

DOCTORAL THESIS SUMMARY
„THERMODYNAMIC AND DYNAMIC PROPERTIES OF ANISOTROPIC
ELLIPSOIDAL MODELS INVESTIGATED BY MOLECULAR
DYNAMICS SIMULATION”

A doctoral dissertation is a collection of thematically related scientific articles published in peer-reviewed journals. The doctoral thesis aims to investigate the influence of anisotropy of intermolecular interactions on the molecular dynamics of glass-forming liquids.

At the beginning of the 21st century, scaling was demonstrated with experimental data confirmed for over 100 different substances. The phenomenon noticed then was called the concept of density scaling. Initially, this phenomenon was associated with the Lennard-Jones potential interactions, combining the repulsive exponent of the potential with a scaling exponent. On this basis, the theory of isomorphs was later derived, which combines the value of the scaling exponent with the value of the slope of the virial and potential energy correlation. On the same basis, an equation of state was later derived, which also returned the same value of the scaling factor, which then successively scaled the data from computer simulations. Unfortunately, using the proposed methods in the case of real liquids led to significant differences in the exponents that actually scale the thermodynamic data in relation to those obtained from the proposed methods.

The reason for these discrepancies is that the shape of real molecules is not isotropic. This led to the modeling of subcooled liquids in computer simulations using the anisotropic Gay-Bern potential, which was performed in paper 1. Using the anisotropic potential made it possible to obtain the experimentally observed discrepancy between the scaling exponents of dynamic data and volumetric data. An important conclusion from the conducted analyses is also the correlation between the value of the exponent scaling the dynamic data and the anisotropy value, which in this case meant the ratio of the length to the width of the molecule. In the further part of the work, the methods for determining the scaling exponent of dynamic data proposed within the concept of density scaling were analyzed in detail in terms of their application in anisotropic models. The results of these analyses show that the methods proposed so far, based on, among others, the equation of state or the slope coefficient of the virial and potential energy correlation, give incorrect values of the scaling exponent of dynamic data. Only one concept of the isochronous criterion gave the scaling exponent correct value, which confirms previous conclusions from real experiments. The work also includes analyses of the relationship between entropy and the concept of thermodynamic scaling presented in article 2. The value of configurational entropy, which was successfully determined for the first time for this type of experiment, is subject to the law of density scaling. The configurational entropy scales with the same exponent as the structural relaxation times. The conducted analyses also show that the suggested alternative concept of using excess entropy in relation to the entropy of an ideal gas does not satisfy the density scaling law.

The presented work's main result is that anisotropy plays a crucial role in modeling the molecular dynamics of glass-forming liquids.