Adsorbed Polymer Chains under Lateral Expansion and Compression: A Molecular Dynamics Study

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ABSTRACT: A molecular dynamics simulation of polymeric chains in contact with an attractive surface under good solvent conditions is presented. The adsorbed chains are in equilibrium with free chains in solution at a very low bulk concentration. The response of the layer to a lateral expansion or compression of the interface area is studied. When the interface is expanded, the total surface excess of the monomers stays relatively constant, due to the slow movement of the chains into the layer. Under compression, expulsion of the chains from the layer into the solution is very rapid. The monomer density at the surface and the surface pressure are calculated as a function of the surface area per chain. Both quantities are found to be monotonically decreasing functions of the surface area, for compressed as well as expanded layers.

I. Introduction

Polymers in contact with a surface exhibit properties significantly different from those in bulk. A rather extensively studied case is that of polymers grafted at one end onto an otherwise repulsive wall.[1] Under suitable conditions, the grafting induces chain stretching to such a degree that the scaling of the chain dimensions with the molecular weight is modified.[2,3] Another example is a system of polymer chains in contact with a surface to which the monomers are attracted. Static properties of such systems have been studied theoretically[4−8] as well as experimentally.[9−13] Scaling arguments suggest that for high enough monomer−surface attraction energy, the adsorbed layer has a self-similar structure,[4] with a power law decay of the monomer density profile with the distance from the surface. Detailed SCF analysis[7] also results in a power law decay of the monomer density, although with a different exponent. The attractive wall affects the dynamics of the polymers as well, slowing down the chain motion significantly. An interesting consequence of this slow motion is the time-dependent effects observed in the interaction of two adsorbed layers.[9] There have been a few theoretical studies probing the dynamics of adsorbed chains. These have been related either to the local monomer motion within the adsorbed layer[14] or to the adsorption and desorption dynamics of a single chain in the vicinity of an attractive surface.[15,16]

Recently, Aharonson *et al.*[17] have investigated the surface tension of polymer solutions in contact with an attractive liquid/air interface, taking advantage of the slowness of the global dynamics of the chains in the adsorbed layer. They calculated the changes in the monomer concentration at the interface and in the surface pressure that result from changing the lateral dimensions of the interface. Since the global chain movement is a much slower process than the local equilibration within the layer, they assumed that there is a quasi-equilibrium state in which the total surface excess of monomers remains constant. Their mean-field treatment gave the interesting prediction that the surface pressure, when plotted as a function of the surface area per chain, exhibits a vanishing slope at the equilibrium value of the surface area. However, the solutions of the mean field equations cease to be physical for compressed layers, so that this result applies only to expanded layers. Similar results were found for the dependence of the monomer density at the interface on the surface area per chain. Possible experimental schemes to verify these predictions were suggested.

In this work, I report on molecular dynamics simulations of the process discussed by Aharonson *et al.*,[17] without making an *a priori* assumption that the total surface excess of monomers remains constant. The simulated system is a layer of chains adsorbed on an attractive surface under good solvent conditions. The adsorbed layer is in equilibrium with free chains in solution at a very low bulk concentration. The system is characterized by the magnitude of the attractive interaction between the monomers and the surface and by the bulk concentration of the monomers in solution. After equilibrating the system, a rapid change in the lateral dimensions of the surface is induced. The response of the chains to this change is monitored. In addition to the density profile of the adsorbed layer, the lateral pressure of the layer is calculated.

In the next section, the simulation method is described. Results for the structure of the adsorbed layer as well as the pressure isotherms are presented in section III.

II. Simulation Method

The equilibrium structure of the adsorbed layers in a good solvent was simulated using a molecular dynamics method in which each monomer is coupled to a heat bath. The equation of motion for monomer i (of mass m) is given by

$$m\frac{\mathrm{d}^2\vec{r}_i}{\mathrm{d}t^2} = -\vec{\nabla}U_i - m\Gamma\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}t} + \vec{W}_i(t) \qquad (1)$$

where Γ is the friction coefficient that couples the monomers to the heat bath. The random part of the monomer−heat bath coupling is given by a white-noise term $\vec{W}_i(t)$, which satisfies

$$\langle\vec{W}_i(t)\cdot\vec{W}_j(t')\rangle = 6k_\mathrm{B}Tm\Gamma\delta_{ij}\delta(t-t') \qquad (2)$$

Here k_B is the Boltzmann constant and T is the

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temperature. The potential U_i is composed of three terms: $U_i = U^0 + U^{ch} + U^s$. U^0 is a Lennard-Jones potential

$$U^0(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r_c}\right)^6\right] \quad \text{if } r \le r_c$$

$$= 0 \qquad r > r_c \qquad (3)$$

In this study I used $r_c = 2^{1/6}\sigma$, such that the potential is purely repulsive. U^{ch} is an anharmonic potential that binds the monomers along a chain. The interaction between the surface and the monomers is taken to have the form

$$U^s = \epsilon^s\left[\frac{1}{5}\left(\frac{\sigma}{z - \sigma/2}\right)^{10} - \frac{1}{2}\left(\frac{\sigma}{z - \sigma/2}\right)^4\right] \qquad (4)$$

where ϵ^s is the interaction strength. This form of the interaction arises from assuming a Lennard-Jones interaction between the monomers and the surface atoms and integrating over the xy plane. The interaction potential has a minimum at $z = 1.5\sigma$, beyond which it is attractive. In the present simulations, I used $\epsilon^s = 5\epsilon$ and cut the potential off at $z = 5\sigma$.

The equations of motion[18] of the monomers are integrated using a velocity–Verlet algorithm with a time step Δt, taken to be as large as possible, while keeping the integration stable. A time step $\Delta t = 0.01\tau$, where $\tau = \sigma(m/\epsilon)^{1/2}$ is a natural unit of time for a Lennard-Jones system, was used. The friction coefficient Γ was set to be $\Gamma = 0.5\tau^{-1}$. I used units in which $m = \sigma = \epsilon = 1$ and measured the temperature in units of ϵ/k_B. The temperature was taken to be $T = 1.2\epsilon/k_B$, making the magnitude of the attractive interface potential $\epsilon^s = 4.2k_BT$. Further details on the simulation technique can be found elsewhere.[19]

The simulations were started by placing chains containing $N = 50$ monomers each in the vicinity of the attractive surface, which lies on the $z = 0$ plane. I took the lateral dimensions (both in the x and y directions) of the surface to be $L_0 = 100/2^{1/2}\sigma \approx 70.7\sigma$. Fifty chains were placed in the simulation volume, allocating an area of $50\sigma^2$ to each chain. This surface density is above the overlapping density of the chains, as the radius of gyration of a single, isolated chain in the vicinity of the adsorbing surface is found to be about 16σ. Such a chain is spread almost totally over the adsorbing surface, and the surface area covered by the chain is about $250\sigma^2$. Thus, the initial chain density corresponds to a rather crowded configuration.

Periodic boundary conditions were used for lateral dimensions. A purely repulsive wall was placed parallel to the attractive surface on the $z = 50\sigma$ plane. This wall keeps all the chains within the simulation volume. The distance between the wall and the attractive surface is large enough so that the properties of the adsorbed layer are not affected by the wall.

During the first stage of the simulations, the system was allowed to equilibrate. Due to the attraction to the surface, the monomer density increased near the surface, eventually forcing some of the chains to be detached from the attractive surface. These chains are expected to move randomly in the space between the adsorbed layer and the repulsive wall, resulting in a constant bulk density of monomers in solution away from the attractive wall. In such low-density regions, chains are isolated from other chains. The simulation of the translational motion of such isolated chains using molecular dynamics is found to be very inefficient. (The motion of the chains within the layer or at the interface between the layer and the bulk solution is driven by the interaction between the chains. For such conditions, MD is quite efficient.[19]) In order to overcome this difficulty, Monte Carlo displacements of an entire chain were incorporated into the algorithm. One of the chains was rigidly translated by a vector $\vec{r}_{MC}$ chosen randomly from within a sphere of radius $N^{1/2}\sigma$ every t_{MC} time steps. The move was accepted only if it did not increase the energy of the system. In principle, one should also allow moves which increase the energy of the system with the usual Boltzmann weight. However, translation of the whole chain over distances comparable to the chain dimensions, as was done in this study, resulted in a prohibitively large increase of the energy, if the move involved moving a chain within the adsorbed layer, from the layer into the solvent, or from the solvent into the layer. The penalty in energy associated with these moves is due either to the loss of the interactive surface–monomer energy or to very large Lennard-Jones interaction energies. In practice, it turned out that all the moves were rejected, except for those that translated an isolated chain into another chain-free region, with no change in the energy of the system. Such Monte Carlo moves, with $t_{MC} = 100$, proved to be very efficient in equilibrating the chains in the bulk solution without increasing the computer time significantly.[20]

One of the physical quantities of interest in this study is the surface (lateral) pressure as a function of the area per chain. For terminally attached chains (brushes), Grest[21] defined the instantaneous value of this quantity as

$$\Pi_a = \frac{1}{L^2}\left[\sum_{\alpha,i} m\dot{r}_{i\alpha}^2 + \sum_{\alpha,i,j>i} r_{ij\alpha}f_{ij\alpha}\right] \qquad (5)$$

α represents the two lateral directions x and y and L is the dimension of the grafting surface in these directions. $r_{ij\alpha} = r_{i\alpha} - r_{j\alpha}$ and $f_{ij\alpha}$ are respectively the α-components of the distance and the force vector between monomers i and j. The lateral pressure is in units of ϵ/σ^2. The same definition was adopted for the present case, with the sum including all the chains in the system, and not only those that are attached to the attractive wall. Contribution of the chains that are completely outside the adsorbed layer is zero, since they are not affected by infinitesimal changes in the lateral dimensions of the interface. Chains that are at least partially within the adsorbed layer do contribute to the lateral pressure, and their contribution to Π_a is taken into account in eq 5.

One of these equilibrium configurations of the layer is then used as the starting point of the second stage of the simulations. The lateral dimensions of the simulation box are rapidly changed (within a few thousand time steps), leading to an isotropic (in the plane) compression or expansion of the layer. The simulation is then continued with the new lateral dimensions. After a sufficiently long time, the chains should regenerate the same equilibrium adsorbed layer with some chains expelled into the bulk solution in the case of compression. Lateral expansion of the layer should result in the penetration of the chains initially in the bulk solution into the layer, until the same equilibrium density is restored within the layer. However, as stated in the Introduction, we are interested in the short-time behavior, before such a mass transport is achieved. Results for the changes in the internal structure of the

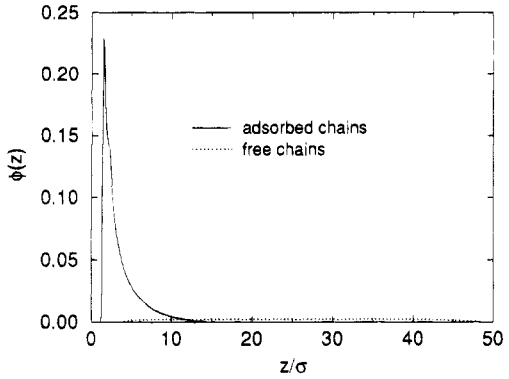

Figure 1. Monomer number density profile as a function of the distance from the attractive surface. Contributions from the adsorbed and free chains are shown separately.

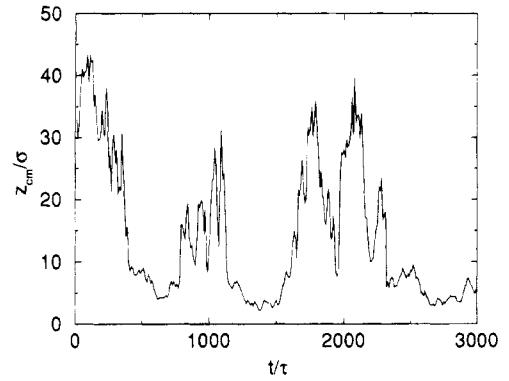

Figure 2. Time variation of the z-component of the center of mass of one of the chains.

layers and in the lateral pressures within this intermediate time scale are presented in the next section. The simulations were carried out for areal compressions to 0.85, 0.72, and 0.50 of the equilibrium area per chain (with the final lateral dimensions being $L = 65\sigma$, 60σ, and 50σ, respectively) and for areal expansions to 1.13, 1.28, 1.62, 2.0, 2.42, 2.88, and 3.92 with respect to the equilibrium (final $L = 75\sigma$, 80σ, 90σ, 100σ, 110σ, 120σ, and 140σ, respectively).

III. Results and Discussion

The monomer number density $\phi(z)$ as a function of the distance from the attractive surface under the conditions described in the previous section is shown in Figure 1. The density is measured in units of monomers per σ^3. The contributions from the adsorbed and the free chains are shown separately. An adsorbed chain is defined here to be one which has at least one monomer within a distance of 3σ from the attractive surface. This distance corresponds to twice the minimum-energy separation of the monomer surface interaction, eq 4. The density profile shown is an average over 300 configurations, taken every 1000 time steps (10τ), after an equilibration run of 2000τ. One can see that beyond the adsorbed layer, the bulk density of the monomers (due to the free chains) is constant, up to a depletion zone near the repulsive wall. The value of the resulting bulk density, ϕ_B is very small; $\phi_B\sigma^3 \simeq 0.0025$ compared to the maximum monomer density of $\phi(z)\sigma^3 \simeq 0.23$ close to the attractive surface.

Figure 2 shows that the equilibrium between the adsorbed layer and the chains in the solution is a dynamic one. The z-coordinate of the center of mass of one of the chains is shown as a function of time. One can see that the chain divides its time between the

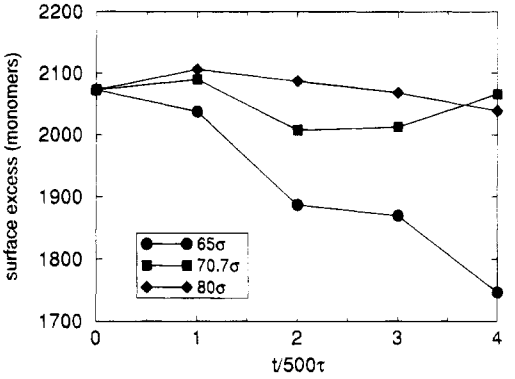

Figure 3. Average number of monomers belonging to adsorbed chains (surface excess) as a function of time for three values of the lateral dimensions of the adsorbed layer. $L = 70.7\sigma$ corresponds to the equilibrium conditions. Each point is an average over 500τ.

adsorbed layer and the bulk solution. The average time it remains within the layer between excursions into the solution is about 500τ. Chain exchange between the adsorbed layer and the bulk, as a result of lateral compression or expansion of the layer, is therefore not expected to be effective within time scales of this order of magnitude. In order to check this point, I have calculated the total surface excess, which is the average number of monomers belonging to the absorbed chains, both for the equilibrium conditions and after the lateral dimensions are changed. This number, averaged over time slices of 500τ, is presented in Figure 3 for three values of lateral surface dimension. Under equilibrium conditions ($L = L_0$), the surface excess fluctuates between 2000 and 2100 monomers. When the surface is expanded to $L = 80\sigma$, the fluctuations remain within this range. Similar results are obtained for higher lateral expansions. Compression of the layer, however, leads to a rather fast expulsion of the chains, as seen for $L = 65\sigma$. Fast expulsion of chains due to osmotic pressure gradient is also observed in other systems of polymers at interfaces, such as grafted layers.[16,22] Penetration of chains into the adsorbed layer proceeds diffusively and is consequently slower. It thus seems that constant surface coverage conditions are not realized in the simulations when the surface is compressed, even for small compressions. On the other hand, slow diffusion of the chains into the layer makes simulations under constant surface coverage possible for expansion.

During the same time scale, the internal structure of the layer has enough time to respond to the changes in the lateral dimensions. The density profile changes significantly, with the layer shrinking in the z-direction and becoming less dense with expanding lateral dimensions. The average of the z-coordinate of all the monomers belonging to the adsorbed chains is shown in Figure 4 as a function of the expansion factor, $(L/L_0)^2$. $\langle z \rangle$ decreases significantly as the layer is expanded, reaching a constant value at high expansions. This apparently corresponds to the situation where the individual chains do not overlap. Compression of the layer, on the other hand, leads to the extension of the chains, resulting in decreased monomer–surface attraction and subsequent chain expulsion. The averages shown are over the first 1000τ of the simulation after the surface dimensions are changed. These values remain almost unchanged for the next 1000τ for expanding layers, while for compressed layers they slightly decrease due to the expulsion of some chains and the relaxation of the remaining ones. Similar changes are

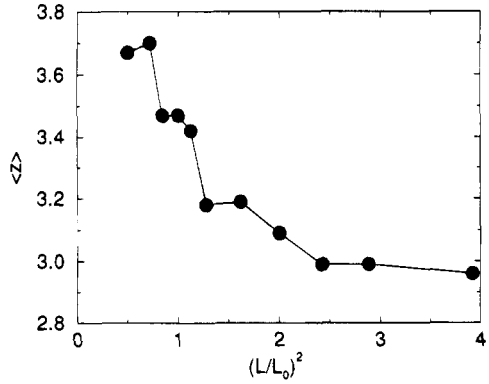

Figure 4. Thickness of the adsorbed layer, as measured by the average of the z-coordinate of the monomers belonging to the adsorbed chains, for different values of the lateral dimensions of the adsorbed layer. The averages are over 1000τ after inducing the change in the lateral dimensions.

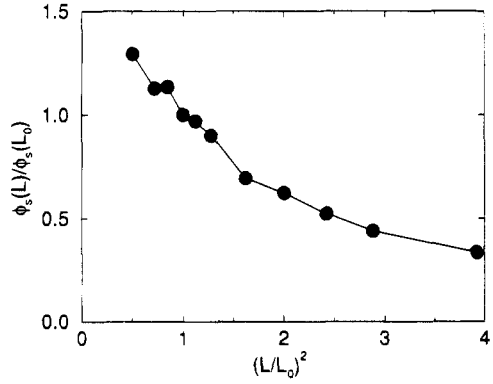

Figure 5. Value of the monomer number density at the attractive surface (ϕ_s) as a function of $(L/L_0)^2$. The surface density at any L is normalized by its value at equilibrium ($L = L_0$).

observed in other measures of the chain dimension, such as $\langle R_{Gz}^2 \rangle$, the z-contribution to the average squared radius of gyration of the chains. The change in the layer density is shown in Figure 5, in which $\phi_s(L)/\phi_s(L_0)$, the monomer density at the surface normalized by the same value under equilibrium conditions, is plotted as a function of $(L/L_0)^2$. ϕ_s is also the maximum value of the monomer density profile. At high values of lateral expansion, ϕ_s decreases linearly with $(L/L_0)^2$, indicating that the chains do not overlap. For smaller values of surface area, interpenetration of the chains results in an increase that is steeper than linear. The increase is monotonic through the equilibrium conditions into the compressed state.

The surface pressure Π_a of the system as a function of $(L/L_0)^2$ is shown in Figure 6. The inset shows the variation of $\Pi_a L^2$. The values for the nonequilibrium conditions ($L \neq L_0$) are averages during the first 500τ of the simulation after inducing the change in the lateral dimensions. It is observed that the instantaneous surface pressure, both for the equilibrium and the nonequilibrium conditions, is a strongly fluctuating function that may have negative as well as positive values. It exhibits a stable average value only when averaged over a time of about 100τ. This is different from the situation observed for the osmotic surface pressure in tethered chains,[21] where the fluctuations are averaged out within a few τ.[23] The pressure decreases with increased surface expansion, going over into an ideal gas behavior, with an approximately constant

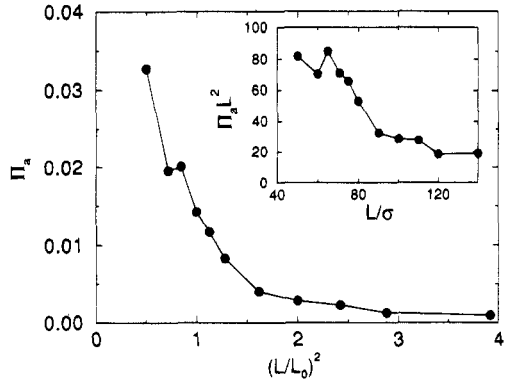

Figure 6. Average surface pressure Π_a of the layers as a function of $(L/L_0)^2$. The points are averages over the first 500τ after changing the lateral dimensions of the layer. The inset shows $\Pi_a L^2$. $L = L_0 = 70.7\sigma$ corresponds to the equilibrium state.

$\Pi_a L^2$. For the compressed surfaces, an overall increase is observed in the pressure with further compression.

Comparing the results for ϕ_s and Π_a with the predictions of Aharonson *et al.*,[17] we find that there is agreement in the limit of large expansion of the layer. Both the mean field treatment[17] and the present simulations indicate an ideal gas behavior, with both quantities decaying as $1/L^2$ in this limit. This is the limit where the surface area per chain is large enough that a chain does not feel the existence of other chains. On the other hand, the mean field treatment[17] predicts that both quantities should exhibit a vanishing slope when the equilibrium state is approached from the expanded side. This was shown analytically for zero bulk concentration and numerically for nonzero bulk concentration. The simulation results, on the other hand, do not indicate a vanishing slope as the equilibrium state is approached, and both quantities increase monotonically into the compressed state. It should be kept in mind, however, that the mean field treatment breaks down when the layer is compressed, as the order parameter $\Psi^2 = \phi$, with ϕ being the local monomer density, becomes negative at the surface. This breakdown may be related to the observation that it is impossible to compress the layer, while keeping the total surface excess constant, as seen in the simulations. It may also affect the regime of small expansions of the layer and lead to the discrepancy between the mean field prediction and the simulation results near the equilibrium conditions.

It would also be interesting to investigate the effect of the chain length on the typical time that it takes a chain to move in and out of the layer. One should bear in mind that the phenomenon discussed here is a transient one. For expanded layers, the chains within the bulk solution will eventually move into the surface layer, bringing the surface pressure, as well as the surface density, to their equilibrium values. (In order to simulate this motion, one should insert additional chains into the simulation volume to keep the bulk density constant, making this stage of the simulation more computer intensive.) The "quasi-equilibrium" state in which the surface excess remains constant can be experimentally observable only if the time scale within which the chain motion is inhibited is macroscopic. A strong dependence of this time scale on the chain length would indicate a macroscopic value of this time for very long chains.

For the case of compressed layers, the simulations reported in this work have shown that the chains leave

the layer immediately, changing the total surface excess as soon as the lateral compression is induced. However, chains much longer than the ones simulated here may have a slower response to compression, leading to a finite time within which the total surface excess remains relatively constant. In a somewhat related system of chains grafted on a surface, the expulsion time of a chain from the layer increases with the chain length. Wittmer *et al.*[24] showed that this process proceeds in three stages. The initial desorption of the grafted head and the local relaxation of the chain near the surface occur on a time scale which is independent of the chain length. The chain is subsequently expelled from the grafted layer with a constant velocity that decreases with the chain length as N^{-1}, so that the time it takes the chain to leave the grafted layer, whose height scales linearly with N, increases as N^2. When the chain reaches the last blob, the motion becomes diffusive. It is not clear whether the expulsion process in the present case can also be separated to similar stages, as the chain may still have some of the monomers attached to the surface while most of the chain is already out of the layer. However, one expects the overall expulsion to proceed more slowly as the chain length increases, since the energy barrier to desorption also increases with the chain length. Investigation of the chain length dependence of the phenomena discussed here (both for expanded and for compressed layers) is presently beyond our computational resources.

IV. Conclusions

This work described the response of a layer of polymers adsorbed on an attractive surface to a change in the lateral dimensions of the surface. For an adsorbed layer in equilibrium with free chains in a good solvent at a low bulk concentration, the total surface excess remains relatively constant for a finite time when the layer is laterally expanded. When the layer is compressed, the chains are rapidly expelled from the layer, reducing the total surface excess immediately. Both the surface pressure and the monomer concentration at the attractive surface are monotonically decreasing functions of the surface area. For strongly expanded layers, the dependence of these functions on the surface area are consistent with isolated chain behavior, similar to the results of Aharonson *et al.*[17] based on mean field calculations. However, unlike the prediction of ref 17, no local maximum is observed in the vicinity of the equilibrium surface area, apparently due to the fact that conditions of constant surface excess assumed in the mean field calculations are not realized in the present simulations. It still remains to be seen whether the qualitative aspects of the results presented here still hold for longer chains.

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