

Steric exclusion/adsorption compensation in partitioning of polymers into micropores in good solvents

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Abstract

Partitioning equilibrium between bulk and slit-like pores in dilute solution was studied by Monte Carlo (MC) simulations on a cubic lattice in the presence of attractive, polymer–pore interaction. Athermal chains with excluded volume of variable lengths were generated in a direct simulation of the equilibrium partition coefficient K . The results show that by the variation of the polymer–pore adsorption energy, ϵ , three modes of liquid chromatography of polymers in good solvents can be reproduced. In contrast to ideal chains, the compensation point where $K = 1$, relevant to critical chromatography, was found to be a function of the chain length. The attraction energy in the compensation point ϵ_c is independent of the slit width and can be identified with the critical energy of adsorption as well as with the adsorption theta point in infinite chains. The counterbalance of steric exclusion (the depletion layer) and wall attraction (the enrichment layer) at the compensation point was confirmed by a flat concentration profile across the pore. The distribution functions of the chain end-to-end distances perpendicular and parallel to slit walls were calculated. It was inferred that in wide pores corresponding to size exclusion chromatography the partitioning proceeds by the coil orientation, and, additionally, that the critical chromatography operates in the regime of weakly adsorbed chains characterized by a diffuse adsorption layer. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Lattice simulations; Partitioning equilibrium; Critical chromatography

1. Introduction

The partitioning of macromolecular solutes between small pores and bulk solution underlies various chromatographic and membrane separation processes. This phenomenon is characterised by the partition coefficient, K , which is the pore-to-bulk concentration ratio at equilibrium. The behaviour of macromolecules in confining geometries was recently reviewed by Teraoka [1]. Theoretical models of partitioning of flexible macromolecules were focused on the pure steric exclusion in infinitely dilute solutions. Owing to the repulsive interaction between a macromolecule and the pore surface there is an entropy cost for the polymers to enter the pore. The analytical approach [2,3] based on the analogy between the diffusion motion of a particle and the conformation of a freely jointed ideal polymer chain provides the relations for the partition coefficient K of the type

$$K \sim \exp(-\alpha_1 \lambda^2) \quad (1)$$

where α_1 is a numerical constant and the coil-to-pore size ratio λ can be expressed as a ratio of the gyration radius of a

chain R_g and a characteristic pore dimension d , $\lambda = R_g/d$. The specific forms of Eq. (1) were derived for various confining geometries such as slit, cylinder or sphere and various chain architectures [1–4]. According to the relation (1), the coefficient K depends on the molecule-to-pore size ratio λ only and not on each of these two parameters taken separately. The steric excluded volume interaction between a macromolecule and a pore is a dominant separation mechanism in the size exclusion chromatography (SEC). The partition coefficient K in SEC of flexible polymers decreases with increasing molecular size of macromolecules.

The computer simulations were method of choice in addressing the steric partitioning of various models of chains and of the confinement geometry. The validity of relation (1) was investigated for the freely jointed chains of variable segment length [5] and for the ideal lattice chains with an adsorbing boundary [6]. The partitioning of the excluded volume chains into a cubic pore was studied by MC simulations on a cubic lattice [7–10]. The comparison [1] of the simulation data [9] with the analytical relation (1) for a cubic pore shows that the excluded volume (athermal) chains enter the restricting geometry more easily than the Gaussian chains of the same R_g . In narrow pores the

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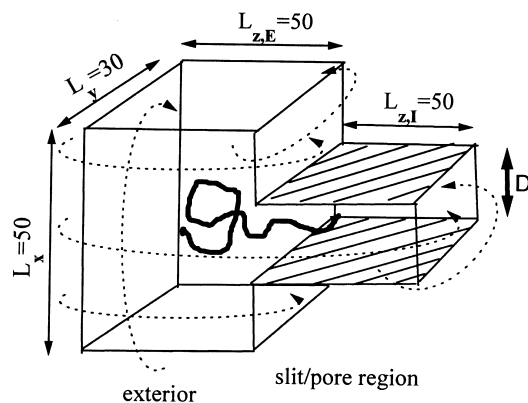


Fig. 1. A scheme of the simulation model.

partitioning of the excluded volume chains was treated by a scaling theory. For infinite chains in the slit-like and cylindrical pores the scaling theory [11] confirms the exponent $x=2$ in relation (1) for the theta solvent but in good solvents the exponent $x=1.7$ should be applied. In the case of athermal chains of finite lengths, scaling arguments were extended [4,12] to deduce the form of an additional pre-exponential factor in relation (1). The concentration of solute is an important variable in the steric partitioning affecting considerably the form of the function K vs λ . An analytical theory [1] and MC simulations [7–9,13] of athermal chains were used to predict the K vs λ curves in dilute and semidilute solutions.

The steric partitioning and molecular separation is substantially affected by attractive interaction between macromolecules and pore walls. To address this problem, the diffusion-equation partitioning theory [2,3] had to be extended to include a short-range adsorption potential and the equation was solved for the various combinations of the molecule-to-pore size ratio λ and the adsorption strength ϵ . The extensive development of this approach by Skvortsov and Gorbunov is summarised in Ref. [4]. The partition coefficient $K(\lambda\epsilon)$ was predicted [4] for the ideal linear and cyclic chains of variable flexibility in the various regimes of narrow and wide pores. The continuum approximation of Casassa was also extended [14] to account for other polymer-pore potentials including the long-range electrostatic interaction relevant for the polyelectrolyte partitioning.

The difference in the adsorption energy of solutes is responsible for the separation in the “ideal” liquid adsorption chromatography (LAC); in contrast to SEC, here the coefficient K increases with the increasing molecular mass M of polymers. In real liquid chromatography (LC) of macromolecules on porous carriers, the combined effect of steric exclusion and adsorption mechanisms is operative. The point where $K=1$ and attractive interaction of walls counterbalances the polymer-pore exclusion is of particular interest in the theory and in chromatographic practice. In the compensation point the entropy losses due to the chain confinement are fully compensated by the adsorption

enthalpy. The chromatography in the range close to the compensation point is termed “critical chromatography”. As at $K=1$ the free energy of a chain in a pore and in bulk is equal, the separation in a column becomes independent of the molecular mass M of solute. This gives the possibility of selectively masking of the component(s) of complex systems or making a part of a macromolecule (a block in block copolymers) chromatographically invisible. Experimental results confirm that the critical chromatography is a versatile method suitable to exploit in separation the difference in the chemical composition of macromolecules (the polymer heterogeneity) in oligomers, block copolymers, polymer blends, etc. [15–17].

The experimental data on the chromatographic separation of polymers by changing the solvent or temperature can be theoretically reproduced using the unified theory of the polymer partitioning by steric exclusion and adsorption [4,18,19]. As a special feature of fitting the chromatographic data by a theory, the independence of the partition coefficient at the compensation point $K=1$ of the molecular mass M was confirmed [18] for ideal chains by using the lattice model [20] with a variable adsorption energy ϵ .

The existing analytical treatments of the exclusion-adsorption compensation phenomenon [4,18] neglect the intrachain excluded volume. As good solvents are frequently used as a mobile phase in LC, we present in this paper the first MC simulations of the steric exclusion and adsorption partitioning of athermal chains into a slit-like pore. The results did not confirm the existence of a single compensation energy ϵ_c predicted for ideal chains. Instead, the compensation point was found to depend on the chain length (or molar mass M). Hence, in critical chromatography in good solvents the steric exclusion/adsorption compensation should occur within a narrow interval of adsorption strengths ϵ_c .

2. The simulation model

Our simulation model is inspired by that of Wang and Teraoka [13] in which we additionally included the polymer-pore wall attractive interaction. Two boxes connected to each other are assumed in simulations on a cubic lattice: the box E, representing the exterior (bulk) phase and the box I, representing the interior slit pore (Fig. 1). The box E has the dimensions $50 \times 30 \times 50$ (in lattice units) along the x , y and z directions, respectively. In the box I of dimension $(D+1) \times 30 \times 50$ there are two solid walls at $x=1$ and at $x=D+1$ extending in the y and z directions and forming a slit. The variable D is defined as a distance between the lattice layers occupied by the walls and is measured in lattice units. The polymer beads are not allowed to occupy the sites on the walls. Periodic boundary conditions apply with respect to all opposite walls in boxes except solid walls.

Selfavoiding athermal walks of the variable length N up

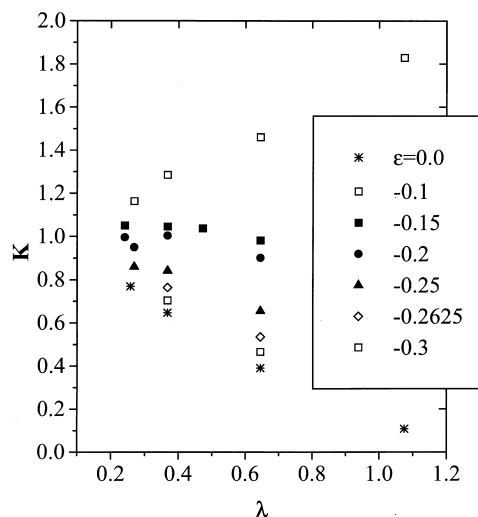


Fig. 2. Plot of the distribution coefficient K vs the ratio $\lambda = 2R_g/D$ for various values of the adsorption energy ϵ .

to 200 beads (199 segments) in the chain were generated. The simulations provide directly the equilibrium concentrations of chains exchanging between bulk and a pore without the necessity to calculate the free energy. Typically the simulations started with two chains in the box E. Chains were equilibrated using the reptation moves and the Metropolis algorithm. The ratio of the volume fractions of a polymer in the interior and exterior boxes at equilibrium, ϕ_I/ϕ_E , gives the coefficient K . The chains in intermediate positions with their parts located in both boxes E and I at equilibrium contributed all their segments either to the volume fraction ϕ_I or to ϕ_E , depending on where the majority of chain segments along the z -axis is located. Up to 2×10^8 chain updates were used; the equilibration required a very long time even for a dilute regime of few chains because all sites in the bulk/pore space have to be sampled.

The short-range adsorption interaction was assumed between the polymer segments and pore wall sites separated

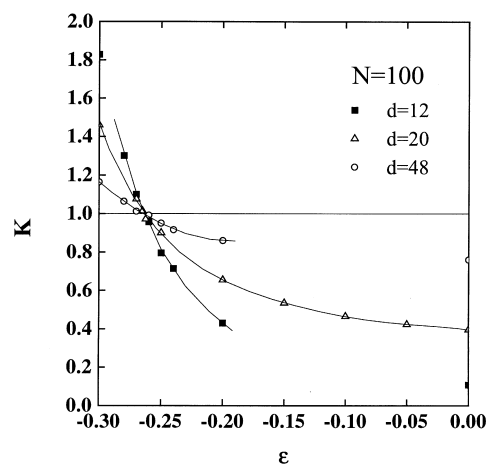


Fig. 3. Plot of the distribution coefficient K as a function of the adsorption energy ϵ for three slit widths $D = 12, 20$ and 48 .

by one lattice unit. The strength of the reduced attraction energy per segment $\epsilon = \epsilon'/kT$ ($\epsilon < 0$) was a variable in the simulation, together with the slit width D and the chain length N . Specifically, we concentrated on finding the reduced adsorption energy ϵ_c where the compensation criterion $K = 1$ was satisfied.

For the chains confined in box I at equilibrium, the end-to-end distribution functions perpendicular, $W(R_{\perp})$, and parallel, $W(R_{\parallel})$, to the walls and the mean-square end-to-end distance $\langle R^2 \rangle$ were calculated. The root-mean-square radius of gyration R_g of free unconfined chains was also determined.

3. Results and discussion

In the athermal system representing good solvents, the volume exclusion of chain segments is secured by the restrictions on the chain conformations imposed by the self-avoiding walks on a lattice. Simulations were performed at slit widths $D = 12, 20$ and 48 . The coil-to-pore size ratio $\lambda = 2R_g/D$ was between 0.2 and 1.1 , covering fully the region of wide pores and partially the region of narrow pores of comparable sizes of a molecule and a pore. We focused on the weakly adsorbed chains; the reduced adsorption strength ϵ was changed from 0 (steric partitioning) up to -0.3 . Variations of the reduced adsorption energy can be interchanged with the variations of temperature.

The gradual change of the shape of the partitioning curve K vs λ with increasing adsorption attraction is shown in Fig. 2 for the chain lengths between 20 and 100 segments. As expected, the coefficient K decreases with λ in the region of prevailing steric exclusion. However, the partitioning curves are shifted to higher λ at $|\epsilon| > 0$, as if the pore width effectively increased with increased attraction. It is interesting that the analogous shifting of the K vs λ curve was observed by an increase in the polymer concentration at pure steric partitioning [1,9]. At present there is no rigorous theory available for the partitioning of linear flexible chains with excluded volume in the presence of attractive polymer-pore interaction. In the ideal chains in the slit-like pores, the steric exclusion equivalent to curve $\epsilon = 0$ in Fig. 2 would be described by Casassa's [2,3] relation (1), and the functions $K(\lambda, \epsilon)$ derived by Skvortsov and Gorbunov [4] would be applicable in the whole regime in Fig. 2 where $|\epsilon| > 0$.

The steric exclusion and adsorption effects in the partitioning compensate in Fig. 2 for ϵ around -0.26 , where K is close 1 and in wide pores, $\lambda < 0.5$, independent of λ . The plot of K as a function of attraction energy for $N = 100$ (Fig. 3) provides a more precise determination of the compensation point. From the intersection of this plot with the line $K = 1$ for $D = 20$ the compensation energy $\epsilon_c = -0.2625$ was determined.

Alternatively, the partitioning can be represented by the dependence of the partition coefficient K on the chain length

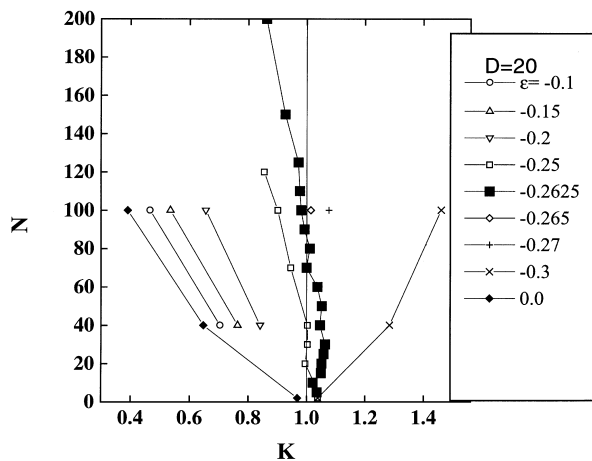


Fig. 4. Distribution coefficient K as a function of the chain length N for various values of the adsorption energy ϵ .

N shown in Fig. 4 for slit $D = 20$ where the simulations of the compensation region are presented in more detail. It is clearly seen that the energy ϵ_c in the compensation point $K = 1$ depends slightly on the chain length N (or molar mass M). For the chain lengths from 70 to 110 the value $\epsilon_c = -0.2625$ is appropriate but in shorter chains the adsorption still prevails ($K > 1$) at this value of ϵ_c , while, on the contrary, in longer chains the above adsorption strength is not yet sufficient to fully counterbalance the steric exclusion ($K < 1$). Thus, in contrast to a single compensation point found in ideal chains [18], in athermal chains the steric exclusion/adsorption compensation occurs within a narrow interval of the adsorption strengths $\epsilon_c(N)$ and by the extrapolation to infinite N the “true” compensation energy ϵ_c may be obtained.

In the ideal chains the steric excluded volume interaction polymer–pore walls is counterbalanced at $K = 1$ by an attraction polymer–pore walls. On the simple cubic lattice this compensation occurs at $\epsilon_c = -0.182$ [4,18]. An inclusion of the intrachain excluded volume into the free energy of partitioning of athermal chains results in the chain-length dependent compensation energy $\epsilon_c(N)$. Moreover, the compensation on a cubic lattice requires a more attractive energy ($\epsilon_c = -0.2625$ at N about 100) for the larger, expanded athermal chains than for ideal chains.

For athermal chains in narrow pores (at $\lambda > 1$) the scaling arguments [4,12] indicated already a possible dependence of the compensation point on the chain length. The scaling functions resembling relation (1) were extended to include the pre-exponential factor and a proportionality was deduced for the partition coefficient in the vicinity of the compensation point, $K_c \sim \lambda^x$, with exponent $x = 5/18$ for a slit-like pore. In order to compare the latter proportionality with data in Fig. 4, the relation can be modified by an introduction of the power law $R_g \sim N^{0.6}$ valid in good solvents. As a result, the function $K_c \sim N^{1/6}$ is obtained, i.e. the partition coefficient in the vicinity of the compensation point should weakly increase with the chain length.

However, the suggested scaling relation [4,12] is apparently inconsistent with the data in Fig. 4 in the region of chain lengths $N > 100$.

The adsorption strength in the compensation point ϵ_c characterising the adsorption in a pore should be closely related to the critical energy for adsorption of a polymer on a single planar surface. In fact, in theoretical treatments of the partitioning of ideal chains [4,18] these quantities were identified. Lattice or off-lattice methods [20–22] were frequently used to study the adsorption of flexible polymers at an attractive planar surface and in the determination of the critical energy of adsorption. This adsorption threshold is characterised by a narrow range of the surface interactions where significant polymer adsorption occurs on the surface. In infinite chains this adsorption transition correspond to a sharp change from the three-dimensional to quasi-bi-dimensional configurations of adsorbed chains [22]. The results in Fig. 3 confirm that in the range of the pore dimensions studied, the adsorption strength at the compensation point ϵ_c can also be in the athermal chains identified with the critical adsorption energy on a single planar surface. All three curves K vs ϵ in Fig. 3 for slits differing in the width intersect at the same energy ϵ_c . This value is evidently determined by the adsorption on individual walls independently, regardless of the distance of the second wall in the slit. In other words, the same attractive energy is needed, for chains to enter a pore and stay there at the concentration corresponding to $K = 1$ in wide pores and in narrow pores, in spite of the intuitively presumed large difference in the steric exclusion between both types of pores, which however applies only when $\epsilon = 0$. Consequently, the chain-length dependence of the compensation energy $\epsilon_c(N)$ observed in Fig. 4 represents also the variation of the critical energy of adsorption with the length of athermal chains.

An interesting parallel exists between the all-included polymer-surface interaction and the intrachain excluded volume interaction in a solvent [23]. The compensation point $K = 1$, counterbalancing the steric exclusion repulsion and adsorption attraction, can be considered in the limit of infinite chains as the adsorption theta point where the polymer–surface interaction vanishes. Such an identification is in full analogy with the definition of the conventional theta point for dilute polymer solutions. The concentration profiles in a pore provide a transparent visualisation of this compensation (see below). A close nature of both types of the theta points is supported by a similarity in respective attraction energies of segment–wall and segment–segment interactions found in the simulations of athermal chains. For a cubic lattice the above-mentioned pore–wall critical energy $\epsilon_c = -0.2625$ differs slightly from the intersegmental interaction energy $\epsilon_\theta = -0.2693$ [24] which reproduces the properties of an unconfined theta chain. The simulations [22] using the coarse-grained off-lattice model provided yet another example of close values of the respective pair of energies, $\epsilon_c = -1.90$ and $\epsilon_\theta = -1.61$.

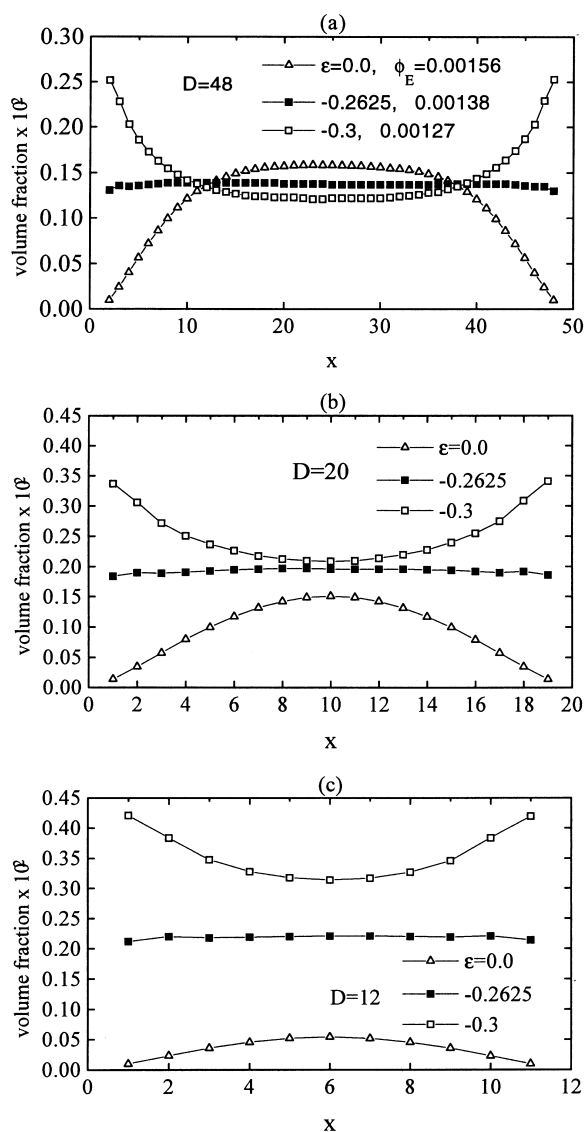


Fig. 5. Variation of the volume fraction of a polymer with $N=100$ in individual layers parallel to the slit walls $\phi_1(x)$ as a function of a distance x across the pore for: (a) $D=48$, $\lambda = 0.269$; (b) $D=20$, $\lambda = 0.645$ and (c) $D=12$, $\lambda = 1.075$.

Microscopic information on the chain confinement across a pore can be obtained from the profiles of local concentrations $\phi_1(x)$ at equilibrium in the layers parallel to the slit (Fig. 5). The averaging of a profile over the span of slit gives the mean intrapore concentration ϕ_1 . The depletion layers on the walls due to steric exclusion of polymer segments are seen on the curves in lower parts of Fig. 5(a)–(c). The wall attraction causes an increase of the chain segment density in the wall vicinity and a layer enriched by a polymer is formed at more attractive adsorption strengths than ϵ_c . The increase of the volume fraction ϕ_1 and of K with an increase in the attraction strength shown in Figs. 2–4 originates in the above mechanism of a gradual change from a depletion layer to an enrichment layer. Both factors, the depletion and enrichment are counterbalanced at the compensation

(or critical) energy ϵ_c for a given chain length. In the compensation point the concentration profiles in Fig. 5(a)–(c) are flat, i.e. the segment concentration is independent of the distance from the pore walls. This unique feature of the behaviour of confined chains, as if there were no walls, is a graphic demonstration of the adsorption theta state. The flat concentration profiles in the compensation point were predicted in ideal chains [4], the inclusion of the intrachain excluded volume makes the occurrence of the flat concentration profiles dependent also on the chain length.

In wide pores the wall confinement and wall attraction effects are discernible up to the distance x about 15 lattice units (Fig. 5(a)). The half of this distance, δ , is called the thickness of the depletion or adsorption layer [21]. As usual, the thickness of the depletion layer is close to the coil radius ($R_g = 6.45$ for $N = 100$). In the pore centre the volume fraction $\phi_1(x)$ approaches the bulk concentration ϕ_E . In pores of intermediate width ($D = 20$), where $\lambda = 0.645$, both the above mentioned effects extend up to the pore centre, but the middle-pore concentrations are still close at the three curves in Fig. 5(b). In a narrow pore where a molecule and a pore have similar dimensions ($\lambda = 1.08$), the confinement effect is strong in the whole span of pore and the concentrations in the profile $\phi_1(x)$ are much reduced (Fig. 5(c)) in comparison with the related profiles in Fig. 5(a) and (b). The pore centre concentration is similarly affected by the wall attraction in a narrow pore; it implies that the thickness of the adsorbed layer is comparable to the coil radius even at $\epsilon = -0.3$, i.e. at the attraction energy stronger than the critical energy.

The confinement and adsorption interaction influence also the chain linear dimensions. The end-to-end distribution functions perpendicular, $W(R_\perp)$, and parallel, $W(R_\parallel)$, to the pore walls are shown in Fig. 6 as a function of the pore width and of the attraction energy. The difference between $W(R_\perp)$ and $W(R_\parallel)$ gives information about the directional anisotropy of coils caused by their deformation or reorientation in the confined geometry. It is apparent from the comparison of Fig. 6(a) and (b) that the confinement geometry has much stronger influence on the chain anisotropy than on the wall attraction, at least in the region of weak adsorption treated here. However, the overall chain dimensions computed for the confined coils are only slightly affected by the pore confinement: the mean-square end-to-end distance $\langle R^2 \rangle$ is 228.4 and 237.6 in pore widths $D = 12$ and 20, respectively. Hence, the observed enhancement of the chain anisotropy by confinement should be caused mainly by an increase of orientation of macromolecules. It is well known that an instantaneous shape of a free unconfined polymer coil resembles the form of a soap bar. The ratio of the shape factors defined along three principal axes of a coil depends on the solvent quality. The off-lattice simulations of athermal chains [25] give the ratio 16.40:3.24:1, i.e. a pronounced coil anisotropy. The principal axes of prolate ellipsoids of unconfined chains

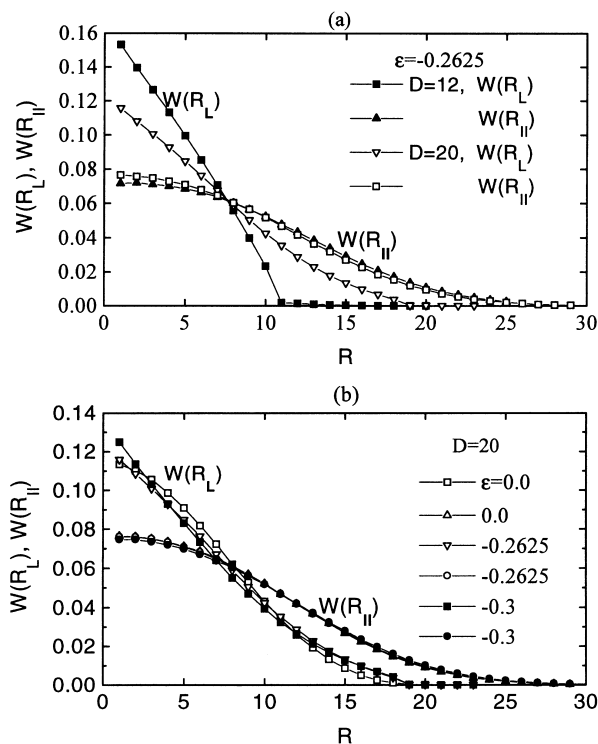


Fig. 6. Plot of the end-to-end distribution functions perpendicular $W(R_{\perp})$ and parallel $W(R_{\parallel})$ to the walls: (a) at the critical adsorption energy $\epsilon_c = -0.2625$ in a slit of widths 12 and 20; (b) in the slit $D = 20$ for various values of the adsorption energy ϵ .

are randomly oriented in a free space. However, in a slit, the preferential alignment of long axes of chains parallel to the pore walls [26,27] results in the difference between the distributions $W(R_{\perp})$ and $W(R_{\parallel})$. In addition, the chains near the walls can also deform by flattening in a direction parallel to the wall, even forming a nearly two-dimensional structure in very narrow pores [27]. Apparently, the reduction of entropy by a steric confinement in a pore is caused mainly by a loss in molecular orientational entropy and to a less degree by a loss in the number of allowed chain conformations. This reasoning is supported by the simulations [28] of incompatible polymer mixtures where the polymer–polymer interface resembles an impenetrable wall. The coils were found to align parallel to the interface and the “true” deformation of the intrinsic shape of coils was considered negligible [28].

The above arguments about the dominance of the chain orientation mechanism over the chain deformation near planar walls referred to pure steric exclusion. Presumably, they can be extended also to weakly adsorbed chains where the alteration of the coil shape by adsorption interaction is minimal. In fact, Fig. 6(b) shows that the increase in the wall attraction brought only the minute increase of the coil anisotropy given by the difference between $W(R_{\perp})$ and $W(R_{\parallel})$. At the same time the overall dimensions of confined chains slightly increase with the adsorption strength, $\langle R^2 \rangle$ is 227.2, 237.6, 244.3 for $\epsilon = 0, -0.2625$ and -0.3 , respec-

tively. In attractive pores of an intermediate size the distribution $W(R_{\perp})$ has a broad shape and exhibits the high number of conformations with end-to-end distances in the x direction of 10 and more units (Fig. 6(a)). This is another indication of a highly diffusional character of the adsorption layers on the walls, with numerous segments extending far to the pore centre and beyond. Even in a narrow, attractive pore the distribution $W(R_{\perp})$ is rather broad and abruptly cut as some of the chains evidently bridge the whole span of the pore (Fig. 6(a)). This observations substantiate our belief that the simulations cover the regime (including the compensation point) of weakly adsorbed chains characterized by a few polymer–surface contacts and numerous loops and tails. The adsorption transition into a compressed quasi-two-dimensional adsorption layer, densely covering the surface by forming the “train” sequences of adsorbed monomers [21], occurs for finite chains at the adsorption strength much higher than the critical adsorption energy [22].

4. Implications for critical chromatography and conclusions

In liquid chromatography (LC) of polymers three modes are exploited: size exclusion (SEC) and liquid adsorption (LAC) chromatography and their combination in the vicinity of compensation point, variably denoted as critical chromatography, liquid chromatography at the critical point of adsorption, liquid chromatography at the point of exclusion–adsorption transition, etc. [15–17]. Three LC modes lead to the different functions of the partition coefficient K (proportional to the retention volume V_R) on the molar mass M . Our results show that all three LC modes can be coherently described by the variation of the polymer–pore adsorption energy ϵ for polymer chains expanded in good solvents. In this way the simulations complement the previous treatments [4,18] of the partition of ideal chains. However, in application of simulations to LC, the attraction energy ϵ should be redefined as the average segment–substrate interaction energy in a given solvent (mobile phase).

In critical chromatography in the vicinity of $K = 1$ macromolecules of any molecular mass are eluted from the column together with the low-molecular solvent, i.e. macromolecules are chromatographically invisible. Experimental results confirm that the critical chromatography is a versatile method suitable to exploit in separation the difference in the chemical composition of macromolecules in oligomers, block copolymers, polymer blends, etc. [15–17]. Our results show that in contrast to the usually presumed existence of a single universal compensation point $K = 1$, in good solvents the compensation point depends on the molar mass M of the solute. In other words, in LC of solutes differing in M , the steric exclusion/adsorption compensation should occur within a narrow interval of the adsorption strengths ϵ_c . Moreover,

the simulations predict that the compensation point (for a given M) is independent of the pore dimensions and thus, of the pore size distribution of column packing.

The microstructural information obtained from simulation indicate that the critical chromatography operates in the regime of weakly adsorbed chains characterized by a diffuse adsorption layer with a numerous loops and tails extending deep to the pore interior. The separation in SEC and in critical chromatography is enhanced in wide pores by orientations of coils shaped as prolate ellipsoids along the pore walls. The deformation of an intrinsic shape of polymer coils becomes important in narrow pores only.

Acknowledgements

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