Preface

Confined at the nanoscale level, soft matter reveals a fascinating behavior, strongly deviating from what is observed in macroscopic samples. Shifts in phase transition temperatures by almost 100 K, impressive increases in elastic moduli, tremendously longer lifetimes of amorphous compounds—these are just a few examples of the *confinement effects* which, for more than 20 years have been fascinating a broad community of researchers.

The classical view of the deviation from bulk behavior focuses on the balance of finite size effects and interfacial interactions in systems at thermodynamic equilibrium. For example, thin films (thickness typically below 100 nm) are treated as slabs where the bulk molecular dynamics is locally perturbed by the presence of free surfaces ($\sim$2 nm layer at the interface with air, other gases, or vacuum) and adsorbing interfaces (proximity of non-repulsive wall). A reduction in the glass transition temperature is commonly imputed to the faster dynamics of free surfaces, while the presence of an adsorbing interface is considered as a source of slower molecular modes.

Such a picture, although very intuitive, cannot describe the peculiar features of soft matter under confinement, including exotic phenomena like the increase in glass transition temperature, T_g, at the free surface of star-shaped polymers and the reduction in T_g of capped films (no free surfaces), in several nanocomposites and in adsorbed layers. It is obvious that one or more key parameters are still missing in our understanding of confined systems.

A solution to this problem could come from the large and growing experimental evidence remarking the presence of ultraslow relaxation processes manifesting at timescales exceeding by several orders of magnitude the bulk equilibration time. These observations aliment the idea that the commonly used preparation protocols (deposition of a solid phase upon rapid solvent evaporation) lock molecular conformations into non-equilibrium states. The deviation from bulk behavior should thus be treated as the manifestation of non-equilibrium phenomena.

In this book, collecting the results of experiments and simulations, we provide the first comprehensive coverage of the impact of non-equilibrium structure and dynamics on the properties of soft matter confined at the nanoscale level.

The 12 chapters of this volume are grouped into three main parts, providing a broad overview of the state of the art in the field. *Equilibration and Physical Aging*: treating non-equilibrium phenomena via the formal methodology of statistical physics in bulk, the analysis of the kinetics of equilibration permits shedding light on the physical origin of the non-equilibrium character of thin polymer films. Both the impact of sample preparation and that of interfacial interactions are analyzed using a very large set of experiments, including dewetting and spinodal decomposition. A historical overview of the investigation of the non-equilibrium character of thin polymer films is also presented. Furthermore, the discussion focuses on how interfaces and geometrical confinement perturb the pathways and kinetics of equilibrations of soft glasses (a process of tremendous technological interest, commonly known as *physical aging*). *Irreversible Adsorption*: the formation of stable adsorbed layers occurs at timescales much larger than the time necessary to equilibrate soft matter in bulk. It is questioned whether this process could be considered as the driving force of equilibration. Recent work showed, in fact, a strong correlation between the behavior of polymers under confinement and the presence of a layer irreversibly adsorbed onto the supporting substrate. This correlation furthermore hints at the possibility to tailor the properties of ultrathin films by controlling the adsorption kinetics. In this section, the investigation of the physics of irreversible chain adsorption is accompanied by a detailed analysis of the molecular dynamics, structure, morphology, and crystallization of adsorbed layers. *Glass Transition and Material Properties*: the discussion covers a broad range of non-equilibrium phenomena affecting different family of soft materials—polymers, low molecular glass formers, liquid crystals. In these systems, geometrical confinement induces the formation of non-equilibrium phases, otherwise not achievable via processing of bulk samples. For example, ferroelectricity is unexpectedly observed in thin films and nanotubes of a polymer being paraelectric in bulk, while the interfacial phases of OH-bonded liquids and of discotic liquid crystals present a remarkable increase in structural order, not achievable via processing of macroscopic samples; an efficient example of chemical engineer at the nanoscale level, where nanopores are employed to obtain stress-free products, is also introduced. These examples show how non-equilibrium phenomena could be exploited as innovative processing parameters to fabricate novel nanomaterials with improved performance.

Finally, the differences between experiments performed under equilibrium conditions (e.g., a frequency sweep at constant temperature) and temperature scan from equilibrium to non-equilibrium states (e.g., differential scanning calorimetry or ellipsometry) at the nanoscale are discussed here.

I sincerely hope that this book can contribute to the progress of understanding soft matter and stimulate the discussion on non-equilibrium phenomena at the nanoscale level.

Bruxelles
May 2015

Simone Napolitano

http://www.springer.com/978-3-319-21947-9

Non-equilibrium Phenomena in Confined Soft Matter
Irreversible Adsorption, Physical Aging and Glass Transition at the Nanoscale
Napolitano, S. (Ed.)
2015, VIII, 300 p. 131 illus., 71 illus. in color., Hardcover
ISBN: 978-3-319-21947-9