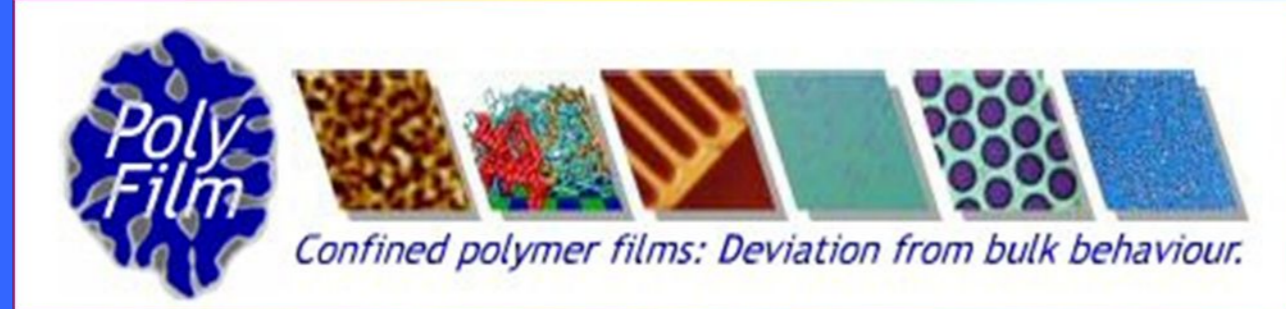




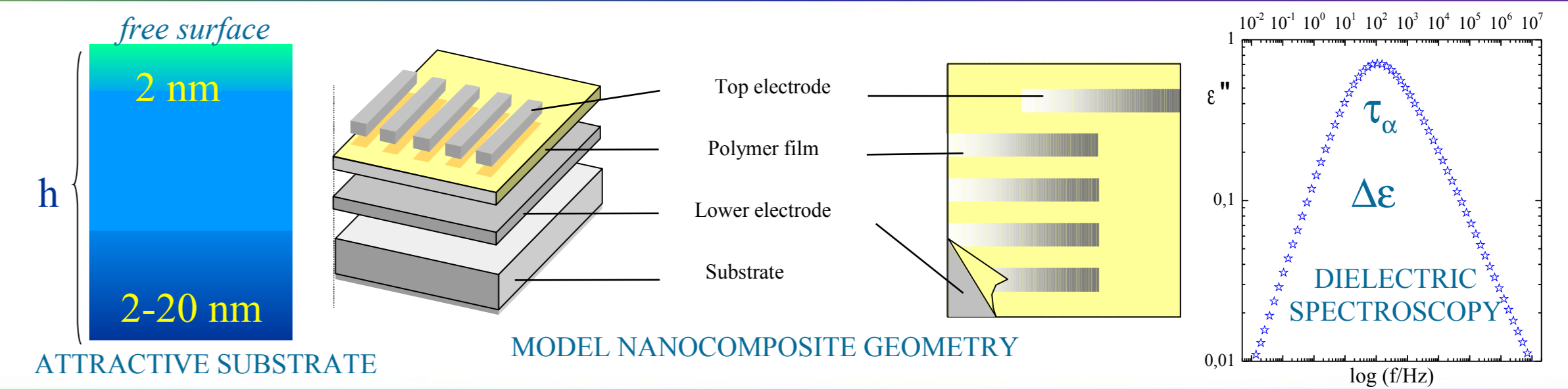
Dielectric signature of dead and reduced mobility layers



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All materials are viscoelastic, i. e. they respond as solids on short time scales and flow as liquids on long time scales. A characteristic time τ separates the solid and the liquid behavior; τ of water at room temperature is around 10^{-12} s, so on the time scale of human life water appears as a liquid. Aim of our work is to understand how and why interfaces may influence the characteristic time of polymers. In order to study the interfacial properties of these materials we prepare ultrathin films thick less than 200 nm and monitor the changes in the material performance upon thickness reduction. We concentrate our attention on interactions between polymers and metals leading to a partial or total immobilization of the polymer chains. We modeled the properties of these attractive interfaces and experimentally verified that τ increases in proximity of the layer in contact with the metal and that the relative variation of τ vanish at high temperatures. Our results are of fundamental interest in the studies on soft matter and of support to the development of polymer based nanodevices.

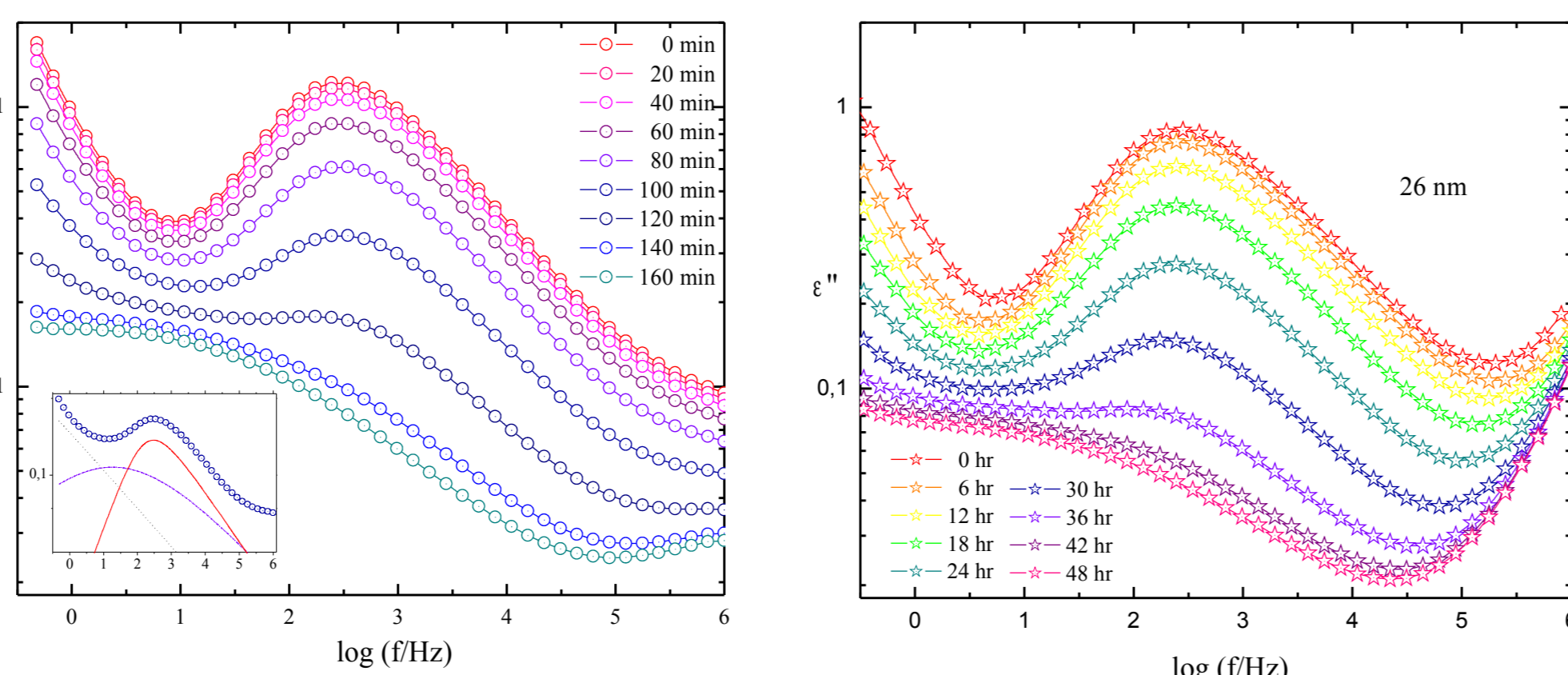


In ultrathin polymer films (thickness < 200 nm), the coupling between the segmental mobility and the crystallization rate is broken down due to interfacial interactions. In particular, in presence of a reduced mobility layer (RML) at the interface with the substrate, the crystallization kinetics slow down at a lengthscale bigger than the one connected with the deviation from bulk behavior of the structural relaxation. By modeling the influence of the substrate interactions on the parameters governing the temperature evolution of the main relaxation time, it was possible to reproduce the effect of geometrical confinement on the quantities connected to the diffusion limited crystallization rate. Upon reduction of the thickness or increasing of the substrate interaction, the films show an apparent higher glass stability in terms of an increase of the cold crystallization temperature and of the crystallization time. The deviations from bulk behavior were found to vanish above a crossover temperature as already observed for the phenomena connected to the glass transition.

Broadband dielectric spectroscopy, BDS, has already been successfully used to detect and study relaxation processes even on the nanoscale. The technique itself has been widely used to monitor crystallization kinetics of polymer chains in bulk, being a sensitive tool to investigate the dynamic changes during the crystals' growth in terms of reduction of the mobility (shift of the structural relaxation towards lower frequency) and the volume fraction (decrease of the relaxation strength $\Delta\epsilon_0$) of the amorphous phase.

In order to prove the feasibility of BDS as an experimental approach to investigate crystallization even in ultrathin polymer films, poly(3-hydroxybutyrate), PHB, a polar biodegradable polyester showing a simple dielectric scenario, has been chosen as sample material. We found an increase of the crystallization time τ_{cr} of more than 1 order of magnitude, not accompanied by any change of the chain mobility. Such a discrepancy is probably due to an RML

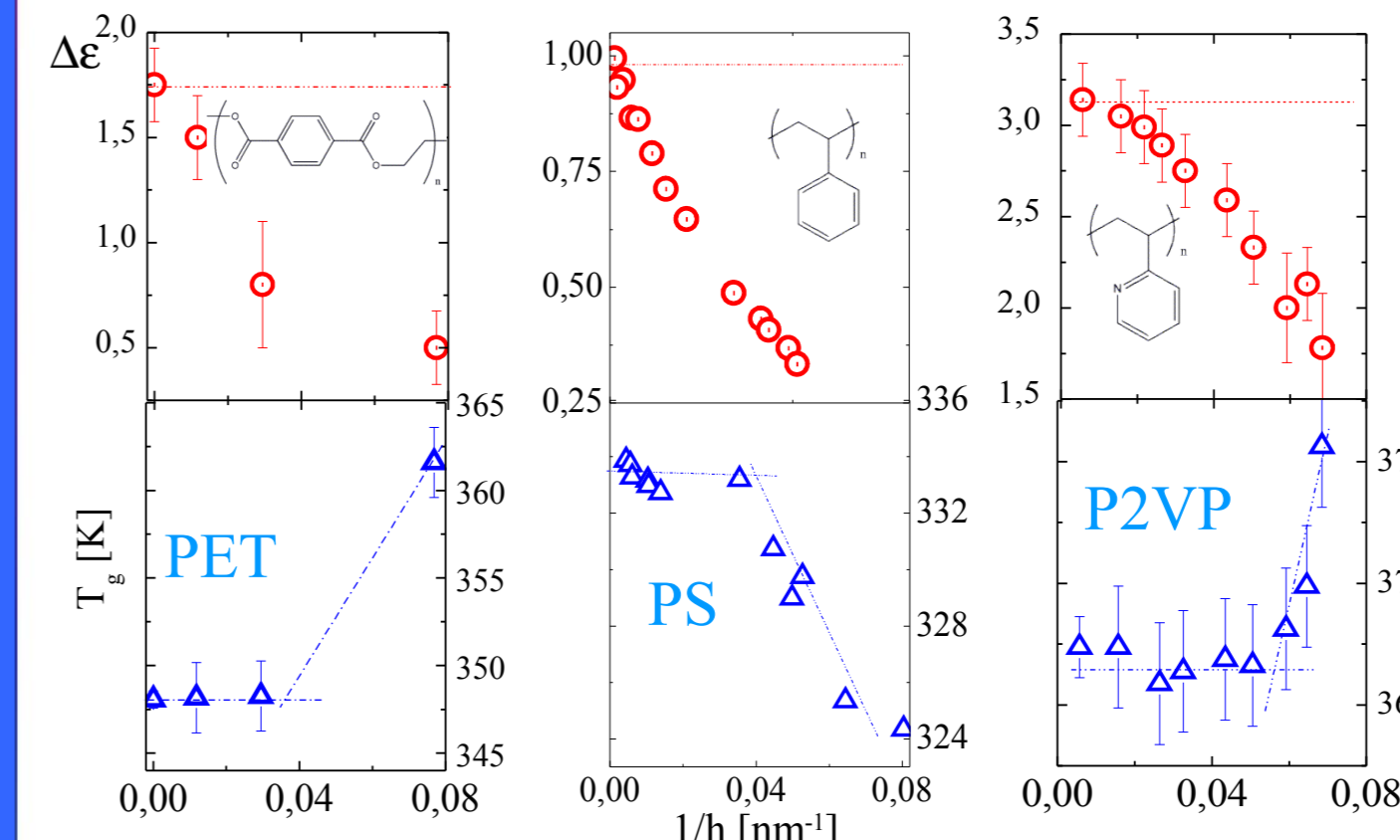
CRYSTALLIZATION OF ULTRATHIN FILMS VIA DS



Dielectric spectra of a 50 nm thick sample during an isothermal crystallization at 18°C. The continuous lines are guides for the eye. In the onset a fit for the spectrum recorded after 105 minutes of annealing.

Dielectric spectra of a 26 nm thick sample during an isothermal crystallization at 18°C. The continuous lines are guides for the eye.

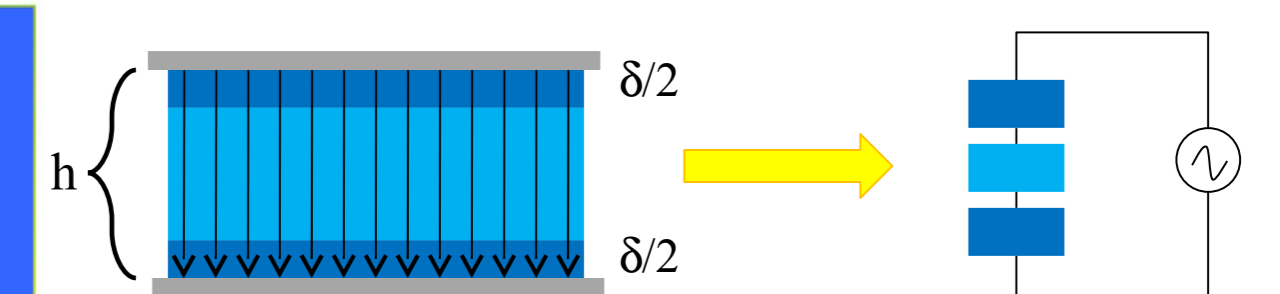
INFLUENCE OF AN RML ON THE STRUCTURAL RELAXATION



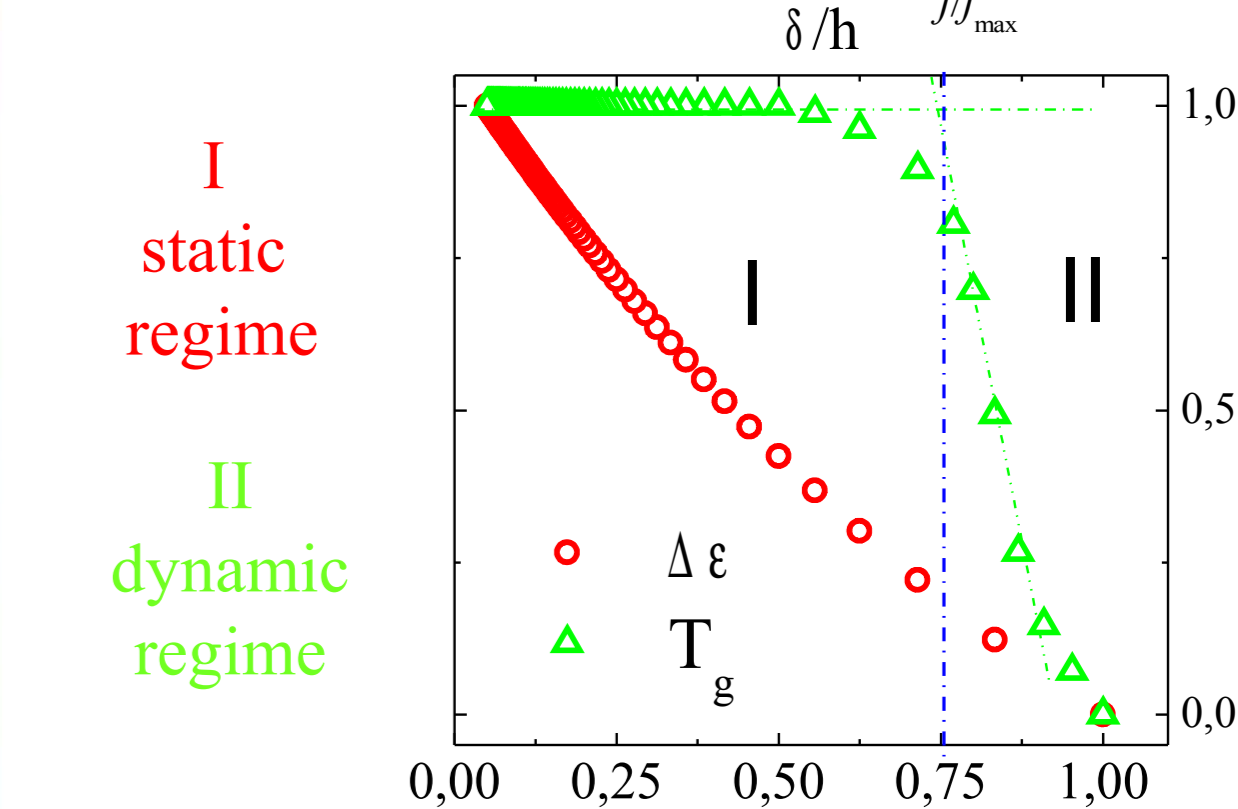
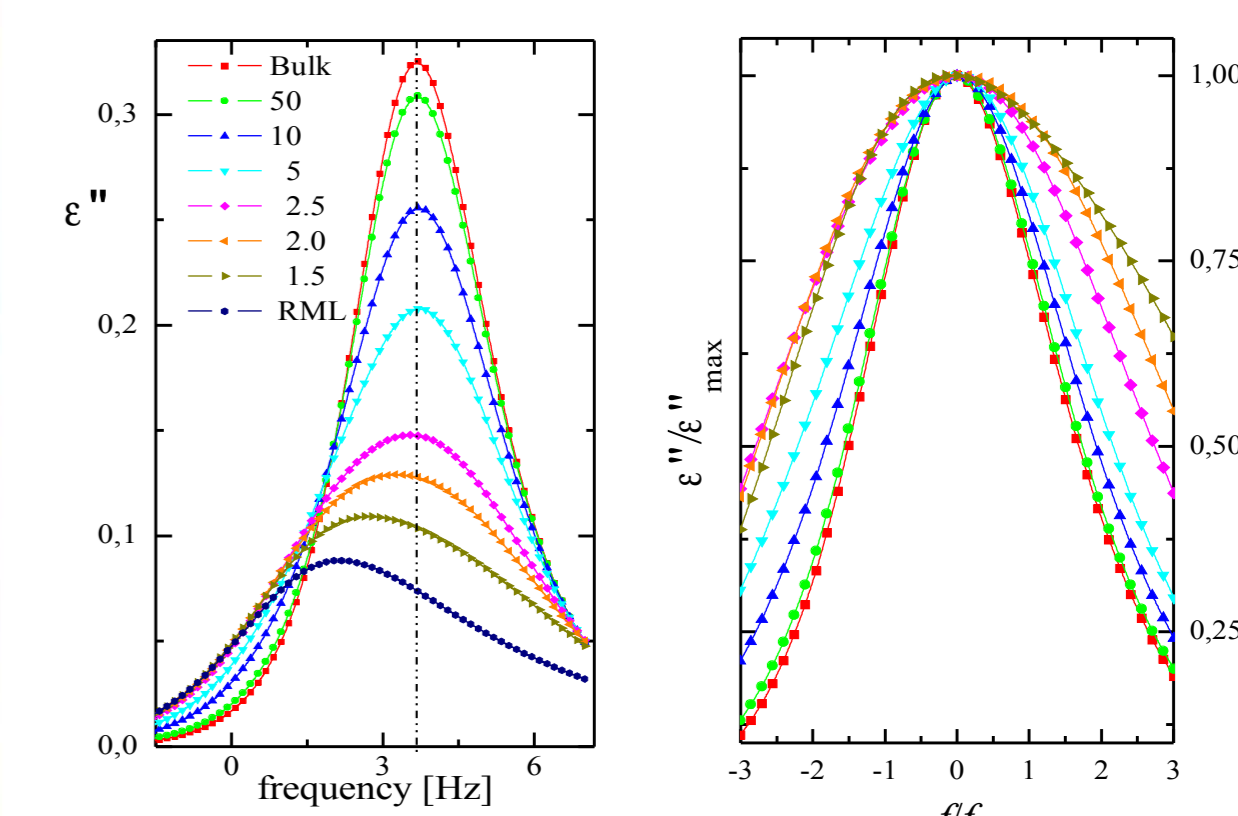
Thickness dependence of the dielectric strength and glass transition temperature for three different polymer systems. PET Napolitano Langmuir 07, PS Fukao PRE 2000, P2VP, Lupascu, PhD Thesis TUDelft 06

By quantifying the linear response of a generalized modulus in a multilayer system, we demonstrated that the presence of a layer with a different mobility acts first on the static properties and then on the dynamical properties of the film itself. In the particular case of a dielectric response, upon thickness reduction, a *Reduced Mobility Layer* first causes the reduction of the dielectric strength, without altering the position of the maxima of the relaxation peaks (*first regime*), and then (*second regime*) leads to an increase of the relaxation time and thus a higher dynamic glass transition temperature at thicknesses comparable to the extension of the RML (7 nm for PET on Al, 20 nm for PV2P on SiO₂).

"BI" LAYER MODEL



$$\frac{1}{C} = \frac{1}{C_b} + 2 \frac{1}{C_\delta} \quad \frac{h}{\epsilon(\omega, T)} = \frac{h - \delta}{\epsilon_b(\omega, T)} + \frac{\delta}{\epsilon_\delta(\omega, T)}$$

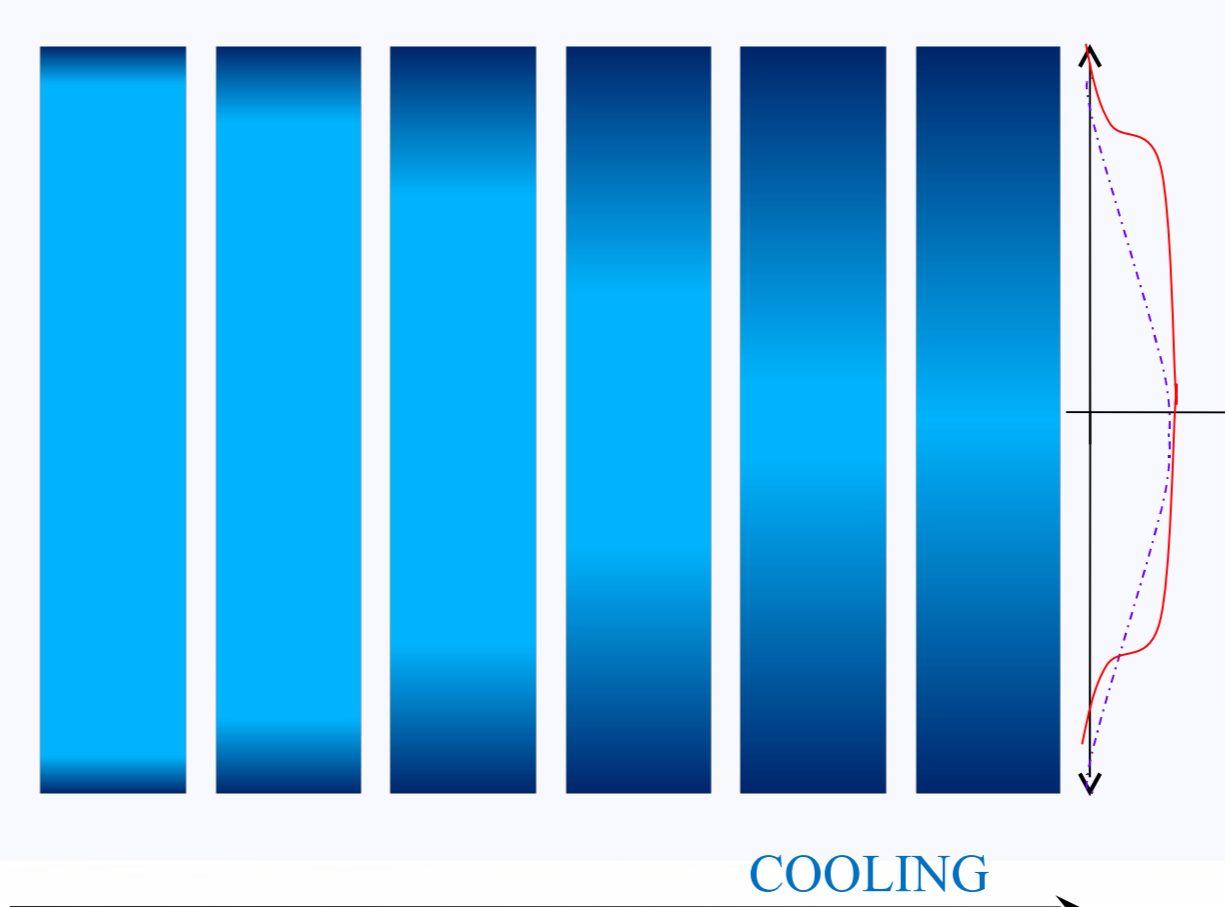


DEAD AND REDUCED MOBILITY LAYERS

Polymer layers at the very interface (2-5 nm) with an attractive substrate are usually modeled as regions with almost null expansion coefficients and absence of molecular mobility; due to these extreme characteristics, those regions are usually denoted as dead layers. Being a direct manifestation of changes in the system properties in proximity of an interface, dead layers are a general issue of the reduction or enhancement of the material performance on the nanoscale, rather than a specific feature of ultrathin polymer films.

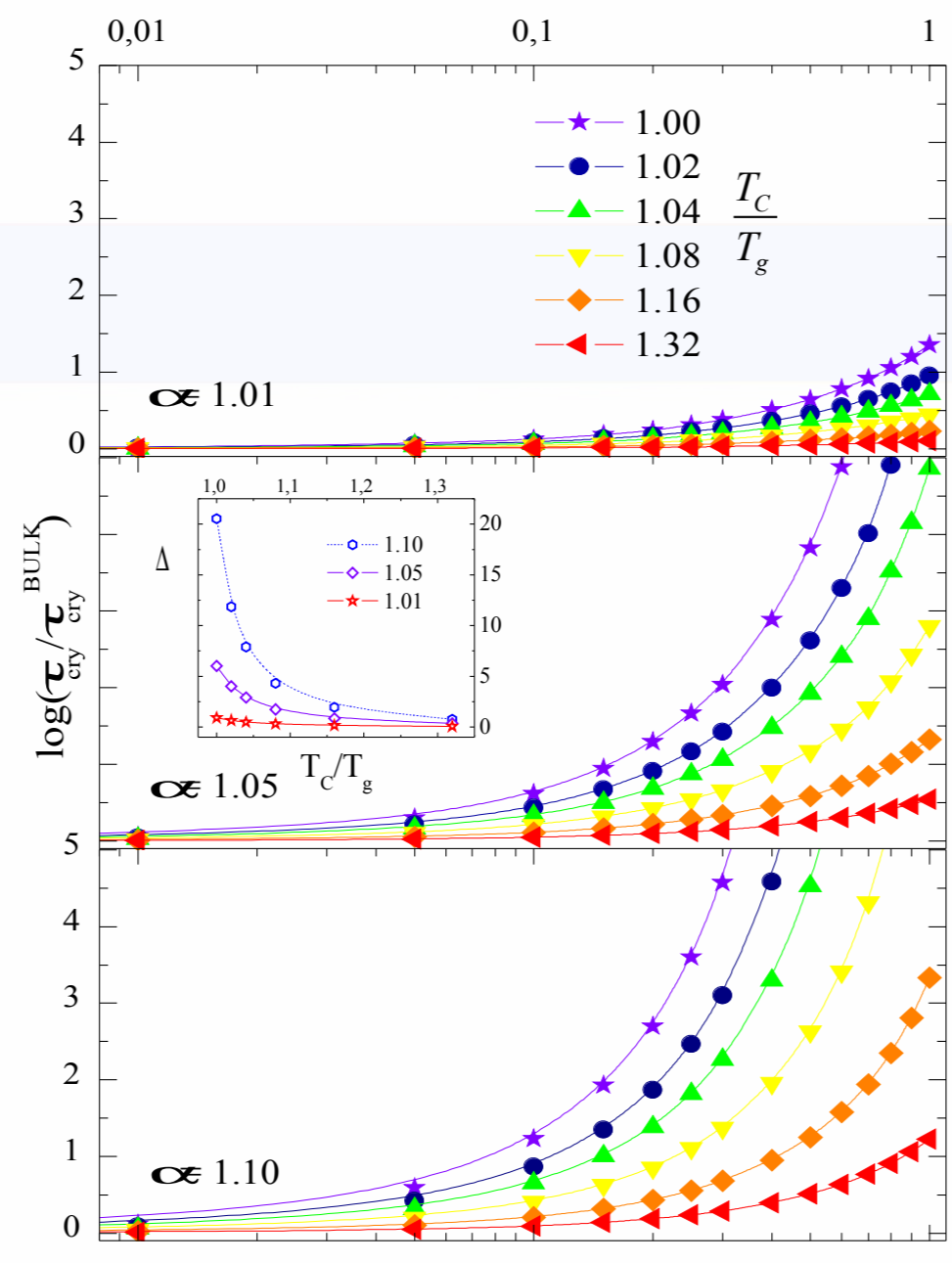
Though the existence of these layers is still a subject of controversy, indirect proofs of their presence in polymer/metal interfaces come from the analysis of the thickness dependence of the expansion coefficients of ultrathin films both in the supercooled and in the glassy state. Similarly, an increase of glass transition temperature, T_g , upon reduction of the sample thickness is usually imputed to the presence of an attractive substrate and thus to a dead layer. In fact, interfaces are treated as boundary conditions, introducing a gradient of mobility within the film thickness, extinguishing over a temperature, process and material dependent lengthscale (reduced mobility layer).

Being almost impossible to characterize these layers in terms of morphological changes or spectroscopic analyses, mostly simulations were carried out to improve the understanding of the structural perturbations generated at the interfaces and their propagation into the core of the sample. The origin of the slowing down in the dynamics of a glass former in the presence of a rough wall was, amongst others, attributed to the longer time intervals necessary for the simulated units to escape the cage formed by the surrounding units. Similarly, in an energy landscape approach, the potential energy minima connected to the different relaxation modes are supposed to be deeper for the molecules in proximity of an attractive interface and smoothly recover the bulk behavior, implying a gradient of the physical properties interrelated with the involved relaxation modes.



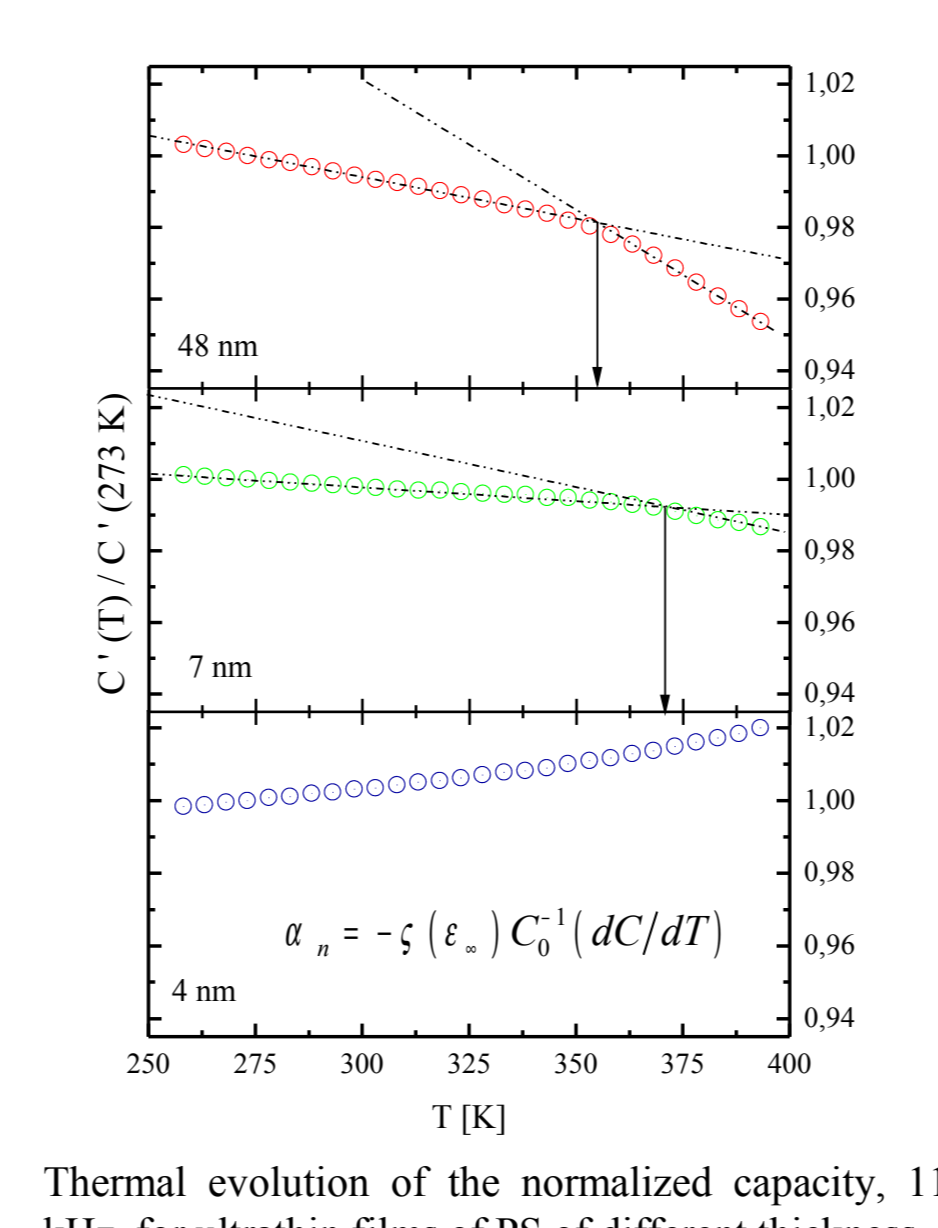
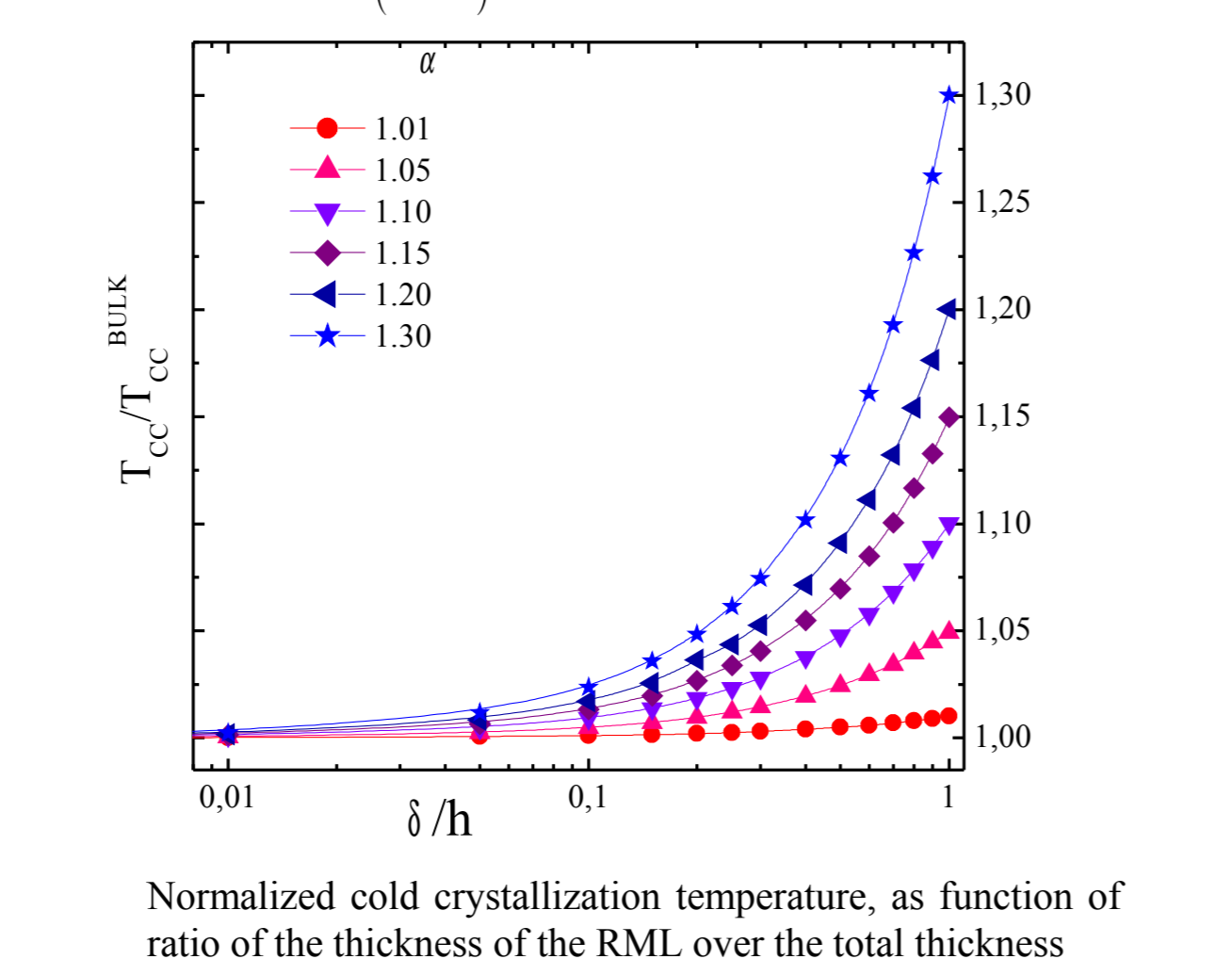
GLOSSARY

- Glass transition** Kinetic transition between a solid and a liquid like response.
- Structural relaxation time τ** Time necessary to a system to relax toward an equilibrium state, after an imposed external disturbance
- Glass transition temperature T_g** Temperature at which the structural relaxation time equals the inverse of the scanning rate of the experiment. T_g can be assigned to the temperature at which the structural relaxation time is 100 s.
- Confinement effect** Change in the material properties when the system confined in a dimension smaller than its characteristic length scales
- Interfacial effect** Change in the material properties at the interface with another medium
- Dead layer** Layer where a given physical property assumes zero value.
- Reduced mobility layer RML** Transition layer between a bulk like zone and a dead mobility layer
- Cold crystallization** Crystallization achieved upon heating an amorphous sample just above its glass transition temperature
- Dielectric spectroscopy DS** Spectroscopic technique based on the interaction between an external electric field and the dipole moments in the sample. The analysis of the frequency and temperature dependent relaxation processes due to polarization gives a unique information on the behavior of the material.
- Capacitive dilatometry** Dilatometric technique based on the measurement of the capacity of a thin layer at frequencies high enough where the contribution of molecular relaxations is negligible.



Deviation from bulk behavior of the crystallization time at different normalized crystallization temperatures, and increasing values of the substrate interaction parameter α .

$$T_g^{BULK} \left(\frac{\delta}{h} \right) = \frac{T_g^{RML} - T_g^{BULK}}{\delta} \frac{T_g^{RML} - T_g^{BULK}}{1 + \frac{\delta}{h}} + T_g^{BULK} \quad T_g^{RML} = \alpha \cdot T_g^{BULK}$$



CAPACITIVE DILATOMETRY

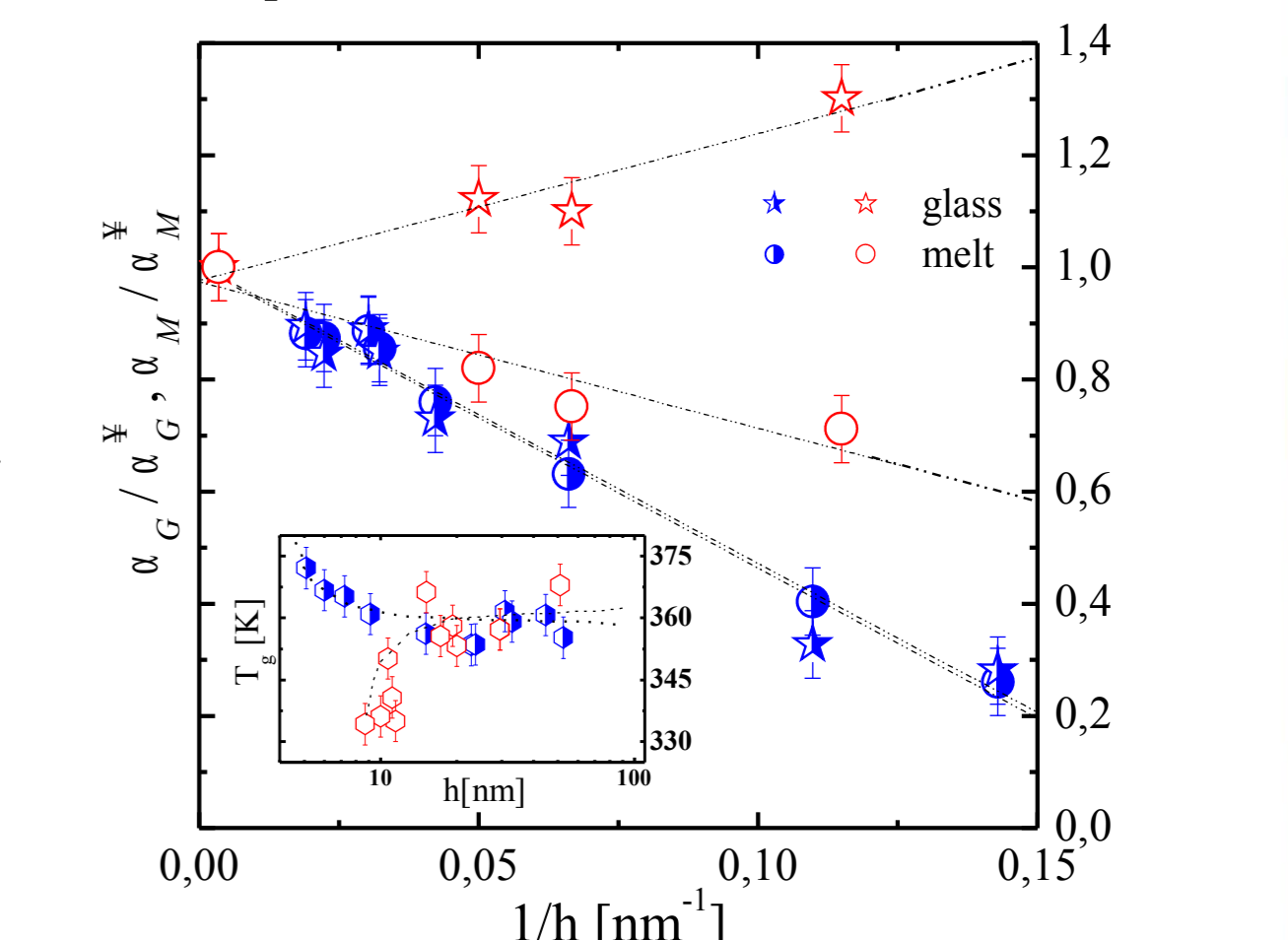
For non-polar systems, at sufficiently high frequencies, where the structural relaxation process appears well above the glass transition region, the temperature dependence of the capacity $C(T)$ can be related to the linear expansion coefficient of the material in the direction normal to the substrate α_n . Thus, similarly to other techniques sensing the temperature dependence of the thickness on the nanoscale, even this approach allows to determine T_g . The glass transition temperature is, in fact, assigned to the temperature at which $C(T)$ shows a kink, separating the glassy state from the melt, as the two regions show a different slope, i.e. different expansion coefficients, α_g and α_m . As already reported for data collected via other techniques, the contrast, i.e. the difference between the slopes in the glass and in the melt, decreases upon thickness reduction.

EXTREMELY THIN FILMS (< 6 nm)

By means of capacitive dilatometry, we investigated the influence of sample preparation on the thickness dependence of the expansion coefficients of ultrathin polymer films of poly(styrene), PS, in the geometry of model nanocomposites. **Series A** was annealed at T_g for 12 hours, **Series B** was annealed for the same time at T_g+25 K. Samples from **Series B** can be schemed as bilayers (dead layer + bulk), while in samples from **series A** the effects of a faster component (free surface, solvent residual) should be taken into account.

$$\begin{cases} T < T_g & a_n(h) = 1 - \frac{\delta}{h} a_g + \frac{\delta}{h} a_m \\ T > T_g & a_n(h) = \left(1 - \frac{\delta}{h}\right) a_m \end{cases}$$

From the fit of the experimental data we obtained dead layers extending over 2-3 nm. Extremely thin films show a continuous increase of the capacitance with temperature.



Normalized expansion coefficients in the melt and the glassy state for ultrathin films of PS as function of the inverse of the sample thickness.

INTERPLAY BETWEEN τ_α AND τ_{cr}

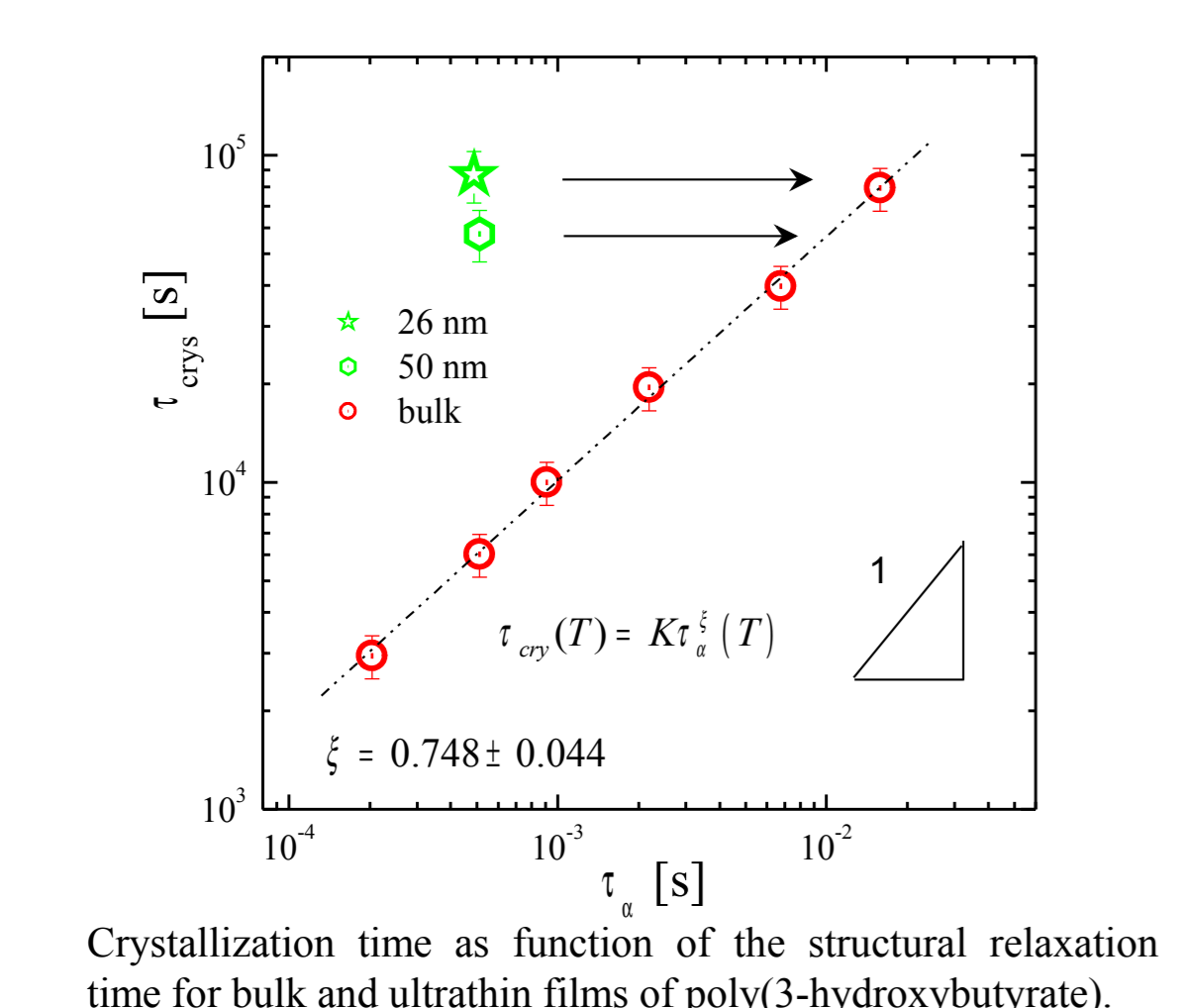
The apparent paradox on the molecular mobility in thin films can be solved by considering the different ways in which a layer with a reduced or enhanced mobility affects the experimental observables: in the first regime, the crystallization rate cannot be related to the molecular mobility probed on the time and lengthscale of the dynamic glass transition (segmental mobility). The crystallization rate has to be connected to an effective glass transition temperature given by the distribution of relaxation times along the film thickness, similar to the one estimated via measurements of the diffusion coefficients.

By modeling a bilayer system consisting of a bulk-like layer and an RML it was possible to reproduce the confinement effects on the diffusion-limited crystallization rate of ultrathin polymer films: an augment of the crystallization time, a reduction of the confinement effects upon increase of the crystallization temperature and modest increase the crystallization temperature in non isothermal conditions.

$$G(T) = f(T) \cdot D(T) \cdot \tau(T) \cdot \eta^{(1)}(T) \cdot f(T) \cdot \tau_\alpha^{-1}(T) \quad \frac{dG(T)}{dT} \ll \frac{dD(T)}{dT} \quad \tau_{cr}(T) = G^{-1}(T) = \frac{1}{f(T)} \tau_\alpha^{(1)}(T) = \frac{1}{f(T)} \tau_\alpha(T)$$

$$\tau_\alpha(T) = \tau_\alpha \exp\left(\frac{BT_\alpha}{T - T_\alpha}\right) = \tau_\alpha \exp\left(\frac{E_a}{R(T - T_\alpha)}\right)$$

$$\tau_{cr}(h, T) = \frac{1}{f(h, T)} \tau_\alpha^{(1,2)}(h, T) = \frac{1}{\Lambda(h) \cdot f(T)} \tau_\alpha(h, T) = \frac{\tau_\alpha(T)}{f(T)} = \tau_\alpha(T) \cdot \exp\left(\frac{BT_\alpha^{off}}{T - T_\alpha^{off}}\right)$$

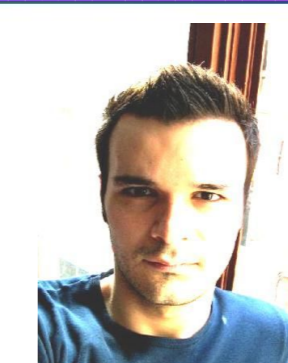


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