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The adsorption and partitioning of self-avoiding walk polymer chains into pores from a bulk theta solution

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Summary

Monte Carlo simulations of self-avoiding walk (SAW) polymer chains on a simple cubic lattice were used to study the adsorption and partitioning of the chains into pores from a bulk Θ solution. The behavior of the SAW chains confined in pores at the bulk Θ temperature was found to differ from that of the Gaussian chains. When confined in a slit or in a square channel, the radius of gyration of a Θ chain perpendicular to the direction of the confinement was shown to increase in comparison with the radius of gyration in bulk solution. The solvent quality in the pore was shown to be better than the Θ solvent, causing the expansion of the chain in the pore. When terminally anchored onto a solid surface, the reduced polymer-surface interaction at the critical adsorption point, ε_w^{ca}, was found to be -0.252 ± 0.001, which differs from the value of ε_w^{ca} for chains without excluded volume effects, a category including random walks and non-reversing random walks on the lattice. When partitioning into a pore modeled as a slit, the polymer-surface interaction at the critical point was shown to be the same as the critical adsorption point and does not shift with the slit width. But when partitioning into a pore modeled as a square channel, the polymer–surface interaction at the critical point was shown to shift with the width of the square channel. At the critical condition point, the partition coefficient of the SAW Θ chains was greater than one in both types of pores. These results differ from the results of the Gaussian chains; instead, they are similar to that of SAW chains in athermal solvent.

Keywords: Monte Carlo simulations; Polymer partitioning; Critical adsorption point

1. Introduction

Liquid chromatography of polymers is governed by two competing forces. First, there is a loss of configurational entropy when a polymer encounters the confined geometries of the pores in a chromatography column. This entropy loss results in the restriction of longer polymer chains from entering the pores, causing shorter elution times for longer polymer chains. In contrast, if there is an attractive interaction, ε_w, between the pore surfaces and the polymer repeating units, the chains can gain enthalpic energy by entering the pores and making contact with the pore surfaces. Longer polymer chains will experience a larger gain in enthalpy, when compared with shorter chains, as the longer chains will be able interact with more sites on the attractive surface of the stationary phase. As a result, longer chains will have longer elution times than shorter chains. It is possible that for some value of ε_w these two forces will cancel with each other, allowing for polymer chains to elute independent of chain length. This condition, where elution time is independent of chain length of a homopolymer has been called liquid chromatography at the critical condition (LCCC) and has been utilized in new chromatographic methods that characterize polymers with complex architectures and chemical compositions [1–11].

The critical condition has been identified theoretically by using the Gaussian chain model, which ignores excluded volume interaction in a polymer chain [12,13]. For Gaussian chains, the critical condition is the same as the critical adsorption point, ε_w^{ca}, of a chain near a single solid surface. At the critical adsorption point, the partition coefficient of a Gaussian chain between the mobile solution and the pores equals one and is independent of the chain length. Computer simulations have studied the partitioning of self-avoiding-walk (SAW) chains into pores with different geometries near the critical adsorption point and found results that differ

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from theoretical predictions based on the Gaussian chain model [14–16]. Notably, one finds that the critical condition likely employed in the experimental LCCC is not necessarily the same as the critical adsorption point and the critical condition can change with the pore size of a square channel pore. These previous simulations, however, were performed for SAW chains in an athermal solvent.

In chromatography experiments, one common method of finding the critical condition is by varying the composition of the mobile phase solvent, resulting in solvents with a quality between the athermal and the Θ condition. It is generally believed that Gaussian chains can be used as models of polymer chains in a Θ solvent, as the scaling behavior of the radius of gyration of the chains with the chain length in a Θ solvent is correctly recovered in the Gaussian chain model. As one may argue that the excluded volume interaction, which gives rise to the observed difference between simulation results and the prediction from the Gaussian chain theory, is only important to consider when the solvent is a good solvent, it would be useful to test if the difference between the computer simulation results and the theoretical predictions is of importance if the solvent is a Θ solvent. Also, although the influence of solvent on polymer adsorption on the porous substrate may not be directly linked with its solvency quality; there is, nevertheless, some link between solvency quality and its influence on polymer adsorption [17]. Therefore, understanding the influence of the solvent quality on the critical condition is also of great importance to experimental studies. Here, the critical condition of SAW polymer chains in a Θ solvent is studied. The results of the Θ chains are compared with previous results [15,16] for SAW chains in athermal solvents and with the Gaussian chains theory. The Θ chains are found to behave much like SAW chains in athermal solvent, and they do not obey the Gaussian chain theory. The reason for such behavior is discussed in terms of the thermodynamic nature of the confined Θ solution.

2. Simulation method

In all simulations, polymer chains are modeled as self-avoiding walks (SAW) on a simple cubic lattice. The partition coefficient, K, is determined for a singe polymer chain by comparing the chemical potential of the chain in a confined geometry, μ_{conf}, with the chemical potential of the chain in a bulk solution, μ_{bulk}, using the chain insertion method [18]. Specifically, K is calculated from the equation

$$-\ln K = \beta \Delta \mu = \beta(\mu_{\text{conf}} - \mu_{\text{bulk}}) \quad (1)$$

where $\beta = 1/k_B T$, and k_B is Boltzmann's constant and T is the temperature. The details of the chain insertion method have been discussed previously [15]. Briefly, a chain is inserted on the lattice bead by bead via a biased insertion and the Rosenbluth weighting factor, W, for the chain is determined. The chemical potential of the chain μ is related to the Rosenbluth weighting factor through $\beta\mu = -\ln\langle W\rangle$.

The simulation box for the bulk solution is a $100a \times 100a \times 100a$ lattice (a is the lattice unit) with periodic boundary conditions applied in all directions. Two confined pore geometries are studied, a slit pore and a square channel pore. The slit pore is represented by a tetragonal box with dimensions of $250a \times 250a \times (D+1)a$ in the x-, y-, and z-directions with values of D between 6 and 30. Two solid walls are located at $z=a$ and $z=(D+1)a$, and periodic boundary conditions are applied along the x- and y-directions. The square channel pore is represented by a rectangular box with dimensions $(D+1)a \times (D+1)a \times 200a$ in the x-, y-, and z-directions. Periodic boundary conditions are applied along the z-direction. Four solid walls were located at $x=a$, $x=(D+1)a$, $y=a$, and $y=(D+1)a$. Typical chain lengths studied were $N=25$–400. The radius of gyration, R_{g0}, for the chains in a dilute bulk solution in the Θ state are given in Table 1.

The adsorption transition of a chain on a single solid surface was studied on a $250a \times 250a \times 100a$ lattice. There were periodic boundary conditions in the x- and y-directions, and two solid walls were located at the $z=a$ and $z=100a$ planes. The polymer chains were terminally anchored to the wall at the $z=a$ by growing the chain with the first bead at $z=2a$. The two walls are separated far enough so that the chain terminally anchored at $z=a$ does not effectively experience the presence of the other wall at $z=100a$ in the simulation.

Two types of interactions were applied in the simulations. First, a polymer-wall interaction, ε_w, is applied whenever a polymer bead occupies a lattice point in direct contact with a wall. The second interaction was an attractive interaction, ε_s, between non-bonded polymer contacts used to simulate the Θ solvent. Throughout the paper, we use values of ε_s and ε_w that are reduced by $1/k_B T$ and will refer them as reduced interactions. In an athermal solvent, $\varepsilon_s = 0$; polymer–polymer interactions are the same as polymer–solvent interactions. As the solvent becomes a worse solvent than an athermal one, ε_s becomes negative; polymer–polymer interactions are attractive when compared to polymer–solvent interactions. For the SAW chains on a simple cubic lattice, the Θ state was found [19] at $\varepsilon_s = -0.2963$ and this value for ε_s was used in all simulations of Θ solvents. More discussion of the Θ state is presented in the next section.

3. Results and discussion

3.1. Definition of the Θ state

Real polymers chains have excluded volume interactions, i.e. no two polymer beads can occupy the same physical space. This is the fundamental difference between a

Table 1
Size of polymer chains in Θ state studied in the simulations

N	25	50	100	200	300	400
$2R_{g0}$	5.42	7.64	11.04	15.46	18.95	21.91

N is the chain length, R_{g0} is the unconfined radius gyration of the chain in the bulk, Θ solution at infinite dilution. The error in R_{g0} is in the last digit. The scaling exponent of R_{g0} on N is 0.504.

real polymer chain and a Gaussian chain. A Gaussian chain always behaves like a random coil and its R_g scales with the chain length N in $R_g \propto N^{1/2}$ regardless of the dimensionality of the system. Under special circumstances, however, the real polymer chain could behave like a random coil in that their $R_g \propto N^{1/2}$. Such special circumstances are found in polymer melt and in polymer solution termed the Θ solution.

In a Θ solution, it is assumed that the repulsive force and attractive force between non-bonded polymer segments cancel with each other exactly. Operationally, one may define the Θ state for a bulk polymer solution in three ways [19]: (i) The point at which the R_g of a single polymer chain will scale with the chain length $N^{1/2}$, (ii) the point at which the second virial coefficient, A_2, between the polymer chains $\rightarrow 0$ in the limit of infinite chain length; (iii) the critical point of the phase transition of a homopolymer solution extrapolated to infinite chain length (note, the attractive interaction between non-bonded polymer segments will lead to phase separation of a polymer solution). It has been shown that in the case of a bulk polymer solution, the three definitions all lead to the same state [19]. In the computer simulation, where a polymer is modeled as the SAW chain on the cubic lattice with a coordination $Z=6$, the Θ state is achieved when an attractive polymer–polymer segment interaction, $\beta\varepsilon_{pp}=-0.2693$ is applied between non-bonded polymer segments (PP model), or a positive polymer–solvent interaction, $\beta\varepsilon_{ps}=0.2693/2$ is applied (PS model). It is the effective interaction between polymer and solvent, $\chi_{ps}=\beta(\varepsilon_{ps}-1/2(\varepsilon_{pp}+\varepsilon_{ss}))$ that determines the thermodynamic state of the polymer solution. Cifra and Terakoa [20] have shown, however, that the two choices to model the bulk Θ solution result in different partition coefficients of polymers into the pores. In the PS model, the Θ solvent would promote adsorption of polymers to the wall, whereas in the PP model, the solvent quality is uncoupled with polymer adsorption onto the wall. They have argued that the PS model is more appropriate for real polymeric systems confined to pores since a bad solvent in experiments is often seen to promote polymer adsorption.

Another subtle issue is the exact location of the Θ temperature for confined polymer solution. Hehmeyer et al. [21] recently assumed that the Θ state of the confined solution could still be defined as the extrapolated critical solution temperature of a polymer solution with infinite chain length, $T_c^*(\infty)$. They determined the Θ state according to this definition for a strictly 2D system, a quasi-2D (a solution confined in a slit) system, and a 3D bulk solution on the simple cubic lattice with a coordination $Z=26$. The Θ temperature is lowered significantly, $T_c^*(\infty)=20.28$ for the bulk 3D solution, $T_c^*(\infty)=11.94$ for a quasi-2D solution (a confined solution), and $T_c^*(\infty)=3.51$ for a strictly 2D system. Moreover, the exponent α in the scaling dependence of $R_g \propto N^{\alpha}$ at the corresponding $T_c^*(\infty)$ was found to be 0.56 for the strictly 2D system, 0.52 for the quasi-2D system, and 0.505 for the bulk solution. Their results indicate that the Θ temperature in a confined solution thus defined shifts (is lowered) from the bulk solution, presumably because there is a stronger excluded volume interaction in a geometry with a reduced dimension, hence a need of a stronger segment/segment interaction (achieved at lower temperature) to offset the excluded volume interactions. Secondly, in the 3D bulk solution at the Θ temperature, the chain behaves like a random coil, a point that has been widely recognized, but in the quasi-2D or strictly 2D at their respective Θ temperatures, the chains do not behave like random coils. The chains are swollen. This effect has not been widely recognized.

In our current study, the Θ state examined corresponds to the Θ state in bulk solution, not the confined solution. We argue that in experimental studies the solvent quality likely is determined in the bulk solution. The relevant 'Θ' temperature to experimental studies would still be the Θ temperature for the bulk solution. We will also use the PP model for the Θ state because we do not want the coupled effect between the solvent quality and the adsorption tendency, allowing more direct comparisons with previous results for both random walks and athermal SAW chains.

3.2. Solvent quality in the pore at the bulk Θ state

The chains at the bulk Θ temperature becoming swollen when being confined in a slit can be seen in their radii of gyration. Fig. 1 presents R_{gxy}, the square of the radius of gyration perpendicular to the direction of confinement, of Θ chains as a function of chain length N when the chains are confined in a slit of dimensions $250a\times 250a\times(D+1)a$, and $D=6$, 8, 10, 12, and 20. R_{gxy} for the confined Θ chains is larger than for the unconfined, bulk Θ chains, and increases with the decrease in D. The exponent α in the scaling dependence of $R_{gxy} \propto N^{\alpha}$, varies from 0.51 in the bulk solution (more accurate estimate of the exponent is 0.505 in our model), to 0.68 when $D=6$, much larger than the exponent, 0.52, found by Hehmeyer et al. [21] for a chain in a quasi-2D solution at the corresponding quasi-2D Θ temperature. Hence the confined chains at the bulk Θ temperature are highly swollen in the pore and experience strong excluded volume interaction upon confinement. The solvent quality in the pore is better than the Θ solvent.

When the SAW chain at the bulk Θ temperature is confined in a square channel, similar results are found (data not shown). If the square channel is narrow, the radius of gyration of the chain along the channel direction increases

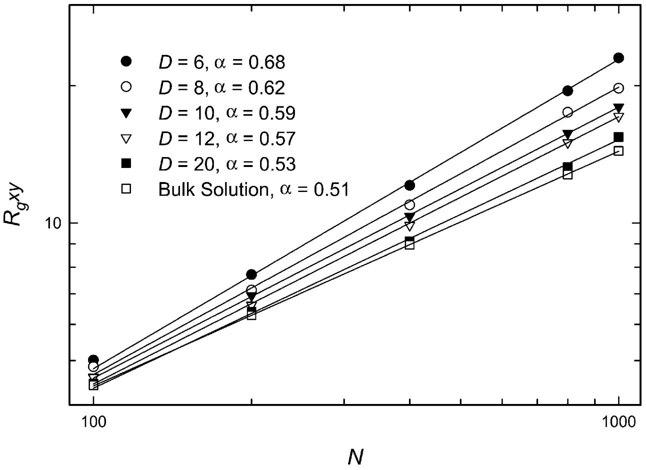

Fig. 1. Double logarithmic plot of R_{gxy}, the radius of gyration perpendicular to the direction of confinement against chain length, N, for a chain confined in a slit of various widths. The lines in the figures are fit to the data from a power law with the exponent α given in the legend.

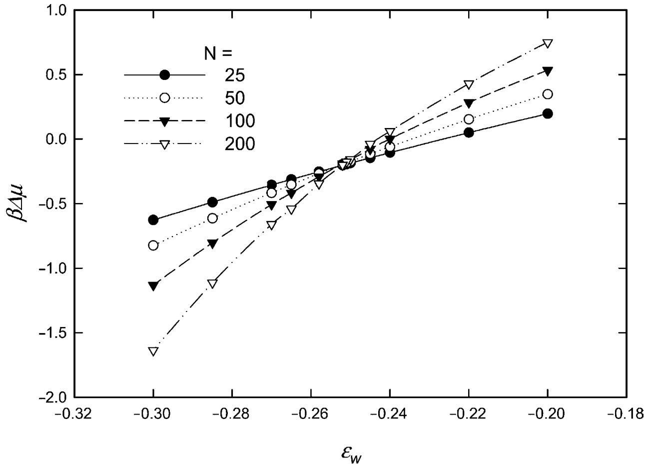

Fig. 2. Plot of reduced chemical potential, $\beta\Delta\mu$, against reduced polymer–surface interaction ε_w for a polymer chain terminally anchored on a solid surface with a chain length $N=25$–200. The data for the different chain lengths intersect at a common point, giving the critical adsorption point, $\varepsilon_w=-0.252$.

and becomes linearly dependent on N. This is to be contrasted to the behavior of a Gaussian chain confined in a channel. A Gaussian chain when confined in a channel does not expand along the channel direction and retains its dimension at its bulk radius of gyration, as discussed by de Gennes [22]. Raphael and Pincus have also shown that, even at the Θ temperature in the pore, the chain is expanded due to the presence of the higher order of excluded volume interactions [23].

3.3. Critical adsorption point of a SAW Θ chain on a single solid surface

The surface adsorption transition of a polymer near an impenetrable wall was extensively studied by the renormalization group theory, the scaling theory and computer simulations because the model provides a link between polymer physics and critical phenomena [24,25]. The exact location of the critical adsorption point is model dependent and has to be determined for each specific system. However, many properties near the critical adsorption point follow universal scaling laws, and hence received extensive studies. For example, the chemical potential of the polymer chain near the critical adsorption $\Delta\mu=\mu_{\text{surf}}-\mu_{\text{bulk}}$, is known to scale with $|\tau|N^{\phi}$, where ϕ is one of the universale scaling exponents, μ_{surf} is the chemical potential of the terminally attached chain, $\tau=\varepsilon_w-\varepsilon_{\text{w}}^{\text{ca}}$ and $\varepsilon_{\text{w}}^{\text{ca}}$ is the critical adsorption point. Most recent studies have suggested that $\phi=1/2$ [24]. We determined the critical adsorption point, $\varepsilon_{\text{w}}^{\text{ca}}$, of the Θ chains by studying the properties of a chain terminally anchored to a solid surface. To find $\varepsilon_{\text{w}}^{\text{ca}}$, the chemical potentials of terminally anchored polymer chains of various lengths are plotted against the values of ε_{w} that was used. The plot of chemical potential reduced by the Boltzmann factor of the polymer chain, $\beta\Delta\mu$, vs. reduced polymer-wall interaction, ε_{w}, for a SAW chain in a Θ solvent is shown in Fig. 2. The plots for the different chain lengths intersect at $\varepsilon_{\text{w}}^{\text{ca}}=-0.252\pm0.001$, which is identified as the critical adsorption point and at the critical adsorption point $\beta\Delta\mu^{\text{ca}}=-0.20\pm0.01$. Fig. 3 presents the scaling plot of $\beta\Delta\mu^{\text{ca}}$ against $|\tau|N^{1/2}$, which confirms the value of $\varepsilon_{\text{w}}^{\text{ca}}$ for the Θ chains. Table 2 summarizes previously reported [11] data of critical adsorption point values for a random walk (RW), a non-reversible random walk (NRRW), and a SAW chain in a good solvent, along with this Θ solvent data. The previous simulation results for $\varepsilon_{\text{w}}^{\text{ca}}$ for RW and NRRW chains agree with known theoretical values, indicating that the method used to locate the critical adsorption point is accurate. The RW and NRRW have no excluded volume interactions and they are the equivalent Gaussian chain models on the lattice.

As can be seen in Table 2, $\varepsilon_{\text{w}}^{\text{ca}}$ for the SAW in Θ solution, -0.252, is in between the $\varepsilon_{\text{w}}^{\text{ca}}$ for SAW in athermal solution, -0.269, and $\varepsilon_{\text{w}}^{\text{ca}}$ for NRRW chain, -0.223, and is closer to the value of SAW in athermal solution than the value for NRRW. This indicates that the SAW in a Θ solvent is more easily adsorbed on the surface than in an athermal solvent. The Θ solvent promotes the adsorption of polymers on the solid surface even with this PP model of the Θ solvent. We envision that the critical adsorption point would shift to a

Table 2
Critical adsorption point values for polymer chains in different models

Chain type	Solvent	$\varepsilon_{\text{w}}^{\text{ca}}$	$\beta\Delta\mu^{\text{ca}}$
RW	Athermal	−0.183 (2)	−0.042 (7)
NRRW	Athermal	−0.223 (2)	−0.07 (1)
SAW	Athermal	−0.276 (1)	−0.346 (3)
SAW	Θ	−0.252 (1)	−0.198 (5)

$\varepsilon_{\text{w}}^{\text{ca}}$ is the reduced polymer–surface interaction and $\beta\Delta\mu^{\text{ca}}$ is the reduced chemical potential at the critical adsorption point. The error in the last digit is shown in parentheses.

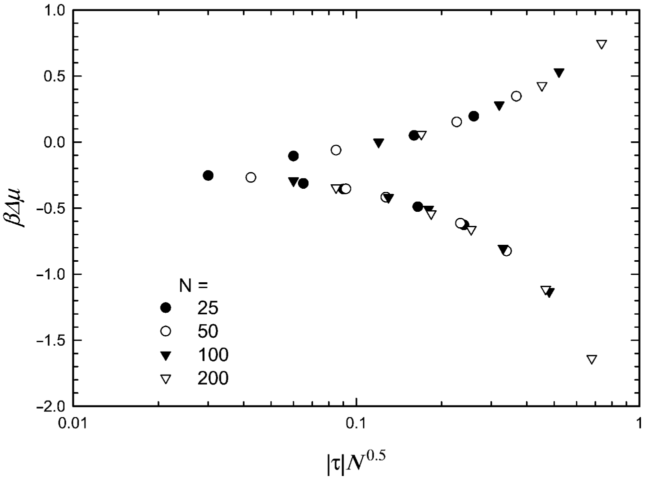

Fig. 3. Linear-log plot of the reduced chemical potential, $\beta\Delta\mu$, vs. $|\tau|N^{1/2}$ near the critical adsorption point, where $\tau=(\varepsilon_w-\varepsilon_w^{ca})$, with $\varepsilon_w^{ca}=-0.252$.

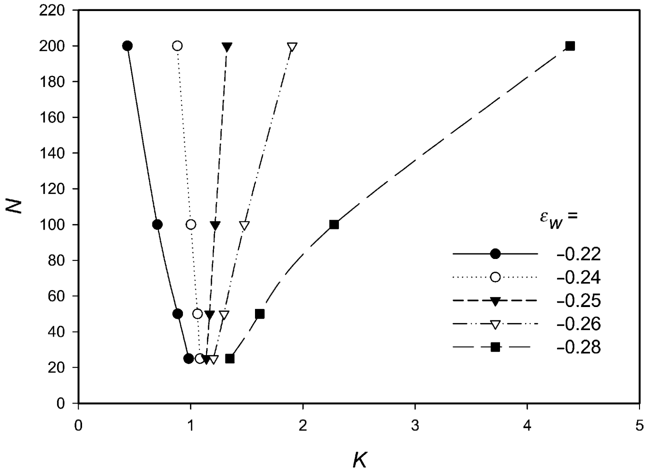

Fig. 4. Plot of K vs. N for polymer chains confined in a slit with $D=10$ for various values of reduced polymer–surface interaction, ε_w.

less negative number if we use the PS model of the Θ solvent. The value of $\beta\Delta\mu^{ca}$ for the four types of polymer chains also varies. Theoretically, $\beta\Delta\mu^{ca}$ for a Gaussian chain would equal zero, but $\beta\Delta\mu^{ca}=0$ was not seen in any of the simulations. This may be because the chain in the simulations is grown with a terminal bead attached to the wall, which is a situation not exactly analogous to a real situation, where the chain would move from a bulk solution to be adsorbed on the wall. For the Θ chain, the value of $\beta\Delta\mu^{ca}$ was again different from that of the Gaussian chain, and is in between $\beta\Delta\mu^{ca}$ for the NRRW and the athermal SAW chain. These results clearly indicate that the SAW chain in Θ solution does not reduce to the Gaussian chain model (the NRRW chain) in adsorption process, even though the scaling dependence of R_g with N may be the same for the two models in the bulk solution.

3.4. Critical condition point in a slit and in a square channel

The separation of polymers in liquid chromatography is based on the partitioning of polymers from unconfined mobile phase into the stationary confined pores in a column. In simulations of athermal SAW chains partitioning into confined pores, the partition coefficient K was found to depend on the chain length at the critical adsorption point [15,16]. Because of this chain length dependence, there is not a common point of intersection in the plots of $\beta\Delta\mu$ against ε_w for multiple chain lengths. A new parameter, ε_w^{cc}, the polymer-wall attraction at the critical condition, was defined through the following process: (1) The standard deviation in $\ln K$ over the chain lengths studied was calculated for several values of ε_w. (2) $\sigma(\ln K)$ was plotted against the corresponding value of ε_w. (3) The value of ε_w, where this plot was at a minimum was defined as, ε_w^{cc}, the polymer-wall interaction at the critical condition, the point where the partitioning coefficients of the polymer chains varied least with chain length. If K is independent of chain length at some value of ε_w, then $\sigma(\ln K)=0$, and this point would be a minimum in the plot of $\sigma(\ln K)$ vs. ε_w.

Previously, the critical condition for athermal SAW chains confined in a slit and a square channel for various sizes have been studied [16]. When confined in a slit, the value of ε_w^{cc} for slit widths $D=6$, 10, and 30 was constant and equal to ε_w^{ca}. In contrast, in a square channel, ε_w^{cc} was shown to vary with the dimension of the channel. If the chains were strongly confined (D was small), ε_w^{cc} was more negative than ε_w^{ca}, indicating that a stronger polymer-wall attraction was needed to reach the critical condition. As the size of the square channel increased, ε_w^{cc} also increased, and approached ε_w^{ca} for the large pore size. An explanation for the dependence of ε_w^{cc} on pore size in a square channel but not in a slit was given earlier and was attributed to the difference in the confinement encountered in the two types of pore.

Figs. 4 and 5 present the dependence of K on N for a SAW chain in the Θ solvent in a slit pore and in a square channel, respectively. The results seen here for the Θ chain is very similar to that for the athermal chain. In both types of pores, K depends on the chain length at the critical adsorption point $\varepsilon_w^{ca}=-0.25$. The dependence is weaker in a slit than that in a square channel with the same width D. Also it is clear from the plot that in the square channel the critical adsorption point is not likely the critical condition point (the chain with $N>100$ is excluded from the channel pore at $\varepsilon_w^{ca}=-0.25$). The new definition of the critical condition, ε_w^{cc} is necessarily. Moreover, K for the Θ chain at the critical condition point (which will be presented in Figs. 6 and 7) is greater than one. We have shown earlier that for the NRRW or RW at the critical adsorption point $K=1$ and is independent of chain length. This was not found for the SAW chain in the Θ solvent in a slit pore or in a square channel pore.

Figs. 6 and 7 show the plots of $\sigma(\ln K)$ against ε_w for the Θ chain in a slit pore and in a square channel, respectively.

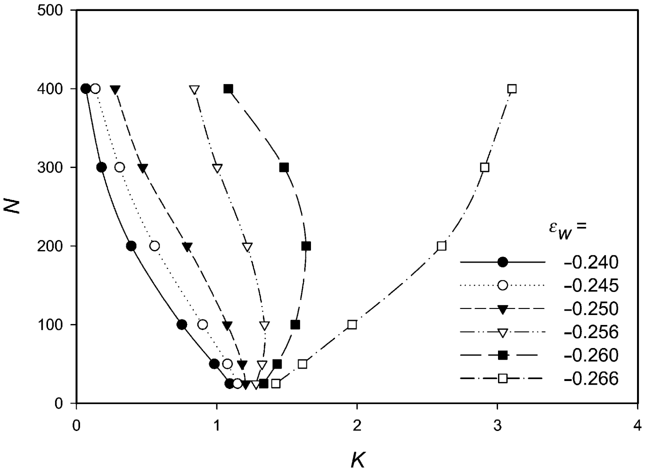

Fig. 5. Plot of K vs. N for polymer chains confined in a 10×10 square channel for various values of reduced polymer–surface interaction, ε_w.

Like the athermal SAW chains, the plot of σ(ln K) vs. ε_w for each value of D has a well defined minimum, ε_w^{cc}, and the value of ε_w^{cc} does not shift with D in a slit pore, but shifts with D in a square channel. The minimum value of σ(ln K) for slits with widths $D=6$, 10, and 30 occurs at $\varepsilon_w=-0.25$, which was closest to the value of $\varepsilon_w^{ca}(-0.252)$ among ε_w values studied, indicating that in slits the value of ε_w^{cc} equals the value of ε_w^{ca}. In contrast, the ε_w^{cc} in a square channel clearly shifts with the width D. The magnitude of the shift in the ε_w^{cc} in the Θ solvent, however, is much less compared with that seen in the athermal solvent. For example in $D=10$, the plot in Fig. 7 for the Θ solvent yields $\varepsilon_w^{cc}(D=10)\approx-0.260\pm0.005$, compared with the determined critical adsorption point $\varepsilon_w^{ca}=-0.252$, almost within the error. In athermal solvent, we have observed a shift of $\varepsilon_w^{cc}(D=10)=-0.295\pm0.005$ from the critical adsorption point $\varepsilon_w^{ca}=-0.276$, much larger than that in the Θ solvent. Overall, results for the SAW chains in the Θ solvent are similar to that in the athermal solvent and differ from the results of the Gaussian chains.

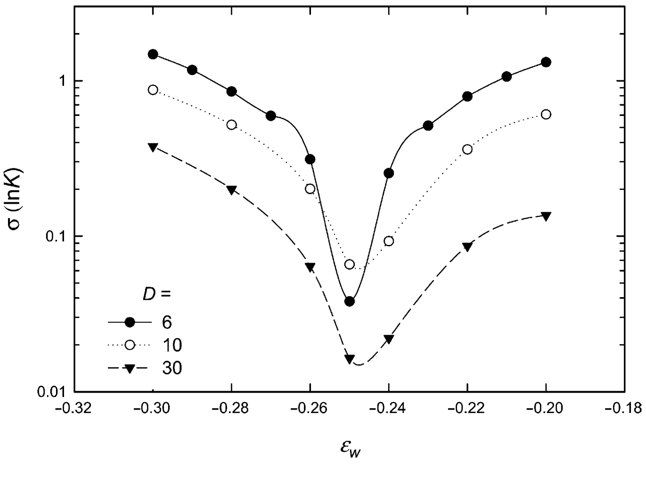

Fig. 6. Plot σ(ln K) vs. ε_w for a self avoiding walk chain partitioning into a slit with width D. The σ(ln K) is computed based on the K for chains with $N=25$–200.

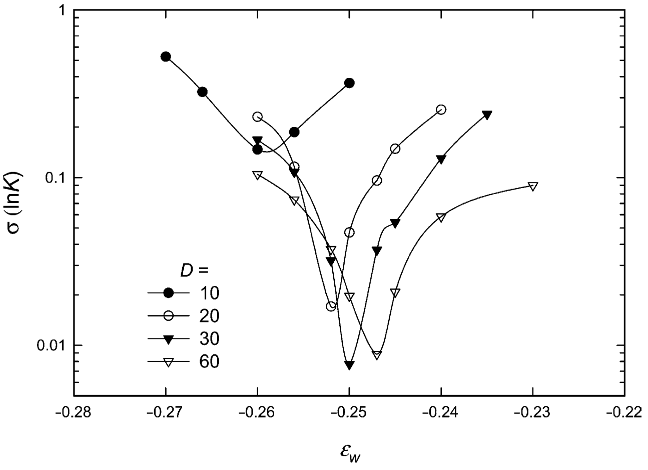

Fig. 7. Plot σ(ln K) vs. ε_w for a self avoiding walk chain partitioning into a square channel with width D. The σ(ln K) is computed based on the K for chains with $N=25$–400.

Another unexpected result, however, emerges from the data in Fig. 7. The value of ε_w^{cc} does not approach ε_w^{ca} for the largest channel widths; instead, for $D=60$, ε_w^{cc} crosses ε_w^{ca} and actually represents a weaker attraction than ε_w^{ca}. To quickly test if the shifting of ε_w^{cc} to a weaker attraction than ε_w^{ca} in an athermal solvent would also occur, simulations were done for athermal chains with a very large channel width, $D=200$. At this large channel width, ε_w^{cc} for the athermal chains shifted to a weaker attraction than ε_w^{ca}, displaying similar behavior to the Θ chains. Hence this phenomenon was inherently present in both cases, and was simply overlooked in the previous study. This result can be explained by considering the differences between the simulations used to determine ε_w^{ca} and ε_w^{cc}. For the simulations used to determine ε_w^{ca}, an attachment between the polymer chain and the surface was required, while in the square channel, the chains were inserted randomly in the pore, making it possible for a chain to be in the middle of the channel without any interaction with the channel walls. Therefore, as D becomes bigger than the bulk sizes of the polymer chains, some of the chains in a simulation will not feel any confinement and be in the middle of the pore, as in a bulk solution. For large pore sizes, ε_w^{cc} will represent a weaker attraction than ε_w^{ca} because the chemical potential calculated in the simulation will become a weighted average of chains that are confined by the walls and chains that are in the middle of a large pore, like in bulk solution.

4. Conclusions

Monte Carlo simulations have been used to study the partitioning of self-avoiding walk polymer chains to pores from a bulk Θ solution near the critical adsorption point. The critical adsorption point, ε_w^{ca}, of the Θ chains was determined by measuring the chemical potential of a chain terminally attached to a solid surface for various values for polymer–surface interaction. The critical adsorption point, $\varepsilon_\mathrm{w}^\mathrm{ca}$, of the Θ chains was found to be in between that for the SAW in athermal solvent and the NRRW chains, an indication that Θ chains do not reduce to the NRRW chains. When partitioning into pores, the Θ chains again do not behave like the NRRW do, but instead behave similarly to SAW in athermal solvents. In a slit pore, the partition coefficient of the Θ chains at the critical adsorption point is greater than one and depends weakly on the chain length. In a square channel pore with small D, there is a strong dependence of K on the chain length at the critical adsorption point, making the critical adsorption point unlikely to be the critical condition employed in experimental LCCC. Instead the critical condition, $\varepsilon_\mathrm{w}^\mathrm{cc}$, was identified by finding the minimum in a plot of deviations in the log of partition coefficients for a given range of chain length against different values for the polymer–surface attraction. The critical condition $\varepsilon_\mathrm{w}^\mathrm{cc}$ thus determined was found to be the same as the critical adsorption point, $\varepsilon_\mathrm{w}^\mathrm{ca}$, in a slit pore. But in a square channel pore, the critical condition $\varepsilon_\mathrm{w}^\mathrm{cc}$ for the Θ chains shifted from the $\varepsilon_\mathrm{w}^\mathrm{ca}$ and varied with channel width D, as it did for athermal chains, although the extent of shift in the surface interaction $\varepsilon_\mathrm{w}^\mathrm{cc}$ from $\varepsilon_\mathrm{w}^\mathrm{ca}$ was smaller than that for the athermal chains.

These results show that partitioning of Θ chains do not follow that of the Gaussian chains. While the Θ solvent is a solvent that will result in real chains with radii of gyration that return to the scaling behavior of Gaussian chains in unconfined, bulk solution, other properties may not return to the results of Gaussian chains. We see here that in confined geometries excluded volume interactions become more prominent, and are not completely canceled with the attractive interactions at the bulk Θ temperature. As a result, the partitioning of the Θ chains into pores does not reduce to the results of the Gaussian chains. Hence, one needs to be cautious about using the Gaussian chain model to study polymer partitioning into pores.

References

[1] Pasch H. Adv Polym Sci 1997;128:1–45.
[2] Pasch H. Adv Polym Sci 2000;150:1–66.
[3] Pasch H, Trathnigg B. HPLC of polymers. Berlin: Springer; 1999.
[4] Baran K, Laugier S, Cramail H. J Chromatogr B 2001;753:139–49.
[5] Brun Y, Alden P. J Chromatogr A 2002;966:25–40.
[6] Chang T. Adv Polym Sci 2003;163:1–60.
[7] Falkenhagen J, Much H, Stauf W, Mueller AHE. Macromolecules 2000;33:3687–93.
[8] Lee HJ, Chang TY. Anal Chem 2001;73:1726–32.
[9] Kitayama T, Janco M, Ute K, Niimi R, Hatada K, Berek D. Anal Chem 2000;72:1518–22.
[10] Janco M, Hirano T, Kitayama T, Hatada K, Berek D. Macromolecules 2000;33:1710–5.
[11] Phillips S, Olesik S. Anal Chem 2003;75:5544–53.
[12] Guttman CM, DiMarzio EA, Douglas JF. Macromolecules 1996;29:5723–33.
[13] Gorbunov AA, Skvortsov AM. Adv Colloid Interface Sci 1995;62:31–108.
[14] Cifra P, Bleha T. Polymer 2000;41:1003–9.
[15] Gong Y, Wang Y. Macromolecules 2002;35:7492–8.
[16] Orelli S, Jiang W, Wang Y. Macromolecules 2004;2004:10073–8.
[17] Berek D, Janco M, Meira GR. J Polym Sci Polym Chem 1998;36:1363–71.
[18] Smit B, Frenkel D. Understanding molecular simulations-from algorithms to applications. San Diego, CA: Academic Press; 2002.
[19] Panagiotopoulos AZ, Wong V, Floriano MA. Macromolecules 1998;31:912–8.
[20] Cifra P, Teraoka I. Macromolecules 2003;36:9638–46.
[21] Hehmeyer OJ, Arya G, Panagiotopoulos AZ. J Phys Chem B 2004;108:6809–15.
[22] De Gennes PG. Scaling concepts in polymer physics. Ithaca, NY: Cornell Univ. Press; 1979.
[23] Raphael E, Pincus P. J Phys II 1992;2:1341–4.
[24] De'Bell K, Lookman T. Rev Mod Phys 1993;65:87–113.
[25] Eisenriegler E, Kremer K, Binder K. J Chem Phys 1982;77:6296–320.