First publ. in: Short and long chains at interfaces : proceedings of the XXXth Rencontres de Moriond, Villars sur Ollon, Switzerland, 1995, pp. 295-301

MOLECULAR EFFECTS IN ULTRA-THIN LIQUID FILM SPREADING DYNAMICS

S.Herminghaus, U.Sigel, U.Albrecht, P.Leiderer
Fakultät für Physik, Universität Konstanz, 78434 Konstanz,
Federal Republic of Germany

The Spreading Dynamics of Silicon Oil Films at thicknesses in the monolayer regime is studied by monitoring the evolution of the coverage profile with optically excited surface plasmons. While for thicknesses above one monolayer the observed profiles agree well with the theory of viscous flow spreading, strong deviations are observed at smaller coverages which point to a diffusivity which decreases with decreasing coverage. This can be qualitatively explained in the framework of the excluded area interaction of the chain molecules. When the coverage decreases, the configurational entropy of the individual molecules changes strongly, leading to a substantially enhanced apparent viscosity for submonolayer films.

The spreading dynamics of oil films on solid surfaces has been studied intensively during the last decade, mainly because of its importance for lubrication and coating applications [1,2]. An extensive theoretical treatment of the spreading of nonvolatile liquids has been set up [3] assuming viscous flow and neglecting the effect of the molecular structure of the oil. Within this framework, many experimental observations could be quantitatively predicted. More recently, one has started to focus on the impact of the molecular structure on the film profiles. In the monolayer regime, a tendency of layering was also observed with chainlike molecules in experiments [4,5] as well as in molecular dynamics simulations [6-8]. In the present work, we investigate the regime of molecular diffusion in the submonolayer regime for chainlike molecules. In experiments with poly(dimethyl-siloxane) (PDMS) films on metal surfaces, we monitored the emerging film profiles optically by means of surface plasmons, as described before [4]. It is observed That the continuum model breaks down quite abruptly at a film thickness corresponding to the backbone diameter of the molecules, crossing over to submonolayer diffusion. This is the regime we want to focus on in the present paper.

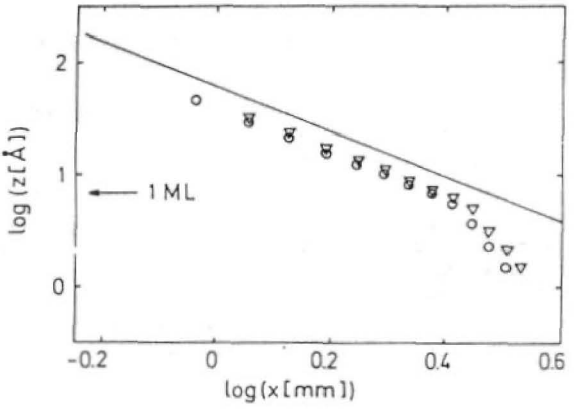

Fig.1. Log-log plot of precursor film profiles of PDMS on an evaporated gold film, measured in vertical rise geometry. Above a thick-ness of 7Å, the profiles agree well with the scaling law predicted for viscous flow (represented by the straight line only the slope of which is significant). Below 7Å, which corresponds to one densely packed layer, significant de-viations are observed.

Fig.1 shows a set of typical data obtained for a vertical-rise geometry. The profiles obtained are plotted on a log-log scale in order to compare with the theoretical prediction that the precursor film thickness d should scale as the inverse square of distance, $d \sim x^{-2}$ [2]. The slope of the straight line is -2, demonstrating the good aggreement of theory with the profiles found experimentally, at least for film thicknesses exceeding 7 Å. This is just the diameter of the PDMS backbone and corresponds to the thickness of one monolayer (ML) of densely packed molecules lying flat on the surface. Below this thickness, significant deviations from the scaling law are observed. Qualitatively, a steeper profile is needed to produce the creep velocity of the precursor film, which points to a reduction of diffusivity for coverages less than one ML.

This is supported by similar data obtained with spreading microdroplets, which have been published before [4]. It was found both experimentally and in Mote-Carlo (MC) simulations that the profile of sub-monolayer 'droplets' was quite well represented by a spherical cap, instead of a gaussian distribution expected for diffusing single monomers

with hard-core interaction. It was shown by MC simulation that the experimental profiles could be well explained by assuming that the chain molecules were lying flat on the surface. If these data are reanalyzed in the framework of the diffusion equation, grad[D(c) grad c] $- \partial_t c = 0$, one can extract the diffusivity D(c), which is plotted in fig.2 (c denotes the coverage, with c=1 corresponding to one ML). It is clearly seen that D(c) increases with increasing coverage for submonolayer films. At first glance, this seems to be a puzzle, since one would expect the mobility of the molecules to *decrease* as they become more densely packed, thus mutually hindering their motion. It will now be shown that although this effect is present, there is also an influence of the conformational entropy of the chains which acts in the opposite direction, overcompensating the former effect. As a result, one obtains, from purely analytical considerations, a simple picture which accounts for the observed behaviour of the diffusivity.

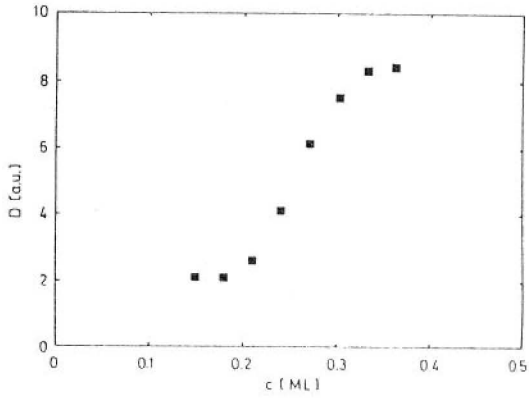

Fig.2. The diffusivity vs. the coverage in the submono-layer regime as derived from the data of ref. [4] (Monte Carlo Simulations). It is clearly seen that the diffusivity increases within the analyzed range of coverage by about a factor of four.

We write the molecular mass current j (in the plane) as [9]

$$j = c \langle v \rangle = c\, m\, \mathrm{grad}\mu(c) = c\, m\, d\mu/dc\, \mathrm{grad}\, c \qquad (1)$$

where c is the coverage, $\langle v \rangle$ is the mean drift velocity of the molecules, $\mu(c)$ is the chemical potential and m is the mobility of the molecules. From the diffusion equation we have $j = D(c)$ grad c and thus

$$D(c) = c\, m\, d\mu/dc \qquad (2)$$

For independent monomers, $\mu = kT \ln c$, and D becomes constant, as expected. For chain molecules, we have an additional term $-TS_c$ in the chemical potential which is connected to the conformational entropy S_c of the chains. This can be written as $-kT \ln w$, where w is the number of possible configurations of the chain. This depends on the coverage c, namely on how many near sites are already occupied by monomers belonging to other molecules. We thus have for the chemical potential

$$\mu(c) = kT\ (\ln n - \ln w) \tag{3}$$

where $n = c/l$ is the number of chain molecules per unit area and l is the number of monomers per chain (i.e., the degree of polymerization). For the diffusivity we thus get

$$D(c) = m\ kT\ \{1 - c\ (d \ln w/dc)\} \tag{4}$$

For further evaluation, we have to find expressions for m and w, which are both affected by neighboring molecules.

We are interested in the coverage dependence of D, whereby we want to compare with the diffusivity D_0 of a free (single) chain molecule diffusing alone on the surface. For the latter, there is also a finite coverage being seen by the monomers, namely the other monomers belonging to the same chain molecule. This gives, for instance, rise to the fact that for the conformation of the single chain, only self avoiding random walks (SAW) are to be taken into account (not the 'phantom chain' configurations). Further reduction of the number of possible conformations is effected only by *other* chain molecules. Similarly, the mobility m of the molecule is effectively (with respect to the mobility of a 'lonely' molecule) reduced only by monomers belonging to other chains, not by those belonging to the same one.

In what follows, we denote the probability that a site next to the chain under consideration is occupied by a monomer belonging to a neighboring chain as c_n. For the mobility, we simply write $m = m_0(1 - c_n)$. Here m_0 plays the role of an attempt frequency for jumps to neighboring sites of the substrate, and c_n is the probability that a jump is not successful because the target site is occupied by a monomer belonging to another chain. Next, we have to derive an expression for the number of conformations of the chain, w. This is given by the number of SAWs possible under the condition that there is a certain density of forbidden (occupied) sites. For zero coverage on a square lattice, we can approximate this by $w \approx 3^l$, since a bond can continue either straight, bend 90 degree to the left, or bend 90 degree to the right (three possibilities). This represents a walk which is self-avoiding only in the first consecutive step, but we will take this as an approximation for the sake of simplicity.

What happens if some of the sites are occupied? In the case that all nearest neighbour sites are occupied, there remains only a single conformation, namely the one which is already realized. Generally, there are $2(1-c_n)+1$ possibilities for a single bond, where again we need to know the foreign occupation of the sites next to the chain. We thus have for the number of conformations

$$w \equiv \{3 - 2c_n)\}^l \tag{5}$$

and for the diffusivity D(c)

$$D(c) = m_0 k\ T\ (1-c_n) \times \{1 + [2c\ l\ /(3 - 2c_n))] \times (dc_n/dc)\} \tag{6}$$

To obtain an expression for c_n, we first calculate the blob size ξ of the chains, along the lines of standard scaling theory. To do this, we first recall that the end-to-end distance R

as derived from Flory's theory of swelling scales as

$$R \sim l^{3/(d+2)} \tag{7}$$

where d is the dimension of the system. For 3D, this leads to the well known law $R \sim l^{0.6}$. The critical concentration (or coverage, respectively) c^* for mutual penetration of the chains is approximately given by the self-density, $c^* \equiv 1/R^2$ (in two dimensions). For coverages larger than c^*, the blob size ξ should not depend on l, since the chains are then longer than the blob diameter. On the other hand, for $c \leq c^*$ we have $\xi = R$. Thus for $c \geq c^*$ we can write a scaling law for ξ:

$$\xi \equiv R\,(c^*/c)^m \tag{8}$$

where m is still to be determined. This obviously behaves as

$$\xi \sim l^{(3 - 2m)/4} \tag{9}$$

where we have used equation (7). To cancel the l-dependence, we have to demand that $3 - 2m = 0$ or, since we are interested only in the c-dependence,

$$\xi \sim c^{-m} = c^{-3/2} \tag{10}$$

Viewed from the chain whose motion is to be examined, the concentration of foreign monomers $c_f(r)$ increases up to the total coverage c within a distance $r \equiv \xi$ (r is the distance to the chain, measured in units of bond length). The probability $c_f(1)$ that a site next to the chain is occupied by a monomer belonging to another chain is thus roughly given by

$$c_f(1) \equiv c_n \equiv c/\xi \sim c^{m+1} \tag{11}$$

The prefactor must be unity, because when c=1, the probability c_n to have a nearest neighbour site (which would else be free) occupied is equal to one. Consequently, we have $c_n = c^{\lambda}$. Inserting this into equation (6), we obtain for the diffusivity D(c)

$$D(c) = D_0(1-c^{\lambda})\,[\,1 + 3\lambda\, c^{\lambda} l/(3 - 2c^{\lambda})] \tag{12}$$

where $D_0 = m_0\, k\, T$ and $\lambda = m + 1 = 5/2$.

The central result of this paper is shown in fig.3, where we plotted $D(c)/D_0$ vs. c for different values of l. For l=10, which is a typical length of the polymers used in our experiments, an increase in the diffusivity similar to the observed one is seen. The small full circles on the curves indicate the estimated limiting concentrations, $c^* = l^{-1/2}$. They correspond in each curve to an increase in D of roughly a factor of two, aside from the 'pathological' case l=1. This case, which should yield $D/D_0 \equiv 1$ [10], is also described rather well by the theory as long as one does not approach c=1 too closely. The

intersection of all curves at (1;0) corresponds to the fact that when the molecules are lying densely, their mobility is equal to zero. For a polymer diffusing on a surface, this case is of course never observed since as $c \to 1$ (from below), it becomes entropically favourable for monomers to leave the first layer, and the model breaks down.

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 306).

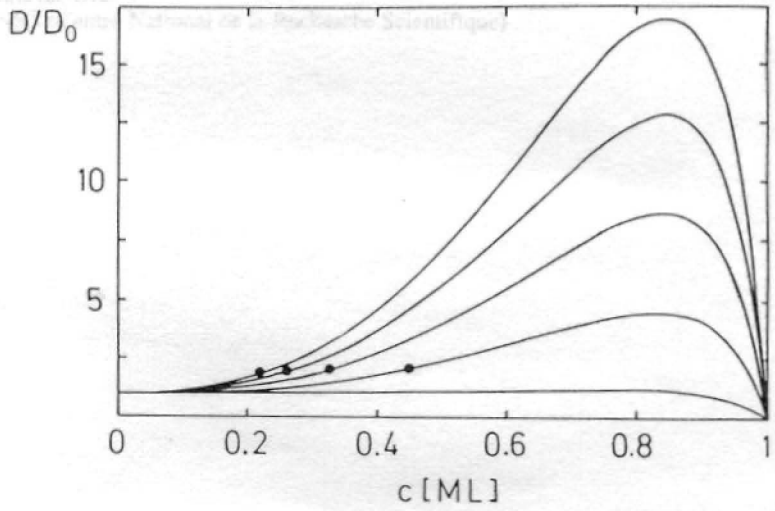

Fig.3. D/D_0 vs. the coverage according to eq.(12) for chain lengths 1, 5, 10, 15 and 20. The maximum value is monotonically increasing with chain length. The qualitative behaviour is obviously similar to what is shown in fig.2

[1] L.Leger, M.Erman, A.M.Guinet-Picard, D.Ausserre, C.Strazielle; *Phys. Rev. Lett.* **60** (1988) 2390.
[2] A.M.Cazabat; *Adv. Colloid Interface Sci.* **34** (1991) 73.
[3] J.F.Joanny, P.-G.deGennes; *J. Physique* **47** (1986) 121.
[4] U.Albrecht, A.Otto, P.Leiderer; *Phys. Rev. Lett.* **68** (1992) 3192.
[5] J.P.Rabe, S.Buchholz; *Phys.Rev.Lett.* **66** (1991) 2096.
[6] R.Hentschke, R.G.Winkler; *J.Chem.Phys.* **99** (1993) 5528.
[7] O. Venäläinen, T. Ala-Nissilä; *Europhys. Lett.* **25** (1994) 125.
[8] J. DeConinck, U. D'Ortona, J. Koplik, J. R. Banavar; *Phys. Rev. Lett.* **74** (1995) 928.
[9] see, for instance: S.R. deGroot, P. Mazur, 'Non-Equilibrium Thermodynamics'. North-Holland 1969.
[10] R.Kutner, Phys.Lett. **81A** (1981) 239.