Unusual Adsorption Behavior of Polymers in Layered Structures

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Abstract: We studied the conformations of polymer chains embedded in regular lamellar matrices such as microphase-separated block copolymer melts or lipid/water systems. In such quasi-one-dimensional systems, the host plays the role of a nearly-periodic external potential. A probe chain can get trapped with the localization length L at isolated defects, when its degree of polymerization N exceeds a cross-over value N_L. Interestingly, the radius of gyration, R_g, of the chain displays a minimum as a function of the defect density, ρ, the minimum being estimated by $\rho_c L \simeq N_L/N$. Using Monte Carlo simulation, we underline the non-monotonic behavior of R_g and calculate Green's function for various defect densities. On the same vein, the mean square displacement of the monomer units at large times shows a pronounced minimum as a function of the defect density, ρ.

Introduction

Microphase-separated block copolymers as well as lipid/water systems can exhibit extended layered structures, patterns which are nearly periodic viewed perpendicular to the interfaces. A long polymer chain embedded in such a host is then subject to a periodic external potential, given that each monomer unit is more attracted to one of the phases than to the other [1, 2]. An alternating AB copolymer whose repeat unit is a short diblock is located preferentially at the interfaces, provided that the host components act selectively on the A and the B species [3, 4, 5]. The interfaces are then adsorbing planes for the repeat units. Common to all of these situations is a one-dimensional (1D) periodic, external potential acting on a tagged chain. This is an interesting problem in theoretical polymer physics since equilibrium statistical properties of ideal chains in 1D potentials can be often obtained exactly. Moreover, as it is well known from the solid state physics [6], disorder effects are most pronounced in 1D. This makes it possible to investigate polymers in disordered environments under extreme conditions and from a new point of view.

Polymers in periodic potentials

We start by displaying the effect of a perfectly periodic potential of the Kronig-Penney form [7] on the chain conformations by using transfer matrix methods. The results can be extended to account for isolated defects of the periodicity. We will show that these defects can localize the chain and that the problem is closely related to the appearance of defect levels in the band structure of solids. Taking into account a finite density of defects, we find that the extension of the chain has a minimum as a function of the defect

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density, ρ. We support our results by Monte Carlo simulations; these also allow insights into the dynamics of chains in 1D disordered media. Our problem is furthermore closely related to the motion of interface lines on a striped surface, as recently considered by Nieuwenhuizen [8].

Here and in the following, we consider an ideal chain of polymerization degree N in an external potential $V(x)$ (given in units of kT). In this case the partition function decouples with respect to the Cartesian x, y and z coordinates. Hence we focus only on the x direction, taken perpendicular to the layers. Green's function $G(x, x'; N)$ of a chain which starts at x' and ends at x obeys the following equation [9]:

$$\frac{\partial}{\partial N} G(x, x'; N) = \frac{l^2}{2} \frac{\partial^2}{\partial x^2} G(x, x'; N) - V(x) G(x, x'; N) \tag{1}$$

with $G(x, x'; 0) = \delta(x, x')$. In Eq. (1), l is the statistical segment length of the chain. For simplicity, we use dimensionless units for all quantities and set $l^2 = 2$ as well as $kT = 1$.

Let us start from an unperturbed periodic potential of the Kronig-Penney form:

$$V(x) = \sum_{\alpha=-\infty}^{\infty} \epsilon \delta(x - \alpha\xi) \tag{2}$$

Depending on the prevailing conditions, ϵ can be either positive or negative. The model given in Eqs. (1) and (2) reproduces the basic features of chains in layered hosts and has the advantage of rendering the mathematics simple. In the following we call $\epsilon < 0$ ($\epsilon > 0$) the attracting (repulsive) case. Now Green's function can be represented as

$$G(x, x', N) = \sum_k e^{-\lambda_k N} \phi_k(x) \bar{\phi}_k(x') \tag{3}$$

where λ_k and ϕ_k are the eigenvalues and eigenfunctions of the equation

$$-\frac{\mathrm{d}^2}{\mathrm{d}x^2} \phi_k(x) + V(x) \phi_k(x) = \lambda_k \phi_k(x) \tag{4}$$

and $\bar{\phi}$ denotes the complex conjugate of ϕ. Equation (4) has the same structure as the time-independent Schrödinger equation. However, because of the exponential term in Eq. (3), modes with $\lambda_k N >> 1$ essentially do not contribute to Green's function. This is the so-called ground state dominance (GSD). Of interest are the solutions with the lowest values of λ.

The Kronig-Penney model is directly solvable by means of the transfer matrix method [6]. In each cell α between two δ-functions, the free solution of Eq. (4) has two components, with prefactors to be determined. We combine these two prefactors into a two-dimensional vector $\mathbf{a}_\alpha$. The solutions between neighboring cells have to obey the standard conditions of being continuous and to have a kink in between, imposed by the delta function. As a result, the coefficients are related by a set of linear equations $\mathbf{a}_{\alpha+1} = T\mathbf{a}_\alpha$, where T is the transfer matrix. We recall here the form of T valid for repulsive ($\epsilon > 0$) interactions [6]:

$$T = \begin{pmatrix} \cos(\kappa\xi) & \sin(\kappa\xi) \\ -\sin(\kappa\xi) + 2\gamma\cos(\kappa\xi) & \cos(\kappa\xi) + 2\gamma\sin(\kappa\xi) \end{pmatrix} \tag{5}$$

Here we set $\kappa = \sqrt{\lambda}$ for $\epsilon > 0$ and introduce the parameters $u = \kappa\xi$, $E = \epsilon\xi$ and $\gamma = E/2u$. This removes all the ξ dependence from the calculations. In the attractive case ($\epsilon < 0$), only $\lambda < 0$ has to be considered, and we set $\kappa = \sqrt{-\lambda}$ [10]. The eigenvalues $t_\pm$ of the transfer matrix T are given by

$$t_\pm = f \pm \sqrt{f^2 - 1} \tag{6}$$

where f stands for $f(E,u) = \cosh(u) + (E/2u)\sinh(u)$ when $\epsilon < 0$ and for $f(E,u) = \cos(u) + (E/2u)\sin(u)$ when $\epsilon > 0$. In an infinite, periodic array, real $t_\pm$ values imply in general eigenfunctions of unbounded growth. For physical reasons, one has from Eq. (6) $f^2 \leq 1$, which determines the allowed values of λ (band condition). Each band is uniquely parametrized by continuous k values in the interval between $-\pi$ and π. For a given value of E, the dispersion relation between λ and k is $\cos k = f(E, u(\lambda))$, the form which replaces the free solution $\lambda = k^2$ for $E = 0$. Because of GSD, we seek a solution in the neighborhood of the lowest band edge λ_g, and introduce $\Delta\lambda = \lambda - \lambda_\mathrm{g}$. Expansion of the dispersion relation to leading order yields

$$\Delta\lambda \simeq \frac{1}{2}(l_\mathrm{eff}/\xi)^2 k^2 \tag{7}$$

Here the effective statistical segment length l^2_eff is given by

$$l^2_\mathrm{eff} \simeq \frac{4u_\mathrm{g}^3}{(-E)(u_\mathrm{g} + \sinh u_\mathrm{g})} \quad \text{and} \quad l^2_\mathrm{eff} \simeq \frac{4u_\mathrm{g}^3}{E(u_\mathrm{g} + \sin u_\mathrm{g})} \tag{8}$$

for the attractive and the repulsive case, respectively. Note the relation $u_\mathrm{g} = \sqrt{|\lambda_\mathrm{g}|}$. In the limiting situations $|E| >> 1$ and $|E| << 1$, a simple analytic solution for λ_g can be given [10]. Generally, we have $l^2_\mathrm{eff} \leq l^2$, i.e., the chain is always squeezed in the periodic potential. Using Eq. (3) and the expression for $\Delta\lambda(k)$, normalized Green's function can be written as

$$G(x, x'; N) \simeq (2\pi l^2_\mathrm{eff} N)^{-1/2} \exp\left\{-\frac{1}{2}\frac{(x - x')^2}{l^2_\mathrm{eff} N}\right\} \tag{9}$$

Hence, a long polymer chain behaves in a periodic potential as a free chain endowed with an effective statistical segment length. However, this ground state approximation holds only for chains whose lengths exceed the cross-over value $N_\mathrm{c} \sim \xi^2/l^2_\mathrm{eff}$.

Localization at isolated defects

We consider now the situation of a single defect site, where two barriers are at the distance ξ' instead of ξ and the deviation from periodicity is thus $\delta = (\xi' - \xi)/\xi$. In this case, there may appear solutions for λ_L outside the bands (so-called defect levels). Again, because of GSD, only defect levels below the lowest band are of interest. The defect states correspond to real eigenvalues $t_\pm$ of Eq. (6) and are localized; their localization length L is given by $L = 1/\ln t_+$. Now, real solutions exist only if the defect (represented by a matrix T') "switches" between a growing (t_+) and a decaying (t_-) solution. This condition can be written in the form [10]

$$\mathbf{l}_+(u_L, E)T'(u_L, E, \delta)\mathbf{r}_+(u_L, E) = h(u_L, E, \delta) \equiv 0 \tag{10}$$

where $\mathbf{l}_+$ and $\mathbf{r}_+$ are the left and the right eigenvectors of T. In the repulsive case, positive δ lead to defect levels below λ_g, whereas the opposite is true in the attracting case; hence

$E\delta > 0$ must be obeyed for defect levels below λ_L. In general, $\lambda_L(E, \delta)$ can be obtained numerically. However, for $0 \leq E\delta << 1$, an analytical solution exists [10]. Denoting now the difference between the lower band edge and the defect level by $\Delta\lambda = \lambda_g - \lambda_L$, we have

$$\Delta\lambda \simeq l_{\text{eff}}^2 \frac{1}{2} \left(\frac{E\delta}{2} \right)^2 \tag{11}$$

and as localization length

$$L/\xi \simeq \frac{2}{E\delta} = \frac{2}{\epsilon(\xi' - \xi)} \tag{12}$$

Now the chain will be localized at the defect if its length is much larger than the cross-over value N_L, where N_L again follows from GSD, $N_L \Delta\lambda \sim 1$. Hence defects of the periodic structure can act as adsorbing sites for the chain and the usual adsorption formalism for polymers may be applied [11]. It is further interesting to note the asymmetry between the case $\xi > \xi'$ and the case $\xi < \xi'$. For instance, in the repulsive case, the removal of a barrier from the regular array results in an *adsorbing* defect; the latter can localize the chain and hence seriously influence its statistical properties. On the other hand, insertion of a barrier creates a repulsive defect which disturbs the chain conformations only slightly.

Finite defect concentrations - unusual behavior of polymers in disordered media

We now turn to the case of a finite concentration ρ of defect levels. In particular, we study the dependence on ρ of the average squared end-to-end distance R^2 of the chain [12]. We assume adsorbing defects, i.e., $E\delta > 0$. Furthermore, we take the chain length N to be much larger than the cross-over value N_L. At very low ρ, the chain will seldom get adsorbed by defects and will spend most of its time in the defect-free region. Once trapped, its escape probability, p_e, is

$$p_e \simeq e^{-\Delta F/kT} \simeq e^{-\Delta\lambda N} \tag{13}$$

where ΔF denotes the difference in Helmholtz (free) energies between the adsorbed and the free conformations. Observed over a sufficiently long time period, R^2 is thus given by $R^2 = g(\rho)R_0^2 + (1 - g(\rho))L^2$, where $g(\rho)$ denotes the probability for the chain to be free at a given ρ and $R_0^2 = l_{\text{eff}}^2 N$ for the defect-free region. Clearly, $g(\rho)$ is monotonic, with $g(0) = 1$, $g(1) = 0$ and, because of detailed balance, $g(\rho)/(1-g(\rho)) = p_e$. Note that defects overlap strongly when their distance is less than L, so that L may be regarded as the eigenvolume (width) of a defect. Thus for $\rho L << p_e$, the ratio $R^2(\rho)/R_0^2$ is a rapidly decreasing function of ρ with a negative slope proportional to $1/p_e$, i.e., very large for $\rho \to 0$ (Fig. 1). When ρL is larger than p_e, the chain is mostly localized at the defects ($R^2 \simeq L^2$).

So far we have assumed that the chain cannot bridge two or more defects. However, even for $\rho << 1/L$, a sufficiently long chain may form bridges between defects, which then allow the chain to extend. We denote by ρ_c the cross-over value where bridging starts and hence $R^2(\rho)$ begins to increase again. In order to estimate ρ_c, we consider two defects at a distance X. Each defect can be again modeled as an adsorbing δ-function in an effective environment. The adsorptive strength Γ of a defect is taken to be $\Gamma = 1/L$;

this leads to one localized state separated from the desorbed states by $\Delta\lambda$ (see Eq. (11)). The corresponding equation for the defect states ϕ_L has then the form

$$\frac{1}{2}l_{\mathrm{eff}}^2\Delta\phi_L(x) + \lambda\phi_L(x) + \Gamma l_{\mathrm{eff}}^2\sum_k \delta(x - x_k)\phi_L(x) = 0 \tag{14}$$

where one sums over the defects. The two defects considered are a two-level system whose lower level corresponds to bridging. Since we assume $N >> N_L$, we expect a solution for $\rho_c << \Gamma = 1/L$. The difference between the two levels due to coupling is $\Delta\lambda_2 \simeq (1/2)\Gamma^2 l_{\mathrm{eff}}^2 \exp(-\Gamma X)$. Consider now the chain fixed at one defect (quenched case). Again, because of GSD, the bridging contribution from the next defect dominates if $\Delta\lambda_2 N > 1$. Hence, for $\rho > \rho_c \simeq 1/\ln(l_{\mathrm{eff}}^2 N/2L^2) \sim 1/\ln(N)$, the chain is more extended than at lower defect densities. However, if the chain is not fixed, it can minimize its Helmholtz energy by moving in the disordered environment (viewed from the chain, this is an annealed disorder) [13]. The chain will prefer defects which are close to each other. On the other hand, the chain will need rather long times to find such places. To estimate the cross-over value ρ_c for bridging, we calculate the Helmholtz energy gain per chain $< N\Delta\lambda_2 >$, averaged over the distribution of distances between two defects $P(X) = \rho\exp(-\rho X)$. Events for $X << L$ do not lead to an extension of the chain. However, restricting the average over distances X larger than $X_0 \simeq L$ only yields a constant factor of the order of unity. When the averaged Helmholtz energy gain $< N\Delta\lambda_2 >$ is of the order of kT (i.e., unity), bridging should dominate the chain conformations. Using the relation $N_L = 2L^2/l_{\mathrm{eff}}^2$, we get for $N >> N_L$

$$\rho_c L \simeq \frac{N_L}{N} \sim 1/N \tag{15}$$

Note that near $\rho = 1$ (so that $1 - \rho << 1$), the situation differs considerably from that near $\rho = 0$ since the ξ cells are now repulsive defects. As discussed above, in the case of very diluted repulsive defects, the chain conformations are only weakly perturbed. This results in a clear-cut asymmetry of the function $R^2(\rho)$, as also obtained in Fig. 1. That $R^2(\rho)$ displays a minimum can be explained by a simple argument. Since only two lengths ξ and ξ' come into play, both limiting situations, $\rho = 0$ and $\rho = 1$, are periodic and therefore lead to extended conformations (cf. Bloch's theorem). On the other hand, the region in between is dominated by disorder (see also [13, 14, 15]), and hence shows localized states which lower $R^2(\rho)$. $R^2(\rho)$ is an increasing function of ρ for $\rho_c < \rho < 1$. For finite chains, there exists additionally the region $0 < \rho < \rho_c$ where single adsorptive defects determine the chain extension. Note that from Eq. (15) it follows that for $N \to \infty$ one has $\rho_c \to 0$ and thus the minimum shifts to zero. There appears a jump (singularity) at $\rho = 0$ for $N \to \infty$. Hence, for infinite chains, only the increasing behavior (disorder effect) for $\rho > 0$ remains. The minimum is a cross-over effect. It is worth noting that the effects discussed here are independent of the underlying periodic background. The role of the latter is included in l_{eff}, Eq. (8), and can in fact be reflected by taking simple voids between the defects, which yields $l_{\mathrm{eff}} = l$ in Eq. (14).

Monte Carlo simulations

The results of the last section were obtained by focusing on the cross-over behavior of a chain bridging between two attracting defect sites. Qualitatively, we have established

two basic features, namely the strong asymmetry between the situations for $\rho << 1$ and for $1 - \rho << 1$ and the fact that the extension of the chain may have its minimum at relatively low ρ_c, i.e. at $\rho_c < 0.5$. To give additional support to our findings, we present now Monte Carlo simulations of single ideal chains in 1D, subjected to aperiodic attractive disorder. We use a striped variant of the well-known bond fluctuation model (BFM) [16] in one spatial dimension, without any excluded volume constraints. The chain consists of N repeat units placed on a 1D grid. The bonds between two repeat units can take all integer values between $-b$ and b. Note that zero values are allowed. It turns out that already $b = 1$ is sufficient to lead to Gaussian statistics for the unperturbed chains reasonably fast. The random jump dynamics for the chain repeat units is now generated as follows. In each attempted monomer move, a repeat unit and a jump direction (± 1 on the 1D lattice) are chosen at random. The repeat unit must again fulfil the bond constraints at its new position. In an external potential, the motion is additionally biased via the standard Metropolis prescription which ensures detailed balance. A Monte Carlo step (MCS) is defined as N attempted monomer unit moves, i.e., during one MCS each monomer has on average one chance to move. This coarsely grained polymer model reproduces the equilibrium properties correctly and leads to realistic diffusional dynamics for times larger than a few MCS [17]. The disorder is taken into account by distributing the traps randomly, in an uncorrelated manner, over the lattice. To reduce the simulation time, we always let the initial chain extend over at least one trap (one trap is always located at the position of the first monomer unit when the chain is created). Each chain is then allowed to relax during 100 000 MCS to remove all statistical artefacts from the chain generation process. Note that the chain can escape from the initial adsorbing site but that in 1D it frequently returns back. On the other hand, if the chain is placed far away from such a site (consider the very dilute limit $\rho \to 0$), it needs a very long time to find it. For finite simulation times, our prescription underestimates $\langle R_g^2 \rangle$ for $\rho \to 0$ (since we always have a trap).
In Fig. 1, we plot the squared radius of gyration $\langle R_g^2 \rangle$ vs. ρ for $N = 80$. The point $\rho = 0^+$ corresponds to a single adsorbing site. The adsorption strength of each defect is chosen as $\epsilon = 0.223$, which corresponds to an escape probability of 0.8 for an individual repeat unit. Note that, as predicted, the curve is not symmetric in the limiting situations, $\rho << 1$ and $1 - \rho << 1$. The minimum of $\langle R_g^2 \rangle$ lies near $\rho \simeq 0.3$. Note further the very steep descent of $\langle R_g \rangle(\rho)$ for small ρ (remember that $\langle R_g^2 \rangle(0)$ is underestimated), in contrast to the behavior for ρ near unity.

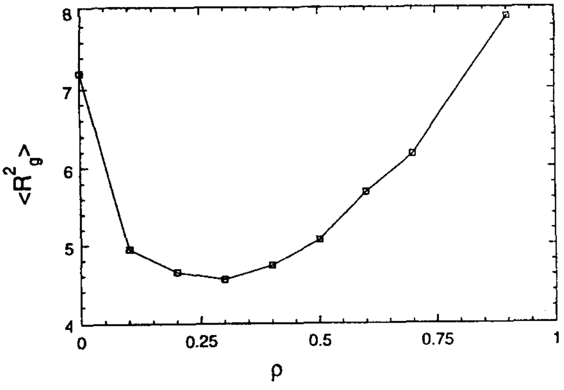

Fig. 1: Radius of gyration vs. the defect density ρ. The data of 100 independent chains comprising 80 repeat units ($N = 80$) are accumulated for $2 \cdot 10^6$ MCS. A pronounced minimum is obtained for $\rho \simeq 0.3$.

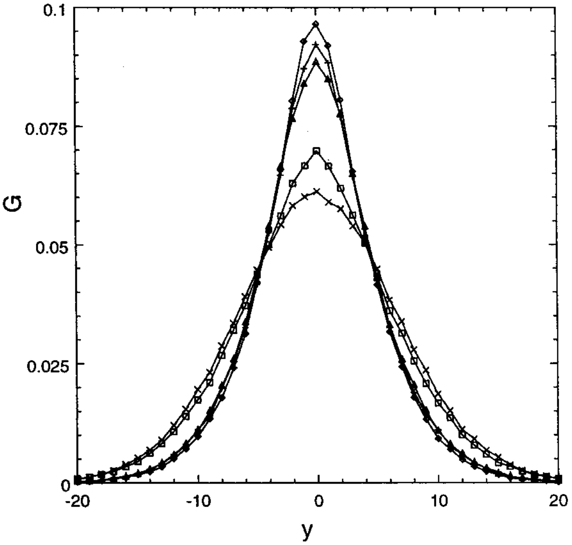

Fig. 2: Distribution function of the end-to-end distance $G(x, x', N = 80)$ vs. the relative distance $y = x' - x$ in lattice units. $\rho = 0^{+}(\square)$, $0.1(+)$, $0.3(\diamond)$, $0.5(\triangle)$ and $1.0(\times)$.

To stress the non-monotonic behavior of the chain extension with ρ, we display in Fig. 2 normalized Green's function $G(x, x', N = 80)$ (probability distribution of the chain end-to-end distance) for five different values of ρ. The non-monotonic behavior of $G(x', x)$ can be nicely seen.

Diffusion of chains under disorder

So far we have investigated the behavior of ideal chains embedded in layered host materials, as frequently realized by structured polymer systems such as diblock copolymers or liquid crystalline polymers. Simplifying the external potential through a Kronig-Penney model, we succeeded in displaying an exact solution for the perfectly periodic case. Now, isolated defects can adsorb the chain, yielding localized states, whose Helmholtz energy lies below that of the extended (Bloch) chain conformations. In the presence of several adsorbing defects, the chain can bridge between them, and thus extend again. As a consequence, the radius of gyration of the chain depends in a non-monotonic fashion on ρ. In all this, the role of the periodic background is marginal. The main results of our approach are that there is an asymmetry in $\langle R_g^2 \rangle$ as a function of ρ (due to the different roles of repulsive and attractive defects) and that $\langle R_g^2 \rangle$ shows a pronounced minimum for a value of ρ smaller than 1/2. Both effects are supported nicely by Monte Carlo simulations.

An interesting open problem concerns the diffusion of polymer chains in such layered structures. However, the transformation of the problem of the polymer *dynamics* in 1D to a quantum mechanical model is not obvious. Moreover, the external potential (periodic or aperiodic) is always a non-linear function of the monomeric unit position. Hence the full Fokker-Planck formalism must be applied, and we recall that determining the dynamics of polymer chains even in perfect periodic potentials is a very hard task. On the other hand, there exists another physical model which leads to a dynamic

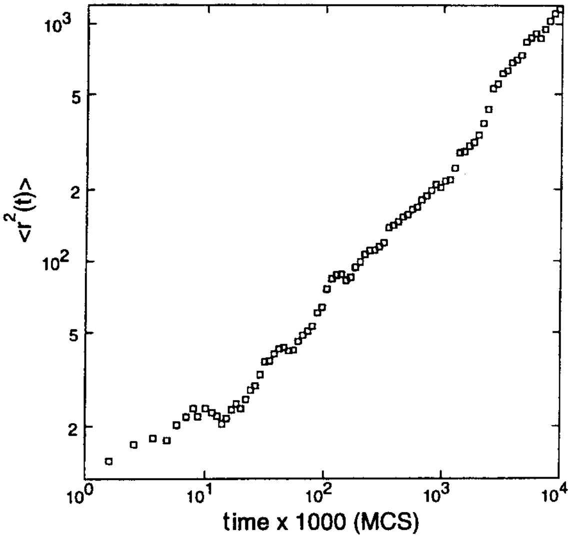

Fig. 3: The mean square displacement averaged over all monomer units and over 100 chains as a function of the simulation time ($N = 80$, $\rho = 0.32$).

problem akin to that of a polymer moving in a 1D disordered medium, namely the analysis of the motion of interfacial lines in a 2D solid-on-solid growth model, as recently discussed by Nieuwenhuizen [8]. Within this approach, the moving interface line is equivalent to a directed random walk in 2D which, in turn, is no more than the graph of a 1D random walk over the monomeric unit positions along the chain.

However, from Monte Carlo simulations, we can obtain valuable information about the dynamic behavior of chains in disordered environments. A first observation is that the chains hardly ever reach diffusive behavior within reasonable simulation times, even if the disorder is not very strong. In Fig. 3, we show $< r^2(t) >$, the mean squared displacement of the monomer units, $< r^2(t) >= (1/N) \sum_{k=1}^{N} < r_k^2(t) >$, as a function of time. The results are averaged over all monomer units within the chain.

Note that within the time scale of 10^7 MCS, a chain of length $N = 80$ is still subdiffusive. In the broad range between 10^4 and $5 \cdot 10^6$ MCS, the slope in Fig. 3 is approximately 1/2. Here the chain explores different areas of the disorder, still finding regions with higher densities of traps and hence with lower local Helmholtz energies [8]. As a consequence, escaping such regions becomes increasingly difficult, thus resulting in subdiffusive behavior. Note that the corresponding time scale is of the order of 10 to 100 Rouse times for the unperturbed chain; the slope of $\sim 1/2$ should not be related to Rousian diffusion. From that it follows that we cannot define a diffusion coefficient for all values of ρ (diffusive behavior is found, however, for very small and very large ρ values). As a measure of the mobility of the chains, we hence use the value $< r^2(\tau) >$ for $\tau = 2 \cdot 10^6$ MCS. This is the longest time used for all systems considered. The results are displayed as a function of ρ in Fig. 4.

One should note that this *dynamic* quantity again shows a pronounced non-monotonic behavior as a function of ρ, the fact qualitatively similar to the static results. However, here the differences between small ($\rho \simeq 0$), large ($\rho \simeq 1$) and moderate ρ values are much larger than those displayed by the static results (note the logarithmic scale in Fig. 4). Our dynamic results are quite similar to those recently reported by Slater and

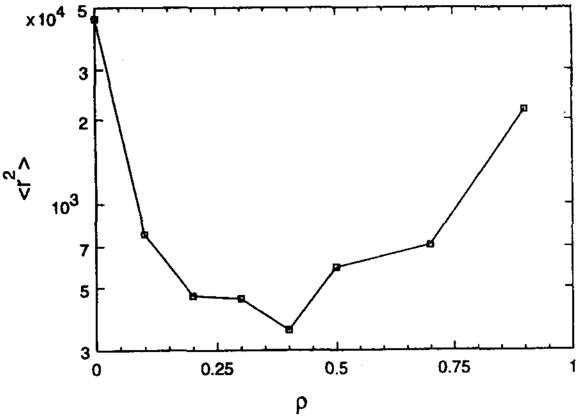

Fig. 4: The mean square displacement of monomer units at $t = 2 \cdot 10^6$ MCS as a function of the defect density ρ ($N = 80$).

Wu [18] from 2D Monte Carlo simulations; this may lead to interesting consequences for the electrophoretic mobility of chains in layered structures.

Acknowledgments

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