Partitioning of Polymers into Pores near the Critical Adsorption Point

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ABSTRACT: We have examined the critical adsorption transition for a nonreversible random walk chain (NRRW) and a self-avoiding walk chain (SAW) at the surface and have identified the critical adsorption point. We then examine the partition coefficient of a NRRW chain and a SAW chain confined in a slit with two adsorbing walls near the critical adsorption point. For a NRRW chain, the partition coefficient at the critical adsorption point is equal to one and is independent of the chain length. This property has been utilized in the liquid chromatography operated at the critical adsorption point (LCCAP). For a SAW chain, however, the partition coefficient at the critical adsorption point K^{cr} is greater than one and is dependent on the chain length and slit width. This confirms the experimental observation of a weak chain length dependence of the partition coefficient at the critical point. Moreover, the study found that K^{cr} for a SAW scales with (R_{g0}/D^2) to a first-order approximation where R_{g0} is the radius of the gyration of the unconfined chain in the dilute solution and D is the slit width.

Introduction

Liquid chromatography at critical adsorption point (LC CAP) is a recent development in the separation and characterization of macromolecules using liquid chromatography.[1−5] This technique makes use of the principles of size exclusion and adsorption compensation of macromolecules in microscopic pores. When there is no attractive interaction between polymer chains and the surface of the microscopic pores, the polymer chains are excluded from the pore according to their sizes relative to the pore sizes. The partition coefficient, K, defined as the concentration in the pore relative to the concentration in the bulk region, decreases as the molecular weight of polymers increases. This is the principle in the gel permeation chromatography (GPC, also called size exclusion chromatography). In GPC, high molecular weight polymers will elute first whereas the low molecular weight polymers will elute later. When the polymers have attractive interaction with the surface of the pores and the interaction exceeds a threshold (the critical point), then polymers will be adsorbed on the surface. The longer the polymer chains, the more they are adsorbed on the surface. Therefore, the partition coefficient K will increase with the molecular weight, contrary to the behavior in the exclusion chromatography. One may envision a threshold at which the partition coefficient or the elution time in the chromatography may become independent of the molecular weight. This threshold is called the critical point and liquid chromatography operated at this critical point is termed as LCCAP. Experimental determination of the critical point however was often complicated by a weak molecular weight dependence of the elution time even very near the critical point. Nevertheless, LCCAP has found use in the analysis of the composition of block copolymers. One can adjust the solvent quality such that one of the blocks is in the critical point and therefore this block will not influence the elution time of the polymers. This block becomes invisible in the chromatography, and the molecular weight of the other block can then been determined.[4] LCCAP also found use in the separation of ring polymers from the linear polymers.[5]

To better understand and make use of LCCAP, one needs to examine the partition of chains into pores near the critical adsorption point. This has not been done extensively. Theoretical investigation of a single polymer chain confined into a slit and a tube was considered initially by Casassa[6] using a diffusion equation. For an ideal flexible chain, this leads to a simple analytical solution for the partition coefficient when the polymer chains do not interact with the walls except the hard wall repulsion. The presence of attractive interaction between polymer chains and pore walls significantly alters the partition coefficients. Guttman et al.[7] used the matrix generation method and considered the polymer chains confined in a pore with attractive surfaces. They examined the critical adsorption temperature for homopolymers, block copolymers, star polymers, and comblike polymers. In their model, chains are random walks with no excluded-volume interactions. Their theoretical considerations provided guidance to the application of critical adsorption chromatography in the separation of polymers with different architecture. Skvortsov et al.[8,9] also considered the critical adsorption chromatography using a continuum model. The theory is again valid for random walk chains. They gave approximate results for the partition coefficient at different adsorption interaction strength and slit width. Both theories confirmed that the partition coefficient at the critical adsorption point is equal to one and is independent of the molecular weight. More recently, Cifra and Bleha[10] used the lattice Monte Carlo simulation and studied the critical adsorption chromatography. The chains modeled in the study were self-avoiding walks. Their results showed that the partition coefficient at the critical adsorption point still have some dependence on the molecular weight of the polymers, unlike the results predicted by the theory.[7−9] The discrepancy was attributed to the ideal chain model used in the theory vs the self-avoiding chains used in the computer simulation.

Theoretically, the critical adsorption point in LCCAP is taken to be the same as the critical adsorption point

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of a single chain near an adsorbing surface. It is also accepted that at the LCCAP the partition coefficient $K = 1$ and is independent of the molecular weight of the chain.[7] Skvortsov et al. indicated that these assumptions may be valid only for random walks (RW) but not for self-avoiding walks (SAW).[8] We reexamine these conclusions about LCCAP using the lattice Monte Carlo simulation for both the RW chains and the SAW chains. We have obtained the partition coefficient of a single polymer chain for a range of slit widths and molecular weights at different polymer–pore surface interactions. We find that for the RW chains the critical adsorption point in LCCAP indeed coincides with the critical adsorption point of a single chain near an adsorbing wall. At the critical point the partition coefficient for a RW chain $K = 1$ and is independent of the molecular weight. However, for SAW chains, the partition coefficient $K \neq 1$ at the critical adsorption point but has a correction term that depends on the molecular weight and the slit width.

Simulation Method

The partition coefficients for a single chain are obtained by comparing the chemical potential of a single chain in the bulk and in the confined slit using the chain insertion method.[11,12] The chain insertion method is well developed and has been reviewed by Frenkel and Smit.[13] One inserts a chain segment by segment using a biased method. During the insertion of the ith segment, if one has a choice of z possible directions, one chooses the direction that favors the largest Boltzmann factor. The sum of the Boltzmann factors of all possible directions during the insertion of ith segment is called the Rosenbluth weighting factor w_i

$$w_i = \frac{\sum_{j=1}^{z} \exp[-\beta u_i(j)]}{z} \tag{1}$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, T is the temperature, $u_i(j)$ is the energy associated with inserting the ith segment in the jth direction. The chemical potential μ of the inserted chain of length N is calculated with reference to $\mu_{\mathrm{id,NRRW}}$, the chemical potential of an ideal nonreversing random walk (monomer overlap is allowed) of the same length on the unconfined lattice. The difference μ_{ex} between μ and $\mu_{\mathrm{id,NRRW}}$ is given by

$$\beta\mu_{\mathrm{ex}} = \beta(\mu - \mu_{\mathrm{id,NRRW}}) = -\ln\langle\prod_{i=1}^{N} w_i\rangle \tag{2}$$

We obtained μ_{ex} for the chains in the bulk solution (μ_{bulk}) and the chains confined in the slit (μ_{conf}). The percent error of the chemical potential determined is typically around 0.05% for short chains and 0.5% for long chains. The partition coefficient for the chain at infinite dilution is given by $-\ln K_0 = \beta(\mu_{\mathrm{conf}} - \mu_{\mathrm{bulk}})$.

The bulk solution is modeled by a simple cubic lattice with dimension of $100a \times 100a \times 100a$ (a is the lattice unit) with periodic boundary conditions applied in all directions. The slit is modeled by a simple cubic lattice with dimensions of $(D + 1)a \times 250a \times 250a$ along the x, y, and z directions. There are two solid walls located at $x = a$ and $x = (D + 1)a$ layers extending in the y and z directions. Periodic boundary conditions are applied in the y and z directions. Polymer beads cannot occupy sites on the wall. D is the slit width, which is the distance between the two walls.

Table 1. Radius of Gyration of the SAW Chain Used in the Simulation

N	R_{g0}
25	2.94 ± 0.03
50	4.34 ± 0.06
100	6.52 ± 0.12
200	9.81 ± 0.39

The polymer chains studied were (i) random walks (RW) and nonreversible random walks (NRRW) and (ii) self-avoiding random walks (SAW) consisting of N beads on the simple cubic lattice. For NRRW model, the chemical potential in the bulk solution is zero according to the above definition. Table 1 presents the radius of gyration of the SAW chain, R_{g0}, used in the simulation. The sizes of the RW and NRRW chain are slightly smaller than that of SAW chain. The interaction between the pore wall and polymer bead is characterized by a nearest-neighbor reduced interaction ϵ_w whenever a polymer bead is in direct contact with the sites on the wall. The terminally anchored polymer chain on a solid surface is modeled by growing the chain with the first bead of the chain on the layer $x = 2a$ in a large slit ($D \gg R_{g0}$).

Results and Discussion

(a) Nonreversible Random Walk at a Solid Surface. The adsorption transition of a polymer chain at a solid wall was extensively studied and is well understood.[14–21] For a random walk chain on a simple cubic lattice, the transition point $\epsilon_w^{cr} = \ln(1 - \lambda_1) = -0.183$ where λ_1 is the ratio of the number of positive directions perpendicular to the layers over the total number of possible directions of the walk and is equal to $^1/_6$ in the simple cubic lattice. For a nonreversible random walk, $\lambda_1 = {}^1/_5$ and $\epsilon_w^{cr} = -0.223$. This result is obtained when one considers the chemical potential of a chain near the surface, which is given by the natural log of the product of the Rosenbluth factors, eq 2. Only the segments near the surface their Rosenbluth factors are modified and are given by $(1 - \lambda_1)e^{-\epsilon_w}$. The Rosenbluth factors for the other segments equal to one. By setting the chemical potential of the chain equal to zero, one obtains $\epsilon_w^{cr} = \ln(1 - \lambda_1)$. Also, very near the critical regime, $\beta\Delta\mu \sim N^{1/2}(\epsilon_w - \epsilon_w^{cr})$, since there are $N^{1/2}$ number of segments in contact with the surface and each segment in contacting with the surface gains the energy $(\epsilon_w - \epsilon_w^{cr})$. The number of segments in contact with the wall can be derived using a simple argument. One assumes N segments homogeneously distributed in a sphere of R_g where R_g is the radius gyration of the chain and $R_g \sim aN^{1/2}$ for a RW chain; a is the monomer size. Only segments in the layer of thickness a above the surface are in contact with the wall. Therefore, the total number of segments in contact with the wall is given by $(N/R_g^3)(aR_g^2) = N^{1/2}$.

The adsorption transition can be studied by examining the properties of a terminally anchored chain.[14–19] Therefore, we first examined a random walk chain terminally anchored at a solid surface to confirm the above known theoretical results. Figure 1 presents the plot of chemical potential $\beta\Delta\mu$ vs ϵ_w for (a) a random walk and (b) a nonreversible random walk chain terminally anchored on the wall for chain lengths $N = 25$, 50, 100, and 200. Before the adsorption transition, long

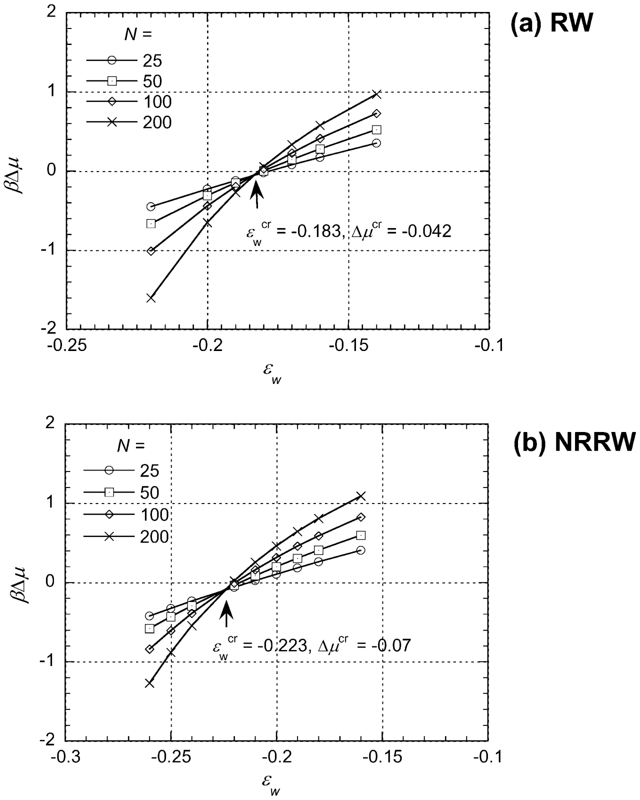

Figure 1. Plots of reduced chemical potential $\beta\Delta\mu$ vs reduced polymer−wall interaction ϵ_w for (a) a random walk chain (RW) and (b) a nonreversible random walk (NRRW) terminally anchored at a solid surface with different chain lengths N. The interception point in the plot gives the critical adsorption point.

chains are repelled more strongly by the surface and hence a large positive $\beta\Delta\mu$. When ϵ_w becomes less than ϵ_w^{cr}, long chains are adsorbed more on the surface. Therefore, the plot of $\beta\Delta\mu$ vs ϵ_w for different chain lengths intersects at the critical adsorption point. For a random walk, the intersection point on the plot corresponds to $\epsilon_w^{cr} = -0.183 \pm 0.002$ and at the critical adsorption $\beta\Delta\mu^{cr} = -0.042 \pm 0.007$. For a nonreversible random walk, we recover the expected $\epsilon_w^{cr} = -0.223 \pm 0.002$, but $\beta\Delta\mu^{cr} = -0.07 \pm 0.01$. Theoretically, one would expect the chemical potential of the chain near the surface at the critical point $\beta\Delta\mu^{cr}$ should be zero. The nonzero value we observed here may be ascribed to the fact that the first monomer of the chain is held fixed on the surface. The critical point was further confirmed by plotting $\beta\Delta\mu$ against $|\tau|N^{1/2}$ where $\tau = \epsilon_w - \epsilon_w^{cr}$. Nice scaling plots were obtained for NRRW and RW (not shown) as shown in Figure 2. These results confirm that we can identify the critical adsorption point clearly and accurately within the range of chain lengths examined.

(b) Nonreversible Random Walk Confined in a Slit. For a NRRW chain confined in a slit, the properties of the chain can be divided into different regimes depending on the interaction strength between the pore wall and the polymer chain and the size of polymer chains relative to the slit width. Gorbunov and Skvortsov[8] developed a rigorous theory based on the continuum model. They gave asymptotic results on the chemical potential and the partition coefficient in different regime. Here, we are only interested in the properties near the critical regime. It was predicted that $\beta\Delta\mu \sim N(\epsilon_w - \epsilon_w^{cr})/D$ near the critical regime. Scaling arguments would also lead to the same results but with the condition that the adsorption blob has to be larger than the slit width. The adsorption blob is the average thickness of the adsorbed layer when a chain is adsorbed on a solid surface and is given by a/τ. When the adsorption blob is larger than the slit width, then D controls the blob size. The number of blobs in a chain is given by N/g, where $g^{1/2}a = D$. Each blob has (g/D) number of monomers in contact with the surface that gain an energy $(g/D)(\epsilon_w - \epsilon_w^{cr})$. Combining these together, one obtains $\beta\Delta\mu \sim N(\epsilon_w - \epsilon_w^{cr})/D$. If, however, the adsorption blob is less than D, deviation from the above equation can be expected.

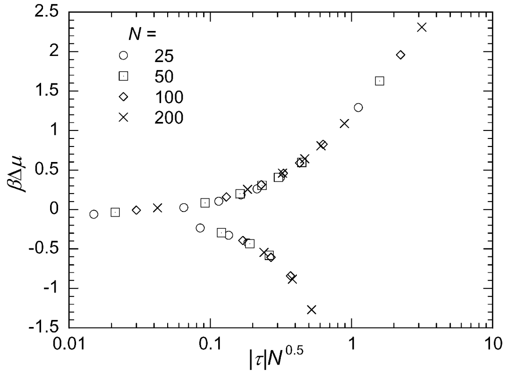

Figure 2. Linear−log plot of reduced chemical potential $\beta\Delta\mu$ vs $|\tau|N^{1/2}$ near the critical adsorption point for a NRRW chain terminally anchored at the surface at different chain lengths N.

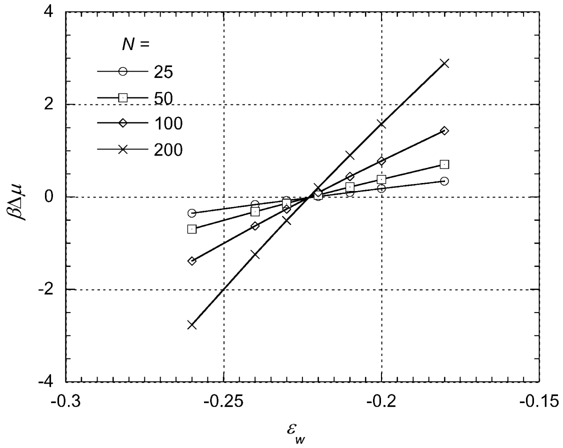

Figure 3. Plot of reduced chemical potential $\beta\Delta\mu$ vs reduced polymer−wall interaction ϵ_w for a NRRW chain with different chain lengths N confined in a slit of width $D = 6$.

Figure 3 presents $\beta\Delta\mu$ vs ϵ_w for a NRRW chain confined in a slit of narrow width $D = 6$. One can see that the critical point was not shifted relative to the single chain anchored at the surface. More interestingly, at the critical points, $\beta\Delta\mu^{cr}$ was zero ($K = 1$). The same results were obtained in a wider slit. Figure 4a presents the scaling plot of $\beta\Delta\mu$ vs $N|\tau|/D$ for the data obtained in $D = 6$. A nice scaling plot is obtained. Figure 4b presents the overlay of the data points obtained in three different slit widths. The scaling dependence on D was obeyed to a good degree, although some deviation was observed for data in $D = 30$. One would expect such deviation according to the scaling arguments given above. These results confirm that for a NRRW at the critical adsorption point the partition coefficient is one and is independent of chain length.

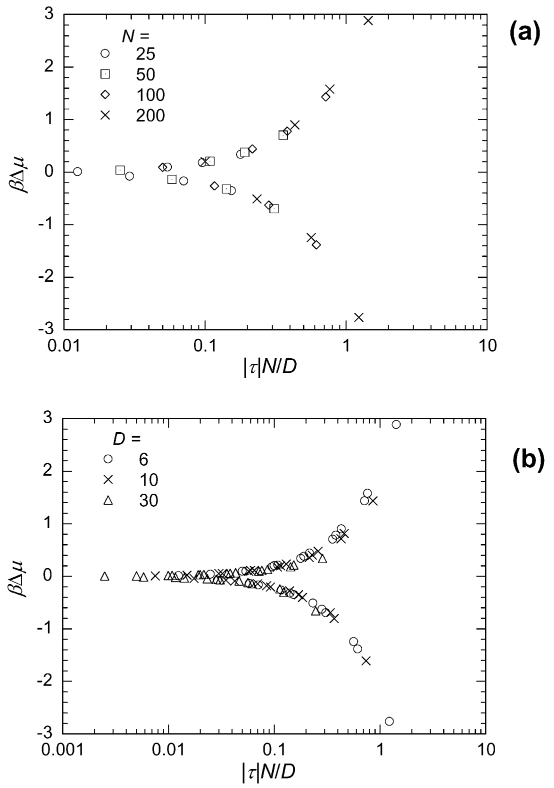

Figure 4. Linear−log plots of reduced chemical potential $\beta\Delta\mu$ vs $|\tau|N/D$ near the critical adsorption point for a NRRW chain with different chain lengths N confined in a slit: (a) in a slit of width $D = 6$; (b) in a slit of different width $D = 6$, 10, and 30.

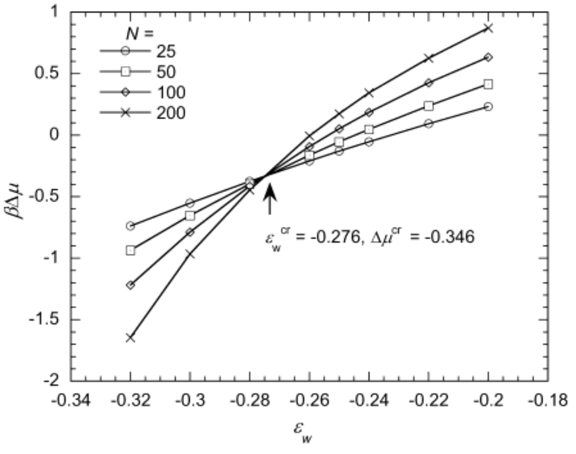

Figure 5. Plot of reduced chemical potential $\beta\Delta\mu$ vs ϵ_w for a self-avoiding walk (SAW) chain with different chain lengths N terminally anchored at a solid surface. The interception gives the critical point $\epsilon_w^{cr} = -0.276$.

(c) Self-Avoiding Walk above a Solid Surface. There is no rigorous theory that can treat the adsorption transition for a SAW chain at a solid surface. Following the same scaling argument as given in section (a), one would predict $\beta\Delta\mu \sim N^{1-\nu}(\epsilon_w - \epsilon_w^{cr})$ near the critical regime where ν is the Flory exponent and is 0.58 in our model. Figure 5 presents the plot of $\beta\Delta\mu$ vs ϵ_w for a terminally anchored SAW chain with different chain lengths. The lines intersect at a common point that corresponds to $\epsilon_w^{cr} = -0.276 \pm 0.001$ and $\beta\Delta\mu^{cr} = -0.346 \pm 0.003$. The value of $\beta\Delta\mu^{cr}$ obtained for SAW chain above the surface was more negative than the value for RW chain or NRRW chain above the surface, which were −0.042 and −0.07, respectively. The nonzero value of $\beta\Delta\mu^{cr}$ again may be ascribed to the fact that the chain is terminally anchored on the wall. Figure 6 presents the scaling plot of $\beta\Delta\mu$ vs $|\tau|N^{\phi}$ with $\phi = 0.5$. Only $\phi = 0.5$ produced a good scaling plot. Using $\phi = 0.42$ gives observable deviations from the scaling law plot. The reported literature value of ϕ ranged[16−19] from 0.67 to 0.53, much larger than the value expected from the prediction based on the scaling theory. We do not know why the observed scaling exponent on N is 0.5 not the expected 0.42 from the scaling theory.

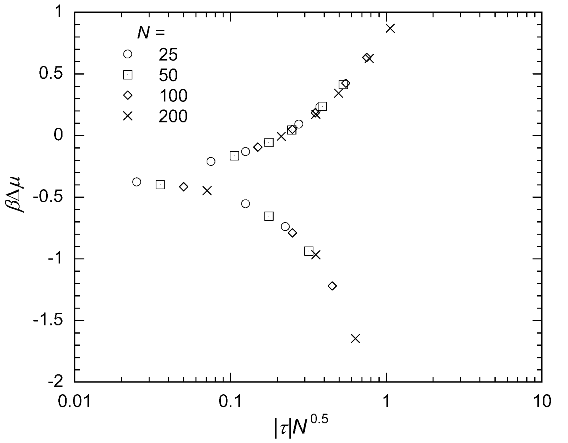

Figure 6. Linear−log plot of reduced chemical potential $\beta\Delta\mu$ vs $|\tau|N^{1/2}$ near the critical adsorption point for a SAW chain terminally anchored at the surface with different chain lengths N.

The critical point determined by us was smaller than the value reported by Meirovitch and Livne,[19] who reported the critical point $|\epsilon_w^{cr}| = \theta_a = 0.291 \pm 0.001$. The methodology they used in determining the critical point was different from ours. Meirovitch and Livne used the dependence of the total energy $E(T)$ on N to determine the critical adsorption point. They plotted $E(T)/N$ vs N for $N = 20-60$, $60-170$, and $170-350$ and seek for the point where the exponent in the plot became the same. Thus, they determined the critical point $\theta_a = 0.291$ and the exponent $\phi = 0.53$. We believe the plot of $\Delta\mu$ vs ϵ_w is a more sensitive test. We suspect that they have overestimated the critical adsorption point.

(d) Self-Avoiding Walk Confined in a Slit. Less was known about the properties of a SAW chain confined in a slit with adsorbing walls near the critical point. Figure 7 presents the $\beta\Delta\mu$ vs ϵ_w for a SAW chain confined in a slit of width $D = 6$. One can see that the four curves do not intersect at a common point. For a wider slit width, deviations between the intersection points are less significant but can still be seen. Therefore, it is not possible to identify the critical point from the plot. However, a nice scaling plot was obtained by plotting $\beta\Delta\mu$ against $N|\epsilon_w - \epsilon_w^{cr}|$ with $\epsilon_w^{cr} = -0.276$, as shown in Figure 8a. It can also be clearly seen that when $|\tau|N \to 0$, $\Delta\mu$ does not approach zero but some finite negative number. Gorbunov and Skvortsov[8] had argued that, for a SAW chain at the critical adsorption point confined in a slit, K is not one but depends on slit width and chain size. They have proposed the following relationship

$$K = \left(\frac{R_{g0}}{D}\right)^{5/18} \exp\left[B\left(\frac{R_{g0}}{D}\right)^{1/\nu}\left(\frac{D}{H}\right)^{(1-\nu)/\nu}\right] \qquad (3)$$

where $H^{-1} = -a\tau^{\nu/(1-\nu)}$ and B is a coefficient of the order

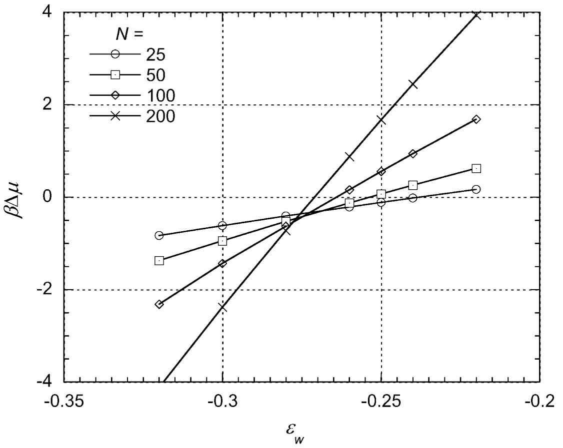

Figure 7. Plot of reduced chemical potential $\beta\Delta\mu$ vs ϵ_w for a self-avoiding walk (SAW) chain with different chain lengths N confined in a slit of width $D = 6$. The four lines do not intersect at a common point.

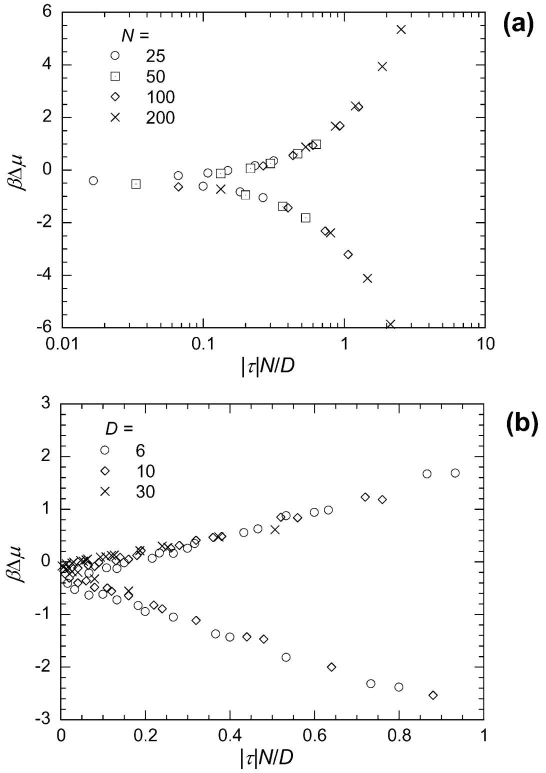

Figure 8. Plots of reduced chemical potential $\beta\Delta\mu$ vs $|\tau|N/D$ near the critical adsorption point for a SAW with different chain lengths confined in a slit. The critical adsorption point used was $\epsilon_w^{cr} = -0.276$: (a) in a slit of width $D = 6$; (b) in a slit of different width $D = 6$, 10, and 30.

of unity, dependent on the form of the pore. The above equation can be rearranged to obtain $\beta\Delta\mu$ near the critical adsorption point.

$$\beta\Delta\mu = -\ln K = BN\tau/D - \frac{5}{18}\ln\left(\frac{R_{g0}}{D}\right) \qquad (4)$$

Figure 8b presents the plot of $\beta\Delta\mu$ vs $N|\tau|/D$ for a SAW confined in three different slits. One can clearly see from the plot when $N|\tau| \to 0$, the interception on the Y-axis for the three sets of data do not coincide. The interception with the Y-axis for the wider slit $D = 30$ is above the interception points for the narrower slits. The three sets of data form a good scaling plot away from the critical region. When one plots $\beta\Delta\mu + (5/18)\ln(R_{g0}/D)$ vs $N|\tau|/D$, data do not collapse into a single curve even for a fixed slit width D. Therefore, the formula in eq 3 suggested by Gorbunov and Skvortsov is not valid, but one may alternatively write the following equation:

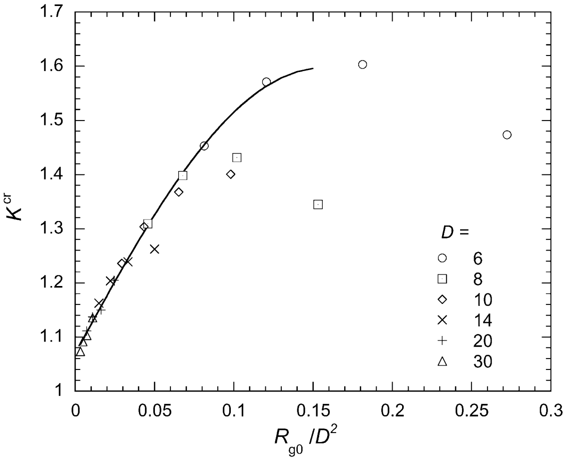

Figure 9. Plot of partition coefficient K^{cr} determined at critical adsorption point $\epsilon_w^{cr} = -0.276$ for a SAW with chain lengths $N = 25$, 50, 100, and 200 confined in a slit of different width D. The points that deviate from the common curve are those with strong confinement ($R_{g0}/D > 0.5$). The solid line is a guide to the eye.

$$\beta\Delta\mu = BN\tau/D + \text{correction term} \qquad (5)$$

We determined the $\beta\Delta\mu^{cr}$ for a SAW chain in different slit widths and chain lengths at $\epsilon_w = -0.276$ in order to investigate the correction term. (The first term in eq 5 will be zero.) We found $K^{cr} = \exp(-\beta\Delta\mu^{cr})$ does not scale with (R_{g0}/D) as suggested by Gorbunov and Skvortsov[8] but scales with (R_{g0}/D^2) reasonably well as shown in Figure 9. Only a few data points corresponding to strong confinement ($R_{g0}/D > 0.5$) show deviation from the common curve. This may suggest that at even stronger confinement, there is another correction term in addition to the term (R_{g0}/D^2) that depends on higher order of ($1/D$). This additional correction term makes the partition coefficient smaller than the value expected from the first correction term. Theoretical investigation on this correction term is definitely needed for a better understanding of the behavior of a SAW chain in confined slit.

It is worth to point out here that if one uses the same scaling arguments presented in section (b) and makes necessary modifications for the SAW chain, one would arrive at $\beta\Delta\mu \sim N|\tau|/D$ for a SAW chain confined in a slit with adsorbing surfaces. But the scaling theory cannot account for the correction term. One may alternatively assume that the critical adsorption point for a SAW chain confined in a slit shifts when the slit width D changes. This interpretation however will make the discussion more complex. It seems more logical to use the concept that the critical adsorption point in the slit does not shift, but the partition coefficient in the slit at the critical adsorption point is not one.

The above results suggest that the critical adsorption point determined for a SAW chain terminally anchored at a solid surface does not shift when the chain is confined in an absorbing slit. However, at the critical adsorption point, the partition coefficient is not one but

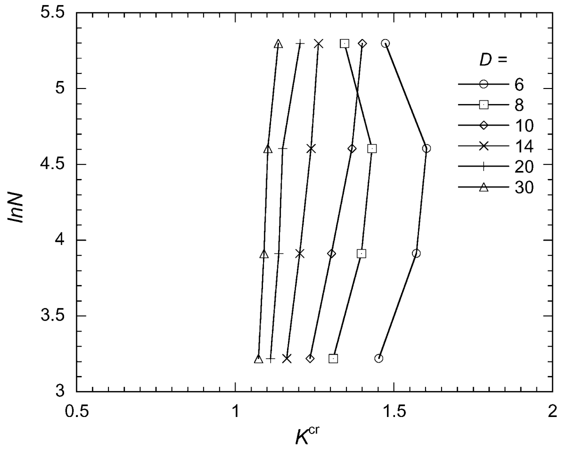

Figure 10. Plot of ln N vs K^{cr} at the critical adsorption point $\epsilon_w{}^{cr} = -0.276$ in different slit widths D.

has a correction term that depends on the size of the chain and the slit width. The variation of K on the molecular weight is the least at the critical adsorption point. In LCCAP, the critical point usually refers to the point at which the retention time of the polymer becomes independent of the molecular weight. In real experiments, the retention time was always found to have some dependence on the molecular weight of the polymers, and the retention time of the polymers at the critical point was larger than that of the solvent.[5] Our results are consistent with the experimental observation. At the critical point, the partition coefficient $K^{cr} > 1$ implies a longer retention time than the pure solvent. Figure 10 presents the results on K^{cr} in the form familiar to the experimentalist, ln N vs K^{cr} for several slit widths D. The curves shown in the plot with small D have also been reported in experiments.[5]

It is also clear from our study that it would be erroneous to determine the "critical point" by varying ϵ_w until $K = 1$ ($\beta\Delta\mu = 0$) as done by Cifra and Bleha.[10] The correction term however is small and scales with (R_{g0}/D^2) to a first-order approximation. Therefore, for long chains τ will be small when $\Delta\mu = 0$. In another words, in the limit of $N \to \infty$, one may determine the $\epsilon_w{}^{cr}$ by identifying the point at which $K = 1$. More interestingly, we also found that when $\Delta\mu$ for a fixed chain length but in different slit widths is plotted as a function of ϵ_w, the curves intersect at a common point $K = 1$, as shown in Figure 11. For short chains like $N = 25$, the interception point was far away from $\epsilon_w{}^{cr}$, but for long chains like $N = 200$, the interception point is close to the critical adsorption point $\epsilon_w{}^{cr}$, although the intersection point for the narrowest slit width $D = 6$ shifts somewhat from the other two slit widths in the latter case. These results show that the compensation point defined as the point at which $K = 1$ is a fixed point for a fixed chain length in different slit widths, but is a different point for different chain lengths in the fixed slit width (from Figure 5). We do not have a clear understanding about this result yet.

Cifra and Bleha[10] used a chain of length $N = 100$ partitioning into a slit of different widths and identified the critical adsorption point by locating the point at which $K = 1$. Not surprisingly, the critical point they reported was -0.2625, slightly larger than our results. At $\epsilon_w = -0.2625$, they also observed the dependence of the partition coefficient on the chain length. Since $\epsilon_w = -0.2625$ is not the critical adsorption point, the dependence they observed is masked by exclusion effect not completely compensated by the adsorption.

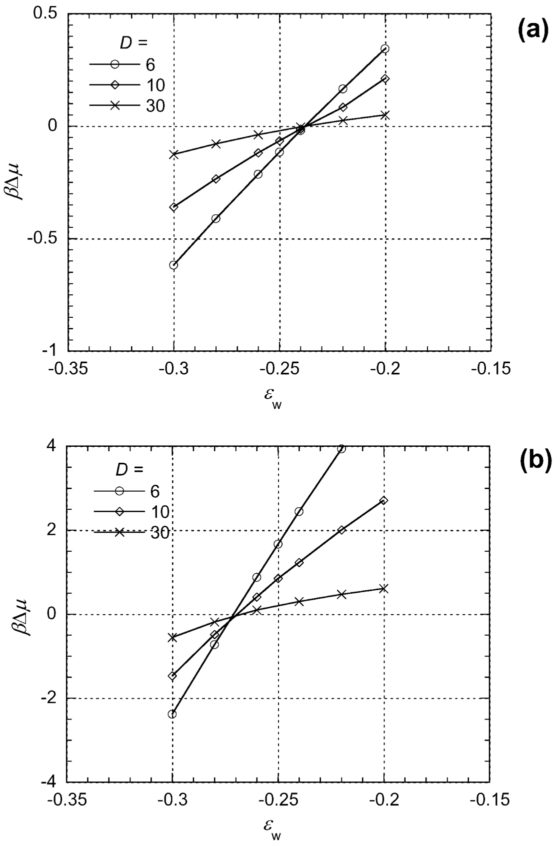

Figure 11. Plots of reduced chemical potential $\beta\Delta\mu$ for a SAW chain with fixed chain length N confined in a slit of different width D: (a) chain length $N = 25$; (b) chain length $N = 200$.

Conclusions

We investigated a single polymer chain near the critical adsorption point confined in a slit using lattice Monte Carlo simulations. For a RW chain or NRRW chain, one found that at the critical adsorption point the partition coefficient is one and is independent of chain lengths. This has been the assumption adopted in interpreting and understanding the critical adsorption chromatography (LCCAP). For a SAW chain, one found that the critical adsorption point is still the same as the SAW chain near a solid surface. However, there is a correction term to the free energy of a SAW chain confined in the slit. The presence of the correction term makes the partition coefficient at the critical adsorption point no longer equal to one, but it is greater than one and varies with the molecular weight. This indicates that if the solvent in LCCAP is good, the partition coefficient will still have some dependence on the molecular size. Such a phenomenon has been observed in experiments.[5] The study also found that the partition coefficient at the critical adsorption point scales with the size of the molecule as (R_{g0}/D^2) to a first-order approximation instead of the predicted dependence $(R_{g0}/D)^{8/15}$.

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