Free Energy and Dimensions of Macromolecules under Confinement in Layered Assemblies

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Summary: The changes in the free energy ΔA accompanying penetration of polymer solutions from bulk into slit-like cavities were determined by lattice simulations. In dilute solutions the thermodynamics of penetration is controlled mainly by the parameter ε_w specifying interaction between polymer and walls of repulsive or adsorptive cavities. However, the magnitude of $|\Delta A|$ is substantially reduced by increasing concentration ϕ in bulk solution. Furthermore, compression of chains by concentration in good solvents and adsorptive cavities was found to be larger in the slit then in the bulk. At intermediate confinement, a region of a minimum coil size was observed at all concentrations and attraction strengths, where molecules are squeezed along all three axes.

Keywords: coil dimensions; intercalation thermodynamics; Monte Carlo simulation; organoclay; polymer adsorption

Introduction

Polymer systems confined on the molecular length scale display the structure and properties differing from bulk systems. Macromolecules constrained by the environments include polymer inclusion compounds and polymer intercalates. In clay-based polymer intercalates the chain molecules diffuse from solutions or a melt into confining spaces formed by galleries (sheets) in layered silicates. It is believed that novel physical properties of materials can be obtained by intimate interaction between chains and a confining medium. On the other hand, the layered composite systems provide unique information on the structure and dynamics of macromolecules in a slit-like confinement which can be confronted with the results of computer modelling.

In this paper the changes in the free energy and the size of flexible macromolecules accompanying penetration of polymer solutions into the repulsive or attractive slit-like cavities are investigated by lattice Monte Carlo simulations. The computational procedure used was

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described in details in our previous papers.[1,2] The excluded volume chains of the length N=100 were generated on a cubic lattice under good solvent conditions. Two interconnected boxes are considered in the simulations, representing the bulk phase and the slit of the width D at equilibrium. Adsorptive cavities were accounted for by assuming attractive interaction ε_w between polymer segments and cavity walls. The simulations provide the ratio of the polymer volume fractions in both boxes at equilibrium $\phi_I/\phi=K$ and the mean-square end-to-end distances of confined chains $<R^2>$.

Free Energy Changes at Penetration of Molecules between Plates

The thermodynamics of the penetration of molecules from a bulk solution into the sheet-like structures was examined as a function of the slit width D, bulk polymer concentration ϕ and wall attraction strength ε_w. Dilute and concentrated solutions placed between slit plates at weak and moderate confinements and segment-wall attractions were considered. The radius of gyration of the free unconfined chains of N=100 in the dilute solution limit is R_g=6.45.

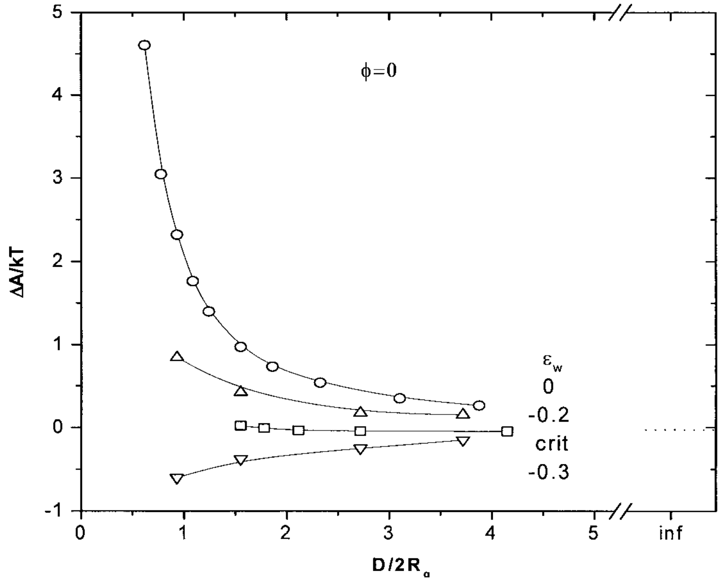

Fig. 1. Variation of the free energy of penetration $\Delta A/kT$ with the normalized plate separation $D/2R_g$ at various attraction strengths ε_w at infinite dilution.

The free energy of confinement $\Delta A/kT$=-ln$K$ in the dilute regime varies considerably with the slit width (Figure 1). For repulsive walls the penalty for penetration, due to a loss of conformational entropy of chains on confinement, increases for narrow slits. In contrast, the free energy gain ($\Delta A/kT<0$) is seen for adsorptive walls, representing a driving force for the chain penetration into a slit. At the critical point of adsorption, ε_c=-0.2625, the free energy of confinement vanishes due to the compensation of steric exclusion (entropy loss) and attraction energy gain.[1]

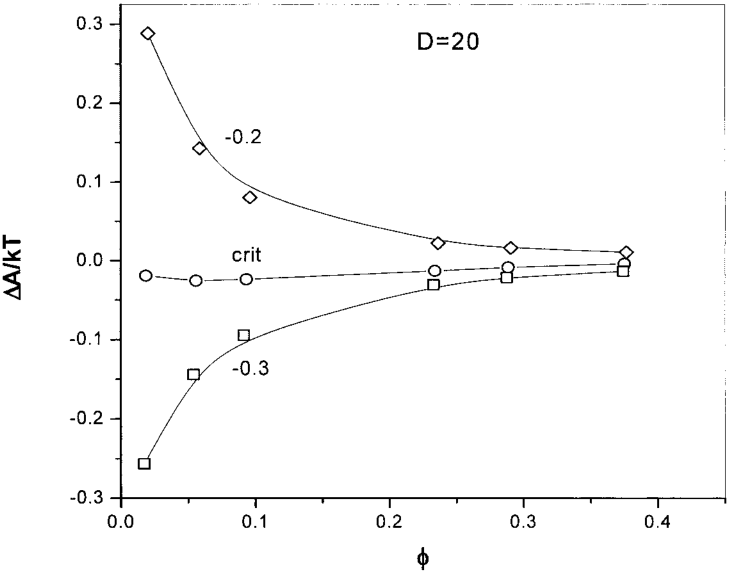

Fig. 2. Variation of the free energy $\Delta A/kT$ with bulk concentration ϕ for various attraction strengths ε_w at weak confinement $D/2R_g$=1.55.

However, an increase in the bulk concentration ϕ markedly affects the free energy changes at penetration (Figure 2). In the region below the critical point, where steric exclusion prevails, the penalty $\Delta A/kT$ is reduced by ϕ and penetration of macromolecules into cavities increases. This phenomenon can be explained[3] by the osmotic pressure, i.e. the repulsion of coils at higher ϕ effectively pushing the chains into cavities. The osmotic pressure-driven increase of penetration occurs around the coil overlap concentration, ϕ^*=0.12 in good solvents. On the other hand, for adsorptive cavities where $|\varepsilon_w|$ is above the critical point of adsorption ε_c, the driving force for penetration is significantly reduced by an increase of ϕ. Evidently, an increase of the bulk concentration ϕ smears the difference between attractive and repulsive cavities and $\Delta A/kT$ approaches zero as the solution changes to a melt ($\phi \rightarrow 1$).

Modelling of penetration via the "confined" adsorption of polymers into slit-like cavities is relevant e.g. to intercalates prepared by exfoliation of layered silicates and adsorption of polymers from solution.[4] For example, the data on the free energy changes on confinement from simulations can be used in the mean-field model[5] of thermodynamics of intercalation into organically-modified layered silicates, instead of an approximate random-flight-chain relation originally employed.[5] The correspondence between universal lattice models and real chains is usually made by equating the lattice modulus with the Kuhn segment length l_K. The length l_k is, for example, about 0.6 in polyethylene oxide (PEO) and about 1 nm in polyethylene (PE). Hence, the lattice simulation data correspond to the above polymers of molecular weights M=7000 and M=14000, respectively. However, since galleries of layered silicates may progressively open at chain penetration the variation of the width D has to be accounted for in computations.

Variations of Coil Dimensions with Confinement

Macromolecules accommodate their size and shape to a one-dimensional confinement in a slit. The mean dimensions of confined chains $<R^2>$ are a complex function of all the three variables examined in simulations: confinement D, bulk concentration ϕ and the attraction strength ε_w. First, variations of the mean dimensions $<R^2>$ of a single excluded volume chain with the slit width D are analysed. The respective curves for various wall attraction ε_w at $\phi \rightarrow 0$ (Figure 3) exhibit a minimum located near the point where the coil-to-pore size ratio $D/2R_g$ is about one. Such a pattern in the variation of the coil size with confinement was previously reported in the case of repulsive walls.[6,7] At large slit widths D, the coil size is slightly reduced relative to the dimensions in bulk and prolate ellipsoids, characteristic forms of coils in dilute solutions, tend to be preferentially aligned by their longest axes along the slit walls. At intermediate confinement, the molecules become squeezed along all three axes and chain dimensions attain a minimum in their dependence on D. Finally, at strong confinement, the chain is severely flattened into a "pancake" shape with the steep increase of its dimensions. The data in Figure 3 show that the characteristic pattern of this dependence is also retained for attractive walls at infinite dilution, just the adsorption effects partially offset the squeezing of coils. In contrast to the free energy dependences, no singular behaviour in the mean dimensions of coils is seen in Figure 3 at the critical point of adsorption. For ideal (Gaussian) macromolecules, the change in their shape from spherical into more or less flattened droplets was suggested[8] to occur at ε_c.

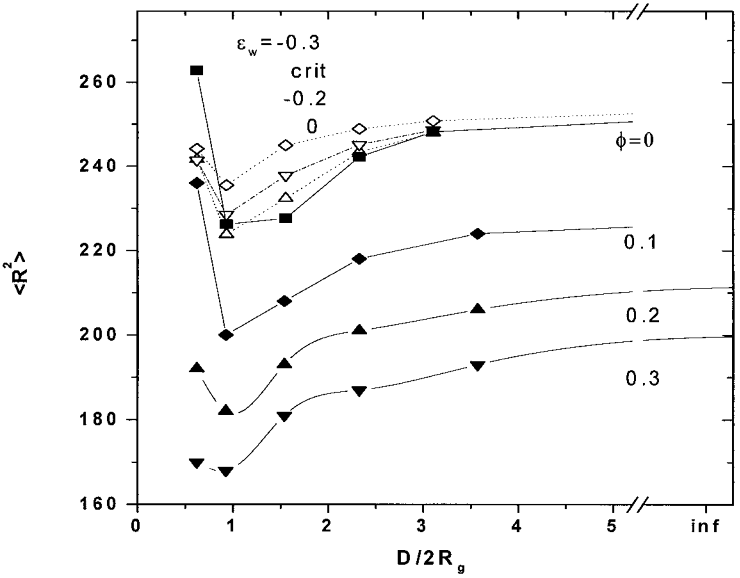

Fig. 3. Variation of mean coil dimensions with confinement in an slit of variable attraction strength ε_w and concentration ϕ.

Next, the concentration dependence of the mean dimension was examined (Figure 4). For bulk solution simulations reproduce the familiar strong reduction of chain dimensions by concentration in good solvents. In confined solutions this concentration-induced compression is even larger for adsorptive cavities; the curves pertaining to the slit are shifted to lower values of $<R^2>$ relative to the bulk.[7] The influence of attractive interaction is noticeable in dilute solutions only, where the adsorption on the walls brings about a slight expansion of the mean dimensions.

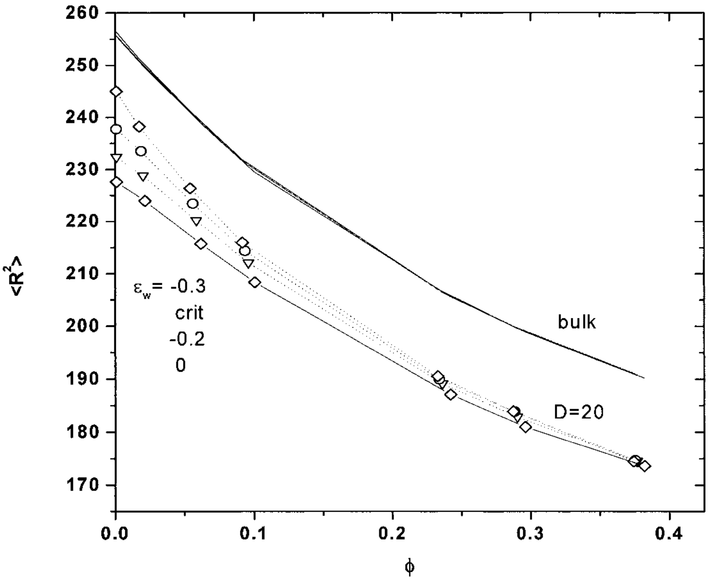

Fig. 4. The change of mean coil dimensions with bulk concentration ϕ in a slit of D=20 at various attractive strengths ε_w.

The data on the concentration-induced compression of chains in Figure 4 can be used in rationalization of the confinement effect on the chain dimensions at finite concentrations (Figure 3). All confinement curves at finite concentrations are shifted to lower $<R^2>$. Nevertheless, the characteristic pattern is maintained, only the minimum becomes less pronounced at higher ϕ. The effect of the attraction strength, which is minor already at low ϕ, further diminishes at finite ϕ. From the pair of variables ϕ and ε_w affecting the coil size in a slit, concentration is evidently the dominant parameter.

Conclusion

The simulations have shown that the free energy change on confinement of flexible polymers in sheet-like structures changes from a penalty (ΔA>0) for repulsive walls to a gain (ΔA<0) for attractive walls. However, the wall attraction strength is a controlling factor of penetration in very dilute solutions only. At higher concentrations the difference between attractive and repulsive cavities gets smaller and $\Delta A/kT$ approaches zero as the solution changes to a melt ($\phi\to 1$). Thus, an increase in polymer concentration in a bulk solution should enhance (reduce) the polymer intercalation into repulsive (adsorptive) layers relative to dilute solutions.

As regards the mean chain dimensions $<R^2>$ it was found that the reduction of the coil size in good solvents at finite concentrations is larger for molecules in the slit than in the bulk. The mean dimensions of confined chains drop by increasing ϕ and rise by increasing the attraction strength ε_w. The variation of the mean dimensions $<R^2>$ with the wall separation D exhibits a minimum corresponding to squeezing of coils along all three axes at all concentrations and attraction strengths. This characteristic pattern of the coil size variations with confinement contrasts with the monotonous changes of the analogous free energy function.

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