

SUMMARY

The submitted doctoral dissertation consists of thematically consistent articles from 2022-2024 published in peer-reviewed journals in Journal Citation Reports. It contains the results of research whose main subject is the molecular dynamics of model van der Waals liquids. The research methodology includes computer simulations of model systems, and it aims to verify theories regarding the molecular dynamics of liquids in terms of free volume and density scaling and to relate these theories to systems of real molecules.

The work proposes an alternative method for determining the excluded volume (the quantity necessary to calculate the free volume), which uses intermolecular distances directly available from molecular dynamics simulations. The excluded volume estimated in this way, contrary to the assumptions commonly made in the literature, is a parameter dependent on the system's state. Interestingly, the determined ratio of excluded to free volume takes the same value at thermodynamic points characterized by the same molecular dynamics. Consequently, relaxation times and diffusion coefficients determined in different thermodynamic conditions can be plotted on one common curve depending only on the excluded to free volumes ratio. An alternative molecular dynamics scaling is known in the literature as density scaling. A comparison of the arguments of both scaling functions suggests that the ratio of determined volumes contains information about the density scaling exponent and, therefore, also contains information about the potential of interactions occurring between molecules. What's more, the demonstration that the volume ratio is invariant in terms of the isomorph theory based on the physical quantity, i.e., excess entropy, suggests that the entropy- and free-volume-based concepts explaining the slowdown of molecular dynamics of supercooled liquids, commonly considered to be competing, may, in fact, be related.

Subsequently, the work focuses on density scaling and an attempt to formulate a definition of the scaling exponent of molecular systems. The research includes a detailed analysis of the isomorph theory explaining the origin of the scaling exponent for simple systems, and their aim is to apply and generalize it to molecular systems with a higher degree of complexity, taking into account the features of real molecules, i.e., structural anisotropy and bond flexibility. As part of the development of the theory, based on the intermolecular relationship of the virial and potential energy, the definition of the scaling exponent of molecular systems with purely repulsive intermolecular interactions described by an inverse power law was derived. According to the formula, the scaling exponent is a weighted average of the exponents describing the intermolecular interactions between specific types of atoms, where the weights are the average potential energies corresponding to these

interactions. The research results for three model rhomboid systems confirmed the validity of the obtained formula.

However, the results of further tests of the newly designed model systems are no longer consistent with the derived definition. Research shows that the scaling exponent of molecular systems with different structures and only one type of intermolecular interaction may have values other than those corresponding to the potential exponent. Thus, the intermolecular potential is not the only factor determining the dynamics of molecular systems. In line with that, relying solely on the intermolecular interaction potential is insufficient to determine the scaling exponent. Going further, it was concluded that, contrary to the practices present in the literature, the value of the dynamics scaling exponent does not enable an unambiguous determination of the characteristics of intermolecular interactions. The final conclusion indicates that to describe the dynamics of real liquids adequately, the theory would need to be formulated anew, or the current theory should be modified to take into account anisotropy and intra-molecular interactions.

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