

Dynamics in ultrathin liquid films studied by simultaneous dielectric spectroscopy (DRS) and organic molecular beam deposition (OMBD)

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Abstract. Real-time dielectric relaxation spectroscopy for a molecular beam deposited glass forming liquids is proposed as a versatile approach for the study of the dynamic glass transition in geometric confinement. To achieve the highest sensitivity down to monomolecular organic layers in a wide frequency range (0.1–10⁷ Hz) during simultaneous deposition and desorption, we have used μm spaced interdigitated electrodes under ultrahigh vacuum conditions. Experiments using glycerol deposited on fused silica at -40°C revealed a dielectric glass transition process for a layer thickness as low as 0.7 nm. While its peak position hardly changes upon thickness reduction, a clear broadening is observed that implies an increasing heterogeneous mobility scenario for the thinnest films caused by molecules being part of a reduced (at the substrate) or enhanced (free surface) mobility layer. This finding is supported by desorption experiments that reveal a strong retardation of the desorption rate for films below 1 nm.

1 Introduction

Many efforts have been undertaken in the last 2 decades to study the deviation of the cooperative dynamics of glass forming liquids from their bulk behavior, when they are confined to nanometer dimensions. While the existence of confinement effects has been demonstrated by numerous work on very different systems including ultra-thin films [1–3], nanoporous glasses and zeolites [4–7], a general conclusive picture of the nature and the origin of such deviations has not yet been achieved, since experimental effects usually dependent on the particular approach and the specific molecular system and the confining geometry. In this context, porous hosts providing spherical or

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cylindrical pores, with typical diameters of few nanometers probably represent a very popular system to study confinement effects on the dynamics of low molecular mass glass formers [4] mainly due to the possibility to prepare robust and large volume samples suitable for bulk-techniques like calorimetry, NMR and neutron scattering. Despite the advantage to provide an effective means to realize a 2- or 3-dimensional confinement [8], nonporous systems unfortunately often exhibit experimental uncertainties regarding the pore-size (distribution), the actual filling factor of the pores and the exact surface chemistry of the solid walls. The widely accepted picture is that both (attractive) surface interactions and size effects are responsible for deviations from the bulk dynamics: while specific interactions between liquid molecules and the solid surface cause a slowdown in the dynamics of the molecules in proximity of the wall, the existence of a finite size of the molecular ensemble should give rise to enhanced mobility due to cooperativity arguments [9]. Ultra-thin films represent a straightforward, alternative geometry to investigate liquid dynamics in confinement since both liquid/surface interactions and the film thickness can be tuned independently to disentangle true size- from interfacial effects in a dynamic experiment. In this paper, we introduce a novel experimental approach able to probe the dynamics of extremely thin layers ($h < 1$ nm) of polar liquids over a broad frequency range (0.1– 10^7 Hz). Taking advantage of the sensitivity of dielectric spectroscopy (DS), such a unique investigation approach allows real time monitoring of the changes occurring in subnanometer films during their deposition and desorption. To prove the feasibility of our technique we followed the kinetics of sorption and desorption of molecular-beam-deposited nanometric layers of glycerol on a glass substrate.

2 Experimental

A scheme of the experimental set-up is presented in Fig. 1. Organic thin layers are grown directly on the surface of an interdigitated comb electrode (IDE), which senses the dielectric properties of the layer. Evaporation is performed in ultra high vacuum (UHV, $p < 10^{-7}$ mbar) generated by a turbo molecular pump in combination with an oil-free roughening pump. A quartz crystal microbalance (QCM) monitors in situ with monolayer sensitivity the growth rate and absolute layer thickness. In the following the essential components and the principle of operation of the OMBD setup [10] will be described in more detail. The controlled deposition of organic material onto the targets (IDE and QCM) is provided by two effusion (Knudsen) cells, which can independently be attached/detached to the vacuum by electro-pneumatic valves. The deposition rate R_d can be tuned by varying the temperature of the Knudsen cell and finally depends on the size of the aperture of the effusion cell, the (ballistic) path length l to the target (here around 20 cm), the molecular mass M and the equilibrium vapour pressure p^e of the organic material according to the equation $R_d \propto \frac{1}{l^2} \frac{(p^e(T) - p^h) N_A}{\sqrt{2\pi MRT}}$ [11]. Here, $p^e(T)$ obeys Arrhenius behaviour with the enthalpy of evaporation being the energetic barrier. In the overlapping plane of the two, slightly inclined, molecular beams, the two sensors (IDE and QCM) are mounted on a temperature stage that allows accurate temperature control of the targets in the range from -40 °C to 100 °C by using an external thermostat. This temperature control has a dual function: it allows to vary the sample temperature during characterisation of the thin film, i.e. taking dielectric relaxation spectra at desired temperature below and above the glass transition temperature. On the other hand, the substrate temperature, T_{sub} , during the deposition process is of importance for the formation of a liquid or glassy film by virtue of the temperature dependent lateral mobility of arriving molecules. By choosing the right combination of target temperature and molecular beam

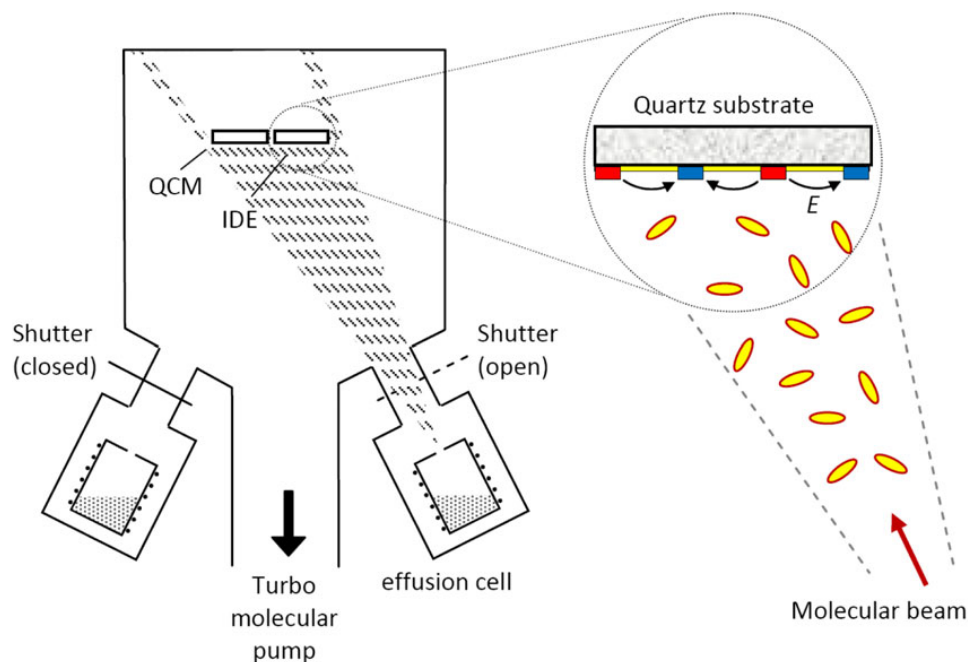


Fig. 1. Scheme of the OMBD setup including an UHV chamber, two effusion cells and a temperature controlled target containing the dielectric sensor (IDE) and the QCM sensor. The close-up on the right illustrates the open electrode structure of the IDE and the lateral electric field.

flux we have been able to realize very low deposition rates in the order of 1nm/min. Measurements of the complex electric capacitance $C^*(\omega) = C'(\omega) + iC''(\omega)$ in a wide frequency range (0.1 Hz–10 MHz) were performed by means of an μm -spaced, interdigitated comb-electrode (IDE) [12,13] in combination with a high-resolution dielectric analyzer (ALPHA N, Novocontrol Technologies), either under isothermal conditions or by varying the sample temperature quasi-linearly in steps of a few K. Such IDE configuration has various specific advantages over the classical parallel-plate configuration: a) the sensing capacitor structure is open and thus accessible by the vapor beam, b) the electrical field is planar ensuring a field direction being parallel to liquid film surface, and c) the electrical sensitivity can be tuned by the effective area and spacing D between the “fingers”. The excellent sensitivity of comb electrodes has been demonstrated in several studies including impedance spectroscopy on self-assembled monolayers [14]. As a consequence of the planar electrical field, the total capacitance of the IDE can easily be decomposed into a background part (empty IDE) and a variable component that linearly increases with the layer thickness h , provided that the film thickness is small compared to the IDE-spacing, i.e. $h \ll D$. This linear relationship provides an independent means to determine the layer thickness from the capacitance response.

3 Results and discussion

Figure 2 shows the time evolution of the dielectric spectrum $C'(f)/C_0$ of glycerol during multiple deposition events (fast rise) followed by a slow decay in the dielectric response due to desorption. A typical spectrum is displayed in the left inset on top revealing two steps in the permittivity at about 10 Hz and 40 kHz. While the

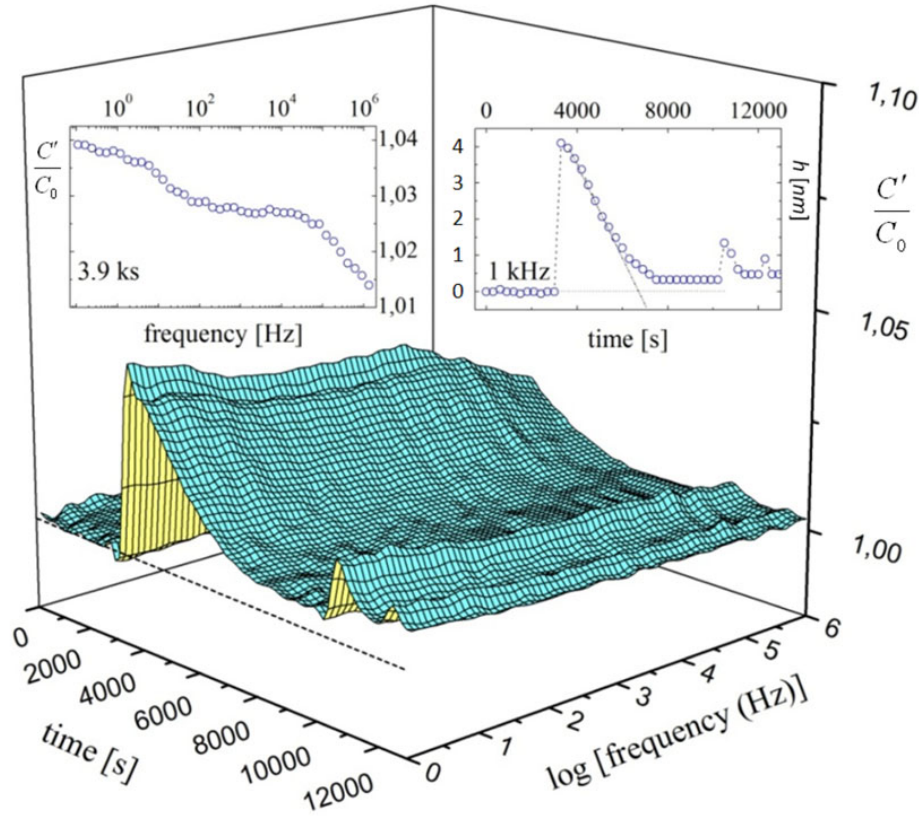


Fig. 2. Time evolution of the real part of the capacitance $C'(f)/C_0$, normalized to the value of the empty IDE, during three successive deposition and desorption cycles. Left inset: Individual spectrum at $t = 3900$ s. Right inset: Layer thickness computed from the permittivity at 1 kHz as function of the time.

high frequency process clearly corresponds to the structural relaxation of glycerol at -40°C , often referred as α -process or the dynamic glass transition process, the presence of another, slower relaxation process, so called electrode polarization, actually confirms the existence of a continuous, electrical conducting liquid film [15,16]. This relaxation, already visible for the thinnest films, originates from the macroscopic separation of charges over macroscopic distances larger than the Debye screening length (for glycerol in the order of $1\ \mu\text{m}$) and disproves the scenario of a dewetted liquid film consisting of nm-sized isolated liquid droplets.

The second inset figure displays the time evolution of the dielectric response at a given frequency, $f = 1\ \text{kHz}$, which reveals particular information about the kinetics of desorption. As expected, the capacitance and thus the layer thickness decrease at a constant rate from initially $h = 4.5\ \text{nm}$, which is in line with the idea that the evaporation rate at a given temperature and pressure solely depend on the molecular mobility at the film surface. However, there is a clear retardation of the desorption process that, around 1 nm, finally reaches a plateau corresponding to a “residual” layer of about 0.5 nm. Considering that the desorption rate $dh(t)/dt$ is proportional to the molecular mobility of the outer molecule layer we can conclude that the molecular dynamics slows down at the very interface to the substrate as expected for strongly H-bonding molecules on an oxide surface.

To study the dielectric α -process in more detail we have performed a complementary experiment under the condition of a very slow layer growth. The results

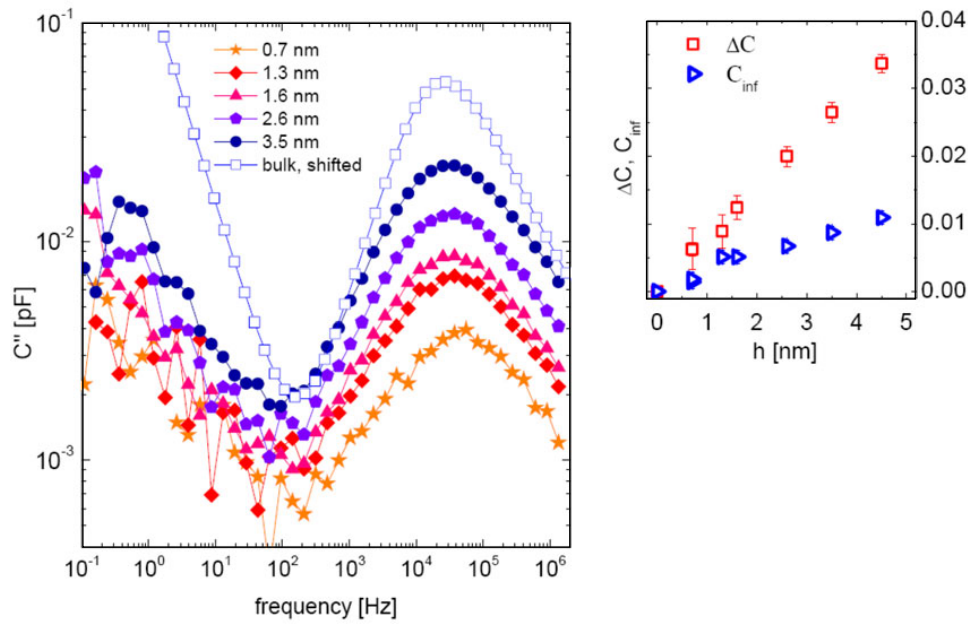


Fig. 3. Left: Evolution of the dielectric loss spectrum of glycerol deposited on a cooled substrate (-40°C). Right: Relation between dielectric relaxation strength ΔC of the α -relaxation process, the capacitance in the high frequency limit C_∞ and the thickness $h(t)$ measured by the QCM.

are presented in Fig. 3 that displays the imaginary part of $C^*(\omega)$ for different layer thicknesses during deposition. Dielectric spectra were analyzed in terms of the empirical Havriliak-Negami (HN) function $C^*(\omega) - C_\infty = \Delta C \cdot (1 + (i\omega\tau)^a)^{-b}$, being $C_\infty = \lim_{\omega \rightarrow \infty} C'(\omega)$ the electric capacitance at optical frequencies, τ the characteristic time of the process, a , b and ΔC respectively the shape parameters and the strength of the relaxation peak [17]. The thickness evolution of the structural relaxation of glycerol layers measured during their deposition is plotted in Fig. 4. Layers as thin as 4.5 nm show a clear trend towards bulk behavior with respect to the peak position (left figure) and the spectral shape (right figure). The validity of this trend is confirmed by a much thicker film ($L = 27$ nm)—obtained after prolonged deposition—that almost resembles bulk properties. In thinner samples ($h < 3$ nm), confinement effects are more prominent in terms of broadening of the α -peak, expressed by a decreasing shape parameter a (Fig. 4, right panel), and a moderate shift of the peak maximum toward higher frequencies. This last feature reflects an overall enhancement of the molecular mobility responsible for the increase of the peak frequency of the loss peak, f_{max} , implying a relatively higher fraction of molecules at the free surface with respect to those being located at the liquid-solid interface [18]. Such scenario might be rationalized by the assumption that thinner layers of glycerol, upon deposition, exhibit a larger roughness due to the statistical nature of the single molecule deposition process and thus a higher ratio between free surface and substrate area compared to bulk like layers. The balance of these effects results in the final value of τ and in an increase of the relaxation breath causing the peak broadening [19].

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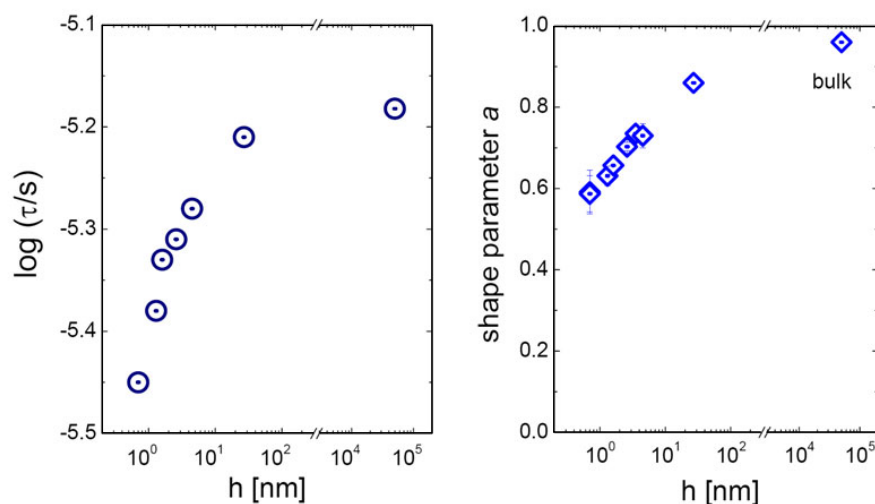


Fig. 4. Thickness dependence of the peak relaxation time (left) and the shape parameter a obtained from a fit of the dielectric loss to a HN-function.

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