Transport Kinetics of Wetting Layers.

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Abstract. – The transport kinetics of wetting layers of ethanol and propane on silver substrates is investigated by monitoring the temporal decay of pulsed-laser-induced spatial thickness modulations. Our method allows to distinguish between different transport mechanisms, such as direct exchange with the vapour phase, viscous flow within the wetting layer, or surface diffusion. In either case, the activation energy found for the lateral transport points to viscous flow as the dominant mechanism in the investigated temperature range. For very thin films, the flow proceeds considerably slower than expected from bulk viscosity data. This suggests that the proximity of the substrate influences the morphology of the liquid, giving rise to an enhanced effective viscosity.

Thin films on solid surfaces have become an attractive field of condensed-matter physics. This is not only due to their technological importance but also for the sake of the fascinating dynamical phenomena discovered in surface diffusion, catalytic surface reactions and the dynamics of wetting far from thermodynamical equilibrium [1-5]. For specific investigations of these phenomena, one has to identify the basic transport mechanisms and determine the corresponding transport coefficients, which may be strongly affected by the confined (film) geometry [6,7]. In particular, it has been reported that the viscosity of a few molecular layers of liquid between solid walls may be enhanced by up to six orders of magnitude [8]. Effects of this kind have not yet been investigated in equilibrium wetting layers due to the lack of experimental techniques.

We monitored the decay of pulsed-laser-induced spatially periodic thickness modulations in wetting layers of liquid ethanol and propane on a silver surface. In the absence of inertial effects, the decay proceeds exponentially in time, with the decay rate depending in a characteristic manner on the wave vector of the spatial thickness modulation, $q = 2\pi/\lambda$. If the modulation decays via exchange of molecules with the surrounding vapour, the equilibration proceeds locally and the decay rate does not depend on q ⁽¹⁾. If, however, the decay proceeds via lateral-transport mechanisms, such as viscous flow within the film or surface diffusion at the liquid-vapour boundary, the decay rate is proportional to q^2 . It should

⁽¹⁾ This is true when the mean free path in the gas is large as compared to the wavelength of the thickness modulation, which was always the case in our experiment.

be noted at this point that in case of the dominance of surface tension as a restoring force, a dependence proportional to q^4 would result. However, since the modulation period is in the micrometre range while the capillary length in the presence of the van der Waals force is on the order of 100 Å, surface tension effects can be neglected.

The substrate consisted of an evaporated silver film (50 nm thickness) whose surface was characterized by scanning tunnelling microscopy. On an atomic lateral scale, the films were smooth with height variations of a few Å. On a lateral length scale of a few hundred Å, variations with typical slopes up to 0.4 were found⁽²⁾. The thickness variation of an adsorbed liquid film due to this roughness can be estimated from the known substrate profiles, liquid surface tensions and typical adsorption energies [10]. We obtain a thickness variation of only about 2 Å for a 30 Å ethanol film. We thus do not expect the substrate morphology to have a dramatic impact on the lateral transport in the film.

Experiments were performed with wetting layers⁽³⁾ adjacent to a vertical substrate. For ethanol, the sample consisted of a closed volume next to the silver-coated glass prism which served as the cell window. The cell was first completely filled with the liquid. Then it was turned upside down and the sealing was carefully opened under vacuum to let the bulk liquid drain out. When the ethanol gas bubble thus forming in the cell filled the volume almost completely, the sample was sealed again and was mounted in the cryostat. After cooling to the desired temperature, a film with a typical thickness around 35 Å (determined optically [11, 12]) formed within a few hours, in the course of thermal equilibration of the sample. For propane the mounted cell was filled through a capillary. This allowed for preparation of films with thicknesses ranging from 15 to 76 Å.

The modulation was created by pulsed-laser-induced thermal desorption using two crossed laser beams [13]. From the thermal properties of the involved materials, we can estimate that about 100 μs after the laser pulse, the amplitude of the temperature modulation at the surface has decayed to less than 10 mK. The spatial average of the surface temperature approaches the equilibrium temperature to within one K within a millisecond. For the measurement of the film thickness and detection of the thickness modulation, we used optically excited surface plasmons as described before [11, 12]. The observed decay times of the thickness modulation ranged from a few milliseconds to several seconds.

Figure 1a) shows the temporal decay constant A of the thickness modulation in an ethanol wetting layer as a function of its wave number, q . At this temperature ($T = 150$ K), lateral transport seems to play an important role, as the strong q -dependence suggests. The solid line represents a least-squares fit of the function $A = aq^2 + b$, where b represents the (q -independent) exchange of material with the vapour and a represents a lateral-transport coefficient. The significance of the fit can be demonstrated by considering the temperature dependence of the constant b . From kinetic gas theory, it is easily seen that the adsorption rate of molecules from the gas phase onto the film surface should scale as $pT^{-3/2}$, where p is the gas pressure. Since we are dealing with almost saturated films, this is very close to the saturated vapour pressure p_s which can be taken from the literature. Accordingly, we plotted the transport coefficient b vs. the quantity $p_s T^{-3/2}$ in fig. 1b). Within experimental scattering, b agrees satisfactorily with the straight line (with unity slope) representing the ideal-gas approximation over more than four orders of magnitude.

Let us now turn to the lateral-transport coefficient a . In the case of viscous flow within the

⁽²⁾ Our findings were consistent with reported tunnelling microscopic images obtained on similar films by other authors before. See, for instance, [9].

⁽³⁾ The purity was 99.9% for ethanol with water being the main contaminant, and 99.95% for propane, with residual impurities being other hydrocarbons.

Fig. 1. – *a*) Plot of the modulation decay time *vs.* the wave number of the modulation for a 30 Å ethanol film at 150 K. The solid line represents a least-squares fit according to $A = aq^2 + b$. The error bars indicate the standard deviation of a number of measurements. *b*) Plot of the *q*-independent part *b* of the decay time *vs.* $p_s T^{-3/2}$. The straight line represents the prediction of the kinetic gas theory.

liquid layer, this is connected to the film parameters by

$$a = \frac{h^3}{3\eta\Omega} \frac{dU}{dh}, \quad (1)$$

as can be derived from the Navier-Stokes equation [14]. The film thickness is denoted by h , U is the substrate potential, η the film viscosity and Ω the molecular volume. An Arrhenius plot of a measured with an ethanol film of 30 Å thickness is shown in fig. 2*a*). From the slope of the fitted line, we obtain an activation energy of (220 ± 50) meV, while from reported data for viscous flow [15, 16] we derived a value of 170 meV. If surface diffusion played an important role here, we would expect the activation energy to be considerably smaller than the reported value for viscous (bulk) flow⁽⁴⁾. This seems not to be the case here. The deviation to *higher* energies, if considered significant in view of the large experimental scattering, may be due to the high van der Waals pressure within the film, which can be several hundred bars, depending on the interaction potential and the film thickness. On judging from available data for the pressure dependence of the viscosity [16], it appears possible that this changes the activation energy by the observed amount.

Similar results have been obtained with propane, which has almost the same molecular weight as ethanol but lacks the hydroxyl group. The latter is responsible for hydrogen bonding and for the dipole moment of the ethanol molecule which may give rise to a significant deviation from a pure van der Waals interaction with the substrate [17]. In contrast, the interaction of propane with the substrate is expected to be solely of van der Waals type, which makes it theoretically easier to describe. Possible deviations from the van der Waals behaviour will be discussed below.

Figure 2*b*) shows our results obtained with propane films of 26 Å thickness. We would like to mention the reproducibility demonstrated by the accordance of the circles with the squares, which were measured in different experimental set-ups. This makes the influence of

⁽⁴⁾ For nickel and platinum, the activation energy for surface diffusion is smaller than for bulk diffusion by a factor of 3.61 and 2.61, respectively [15]. In experiments with solid hydrogen, we found this ratio to be even 8.7.

Fig. 2. - Arrhenius plot of the fit parameter a for ethanol (a) and propane (b) films. The slope, which corresponds to the activation energy of the transport process, suggests that viscous flow is the dominant mechanism. The dashed line represents what one would expect from bulk viscosity data.

contamination effects on our results appear very unlikely. Furthermore, the experimental scattering is considerably less than in the case of ethanol. The slope of the data in the Arrhenius plot yields an activation energy of (73 ± 7) meV, while the reported value for bulk viscous flow is (50 ± 4) meV [16, 18]. The deviation is similar to what we found for ethanol, pointing again to viscous flow as the dominant transport mechanism, with the activation energy being slightly enhanced, perhaps due to the van der Waals pressure. Surface diffusion does not seem to play an important role.

In order to obtain a prediction not only for the activation energy, but also for the prefactor in the Arrhenius plot, we have to know the Hamaker constant for the interaction of the propane molecules with the substrate. The Hamaker constants do not vary dramatically for different liquids, as long as quantum liquids are disregarded. Even for systems as different as nitrogen, methane and krypton, the calculated Hamaker constants lie within 25 per cent [19]. For the alkanes, the polarizabilities of the C-H bonds can be regarded as additive [20]. We can thus obtain a reasonable estimate for the Hamaker constant of the propane/silver system by appropriate scaling of the value of $23.8 \cdot 10^3 \text{ K}\text{\AA}^3$ reported for the methane/gold system [19].

The dashed line in fig. 2b) represents what one would expect accordingly for the viscous transport in the propane film. As already mentioned, the slope representing the activation energy is not far from the observation. However, the prefactor of the decay rate differs by more than an order of magnitude. This discrepancy is too large to be explained by the van der Waals pressure in the film. A possible explanation is that the confined geometry of the thin film (i.e. the proximity of the substrate) gives rise to a substantial enhancement of the effective viscosity, similar to what has been observed by other authors for liquid films between solid walls [8]. In fact, a strong tendency to liquid-crystal-like order near the substrate has been reported for alkanes and other liquids both experimentally [8, 21, 22] and theoretically [23]. An effect of these structures on the transport properties of a wetting layer may be expected, but the crucial test whether this is actually the case is to measure the dependence of the transport kinetics as a function of the liquid-film thickness.

This is shown in fig. 3, where we have plotted the decay coefficient a vs. the film thickness in a log-log plot at $T = 90 \text{ K}$. From eq. (1) we see that for a van der Waals potential which scales as $U \propto (\text{distance})^{-3}$ [24], a should vary inversely proportional to the film thickness. This is indicated by the solid line where the Hamaker constant has been estimated as discussed above. As one can see, the discrepancy in the transport rates almost vanishes as

Fig. 3. – Log-log plot of the decay rate coefficient a vs. the film thickness for propane at $T = 90$ K (a similar behaviour has been observed at $T = 110$ K). The data show a crossover to bulk viscous transport at film thicknesses above $70 \text{ \AA}$ when one compares with the usual van der Waals behaviour (solid line). For small film thickness, the decay rate coefficient deviates by more than an order of magnitude from the expected value, suggesting that the effective viscosity of the film seems to be strongly enhanced. The discrepancy with experimental work on the adsorption potential of similar compounds (dashed line) is even larger. Assuming a stagnant layer of $10.5 \text{ \AA}$ thickness with the remaining part of the film having the standard bulk viscosity, we obtain the dotted line, which shows satisfactory agreement with the data.

the film thickness exceeds $70 \text{ \AA}$. On the other hand, it increases steadily as the films become thinner, just as expected in the case of a substrate-induced effect. A simple picture to account for the substrate effect is that there may be a stagnant layer of film material which does not participate in the flow, as suggested also by recent experiments with solid particles in a liquid suspension [25]. In this case, we have to replace the h^3 -term in eq. (1) by $(h - h_0)^3$, where h_0 is the thickness of the stagnant layer. If we treat the latter as a free fit parameter for the data in fig. 3 while treating the remainder of the film as liquid with the standard bulk viscosity, we obtain the dotted line. In view of the error bars, this fits the data quite satisfactorily, corresponding to a stagnant layer thickness of $10.5 \text{ \AA}$ (approximately three monolayers). It approaches the solid line asymptotically to within 10 per cent, which is well within the uncertainty of the estimated Hamaker constant.

In the above discussion we have tacitly assumed the interaction potential $U(h)$ to be purely van der Waals like. Finally, we want to discuss the possibility of a non-van-der-Waals surface potential. In fact, it has been reported that the van der Waals potential might be inadequate for the adsorption behaviour of similar compounds [26, 27], among others pentane, a homologue of propane, and ethanol. In contrast, a potential scaling approximately as $U \propto (\text{distance})^{-2}$ has been found, along with an adsorption energy which exceeded the typical van der Waals energy by orders of magnitude for film thicknesses similar to those investigated in our experiment. If we adopt this (yet unexplained) potential, along with the high binding energies found, we obtain for the decay rate coefficient a the behaviour indicated by the dashed line in fig. 3. Although the general trend that a be more or less independent of the film thickness is in accordance with our results, the discrepancy in the absolute value is even larger, and independent of film thickness. A large discrepancy in the apparent viscosity is then found for ethanol as well. As an alternative interpretation of our data, we should thus take into account the possibility that some (yet unknown) mechanism which gives rise to the unexplained non-van-der-Waals potential in the reported iso-

therms [26,27] may also be responsible for the (in this case dramatically) enhanced viscosity we have observed.

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