Relaxation pathways in ultra-thin, spontaneously polarised molecular glasses

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Molecular glasses are ubiquitous in nature, from ice mantles in the interstellar medium [1] to the internal structure of freeze-tolerant insects [2], and have wide ranging technical applications in the pharmaceutical and electronic industries [3,4]. The kinetic stability of a molecular glass is determined by a complex interplay between competing relaxation mechanisms. Recently, glasses with unparalleled kinetic stability have been prepared as ultra-thin films via physical vapour deposition techniques on a range of substrates [5]. This discovery has coincided with reports that ultra-thin molecular films harbour static electric fields, up to 10^8 Vm^{-1}, generated spontaneously via collective dipole orientation upon film growth [6].

Here, we combine these two fields and describe how the dynamics of molecular motion in ultra-thin molecular glassy films may be followed, exploiting the presence of spontaneous electric fields in these films and measuring the decay of such fields in real time. We couple this with pioneering neutron scattering data that probe accompanying changes in macroscopic molecular diffusion in the film. The results point to a decoupling of electric field decay and molecular diffusion, showing that the two processes proceed via different mechanisms with different temperature dependencies. We present a case for the use of surface potential measurements to understand the relaxation pathways available to ultra-thin molecular glasses produced by physical vapour deposition.

Molecular glasses were prepared via condensation of methyl formate onto cryo-cooled substrates under ultra-high vacuum conditions. Neutron reflectivity measurements were performed *in situ* on these films, as a function of temperature. The inclusion of a Co magnetic tracer layer in the substrate and use of a spin-polarised neutron beam gives nm resolution when tracking molecular diffusion, as a function of film temperature, with this technique. Electric fields of up to 10^8 Vm^{-1}, internally generated by the films following spontaneous molecular-dipole alignment, manifest as voltages, detectable at the surface-vacuum interface. These voltages were measured using an electron-beam irradiation technique and we will discuss the evolution of the voltages in real time as a function of the film growth conditions.

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