Abstract

Author:	Mgr. Dominika Melicherová
Title:	Study of polymerization of nitrogen at high pressure by molecular dynamics
University:	Comenius University in Bratislava
Faculty:	Faculty of mathematics, physics and informatics
Department:	Department of experimental physics
Supervisor:	Prof. Ing. Roman Martoňák, DrSc.
City:	Bratislava
Date:	3.7.2023
Number of pages:	80
Type of thesis:	Doctoral thesis

A first-order liquid-liquid phase transition is a rare and not fully understood phenomenon that has only been confirmed for one pure element, phosphorus. A first-order liquid-liquid phase transition between molecular and polymeric liquid states has been proposed for nitrogen but there are some discrepancies between experiment and simulations regarding the transition pressure. A similar discrepancy is also present in the solid state where molecular and polymeric liquid states also compete. We performed *ab initio* molecular dynamics simulations at temperature 3000 K and pressure interval 100-125 GPa using SCAN functional and system sizes of 192 and 288 atoms to reduce finite size effects. We carried out compression and decompression and we found a transition between 110 and 115 GPa, which is closer to the experimental data. We also performed molecular dynamics simulations of molecular crystal and polymeric crystal close to the melting line and we found that molecular crystal has high orientational and translational disorder of molecules and is likely to be a plastic crystal with high entropy. The high entropy of the molecular crystal stabilizes the molecular phase to high pressures at high temperatures. However, *ab initio* molecular dynamics simulations are extremely time-consuming especially in the case of liquids where large simulation cells are required. We have therefore

trained a machine learning potential for liquid nitrogen which would allow us to scan more temperatures and study the liquid-liquid phase boundary in detail.

KEYWORDS: liquid nitrogen, liquid-liquid phase transition, molecular dynamics, DFT, machine learning potentials