SIMULATION-EXPERIMENTAL INVESTIGATIONS OF GLASS-FORMING LIQUIDS BASED ON A NEW STRATEGY FOR EFFECTIVE MOLECULAR MODELING

Undeniably, the discovery of the first computer could be recognized as one of the most breakthrough events in the last century. These machines completely revolutionized the science and industry. It is due to not only the extreme increase in the speed of calculations but also the emergence of the entirely new methods for studies. Examples of the latter are the computer simulations, which nowadays are commonly applied to model behaviors of many physical, chemical, biological, meteorological, as well as human systems. The scientific importance of the above method results from the fact that it links experimental results with the theoretical predictions. The findings obtained from computer simulations of model systems are compared with the experimental results to verify the correctness of the models. On the other hand, use of certain approximations enables the theoretical solution of the model systems, yielding the results, which are subsequently compared with findings of computer simulations verifying the validity of applied approximations. Thus the computer simulations are recognized as an inherent part of the modern research.

One of the first studies for which computer simulations were applied is the modeling of the dynamic behavior for liquid. Interestingly, the model systems, which have been studied in the middle of the last century are still also of great interest. They are so-called simple-liquids, i.e., systems of which molecules are treated as spheres and interact in the defined manner depending only on the distance between them. It is worth noting that above form of the intermolecular interactions has a strong theoretical basis because the well-known Lennard-Jones potential is an example of simple-liquids' potential. Consequently, the theoretical framework of simple-liquids together with computational ease of simulations of their dynamics make that simple-liquids are still very willingly used to examine the nature of physical phenomenon on the fundamental level of intermolecular interactions. One of the nowadays widely discussed examples is the density scaling law. According to this concept the dynamic properties of supercooled liquids, X, e.g., structural relaxation times, diffusion constants or viscosity, could be scaled onto one master curve, independently on thermodynamic conditions. Moreover, the master curve follows the scaling equation, $f\left(X\right)=TV^{\gamma}$, where T is a temperature, V is a volume, whereas γ is a material dependent constant directly related to the intermolecular potential of simple-liquids. The facts (i) that density scaling law directly connects intermolecular interactions potential with observed macroscopic parameters, and (ii) that the more than one hundred materials satisfy the scaling equation, make density scaling is presently one of the most frequently studied feature of supercooled liquids. Interestingly, the form of the intermolecular interactions potential, which leads to the density scaling, implies also the equation describing the dependence of the pressure on volume. The latter possesses the parameter, γ_{EOS}, which is also related to the intermolecular potential. Moreover, the definitions of both parameters imply the equality $\gamma=\gamma_{EOS}$. However $\gamma=\gamma_{EOS}$ have never been reported for real materials, whereas it was exclusively observed for simple-liquids. That fact implies the natural question concerning the extent to which the simple-liquids can mimic the behavior of real materials and what are the reasons for the observed discrepancies between results obtained for the model and real systems.

In the framework of the research project, we plan to introduce the new model, quasi-real systems. The idea is to project molecules which exhibit the feature of real molecules (omitted in the simple-liquids) keeping the simplicity of the standard model systems. Consequently, the simplicity of novel systems enable obtaining of theoretical solutions (like it is in the case of simple-liquids) and ensures that the influence of other factors is minimized. Basing on our model molecules we will investigate how the molecular architecture, spatial charges distribution, and molecular flexibility influence on the structure, dynamics, and thermodynamics of the system. In this context is worth noting that our initial studies suggest that the structural anisotropy of the molecules is a reason for observed inequality between γ and γ_{EOS} for real liquids. Taking above into account, we plan to determine the intramolecular features, which are crucial for the density scaling, the tendency of the system to crystallization, the increase in the dynamic heterogeneity during approaching the glass transition or any other physical process characteristic for supercooled liquids. Hence, the planned researches constitute the natural step towards a deeper understanding of the nature of the above physical processes because obtained results enable unification of results obtained for simple-liquids and real materials.

However, the realization of the above very challenging task requires not only computational but also experimental studies. Therefore, within the scope of planned research, we perform the experimental verification of simulations results. For this purpose, we find the real analogs of our model systems differing mainly in studied intramolecular property. Discussed choice minimizes effects of other intramolecular features are minimized and enables experimental confirmation of computational results. Consequently, we sincerely believe that planned researches provide valuable hints to the prediction of the physical properties of the system basing only on the chemical structure of the molecule. Thus the planned research would be the cornerstone for the unification of supercooled liquids' chemistry and physics.