

The main purpose of this project is to study the phase transitions and molecular dynamics in the supercooled and glassy state, in low and high molecular weight liquids of varying intermolecular interactions, under 1 D and 2 D spatial confinement. This issue seems to be extremely important in the context of the current discussion on the molecular origin of the glass transition, which is one of the fundamental unsolved problem of condensed matter physics. It is worth mentioning, that upon cooling liquids the drastic increase in viscosity and slowing down of the dynamics at relatively narrow range of temperatures close to T_g is observed. To explain this experimental universal finding different theoretical models based on the free volume, entropy and cooperativity concepts were developed. Recent progress in the current scientific instruments, neutron and nuclear magnetic resonance spectroscopies, supported by sophisticated theoretical simulations and considerations showed, that drastic slowing down of the dynamics close to T_g can be connected to increased length scale of cooperativity (ξ), as proposed in 1965 by Adam and Gibbs. On the other hand the spatial confinement offers unique opportunity to go even below that predicted value of ξ . Hence, the new experimental way to study molecular dynamics and glass transition phenomenon emerged. However as shown recently, the situation is far more complicated due to perturbations introduced by the surface and interface substrate-liquid effects. As a consequence, the shift of the dynamic glass transition does not have to be necessarily just a function of the degree of spatial restriction. Thus positive or negative shift of the phase transition can be recorded. What is more, current papers on the dynamics of thin films made of polymers present completely contradictory results. It should be added, that there are works that show, that segmental relaxation does not change even for the single coil of polymer, while others demonstrate, that T_g can be shifted by more than 50 K. Hence, both results seem to be in clear conflict, leading to a hot debate on the nature of the glass transition temperature. New theoretical models are proposed and developed to account experimental observation. The newest research published in the best journal including Science, Nature etc. indicated strong heterogeneous structure of the confined liquids, which seems to be a key to understand reported discrepancies. It is worth mentioning, that our studies carried out in pores showed, that there are at least two fractions of molecules i.e. interfacial and core ones, which demonstrate completely different dynamics, as revealed by dielectric and calorimetric measurements. Moreover, strong interplay between the core and interfacial mobility as well as thermal history of the sample was found to contribute to different shift of the dynamic glass transition temperature. We would like to continue this research to see, if such observation is universal for all kinds of glass formers. Beside, we plan to develop the concept of negative pressure in pores proposed by Zhang, furthermore criticized by others. The other, completely not explored, but very excited issue is related to determination of repulsive index from the Lennard-Jones potential. It turns out, that the calculation of the ratio of the activation barriers for the relaxation times measured below and above the crossover temperature corresponds very well to the ratio E_v/E_p (enthalpy at constant volume and pressure, respectively). Hence using simple relations reported in literature it is possible to determine the scaling exponent ν . On the other hand, this parameter was shown to correlate to the repulsive exponent in the Lennard Jones potential. Thus exceptional and unique opportunity to get insight into intermolecular interactions in the studied systems appeared. What is more, knowing ν one can predict further basic properties of the bulk materials, such as pressure sensitivity of the structural dynamics, pressure coefficient of the glass transition, relaxation times at given thermodynamic conditions, without any pressure experiments!

Undoubtedly in the course of better understanding of the processes and experimental results obtained for the spatially restricted soft matter further systematic and comprehensive studies on the other aspects of molecular dynamics and the glass transition phenomenon will be carried out. Thus, we plan to focus on:

- 1) physical aging,
- 2) crossover temperature,
- 3) dynamics of secondary relaxations,
- 4) crystallization, polymorphism, tuning morphology of the crystals, description of the kinetics,
- 5) dynamics of supramolecular structures.

All these issues obey fundamental problems of the physics of condensed matter and can be separately considered as a subject of the proposal. It should be stressed, that these aspects were intensively investigated in the literature for the bulk materials. On the other hand, in many times due to accuracy, resolution of the applied instruments and very small amount of the sample they were not studied thoroughly by the scientists dealing with the confinement effects. Extremely interesting seems to be studying the impact of 1 D and 2 D confinement, strength of host-guest interactions, morphology and geometry of nanoporous materials and intermolecular interactions on the mentioned above issues. In this context it should be stressed, that proposed plan of research goes much beyond the current state of art. One can also mention, that our preliminary measurements show, that due to finite size scale, as well as perturbation of the substrate, physical aging, kinetics of crystallization, aging, dynamics of secondary relaxation and supramolecular structures are significantly modified.

As a final point we plan to run pioneering high pressure measurements on the dynamics of confined system. It should be added, that up to now pressure was regarded as invaluable thermodynamic variable providing complementary information on the properties of the bulk materials. Within this project we would like to see, is there any impact of confinement on the pressure coefficient of the glass transition, activation volume, does it change with the pore size, strength of host-guest interactions and geometry of nanoporous materials. We also wish to study all the mentioned above aspects of the glass transition temperature at high pressure. This kind of research opens new ways of studying the soft matter confined in porous media not touched in the literature at all. As a consequence validity of all current models can be tested or alternatively new models of the glass transition temperature under confinement will be developed.

The proposed research on the soft matter under 1 D and 2 D confinement obeys fundamental issues concerning the dynamics and physics of the glassy transition phenomenon. We expect that data obtained within this project should provide significant progress in this field and serve to verify current or alternatively build new models of glass transition phenomenon under confinement. Simultaneously we believe that new nanotechnologies devoted to the application of nanoporous matrices as efficient drug carriers, templates to control morphology and basic physico-chemical properties of the recovered crystals, will be developed.