

Mean Chain Length of Adsorbed Supramolecular Polymers

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We present a theoretical study of reversible supramolecular polymers near an adsorbing surface. Mean chain lengths for free and adsorbed supramolecular polymers were calculated for a broad range of concentrations. As far as we know, this is the first report that describes a regime where the mean chain length *decreases* with increasing monomer concentration. It is shown that this anomalous behavior is caused by a change of the structure of the adsorbed layer.

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Polymers with reversible bonds have provoked a lot of excitement in the scientific community in recent years. Many new types of these novel polymers have been synthesized recently, and these compounds have become known in the field as *supramolecular polymers* [1]. It is to be expected that materials with tailored mechanical and structural properties can be devised from these polymers, since the chain length of supramolecular polymer can be changed reversibly [1]. This gives supramolecular polymers distinct advantages over ordinary polymers with a quenched weight distribution. For example, supramolecular polymers can be used to regulate colloidal stability in suspensions or modify the properties of a surface in ways that are qualitatively different from ordinary polymers [2]. To obtain an understanding of the behavior of supramolecular polymers is crucial in controlling the properties of supramolecular materials.

We present a theoretical study of supramolecular polymers in this Letter. The arguments proposed here are kept general, so the results presented in this Letter are applicable to any material containing linear reversible aggregates. Examples of such systems are liquid sulfur [3], selenium [4], actin filaments [5], and wormlike micelles [6,7]. Moreover, the results presented here are also valid for ordinary polymers with the same size distribution (e.g., condensation polymers) [8].

Supramolecular polymers consist of monomers that are joined by reversible bonds. The number averaged degree of polymerization $\langle N \rangle$ of supramolecular polymers is the most interesting parameter to characterize the system because it depends on the system in the case of supramolecular polymers but is constant for ordinary polymers. In this Letter, a comparison is made between the average chain length of free chains in solution, $\langle N_{\text{bulk}} \rangle$, and the average length of chains that are adsorbed to a surface, $\langle N_{\text{ads}} \rangle$.

While expressions are available for $\langle N_{\text{bulk}} \rangle$, the calculation of $\langle N_{\text{ads}} \rangle$ has not yet been addressed in literature. This issue is essential in understanding the behavior of supramolecular polymers near interfaces. Here, we report numerical calculations of $\langle N_{\text{ads}} \rangle$ and show that $\langle N_{\text{ads}} \rangle$ has a qualitatively different concentration dependence than $\langle N_{\text{bulk}} \rangle$.

Predictions for the weight distribution of supramolecular chains in a homogeneous, isotropic environment go back to a classic paper by Flory [9]. The Flory theory was derived in the context of reacting condensation polymers, but the theory is also applicable to supramolecular polymers. Within the Flory mean-field approximation, it is assumed that the scission energy E_{scis} is independent of chain length and that long chains are formed. It can then be shown [6] that

$$\langle N \rangle \approx \sqrt{\phi} \exp\left(\frac{E_{\text{scis}}}{2kT}\right). \quad (1)$$

Here ϕ is the volume fraction of monomers, k is Boltzmann's constant, and T is the temperature. The result 1 does not depend on the stiffness of the chain.

Lattice models can be useful if a thorough analysis of the model system is desirable. We consider a system that is partitioned into cubic lattice sites with lattice spacing unity. Each lattice site has q neighboring sites, where q depends on the dimensionality of the system. The sites are occupied by either a solvent molecule or a monomer. The solvent molecules are engaged in isotropic interactions with their neighbors. On the other hand, monomers have different faces, and the interaction with a neighboring site therefore depends on their mutual orientation. The monomers have two linking faces, denoted by L , which have a special affinity for each other. The other $q - 2$ "indifferent" faces on the monomer are designated by the letter I . A bond is then formed if linking faces of two adjacent monomers are directed toward each other, and a chain consists of monomers that are connected by such bonds.

An energy u_{ij} is assigned to each contact between a face of type i and a face of type j . For instance, the energy of a contact between two linking faces, u_{LL} , has to be negative in order to obtain appreciable chain formation. Obviously, u_{LL} is related to E_{scis} if all other interactions are zero: $u_{LL} = -E_{\text{scis}}$.

The stiffness of the chain is controlled by means of the energy u_{bent} , which is assigned to each monomer of which the two linking faces are perpendicular to each other. u_{bent} can be related to the persistence length ℓ_p : $\ell_p = 1 + \frac{1}{4} \times \exp(u_{\text{bent}}/kT)$ in a cubic lattice [10].

van der Gucht and Besseling recently applied the Bethe-Guggenheim, or quasicheical, approach to supramolecular polymers in homogeneous and inhomogeneous systems [2,11,12]. Correlations in the occupation of adjacent lattice sites are accounted for in this approach, but pairs of sites are considered to be occupied independently. The Bethe-Guggenheim approach can therefore be regarded as a first-order correction over the random-mixing approximation, in which the occupation of lattice sites is assumed to be stochastically independent.

Usually, only numerical results can be obtained at the level of the Bethe-Guggenheim approximation, but in some limiting cases, analytical results can be found. van der Gucht and Besseling derived an expression of $\langle N \rangle$ for free chains in a homogeneous, isotropic environment [11]. Their result is

$$\langle N \rangle = 1 + \sqrt{\frac{\phi}{q/2 - \phi}} \exp\left(\frac{-u_{LL}}{2kT}\right). \quad (2)$$

The above equation gives a more accurate expression of $\langle N \rangle$ than Eq. (1). It is exact within the Bethe-Guggenheim approximation. Note that the above equation collapses to Eq. (1) in the limit of long, linear chains and low monomer concentrations.

Moreover, Eq. (2) allows us to compare the mean chain lengths for different dimensionalities. For example, in the three-dimensional simple cubic lattice used here $q = 6$, and in the corresponding two-dimensional square lattice $q = 4$. In the concentrated regime, assuming that long chains are formed, we find that $\langle N \rangle_{\text{cubic}} : \langle N \rangle_{\text{square}} \approx 1 : \sqrt{2}$. In general, a lower dimensionality of the system leads to a higher average chain length.

To summarize, both the Flory and the more accurate Bethe-Guggenheim approaches predict that $\langle N \rangle$ of free chains increases monotonically with concentration. This result is compared with the mean chain lengths of adsorbed chains.

Direct Monte Carlo methods are unsuitable to calculate $\langle N_{\text{ads}} \rangle$ for realistic chain lengths, because E_{scis} is easily of order $10kT$ [1]. Therefore, the acceptance probability of breaking a chain is very low, and hence excessive equilibration times are needed. Therefore, $\langle N_{\text{ads}} \rangle$ is calculated by means of the Bethe-Guggenheim approach, because this leads to a far better description of polymeric behavior than random-mixing mean-field theories can provide. It was shown by Dickman and Hall [13] that the Bethe-Guggenheim approach gives a much better description of the equation of state than the Flory method. Unfortunately, no analytical expressions are available in this case, so $\langle N_{\text{ads}} \rangle$ has to be calculated numerically.

Still, indirect correlations between monomers are approximated, and the occurrence of rings is disregarded. Although the severity of the approximations is not exactly known, it is obvious that the description becomes better at high monomer densities, since the local environment of the

monomers is then well captured by a mean-field approach. Furthermore, the calculations are more accurate when long chains are formed, because the probability of ring closure then becomes extremely low. Both these conditions are met near the interface for a large concentration range (nearly full coverage, $\langle N \rangle \gg 1$). It is therefore not to be expected that a more elaborate type of calculation will lead to different conclusions than ours.

It should be noted that a nematic environment promotes chain formation [14]. While this effect is ignored in the random-mixing approximation, it is included to some extent in the present approximation. However, it remains questionable whether lattice models are suitable to study condensation of rods on the surface [15]. The results for flexible chains might therefore be more accurate than the results for very stiff polymers.

The lattice model described above is therefore extended to account for the presence of an interface. Our system of interest is then a wide slit with a reflecting boundary parallel to the surface. The slit is in equilibrium with a large, homogeneous reservoir with monomer concentration ϕ . It has been checked that the slit width is large enough that adsorption can be assumed to occur on an isolated surface.

The surface is also covered with faces of a certain kind, and they are hereafter referred to as S . Adsorption of the supramolecular polymers is governed by the interaction between the faces on the surface and those on the monomers. The case of adsorbed chains that are in full equilibrium with the chains in the bulk is of interest here. A schematic representation of the model system is shown in Fig. 1.

The mean chain length and other properties of the system can be calculated numerically if the distribution of monomers over the system is known [11]. This distribution depends on ϕ , T , u_{bent} , and the contact energies $\{u_{ij}\}$. The appropriate partition functions and minimization scheme are described elsewhere [11,16].

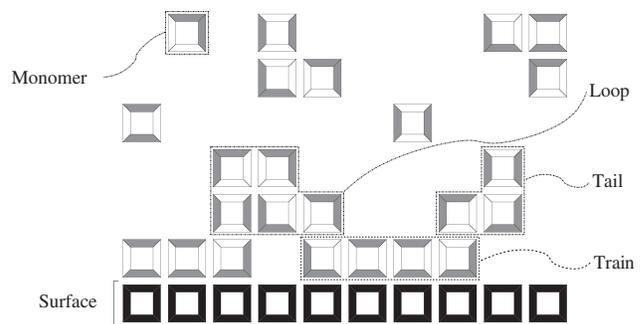


FIG. 1. Two-dimensional representation of the lattice model described in this Letter. Monomers are indicated by the squares with two white sides and two gray sides, which indicate the linking and indifferent faces, respectively. The surface is represented by black squares. Solvent molecules are not depicted. A loop, a tail, and a train are also indicated.

A chain is defined to be “adsorbed” if at least one monomer of the chain is adjacent to the surface. Using this definition, the average length of the adsorbed chains can be calculated from the occupation of lattice sites in the same way as mean lengths of ordinary chains in a homogeneous environment are calculated [11]. Similarly, the mean length of substructures of adsorbed chains can be calculated. A train is defined as a sequence of monomers in the lattice layer adjoining the surface, a loop connects two trains, and a tail is connected at one end to a train (Fig. 1).

The mean length of the adsorbed chains is plotted in Fig. 2 against bulk monomer concentration for different adsorption energies. Note the emergence of a peculiar nonmonotonic concentration dependence of the chain length for $u_{IS} \lesssim -2kT$. This behavior is qualitatively different from Eqs. (1) and (2) since both formulas predict that $\langle N \rangle$ increases with ϕ at all concentrations. The plots in Fig. 2 merge at $\phi \rightarrow 1$ because adsorption energy is irrelevant in a polymer melt: a monomer is then replaced by another monomer upon removal from the surface.

Mean chain lengths of adsorbed supramolecular polymers with varying flexibility are shown in Fig. 3. Figure 3(a) shows that the nonmonotonic concentration dependence is not found for very stiff polymers. This is related to the fact that stiff chains do not form loops and tails, but instead remain adsorbed as trains over the entire concentration regime. Figure 3(b) shows that, at low ϕ , even flexible monomers adsorb predominantly as trains, and loops and tails are formed at higher concentrations. The explanation for the reduction of the mean chain length during this transition is given below. Consider a system at a ϕ where the surface area is completely filled with trains. If the monomer concentration is increased, more monomers are added to the adsorbed chains due to the favorable u_{LL} interactions. Monomers can be added at the end or in the middle of a train. The latter leads to a bisection of the train,

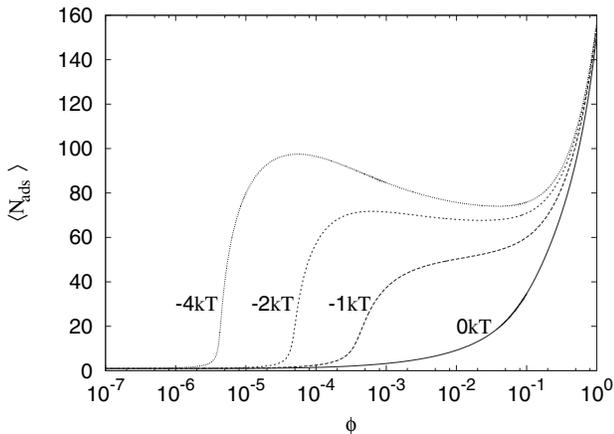


FIG. 2. The mean chain length of the adsorbed chains versus the monomer concentration in the reservoir. Results for monomers with different adsorption energies u_{IS} (in units kT) are shown. $u_{LL} = -10kT$, $u_{\text{bent}} = 0kT$.

and hence to a shortening of the adsorbed chain. Bisection is energetically unfavorable, since an LL pair is lost, but will sometimes occur for entropic reasons. Hence, $\langle N_{\text{ads}} \rangle$ decreases with ϕ when chain shortening due to bisections is more important than lengthening of the chains by adding monomers at the ends of the trains.

A comparison between the calculations regarding flexible polymers in Figs. 3(a) and 3(b) reveals that the sudden increase of the mean length coincides with the filling of the layer next to the surface, and that the mean length, indeed, decreases when loops and tails are formed. Figure 3(b) shows that stiff polymers adsorb more strongly than flexible monomers, in line with earlier predictions [17].

The reduction of $\langle N_{\text{ads}} \rangle$ is equivalently explained by Eq. (2). The chains are confined to the layer next to the surface in the “train regime” so the adsorbed layer is then effectively a two-dimensional system. When the monomer

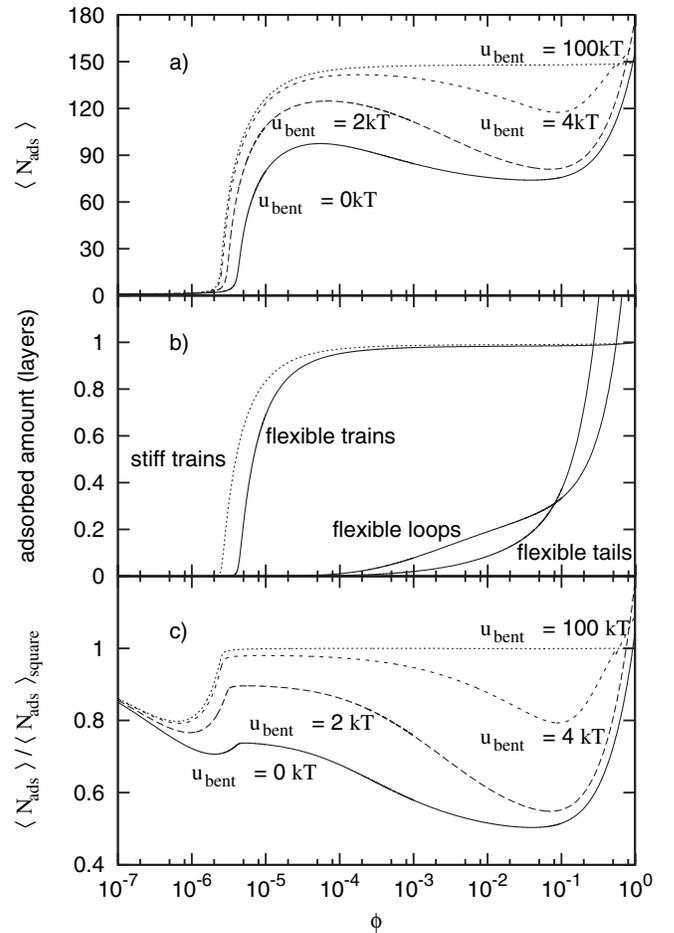


FIG. 3. (a) The dependence of the mean length of adsorbed chains versus ϕ . (b) The total adsorbed amount for various chain substructures, expressed in equivalent lattice layers, depicted on the vertical axis. (c) The quantity shown on the vertical axis is the quotient of $\langle N_{\text{ads}} \rangle$ [same quantity as plotted in (a)] and $\langle N_{\text{ads}} \rangle_{\text{square}}$, which is the mean length calculated with Eq. (2) where $q = 4$ and the monomer concentration is the volume fraction of monomers in the layer adjacent to the interface.

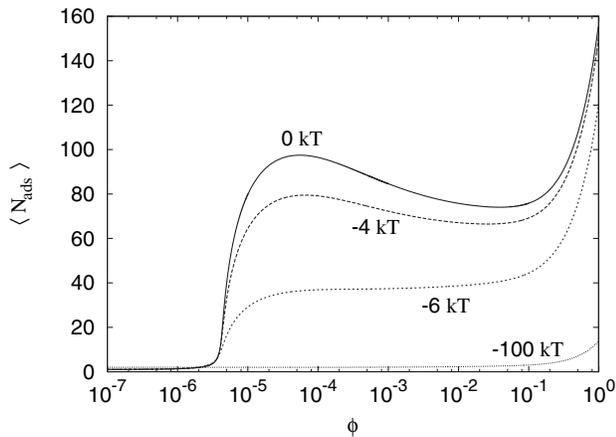


FIG. 4. $\langle N_{\text{ads}} \rangle$ is plotted versus the bulk monomer concentration for different values of u_{LS} . $u_{LL} = -10kT$ and $u_{IS} = -4kT$.

concentration increases, more tails and loops are formed, so the chains transform into an arrangement of higher dimensionality. Remember that it can be inferred from Eq. (2) that the mean length decreases as the dimensionality of the systems increases. This also explains the reduction of the mean length of adsorbed chains at intermediate concentrations. Furthermore, this behavior is not found for stiff supramolecular polymers for that reason. They remain adsorbed as trains at all concentrations so the adsorbed chains remain in a two-dimensional arrangement. The chain length for adsorbed stiff chains is therefore exactly reproduced by Eq. (2) if we choose the occupation of the first layer as the monomer concentration and $q = 4$, which is the coordination number of a square lattice [Fig. 3(c)]. It appears from 3(a) that $\langle N \rangle$ of adsorbed flexible chains passes a minimum as well and is longer than stiff polymers at very high concentrations. As yet we do not have an explanation for this phenomenon.

The results presented in this Letter describe adsorption that is induced by a favorable energetic interaction between the surface and the indifferent faces of the monomers. Our results for nonzero interaction energy between the linking face and the interface, u_{LS} , are shown in Fig. 4. The nonmonotonic behavior is still present when the affinity for the surface is identical for linking faces and indifferent faces.

$\langle N_{\text{ads}} \rangle$ strongly decreases if u_{LS} is made even more negative, and eventually the maximum disappears altogether (Fig. 4). The trains become shorter when u_{LS} becomes more negative because the probability increases that a train ends by means of a linking face pointing towards the

surface. Eventually, at $u_{LS} = -\infty$, only dimeric structures at the surface are formed, so $\langle N_{\text{ads}} \rangle$ equals 2 in that case.

In conclusion, we have shown that the mean chain length of supramolecular polymers has a nonmonotonic concentration dependence in the presence of an adsorbing surface. This phenomenon is caused by a transition from a two-dimensional to a three-dimensional arrangement at the surface. It is to be expected that this behavior is important in experimental systems of supramolecular polymers near interfaces.

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