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Density of polymers in a layered structure: An exactly solvable model

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We have developed an exactly solvable model that makes it possible to calculate the density profile of polymers filled inside a chemically nonuniform structure that consists of alternating layers that have different affinity for polymers. It is shown that the mean density of polymers in this layered structure is in excess relative to that in the uniform system that has the same average affinity for polymers. The average excess density of polymers in the layered structure is calculated as a function of their degree of polymerization, layer thickness, and affinities of the layers for polymers. The developed theoretical model is shown to have relevance to several experimentally important chemically nonuniform layered systems like microphase separated diblock copolymers and selective mixed brushes.

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Being placed inside a spatially nonuniform host system, polymers can significantly change their density structure. This change of the structure relative to the uniform polymer system results from that the polymer chains adjust their conformations in order to lower the enthalpy of their interaction with the nonuniform host system. This enthalpic effect is opposed by the loss of the polymer entropy that accompanies the above interaction-induced reduction of the conformational degrees of freedom of polymers. The counterbalance between the enthalpic gain and entropic loss associated with any given polymer conformation determines the relative contribution of this conformation to the structure of the polymer density in thermal equilibrium.

A fertile ground for the interplay between the above enthalpic and entropic effects on the structure of polymers is provided by a chemically nonuniform host system composed of alternating layers that have different affinities for polymers. For a common example of such systems we refer to the lamellar microphase-separated diblock copolymers and lipid/water systems. Yet another, more recent example of the periodic chemically nonuniform host system is provided by the binary mixed brush [1,2], the self-adoptive responsive material that can change its morphology in response to altering external conditions (e.g., the quality of the solvent). Once the degree of incompatibility between the brush species A and B reaches its critical value, the binary brush microphase-separates by splaying the chains of the same type together. The thus formed "ripple" [1,3] morphology of the brush consists of a set of alternating distinct clusters of species A and B separated by a solvent [2,4]. Being adsorbed in the top layer of the ripple brush morphology, the "foreign" polymer experiences the action of the nonuniform potential V that comprises the interactions of this polymer with the clusters of species A, B and the solvent. At high degrees of incomparability between species A and B, the clusters of these species are well segregated in the top layer of the brush, so that the above potential V can be taken in the form

$$\beta V = c_0 + c\sum_m [\delta(x-(2m+1)d) - \delta(x-2md)], \qquad (1)$$

where c_0+c and c_0-c are the Flory-Huggins parameters that describe the strength of the interaction between the foreign polymer and the species A and B, respectively, and d is the separation between the neighboring clusters. In the case of the ripple morphology of the mixed brush, each positive (negative) delta functional term in Eq. (1) represents the cluster of the species A (B).

Note that the potential V given by Eq. (1) is nothing but a sum of the attractive and repulsive delta comb potentials. In spite of its highly idealized nature, the delta comb potential is known to adequately describe the structure of polymers in the previously investigated periodic systems [5,6], the use of this singular potential being tantamount to the considerable simplification of the mathematical description. Strictly speaking, modeling the extended clusters by the one-point delta functions is well justified in the case of high incompatibility between the species A and B only. In this case the lateral dimension of the above clusters in the top layer of the brush is of the order of several monomer units [4]. The external field produced by the clusters of such small extensions can be reduced to the action of one-point delta potentials in the framework of the diffusion approximation [7]. This approximation, which will be used to describe the structure of foreign polymers in a layered host, is based on the realistic assumption that the typical length of spatial inhomogeneity in the system is much bigger than the monomer unit. The same assumption justifies neglecting the imperfections that arise from the lateral inhomogeneities in the periodic brush structure. At moderate degrees of incompatibility, where the clusters of A and B species become quite extended, the potential V in Eq. (1) retains only key properties of the true layered host, such as the periodicity of the system and selectivity of the host species with respect to the foreign polymer. As will be shown in the present work, the periodicity of the external field produced by a layered host, as expressed through the potential V, by itself leads to a significant enhancement of the total amount of polymers that can be "stored" in this periodic system. Specifically, the total amount of polymers that must be placed into the host mate-

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*Corresponding author. Email address: chervanyov@ipfdd.de rial in order to attain thermodynamic equilibrium with the external bulk system is proven to be larger for the layered host structure than for its uniform counterpart. The above described reversible switching between the ripple and random morphologies of the mixed brush that produces or, alternatively, destroys the described structure of alternating clusters of A and B species can therefore be used for absorbing foreign polymers from ambient polymer systems (e.g., semidilute polymer solution).

Yet another mathematical simplification comes from the fact that we restrict the consideration to the case of the dilute solution of polymers in the host system. In this case, both the intra- and interpolymer interactions are well screened in the interior of the layers. This screening provides justification to neglect the above intra- and interpolymer interactions, as compared to the interaction between the foreign polymers and the species A and B comprising the layers.

A technical side of the calculation of the density structure of polymers immersed in a layered structure also merits a few comments. First of all, to the best of the authors' knowledge, no exact solvable models of this system are proposed to date. The previous work [5,8,9] gives valuable insight into the structure of an *individual* Gaussian polymer chain in the periodic potentials and localization of this chain in aperiodic potentials. This study relies on the analogy between the relevant mathematical problem and the solid state theory of the motion of electron in a periodic crystal, which has been first pointed out by de Gennes in Ref. [10]. A rigorous treatment of this problem is prohibitively complicated, as it requires the calculation of the two-point propagator of the polymer chain in the direct space, so one has to resort to appropriate approximation schemes (e.g., the ground state dominance).

In the present work we propose a different, entirely rigorous approach that is suited for the consideration of the many-chain polymer system in terms of its coordinate-dependent density. The proposed method of calculation takes full advantage of the spatial periodicity of the polymer density in the layered host structure, which produces a considerable simplification of the mathematical formalism. Being combined with the symmetry of the potential considered, the above simplification leads to analytically solvable model for the polymer density distribution in the host system of alternating layers.

A minimal model to describe the counterbalance between the volume interactions and altering the conformational entropy of polymers in the nonuniform layered structure, which is outlined in the introductory part, is provided by the Edwards diffusion equation for the propagator $Q(\vec{r},n)$ of Gaussian (ideal) polymers in an external field V, of the form

$$\partial_n Q(x,n) = \nabla^2 Q(x,n) - \beta V(x) Q(x,n). \tag{2}$$

Here β is the reciprocal temperature, n is the natural parameter of the polymer contour curve, and x is the coordinate along the direction normal to the interfaces between layers. Hereafter, all lengths are measured in the polymer segment Kuhn length b divided by $\sqrt{6}$, so that, for instance, the radius of gyration of the polymer reads $R_G = \sqrt{N}$, N being the degree of polymerization. The propagator Q in Eq. (2) describes the probability to find one end of the polymer of the degree of polymerization N at the position x given that its other end is uniformly distributed in space. This latter condition is described by the initial condition $Q(x,0)=1$ imposed on the solution of the modified diffusion equation in Eq. (2). The foreign polymers in the layered structure are assumed to be in thermodynamic equilibrium with the external homogeneous polymer system, which is described by the bulk density ρ_b and temperature T.

It proves convenient to rewrite the Edwards equation in the integral form in terms of the Laplace transform of the propagator Q defined by $\widetilde{Q}(x,s) = \int_0^\infty \exp(-sn) Q(x,n) dn$. This reads

$$\widetilde{Q}(x,s) = s^{-1} - \int_{-\infty}^{\infty} V(x_1) \widetilde{Q}(x_1,s) \widetilde{\kappa}(x - x_1, s) dx_1, \tag{3}$$

$\kappa(x,n) = (4\pi n)^{1/2} \exp(-x^2/4n)$ being the Gaussian.

Now we will demonstrate that the linear integral equation in Eq. (3) can be easily solved by recognizing the fact that the propagator Q must be a periodic function of the coordinate x. In particular, $\widetilde{Q}$ has the same values at $x=2md$ and $x=(2m+1)d$, the values of the x coordinate that describe the location of the attractive and repelling delta peaks, respectively. It is therefore possible to introduce the common notations $q_\pm(s) = [\widetilde{Q}(2md) \pm \widetilde{Q}((2m+1)d)]/2$ and rewrite Eq. (3) in the form

$$\widetilde{Q}(x,s) = s^{-1} - c[q_-(s) \widetilde{\sigma}_+(x,s) + q_+(s) \widetilde{\sigma}_-(x,s)], \tag{4}$$

where the sums $\sigma_\pm$ are defined by

$$\sigma_\pm(x,n) = \sum_m (\pm 1)^m \kappa(x - md, n), \tag{5}$$

and we have omitted the constant part of the potential c_0 for the sake of brevity. Note that this omitted part can be easily taken into account by multiplying the final result for the propagator Q by the factor $\exp(-c_0 n)$.

Substituting $x=md$ into Eq. (3) and solving the obtained set of linear equations for $q_\pm(s)$ one finds

$$q_+ = \frac{s^{-1}}{1 - c^2 \widetilde{\sigma}_+(0,s) \widetilde{\sigma}_-(0,s)}, \quad q_- = \frac{c s^{-1} \widetilde{\sigma}_-(0,s)}{1 - c^2 \widetilde{\sigma}_+(0,s) \widetilde{\sigma}_-(0,s)}, \tag{6}$$

and

$$\widetilde{Q}(x,s) = s^{-1} + \frac{s^{-1} c [c \widetilde{\sigma}_+(x,s) \widetilde{\sigma}_-(0,s) + \widetilde{\sigma}_-(x,s)]}{1 - c^2 \widetilde{\sigma}_+(0,s) \widetilde{\sigma}_-(0,s)}. \tag{7}$$

The obtained result for the propagator Q in Eq. (7) can be further simplified by calculating the sums $\sigma_\pm$. Taking the Laplace transform of $\sigma_\pm$ given by Eq. (5) and performing the summation in the interval $x \in [0,d]$ result in

$$\widetilde{\sigma}_+ = \frac{\cosh((d/2 - x)\sqrt{s})}{2\sqrt{s} \sinh(d\sqrt{s}/2)}, \quad \widetilde{\sigma}_- = \frac{\sinh((d/2 - x)\sqrt{s})}{2\sqrt{s} \cosh(d\sqrt{s}/2)}. \tag{8}$$

Note that the formulas for $\widetilde{\sigma}_\pm$ in Eq. (8) that are valid only for $x \in [0,d]$ can be extended over the entire x axis by making use of the equalities $\widetilde{\sigma}_\pm(x+d,s) = \pm \widetilde{\sigma}_\pm(x,s)$ that stem from the periodicity of the potential V. It is also important to note that, as follows from Eq. (8),

$$\tilde{\sigma}_{+}(0,s)\tilde{\sigma}_{-}(0,s) = (4s)^{-1}, \tag{9}$$

which makes it possible to directly invert the Laplace transform in Eq. (7) and calculate the propagator $Q(x,n)$. The results reads

$$Q(x,n) = 1 + c\exp\left(\frac{c^2 n}{4}\right) \otimes \left\{ \kappa(x,n)\,\theta_4\left(\frac{xd}{4in}, e^{-d^2/4n}\right) + c\left[\kappa(x,n)\,\theta_3\left(\frac{xd}{4in}, e^{-d^2/4n}\right)\right] \otimes [\kappa(0,n)\,\theta_4(0,e^{-d^2/4n})] \right\}, \tag{10}$$

where $\otimes$ stands for the convolution in n, and $\theta_n(z,x)$ is the elliptic theta function [11].

The explicit expression for Q in Eq. (10) gives the solution of the initial value problem given by Eq. (2) with the potential defined by Eq. (1) and the initial condition $Q(x,0)=1$. This solution describes altering the polymer free energy due to the redistribution of the polymer density in the layered A-B structure relative to the homogeneous density distribution in the Gaussian polymer system. The above distribution of the polymer density in the alternating A, B layers can be calculated by making use of the standard [7] formula

$$\rho(x) = \frac{\rho_b}{N}\int_0^N Q(x,n)Q(x,N-n)dn, \tag{11}$$

where ρ is the coordinate-dependent monomer number density. Note that in the absence of the external potential V one has $Q=1$ so that $\rho(x)$ in Eq. (11) reduces to its bulk value ρ_b. As is expected, the monomer number density $\rho(x)$ given by Eq. (11) and propagator Q given by Eq. (10) are periodic functions of the coordinate x with the period $2d$.

Substituting propagator Q given by Eq. (10) into Eq. (11) leads to a quite cumbersome expression for the density profile $\rho(x)$ in terms of the strength c of the delta potentials, the separation d, and the degree of polymerization N. For the sake of brevity we restrict ourselves to the detailed consideration of the excess number density defined by

$$\eta = \int_{-\infty}^{\infty} [\rho(x)/\rho_b - 1], \tag{12}$$

which proves to be beneficial for that this quantity can be reduced to a tractable analytic form. Note that the magnitude of η equals the difference between the total amount of foreign polymers per unit volume of the layered structure and the bulk density ρ_b. Positive values of η describe the excess (above the bulk) amount of polymers in the layered structure.

Substituting $Q(x,n)$ given by Eq. (11) into Eq. (12) and integrating the result according to Eq. (12), one finds

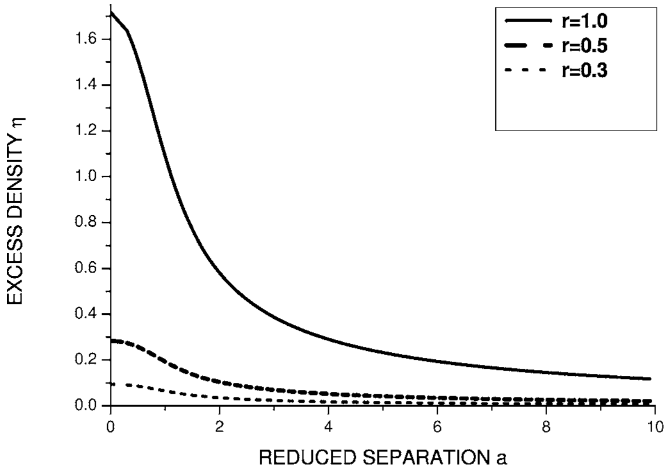

FIG. 1. Average excess monomer number density η given by Eq. (13) as a function of the reduced separation a for several values of the interaction parameter r.

$$\eta = \frac{2}{a\sqrt{\pi}}\int_0^1 (e^{r^2(1-y^2)} - 1)\,\theta_4(0,e^{-a^2/y^2})dy, \tag{13}$$

where we have introduced the notations $r=c\sqrt{N}/2$ and $a=d/2R_G$.

The expression for η given by Eq. (13) is the central result of the present work that will be analyzed with help of Fig. 1 that shows $\eta(a)$ as a function of the reduced separation a for several values of the interaction parameter r. Figure 1 clearly shows that in spite of that the spatial mean of the potential V is zero, the total amount of polymers located inside the layered structure is different from what would have been observed if had there been no attractive and repelling layers (i.e., in the bulk, as defined by the homogeneous density ρ_b). This qualitative conclusion can be rationalized by saying that the chemical nonuniformity of the layered structure acts as an effective attractive potential. This effective potential leads to a decrease in the chemical potential of the polymers filled in the layered structure relative to the chemical potential of the polymers in the bulk. In order to compensate for thus created "osmotic" pressure that stems from the above difference between the chemical potentials, the system responds by increasing the density of polymers in the layered structure relative to that in the bulk. In full accordance with the above arguments, the thus occurred excess (above the bulk) of polymers in the layered structure is described by the positive values of η depicted in Fig. 1 for different values of the parameters a and r.

As is seen from Fig. 1, the average excess monomer number density η is a monotonic decaying function of the reduced separation a for any value of the interaction parameter r. This function has a finite value for $a=0$ and it tends to zero as the separation approaches infinity. The described behavior of the polymer density as a function of a can be understood by recognizing the fact that η in Eq. (13) can be presented as a product of the spatial density of delta potentials ρ_δ and the average excess polymer density produced by one delta potential $\Delta\eta_1$. The above spatial density of delta potentials ρ_δ

(the number of potentials per unit length) is nothing but a reciprocal separation $1/d$. The excess polymer density $\Delta\eta_1$ per delta potential is an increasing function of the separation that turns to zero at $a=0$ and saturates to an r-dependent finite value at $a\to\infty$. The behavior of η at large separations is therefore fully determined by the behavior of ρ_δ, i.e., one has $\eta\sim a^{-1}$ for $a\gg 1$. For small separations $a\ll 1$, an infinite increase of $\rho_\delta=1/d$ is compensated by the linear decrease of $\Delta\eta_1\sim d$, so that the excess density η tends to a finite value that can be evaluated as $\exp(c^2N)-1$. However, it must be noted that the limit $d\to 0$ is rather unphysical. This is because the real potential always has a nonzero radius, in contrast to its idealized counterpart presented by the delta function in the above consideration. So, strictly speaking, the above radius is to be considered a lower bound for the allowed values of the separation d, which therefore never turns to zero.

It is interesting to investigate how well the exact result for η given by Eq. (13) agrees with its "ground state" (i.e., the limiting case $N\to\infty$) counterpart. Taking the asymptotic limit $N\to\infty$ results in

$$\eta = 4e^{r^2}(cd)^{-1}\tanh(cd/4) - 1. \tag{14}$$

The result for η in Eq. (14) describes the limiting case where the radius of gyration R_G of the polymer is much bigger than the host periodicity d. Note that even in the above limit $N\to\infty$ the interaction parameter $r=c\sqrt{N}/2$ has typical values of the order of unity. This evaluation of r stems from the fact that the realistically high degree of polymerization $N\sim 10^4-10^6$ is compensated by small [13] values of $c\sim 10^{-2}$ in the product $r=c\sqrt{N}/2$.

The ground state limit of η calculated by Eq. (14) for $r=1$ is plotted in Fig. 2 against its exact counterpart given by Eq. (13). According to this figure, the ground state limit and the exact result for η are in reasonably good agreement in the range $d<2R_G$. For $d>5.4R_G$ the ground state limit in Eq. (14) gives a qualitatively incorrect result: the density of foreign polymers in the host system is depleted relative to the bulk. This conclusion calls for care to be exercised in using the ground state approximation for calculating the structure of nonuniform polymer systems with typical size of inhomogeneity of the order of R_G or bigger. This situation is typical, for instance, for the diblock copolymer systems that host foreign homopolymers of the comparable degree of polymerization.

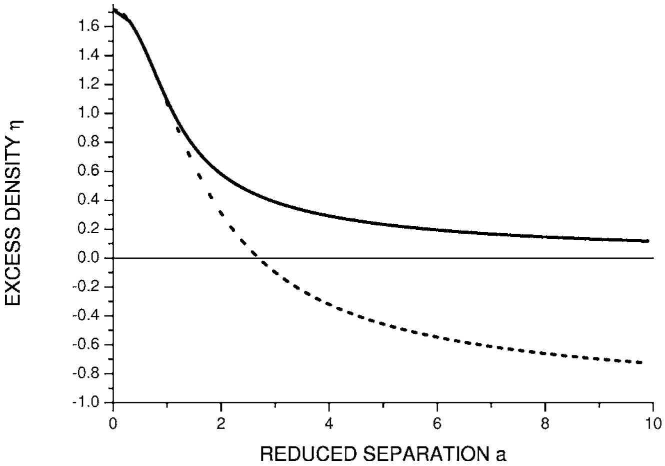

FIG. 2. Comparison between the ground state limit of the average excess monomer number density η given by Eq. (14) (dashed line) and its exact counterpart given by Eq. (13) (solid line). The interaction parameter r is taken equal to 1.

The next important point to be mentioned here is that the aforedescribed "nonuniformity induced" enhancement of the polymer density inside the layered structure is quite analogous to the enhancement of the polymer adsorption onto the patterned surfaces described in Ref. [12]. In the case of polymer adsorption, the patterned surface can be viewed as a two-dimensional layered structure bearing the reversibly adsorbed polymers that are maintained in thermal equilibrium with the "free" polymers in the bulk. The qualitative agreement between the present results and those described in Ref. [12] enhances credibility of the main message of these two works: chemical nonuniformity of the system that serves as a host for foreign polymers causes enhancement of the polymer density relative to the equivalent (in average) uniform host system.

In summary, we calculated the density of polymers filled in the layered host system that has zero average affinity for polymers. The obtained results clearly show that the nonuniformity of the layered structure leads to the enhancement of the average density of foreign polymers relative to its bulk value. Financial support from DFG, SFB 287 is gratefully acknowledged.

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[13] Note that c can be identified with the Flory-Huggins parameter of the interaction between the polymer and host material, which is typically of the order of 10^{-2}.