ in free solution) using the incremental gauge cell method²⁵. The difference between the incremental

chemical potential of the adsorbed chain and a free chain, $\Delta\mu = \mu_{incr} - \mu_{incr}^0$ acts as an indicator of the regime of adsorption.

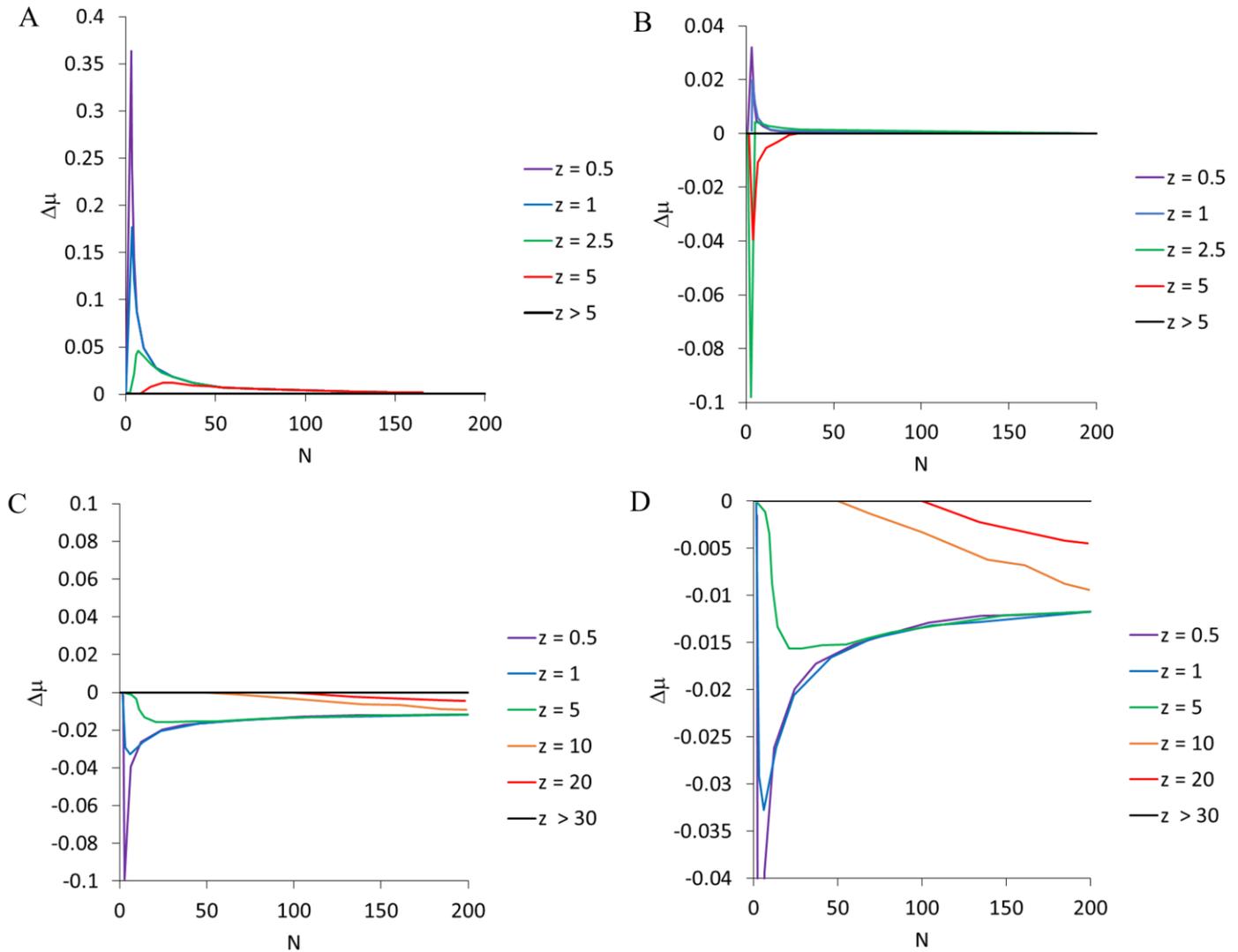


Figure 2. Chain length dependence of the incremental chemical potential difference $\Delta\mu(z, U)$ of anchored chains at several U . A) $U = 0$. B) $U = -0.725$ (CPA), C) $U = -1$. D) Zoom of case C for large N . The range of anchoring distances z varies from 0.5 to 200.

The plots in Fig. 2 show the incremental chemical potential difference $\Delta\mu$ as a function of chain length N for chains anchored at different distances z from the surface. For the case of zero adsorption potential ($U = 0$, Fig. 2. A), $\Delta\mu$ is positive reflecting effective repulsion from the surface due to entropic restrictions. As chains become longer or are anchored farther away from the surface, the surface effect diminishes and the incremental chemical potential tends to that of a free chain. The critical conditions are found for $U = -0.725$ (Fig. 2. B). At

the CPA, the difference in chemical potentials $\Delta\mu = 0$ for all anchoring distances z for chains longer than a certain length $N^*=20$. The chemical potential for chains close to the surface is either slightly positive (for very short chains, which are unlikely adsorbed) or negative (for longer chains, for which the probability of adsorption is higher). Beyond the critical point (Figs. 2. C, D), the incremental chemical potential of the adsorbed chains is negative, since the majority of chains are strongly adsorbed. Interestingly, long chains ($N > 100$) tethered at distances $z = 10-20b$ do come into contact with the adsorption well (see Fig.2.D), indicating the existence of “stretched” states with chain gyration radii exceeding the maximum gyration radius $R_G(N=200) \sim 10b$ of free chains. These “stretched” states (Fig. 1.2) are entropically less favorable than free chains (Fig. 1.1), but their free energy is partially compensated for by the strong adsorption interaction. Notably, the CPA determined by this method is identical to that found by the geometrical method whereby chains tethered directly to the surface are exposed to an increasing potential field²⁴.

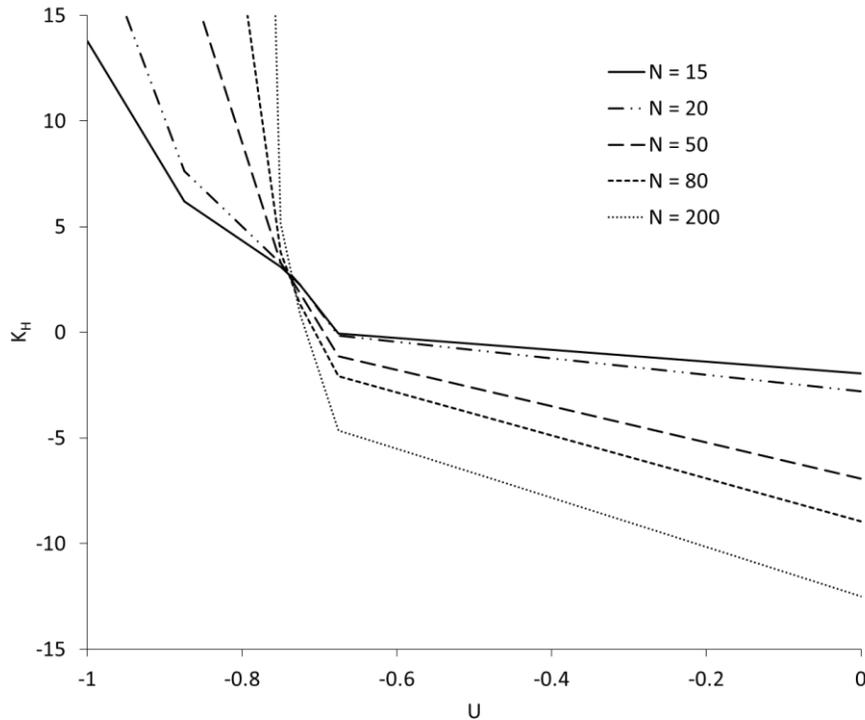


Figure 3. The Henry coefficient $K_H(N)$ computed for a series of characteristic chain lengths ($N = 15-200$) as a function of the adsorption potential U . The intersection point corresponds to the CPA at $U = U_C = -0.725$. Here, K_H is given in units of b .

The transition from weak to strong adsorption conditions and the existence of a well-defined CPA are reflected in the dependence of the Henry adsorption coefficient^{12, 20} on the adsorption potential (see Fig. 3). The Henry coefficient, which represents the ratio of the surface excess concentration of chains c_s to their bulk concentration c_0 , $K_H = c_s/c_0$, is calculated using the following equation¹²:

$$K_H(N) = \int_{z=0}^L [\exp[-(F(N, z) - F^0(N))] - 1] dz \quad (3)$$

Notably, the Henry coefficient K_H has the dimension of length, presented in Eq. (3) and below in terms of Kuhn segments, b , since z is also measured in b . Equation (3) states that the Henry coefficient is the integral of the Boltzmann weighted difference in the free energy of anchored $F(N, z)$ and free $F^0(N)$ chains. The plot of the Henry coefficient K_H as a function of the adsorption potential illustrates several key features of adsorbed chains. For weak potentials, $|U| < |U_C|$, the Henry coefficient is negative, reflecting effective entropic repulsion and respectively, negative excess adsorption. As a consequence, weak potentials produce a significant spread of the Henry coefficient values across different chain lengths. The chains are mostly repelled from the surface in proportion to their size and K_H decreases with chain length. As the adsorption potential approaches the critical condition, $U \sim U_C = 0.725$, the Henry coefficients for all chain lengths intersect at the critical value $K_H \sim 1.25$. At these conditions, which are identical to the case of a tethered chain^{20, 24}, all chains are equally likely to adsorb or to remain free, so the Henry coefficient is chain length-independent. Noteworthy, the critical value of K_H is not zero reflecting the CPA condition of the equality of the incremental chemical potentials rather than chain free energies. Above the critical potential $|U| > |U_C|$ there is a sharp transition wherein the chains become strongly adsorbed to the surface. Smaller chains are less likely to adsorb than larger ones, and so the Henry coefficient increases with chain length.

5. Probing the existence of critical conditions for completely confined chains

The value U_C of the critical potential on the nonporous surface acts as a benchmark to probe the critical point on porous surfaces. In this and the following section, the existence of critical conditions is investigated using simple model pores under two different geometric constraints: complete or partial confinements. It will

be shown that, under specific circumstances, critical conditions exist on porous surfaces and the critical adsorption potential on a porous surface is equal to the critical potential on a nonporous surface.

Adsorption in pores is modeled by confining chains to spherical pores of various sizes. We explore the range of pore radii $R_{pore} = 1.5-6b$ that corresponds to the conditions of strong $R_G/R_{pore} \sim 10$ to moderate $R_G/R_{pore} \sim 2$ confinement for the largest ($N = 200$) chains considered. The adsorption potential at the internal surface of pores is assumed to have the same square-well form as the potential at the external surface.

To demonstrate the effect of pore size on adsorption behavior, we present in Fig. 4 the results of two computational experiments. In the first experiment, chains of lengths $N = 1-200$ were completely confined within pores of a range of pore sizes $R_{pore} = 2, 3, 4, 5$ and $6b$ at $U = U_C$, and the chains were allowed to equilibrate. The incremental chemical potential of these chains was measured and plotted as a function of the chain length (see Fig. 4.A). It is clear from Fig. 4.A that the incremental chemical potential of confined chains is a monotonically increasing function of chain length due to the increasingly prohibitive entropic penalty to insertion of additional beads in a pore volume. The incremental chemical potential intersects the unconfined (free) chain value for some chain length $N = N^*$, (equivalently, gyration radius $R_G = R_G^*$), referred to here as the *critical chain length* and *critical gyration radius*, respectively. At N^* (R_G^*), the enthalpic and entropic interactions are exactly balanced. The values of the critical chain length/gyration radius are dependent on the pore size R_{pore} and decrease progressively as R_{pore} gets smaller. The dependence of N^* and R_G^* on R_{pore} is plotted below in Fig. 4.B.

The critical chain length N^* is quadratic in R_{pore} ($N^* \sim R_{pore}^2$) (equivalently, $R_G \sim N^{0.5}$) indicating that chains of length $N < N^*$ behave as *free chains* in the pore when the adsorption potential is at its critical value, $U = -0.725$. However, any chain larger than N^* will not hold to this scaling, due to the penalty imposed by the positive incremental chemical potential. The dependence of the critical gyration radius R_G^* on the pore size approaches a linear asymptote ($R_G^* \sim R_{pore}$) (Fig. 4.B, solid line) for large pores ($R_{pore} \geq 4$), indicating that as pore size increases, it is possible to directly predict the maximum chain size that will adsorb in the pore. There

is deviation from the asymptote for small pores $R_{pore} \leq 4$, which is explained by the increasing effect of entropic confinement.

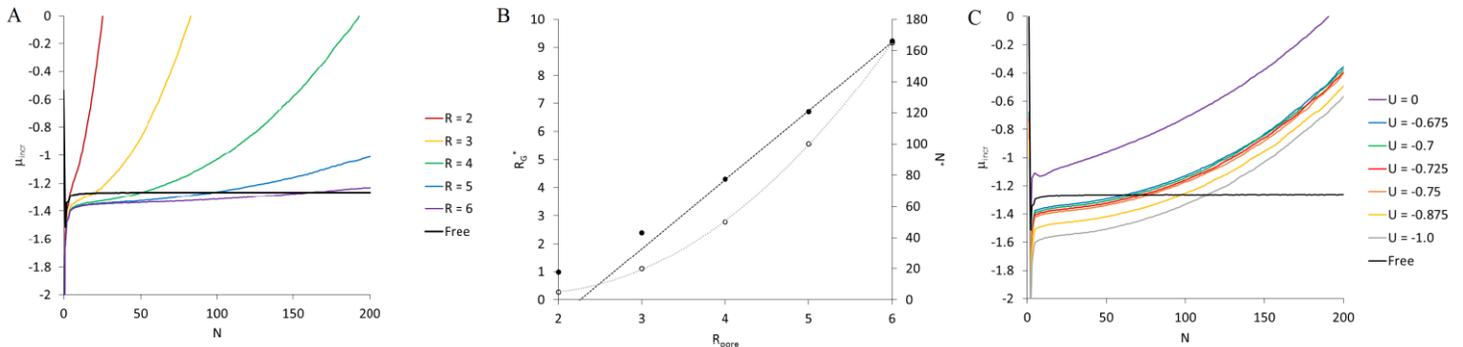


Figure 4. Incremental chemical potential as a function of N for chains of length $N = 1-200$. A - chains confined to pores of size $R_{pore} = 2, 3, 4, 5$ and $6b$ at $U = -0.725$. Black line represents the incremental chemical potential of unconfined ('free') chain. B – Chain length N^* (open circles) and gyration radii R_G^* (closed circles) for which $\mu_{incr} = \mu_{incr}^0$, both as a function of R_{pore} for $U = -0.725$. Solid black line – asymptotic dependence of R_G^* vs R_{pore} for larger pores. Dashed line – parabolic dependence of N^* on R_{pore} . C - Chains confined to a pore of size $R_{pore} = 4b$ for various adsorption potentials U spanning from 0 to -1. Black line represents the incremental chemical potential of unconfined chains.

In the second experiment, the incremental chemical potential of the chains was measured as a function of the adsorption potential U , for a single pore size, $R_p = 4b$ (see Fig.4.C). At this pore size, chains of $N < 50$ beads ($R_G \leq 4$ in free solution) fit comfortably within the pore when exposed to adsorption potential U corresponding to critical conditions on a plain surface $U = -0.725$ (as per Fig. 4.B). However, beyond $N = 50$, the incremental chemical potential increases rapidly with N for all adsorption potentials considered. In the limit of an extremely strong potential, it is conceivable that any chain consisting of $N < 200$ beads could adsorb within the pore. However, the monotonically increasing chemical potential indicates that longer chains ($N \gg 200$) would be totally excluded from this pore.

Fig. 4.C clearly demonstrates the absence of the critical adsorption conditions for this pore. This situation is applied in general case: critical conditions (Eq. 1) do not exist for real chains confined to pores of comparable or smaller size than that of the free chain. The results illustrated in Figs. 4 confirm the earlier findings for excluded volume chains, which were reported for various pore geometries^{8,29}. To further illustrate

this point, the difference in free energy $\Delta F = F(N) - F^0(N)$ and the partition coefficient $K_p = \exp[-\Delta F]$ for chains confined to pores of sizes $R_{\text{pore}} = 1.5b$ and $4b$ are plotted as functions of N in Fig. 5 below.

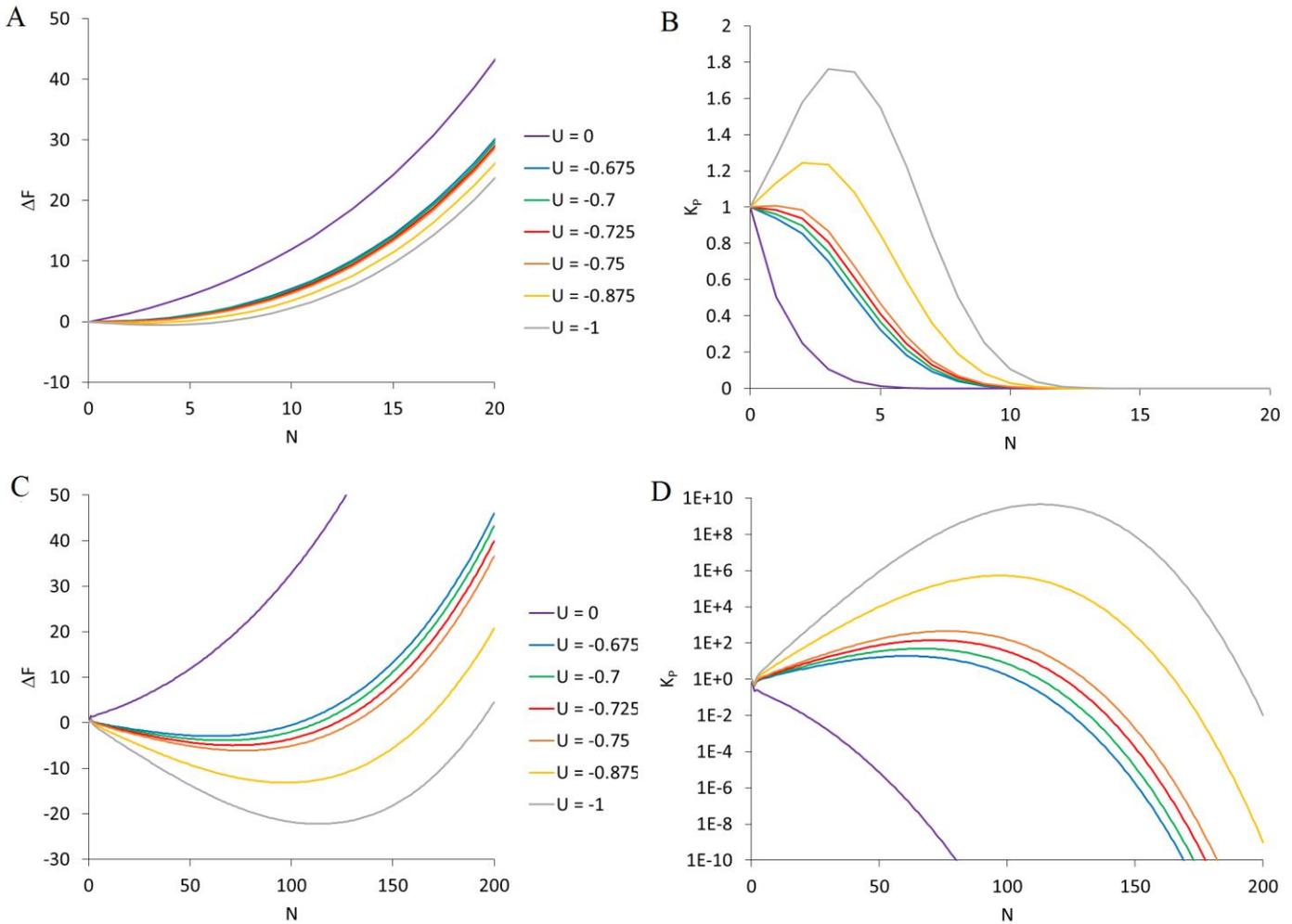


Figure 5. The chain length dependences of the free energy difference $\Delta F = F(N) - F^0(N)$ (A,C) and the respective partition coefficient K_p (B,D) for the chains completely confined to a pore of $R_{\text{pore}} = 1.5b$ (top) and $4b$ (bottom) for a series of adsorption potentials $U = 0$ to -1 .

The difference in free energy ΔF of confined chains plotted in Fig. 5.A,C shows several interesting features. First, in the absence of adsorption ($U = 0$), the free energy is monotonically increasing with N regardless of the pore size. This is consistent with the effect of a pore being gradually filled up with the chain of beads – as the pore fills, the work required to add another bead to the chain increases due to strictly entropic forces. In the presence of an adsorption potential, the shape of the free energy dependence changes dramatically. Instead of being monotonically increasing, the free energy experiences a minimum³⁰, after which

the free energy becomes progressively positive as N increases. This minimum is more pronounced for the larger (4b) pore (Fig. 5.C) than the smaller pore (Fig. 5.A), and the chain length N_M at the point of minimum varies with U and R_{pore} .

The partition coefficient K_P for chains completely confined to pores is defined in terms of the exponent of the difference in free energy of confined and unconfined chains $K_P = \exp[-\Delta F]$. The plots of K_P as a function of chain length (Fig.5, B,D) further illustrate the absence of critical conditions for finite length chains, regardless of pore size. At zero adsorption potential, the partition coefficient monotonically decreases as chain length increases, reflecting the increasing difficulty to force larger excluded volume chains into the pores. In the presence of adsorption potential, the partition coefficient is non-monotonic in a manner similar to the free energy. The partition coefficient increases with chain length for chains, which can fit in the pore with minimal restriction ($N < N_M$). The length N_M of the chains “most likely” residing inside the pore shifts to slightly larger values as adsorption potential increases. However, for $N > N_M$, the partition coefficient rapidly decreases with the chain length for all adsorption potentials due to severe entropic limitations, with the smaller (1.5b) pore (Fig. 5.B) accommodating roughly 10 beads ($R_G = 1.6b$ in free solution), and the larger (4b) pore (Fig. 5.D) up to 40 beads ($R_G = 4b$ in free solution) . The non-monotonic behavior of the partition coefficient reinforces the conclusion that critical conditions do not exist for the real chains completely confined to pores, when pore size R_{pore} is comparable to chain size R_G . This effect would not be observed for ideal chains, for which the CPA does exist³¹. Below, we show that the critical behavior observed in experiments is due to the adsorption mechanisms involving the external surface of the substrate.

6. Partially confined chains

The characteristic chain length N_M mentioned above is of special interest. Provided the pore has an opening, chains of length $N > N_M$ tend to escape from the pore, at least partially, forming so-called flower conformations¹². Depending on the pore size, these partially confined states have been shown to make up a significant portion of chain's conformations¹². A flower conformation consists of a “root” or *trans* section of the

chain residing inside the pore and a “stem” or *cis* section hanging out of the pore. The stem of the flower conformation may either be adsorbed, if the adsorption potential U is strong, or protrude into the bulk solution, if U is weak, see Fig. (6. A, B). Partially confined flower chains help us to explain the presence of critical conditions on porous substrates where the pores are of smaller size than the polymer chains in free solution $R_{pore} < R_G$.

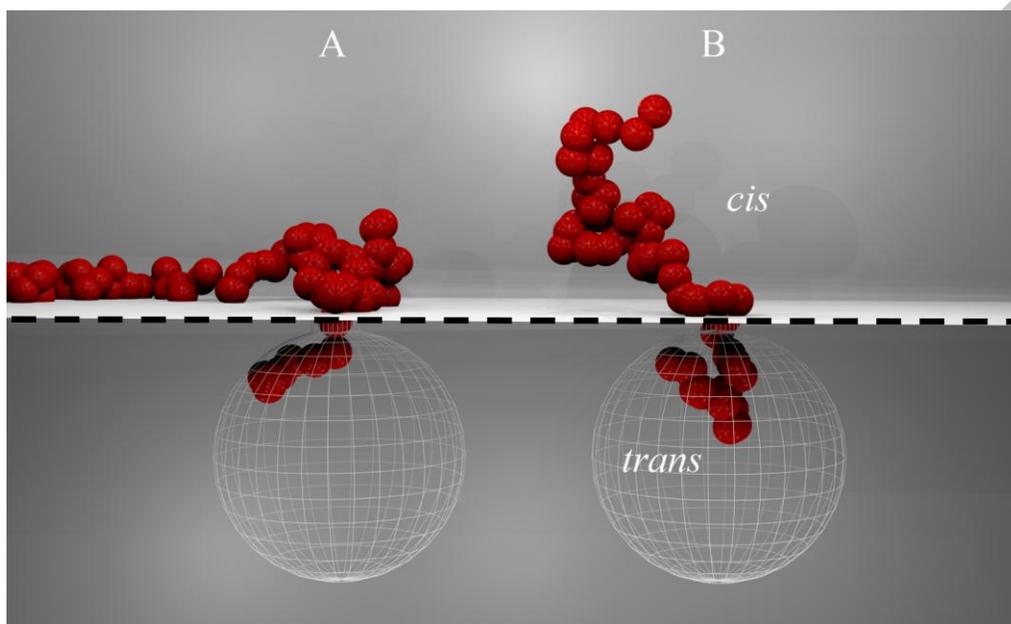


Figure 6. Partially confined chains in two conformations: (A) strong adsorption ($|U| > |U_c|$) and (B) weak adsorption ($|U| < |U_c|$). Dashed line represents delineation between *cis* and *trans* states.

The free energy of partially confined chains was a subject of detailed studies related to the translocation of chain molecules into nanopores^{30, 32}. The free energy of a partially confined chain of length N is presented as a function of the degree of translocation s – the number of monomers inside the pore. The free energy $F(N, s)$ is composed of the free energies of *cis* $F^C(N-s)$ and *trans* $F^T(s)$ subchains: $F(N, s) = F^C(N-s) + F^T(s)$, where *cis* denotes beads outside the pore, and *trans* - inside the pore (See Fig. 6.B). The sub-chain free energies are themselves composed of the sum of the incremental chemical potentials for *cis* and *trans* chains of length $N-s$ and s respectively. For details of the free energy calculations of flower conformations, see *Supporting Information*.

The *cis*- and *trans*- sub-chains are simulated independently, in a manner similar to that used for externally adsorbed or completely confined chains. In each case, sub-chains are tethered by a terminal

monomer with a center distanced $0.5b$ from the surface separating *cis* and *trans* conformations (denoted by the dashed line in Fig. 6). Upon equilibration, the incremental chemical potentials of the *cis* and *trans* sub-chains are measured and the free energies of *cis* $F^C(N-s)$ and *trans* $F^T(s)$ subchains are calculated. The sum of sub-chain free energies gives the free energy $F(N,s)$ of the partially translocated chains with given degree of translocation.

In order to determine the free energy $F(N)$ of the ensemble of flower chains with different degrees of translocation $s = (1 \dots N)$, one has to sum the Boltzmann-weighted free energies $F(N,s)$ of the chains with given degree of translocation¹² :

$$F(N) = -\ln\left(\sum_{s=1}^N \exp(-F(N,s))\right) \quad (4)$$

It is important to note that each state $F(N,s)$ is itself an ensemble average of the chain free energy representing the free energy of the most favorable conformations at given degree of translocation. Fig. 7.A-B below shows the incremental chemical potential and free energy difference $\Delta F = F(N) - F^0(N)$ as functions of the chain length N for chains partially confined to a small pore ($R_{\text{pore}} = 1.5b$) and exposed to different adsorption potentials.

The effect of the pore is evident from the behavior of the incremental chemical potential of the partially confined chains. For all but the smallest chain lengths, the incremental chemical potential is a constant in chain length and resembles the behavior of an end-tethered chain²⁴. For strong potentials $|U| > |U_C|$, where $U_C = -0.725$ is the CPA found previously for non-porous surface, the incremental chemical potential is more negative than that of the free chain, indicating that the *cis* sub-chain is mostly adsorbed (Fig. 7.A). The incremental chemical potential for weak potentials $|U| < |U_C|$ however approaches the free chain value, indicating that most *cis* beads are not adsorbed (see Fig. 7.B). Noteworthy, at $U \sim U_C$, the incremental chemical potential equals that of an unconfined chain, fulfilling the CPA condition Eq. (1).

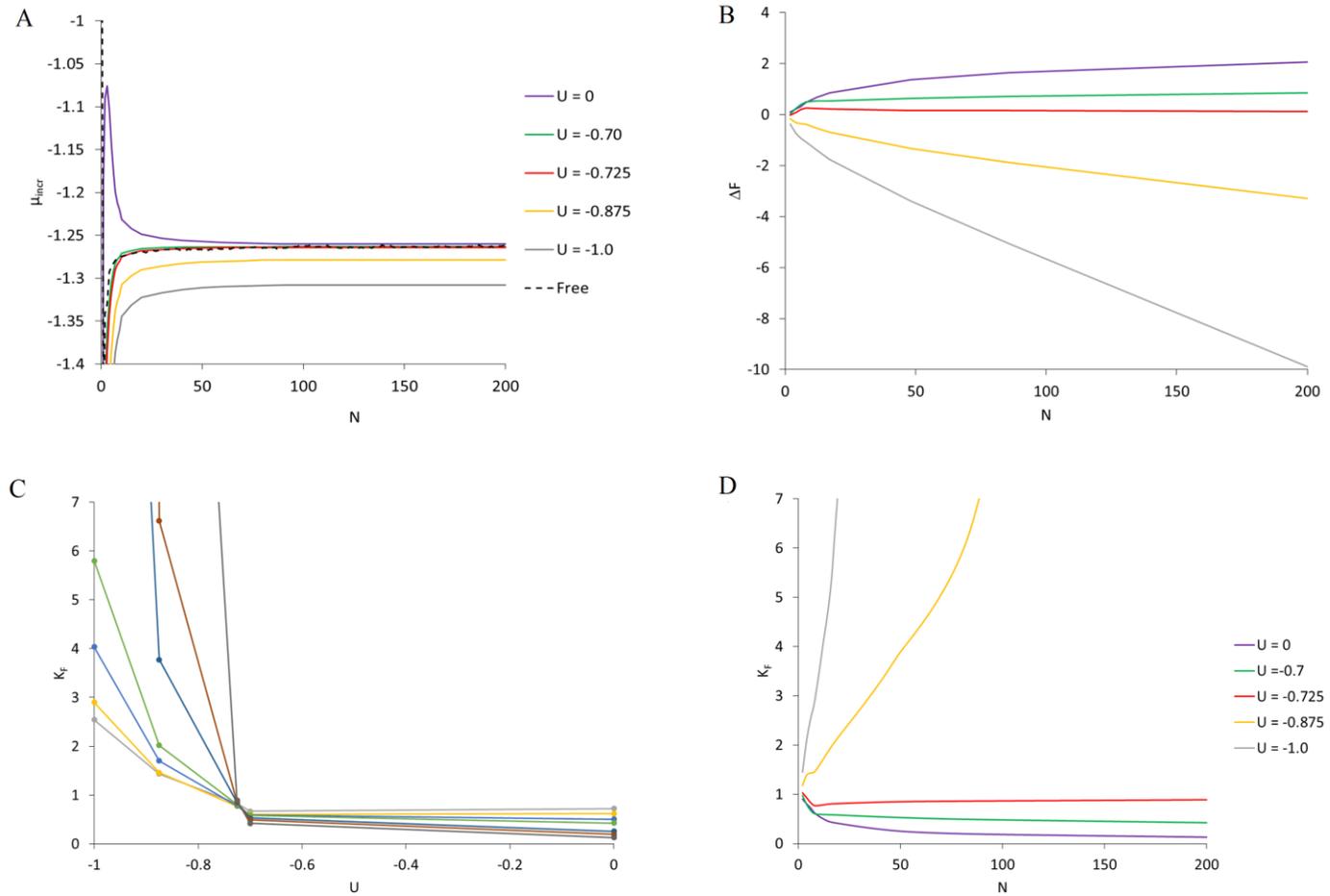


Figure 7. (A) Incremental chemical potential, and (B) free energy difference as functions of chain length N for chains partially confined to a pore of radius $1.5b$ for several adsorption potentials $U = 0$ to -1 . Partition coefficient K_F for chains partially confined to a pore of radius $R_{pore} = 1.5b$ as (C) a function of adsorption potential U for several N and (D) for $N = 1-200$ for several U .

The difference in free energy (Fig. 7.B) as a function of the chain length is a clear indicator of the existence of critical conditions for partially confined chains. For adsorption potentials stronger than U_C , ΔF decreases with chain length, indicating that longer chains are more likely to be adsorbed than shorter ones. For potentials weaker than U_C , ΔF increases with chain length, meaning short chains are more likely to be adsorbed. At the critical conditions, the free energy difference becomes constant, and notably, this critical condition $U_C = -0.725$ is the same as for the externally adsorbed chains.

In a manner similar to completely confined chains, we define the partition coefficient for flower conformations as the exponent of the difference in free energy between a confined and unconfined chain: $K_F =$

$\exp[-\Delta F]$. The partition coefficient for chains partially confined to a pore of size $R_{pore} = 1.5b$ is given in Fig. 7.C-D as a function of adsorption potential U and chain length N , respectively. The partition coefficient of partially confined chains demonstrates several key features, which differentiate it from the case of complete confinement. First, for potentials stronger than the critical conditions $|U| > |U_C|$, the partition coefficient is monotonically increasing in chain length. (Fig. 7.C, $|U| > 0.725$; 7.D, yellow, gray lines). These potentials ($|U| > |U_C|$) indicate enhanced adsorption of longer molecules (LAC conditions). Second, there exists a characteristic potential (the critical point, $U_C = -0.725$), where the partition coefficient switches from a decreasing function of N to an increasing one (Fig. 7.C intersection point, 7.D red line). At the critical potential U_C , the partition coefficient does not depend on N . This potential is identical to the critical potential of chains adsorbed at a non-porous surface, which was described above. For potentials weaker than that corresponding to the critical condition $|U| < |U_C|$, K_F decreases with chain length, indicating enhanced partition of small molecules (SEC conditions) (Fig. 7.C, $|U| < 0.725$, 7.D, green, purple lines). The transition from SEC to LAC through the CPA is very sharp – adsorption is greatly enhanced (relative to the weak adsorption case) for all molecules beyond the critical conditions at $|U| > |U_C|$.

The ability of partially confined chains to experience critical adsorption conditions illustrates the importance of accounting for the mechanisms which include external surface adsorption in the case of porous substrates. Indeed, the mechanism of partial confinement offers an explanation for experimental observations of critical conditions. In the final section below, we explore the application of external surface adsorption and in particular, the contribution of partial confinement to chain retention in polymer chromatography on porous substrates.

7. Chain Retention on Porous Substrates

Assuming the thermodynamic equilibrium between unretained and retained analyte (chains), the retention volume V_R is defined as the ratio of the total quantity N_{tot} of analyte in the column to the bulk

concentration c_0 of the unretained analyte in the interstitial volume, $V_R = N_{tot}/c_0$. Accounting for all three possible mechanisms of retention, N_{tot} can be expressed as

$$N_{tot} = c_0[V_I + K_H S_{ext} + K_P V_P + K_F V_O] \quad (5)$$

Equation 5 states that the total amount of analyte in the column is divided into four contributions from chains located: (1) in the interstitial volume V_I (unretained), (2) on the external surface of the stationary phase particles of area S_{ext} , (3) completely within the pores of accessible volume V_P , and (4) at the external surface of stationary phase particles in flower conformations, where V_O is the volume of surface pore openings. Normalizing Eq. (5) by the bulk concentration c_0 , one arrives at the equation of the retention volume

$$V_R = V_I + K_H S_{ext} + K_P V_P + K_F V_O \quad (6)$$

In the spirit of the Gibbs adsorption theory³³ the sum of the last three terms in the right-hand side of Eq. 5 represents the excess adsorption $N_{ex} = c_0[K_H S_{ext} + K_P V_P + K_F V_O]$ of analyte in the column, as compared to the amount of analyte in the interstitial volume at the bulk concentration, $N_0 = c_0 V_I$. Provided the excess adsorption is attributed to the retained analyte, the overall partition coefficient K can be defined as the ratio of the *excess adsorption* concentration, $c_{ex} = N_{ex}/V_S$, per unit volume of the porous solid particles of volume $V_S = V_{col} - V_I$ and the bulk concentration c_0 in the solvent, $K = c_{ex}/c_0$ ²⁰. Note that the volume V_S includes the volume of pores inside the particles. As such, the retention expression (6) may be rewritten as $V_R = V_I + K V_S$, with the overall partition coefficient

$$K = K_H \hat{S}_{ext} + K_P \varepsilon_P + K_F \varepsilon_S \quad (7)$$

Here, $\hat{S}_{ext} = S_{ext}/V_S$ is the specific external surface area per unit volume of solid phase, $\varepsilon_P = V_P/V_S$ is the accessible porosity of the substrate, and ε_S is the surface porosity. The surface porosity is defined as $\varepsilon_S = n_S v_O \hat{S}_{ext}$; n_S is the number of pore openings per unit of external surface area and v_O – the volume of one pore opening. These parameters are determined by the column packing geometry and particle structure. Eq. (7) represents the extension of the definition of the partition coefficient for a nonporous surface²⁰ to a porous substrate.

The chain model employed is described in Section 3 with the monomer size scaled to represent the Kuhn segment of polystyrene at good solvent conditions (molar mass 832 Da, $b=2\text{nm}$)³⁴. The chain length in the

simulations varies from $N = 2$ to 200 that corresponds to the variation of molecular mass M of polystyrene fractions from 1,664– 166,400 Da. In Fig. 9, chain length N is converted to molecular mass M via the Kuhn segment mass.

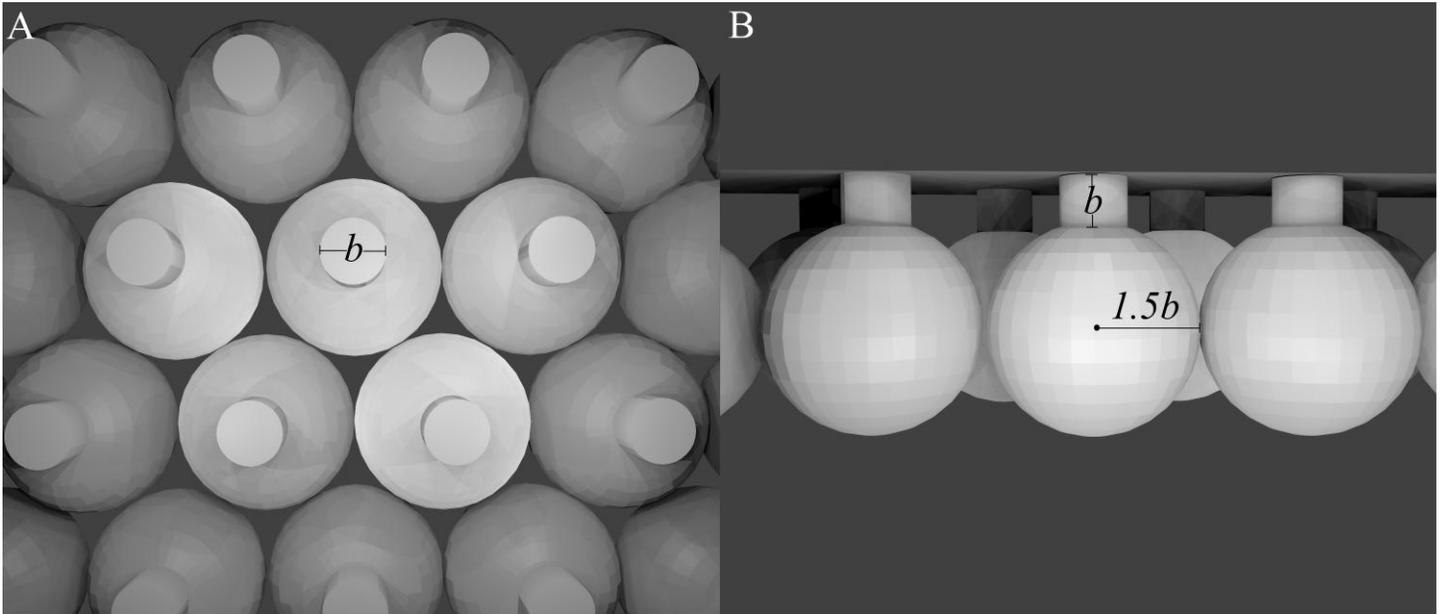


Figure 8. Model porous substrate: plane surface perforated by ink-bottle pores with spherical bodies and cylindrical openings. (A) Top-view (B) Side-view.

As a structural model of porous substrate, we use the surface perforated by ink-bottle pores with cylindrical pore openings and spherical pore bodies, Fig. 8. The diameter and length of the pore opening are set equal to the bead diameter b , so that $v_0 = \pi b^3/4$. The size of pore bodies is set to $R_{pore} = 1.5b$, reflecting the nominal pore width of 6nm of NovaPak® C₁₈ substrate from Waters Tech. (Milford, MA), used in¹¹. Assuming a dense packing of spherical pores, the surface pore density is set to $n_S = 0.13/b^2 = 3.2 \times 10^{12}/\text{cm}^2$. The fixed density n_S corresponds to a surface porosity of $\varepsilon_S = 0.1$ and an accessible volume porosity of $\varepsilon_P = 0.09$. This model implies that the retention volume (6) depends only on two column parameters, the packing porosity $\varepsilon_C = V_I/V_{col}$, where V_{col} is the total column volume, and substrate external surface area S_{ext} :

$$V_R = \varepsilon_C V_{col} + S_{ext} [K_H + 1.8bK_P + 0.1bK_F] \quad (8)$$

Equation (8) is used directly to calculate the theoretical retention plotted in Fig. 9.B. To illustrate the influence of multiple retention mechanisms – and in particular the role of partial confinement (flower

conformations) – on chain adsorption and partitioning, we have applied our model to a well-characterized example of isocratic elution of polystyrene (PS) fractions in binary mixtures of THF and ACN on a chromatographic column packed with porous particles ¹¹.

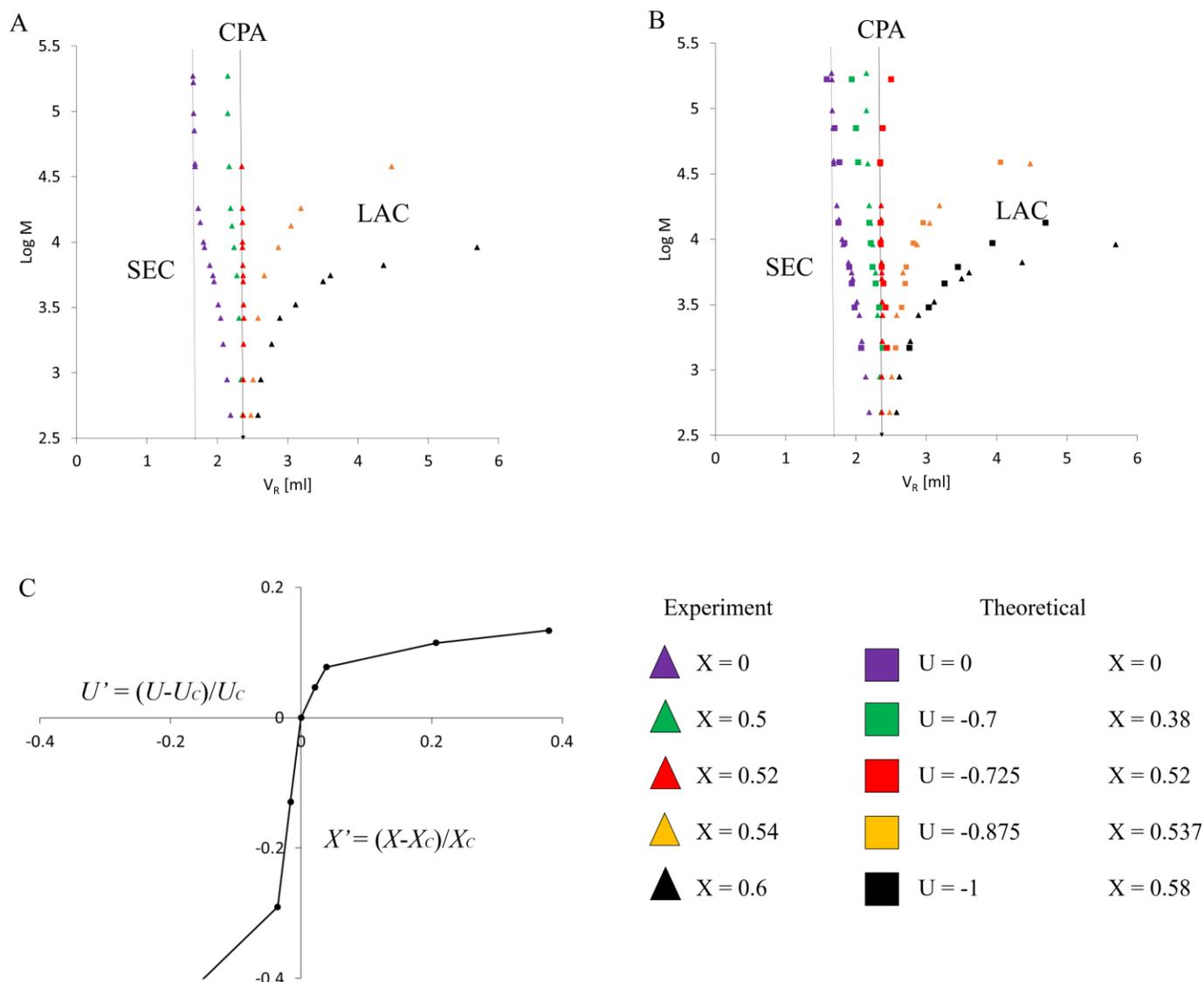


Figure 9. (A) Molecular mass M elution profiles for the isocratic separation of polystyrene ¹¹. The solvent composition X of the experimental data is given in terms of the volume fraction of acetonitrile, $X = 0$ to 0.6 . Three chromatographic modes, SEC, LCCC (elution at CPA) and LAC are clearly distinguished by the shape of elution profiles. (B) The same experimental data (triangle symbols) alongside theoretical retention volumes (square symbols) calculated using the retention equation (8) in conjunction with the partition coefficients derived from simulations. In both graphs, solid vertical line denotes CPA retention volume, $V_{CPA} = 2.35$ ml, dashed line – retention volume of largest chains, $N = 200$ in SEC mode ($X = 0$), fitted by adjusting the column porosity to $\varepsilon_c = 0.53$,

corresponding to interstitial volume $V_I = 1.9$ ml. (C) Correlation between effective adsorption potential U and solvent composition X in terms of dimensionless deviation U' , X' from the critical values, U_C and X_C , for a nonporous column.

The diagram in Fig 9.A shows the experimental correlation between the chain molecular weight and the retention volume for a range of solvent compositions in terms of volume fraction X of ACN recalculated from the data presented in ¹¹. As clearly seen, the composition of $X_C = 0.52$ corresponds to the critical conditions of molecular weight independent elution with the CPA retention volume $V_{CPA} = 2.35$ ml. Compositions $X < X_C$ correspond to the SEC order of elution with larger chains eluted first, most prominent for the limiting case of pure THF ($X = 0$). At this mobile phase composition, ($X = 0$) the chain retention exhibits a characteristic shape that points toward different states of polymer chains depending on molecular weight. Larger chains are excluded from the surface and it is less probable for them to enter the pores of the substrate than for smaller chains. Conversely, it is possible for smaller chains to penetrate into the pores of the substrate and the retention of these chains may be influenced by the presence of partially confined (flower) conformations. Above the CPA ($X > 0.52$), the elution volume increases with the molecular weight that implies the LAC regime, with chains strongly attracted to the substrate and the reverse sequence of elution. Larger chains have a higher probability to interact with the substrate than smaller ones, and therefore are more strongly retained. When chains are strongly adsorbed, the enthalpic effects favor the chains to penetrate into the pores and therefore one may expect a larger contribution of flower conformations for chains of all molecular weights than is present in the SEC regime.

To describe the chain retention in this system, we made the following assumptions. First, we associated the SEC conditions observed in pure THF ($X=0$) with the negligible adsorption potential, $U = 0$, and the CPA conditions at $X_C = 0.52$ with the critical adsorption potential $U = U_C = -0.725$. Next, we determined the packing porosity ε_C , and the external surface area, S_{ext} , which are the only two adjustable parameters in our model. The packing porosity $\varepsilon_C = 0.53$ (corresponding to $V_I = 1.9$ cm³, for a column of volume $V_{col} = 3.58$ cm³) was adjusted to fit the theoretical retention volume of chains of length $N = 200$ ($V_R = 1.6$ ml, Fig. 9.B, dashed line) for the case of zero adsorption potential ($U = 0$) to the experimental retention of the largest (166,400 Da) chains in pure THF ($X = 0$). $S_{ext} = 4 \times 10^5$ cm² was chosen to best reproduce the critical retention volume $V_{CPA} = 2.35$ ml

(Fig. 9.A, B solid line). The value of S_{ext} is larger than the estimate made by assuming smooth, spherical particles of nominal radius $R_p = 2\mu\text{m}^{11}$, which may imply a significant degree of surface roughness and particle size heterogeneity. With these parameters, we predicted the retention behavior at different molecular weights and selected adsorption potentials ($U=0, -0.7, -0.725, -0.875, \text{ and } -1$).

The experimental and theoretical retention are overlaid in Fig. 9.B. The square symbols correspond to the theoretical retention of chains exposed to a range of adsorption potentials $U = 0$ to -1 . The experimental and theoretical retention volumes at SEC ($X=0, U=0$) and CPA ($X=0.52, U = U_C = -0.725$) conditions are in good agreement, since the selected points at these conditions were chosen for the fitting of model parameters. For potentials weaker than U_C , retention is a decreasing function of molecular weight. For potentials stronger than the critical value, the theoretical retention mimics qualitatively the behavior of chain retention in the LAC regime. Note that the shown experimental and theoretical dependences deviate because the chosen values of the adsorption potential do not match the experimental compositions.

In order to match the effective adsorption potential U employed in simulations and the solvent composition X , we employ the correlation derived in our previous work²⁰ for chain separation on a non-porous column, Fig.9.C. This correlation relates the dimensionless deviations of the potential $U' = (U-U_C)/U_C$ and composition $X' = (X-X_C)/X_C$, both reduced to their respective critical values. Using this correlation, the potentials employed in calculations $U = (0, -0.7, -0.725, -0.875, \text{ and } -1)$ correspond respectively to the solvent compositions $X = (0, 0.38, 0.52, 0.537, 0.58)$. (See legend in Fig.9). This correlation leads to logical results: theoretical and experimental retention volumes are properly ordered and theoretical data for $X=0.38, 0.537, \text{ and } 0.58$ are located to the left of experimental data at $X=0.5, 0.54, \text{ and } 0.6$, respectively. Noteworthy, the quantitative agreement found with the correlation derived for a non-porous column confirms the robustness of our model and transferability of obtained parameters.

In Fig. 10, we present the calculated contributions of different adsorption mechanisms in retention of polymer chains of different length at three different adsorption potentials $U = 0, -0.725$ and -1 , which have been shown to correspond to the SEC, LCCC and LAC conditions from the experiments. We quantify the

contribution of each mechanism to theoretical retention using the components of Eq. 8 attributed to external surface, complete confinement to pores, and flower conformations, respectively:

$$V_{R,ext} = K_H S_{ext}; V_{R,pore} = K_P I.8b S_{ext}; V_{R,fl} = K_F O.1b S_{ext} \quad (9)$$

The contributions (9) in cm^3 are plotted as functions of the chain length. For the SEC regime ($U = 0$), the (exclusion) contribution from the external surface $V_{R,ext}$ dominates (Fig. 10.A); it is negative due to the excluded volume effects prominent in the absence of adsorption potential. The complete confinement contribution is negligible and the flower conformations contribute only into the retention of smaller chains. At the critical conditions ($U = U_C$), the contributions of external adsorption and flower conformations are comparable and constant for larger chains (Fig. 10.B). The contribution from the complete adsorption is notable only for the smallest chains and rapidly decreases with the chain length. Even at strong adsorption ($U = -1$), external adsorption and flower conformations dominate for all but the smallest chains (Fig. 10, C). Noteworthy, the contribution from complete adsorption progressively vanishes with the increase of the chain length and the decrease of adsorption potential, see Fig. 10.D.

This analysis indicates that adsorption on the external surface and partial confinement in pores represent the major factors determining chain partition. The mechanism of partial confinement (flower conformations) helps one explain the presence of critical conditions observed in polymer chromatography with porous substrates and resolve the controversy between the experimental observations and prior molecular simulations⁷⁻⁸ which focused entirely on the behavior of chains completely confined in pores neglecting the external surface effects.

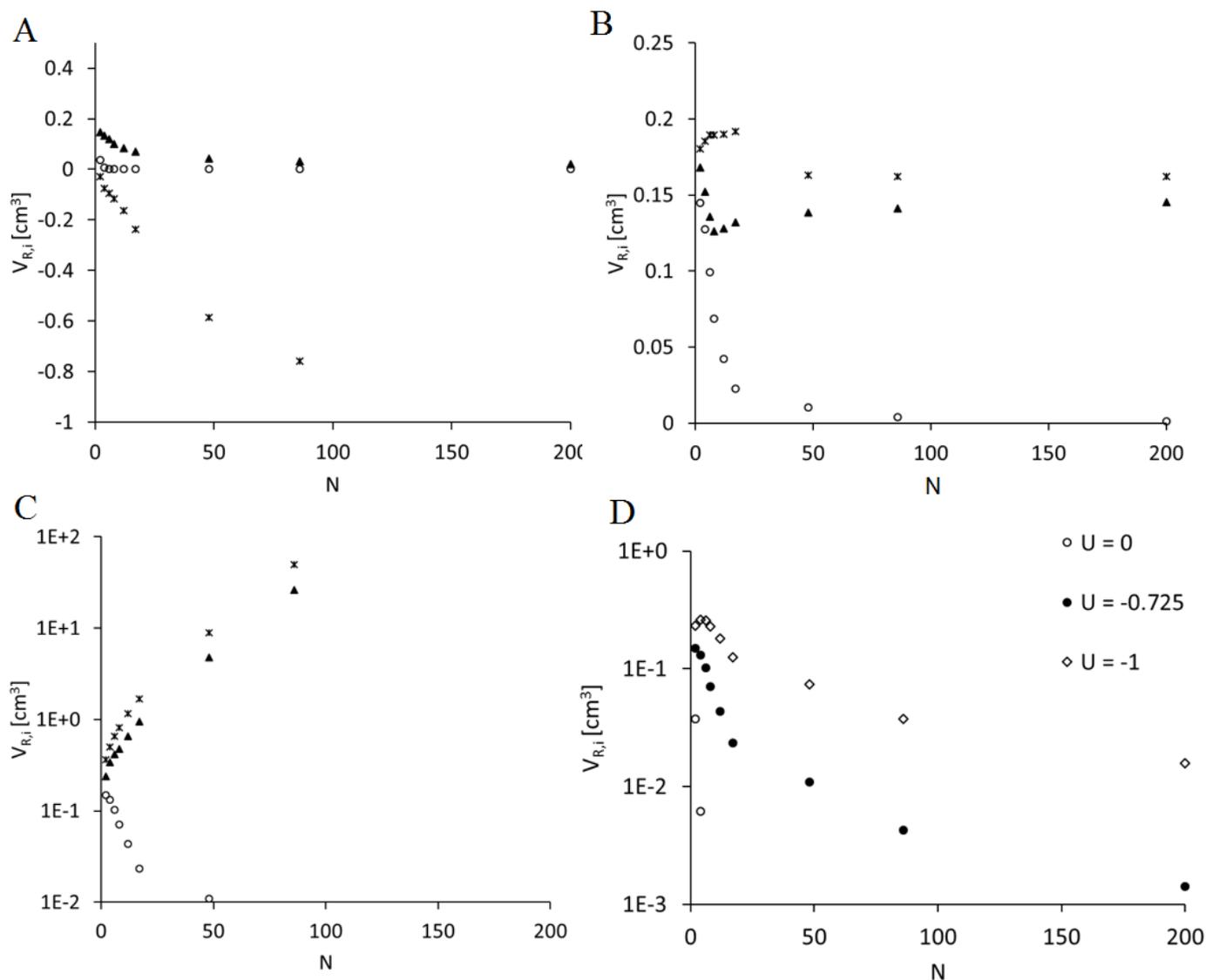


Figure 10. Contributions of adsorption mechanisms in SEC, LCCC, and LAC regimes: A. $U = 0$, B. $U = U_C$, and C. $U = -1$. Symbols for A-C: Stars—external adsorption. Open circles – complete confinement. Filled triangles –flower conformations. D. Comparison of contribution of complete confinement across adsorption potentials – rapidly diminishes with the decrease of adsorption potential and increase of the chain length.

8. Conclusion

Using a simple excluded volume chain model and MC simulations of thermodynamic equilibrium between adsorbed and free chains, we examine mechanisms of chain adsorption on a model porous substrate

searching for conditions of the critical point of adsorption (CPA), at which the partition coefficient in the process of chromatographic separation is chain length independent. We distinguish three adsorption mechanisms depending on the chain location: on external surface, completely confined in pores, and also partially confined in pores in so-called “flower” conformations. The chain adsorption is treated in terms of the Gibbs excess adsorption theory developed earlier for non-porous surfaces³³. The thermodynamic condition of the CPA is defined from the equality of the incremental chemical potentials of adsorbed and free chains²⁴. The free energies of different conformations of adsorbed chains are calculated by the incremental gauge cell MC method²⁵ that allows one to determine the partition coefficient as a function of the adsorption potential, pore size, and chain length. We confirm the existence of the CPA for the chain length independent separation on porous substrates, which is explained by the dominant contributions of the chain adsorption at the external surface, in particular in flower conformations. The CPA, known in chromatography as the LCCC regime, separates the regime of weak adsorption with SEC sequence of elution, with longer chains spending shorter time in the column, and the LAC regime of strong adsorption with the reverse sequence of elution. We show that as the magnitude of adsorption potential becomes stronger and approaches the CPA, the chains completely confined in pores are expelled to the external surface forming flower conformations. This mechanism was neglected in previous studies of excluded volume chains in pores, which questioned the very existence of the CPA for porous substrates. Moreover, we show that the critical conditions for porous and nonporous substrates are identical and depend only on the surface chemistry.

It is hypothesized that the experimentally observed critical adsorption on porous substrates may be explained by the presence of external adsorption and partially confined or ‘flower conformation’ chains, and it was shown that flower conformations exhibit the same critical point as externally adsorbed chains.

The theoretical results are confirmed by comparison with experimental data on chromatographic separation of a series of linear polystyrenes with variable solvent composition¹¹. The overall partition coefficient, which included contributions from all three adsorption mechanisms, was calculated for chains adsorbing to a model porous substrate perforated by ink-bottled pores. Although this model does not imitate the

pore structure of real chromatographic substrates, it captures the major physical mechanisms in a coherent fashion. The advantage of this model is a minimal number of adjustable parameters, the column packing porosity and packing external area, which were determined to get the best fit to the experimental data on the retention volumes at the non-adsorption surface (SEC regime) and at CPA. The presence of molecular weight independent elution at CPA and SEC-, LAC-like behavior was confirmed by varying the adsorption potential. The retention volume contributions of each adsorption mode were calculated and compared at characteristic adsorption potentials, corresponding to SEC, LCCC, and LAC conditions. It was found that external adsorption and flower conformations dominate over the mechanism of complete confinement, providing an explanation for the disagreement between the results of previous simulations and experimental observations. Finally, using a correlation between the effective adsorption potential in our model and the solvent compositions previously determined for separations on nonporous substrate²⁰, the adsorption potentials in the porous substrate model were related to the expected solvent compositions that led to a quantitative agreement with the experimental observations.

In conclusion, we developed a thermodynamic framework for modeling chain adsorption on porous substrates that is based on the Gibbs excess adsorption theory and the establishment of the equilibrium conditions from the equality of excess free energies of the adsorbed and free chains. The critical conditions of chain length independent separation are defined by the additional condition of equality of the incremental chemical potentials of the adsorbed and free chains. Using a simple yet instructive model of porous substrate, we show the existence of the CPA for excluded volume chains and describe the SEC, LCCC, and LAC regimes observed for separation of linear polystyrenes on non-porous and porous chromatographic columns in a unified fashion. A quantitative agreement was achieved with transferring the adsorption potential – solvent composition correlation determined for the non-porous column to the porous column. This confirms the robustness of the proposed methodology and its potential applicability, with proper extensions to more complex systems including block-copolymers, star polymers, end-functionalized chains, as well as to the challenging problem of separation of polymer grafted nanoparticles.

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Supporting Information

- A. Glossary of terms and abbreviations.
- B. Derivation of the Critical Conditions of Adsorption: General Case.
- C. Calculation of Free Energy of Partially Confined Chains.

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