Anomalous Properties of Condensed Hydrogen Molecules under Extreme Thermodynamic Conditions Revealed by the Non-Empirical Quantum Molecular Dynamic Simulation Method

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The nuclear and electron wave packet molecular dynamics (NEWPMD) method describes floating and thawed Gaussian nuclear wave packets (NWPs) via the time-dependent Hartree method, and electron wave packets (EWPs) through the perfect-pairing valence bond theory that treats the Pauli exclusion energy. [1,2] The non-empirical ab initio intramolecular and intermolecular interactions were explicitly derived with which the equations of motion (EOMs) for a time-dependent wave function composed of the NWPs and EWPs are time-evolved. The simple EOMs ensure a stable long-time solution, that is, the time-dependent wave function even for condensed hydrogen molecules. In addition, the NEWPMD approach reproduces a long-range intermolecular dispersion force between H_2 molecules which the conventional density functional theory cannot provide.

The NEWPMD method has successfully reproduced various experimental observations without any model potential and empirical parameter such as (1) the radial distribution functions, diffusion coefficients, viscosity and shifts of the H-H vibrational frequency in liquid hydrogens [2,3], (2) the stable crystal lattice structure below the freezing temperature(13.8 K), vibrational displacement and reasonable lattice phonon frequency in solid hydrogens [4], (3) the discrete jump of the H-H vibrational frequency at the liquid-solid phase transition [4,5], (4) the thermal conductivity of non-equilibrium liquid hydrogens under a temperature gradient[6], (5) the isotope-dependent bond length and diffusion coefficient in liquid deuterium[7], (6) the decelerated diffusive dynamics at an optimal mixing rate for the H_2-D_2 mixture[8], and (7) the Widom line to divide liquid-like and gas-like regions hidden in supercritical hydrogens [9]. The temperature and density were never adjusted or scaled in any of these simulations. All the above-mentioned successful agreements with the experimental results in the far-different various phases and thermodynamic states demonstrate that the NEWPMD method not only reflects the real thermodynamic states of hydrogen systems at the same temperature and densities as the experimental values but also successfully reproduces the appropriate intermolecular interaction potential which essentially influences the thermodynamic properties.

In this presentation, we will report our computational results especially focusing on the latest computational findings on the two extreme thermodynamic conditions: (1) the decelerated liquid dynamics induced by component-dependent supercooling in hydrogen and deuterium quantum mixtures at low temperature, and (2) the distinct molecular dynamics dividing liquid like and gas-like supercritical hydrogens at higher temperature than the critical temperature (33K). In the former, we computationally found that the dynamics of the quantum H_2-D_2 mixtures significantly slows down at a specific mixing ratio, which is directly connected to the experimentally observed anomalous slowdown of crystallization in quantum H_2-D_2 mixtures at extremely low temperature. The latter proposes a new index to monitor the supercriticality and especially to distinguish liquid-like and gas-like supercritical regions which are different from normal liquid and gas. Both of the computationally predicted properties and obtained insights will help future experimental searching and understanding

anomalous and unknown hydrogen molecular dynamics which could play an important role in interstellar space.

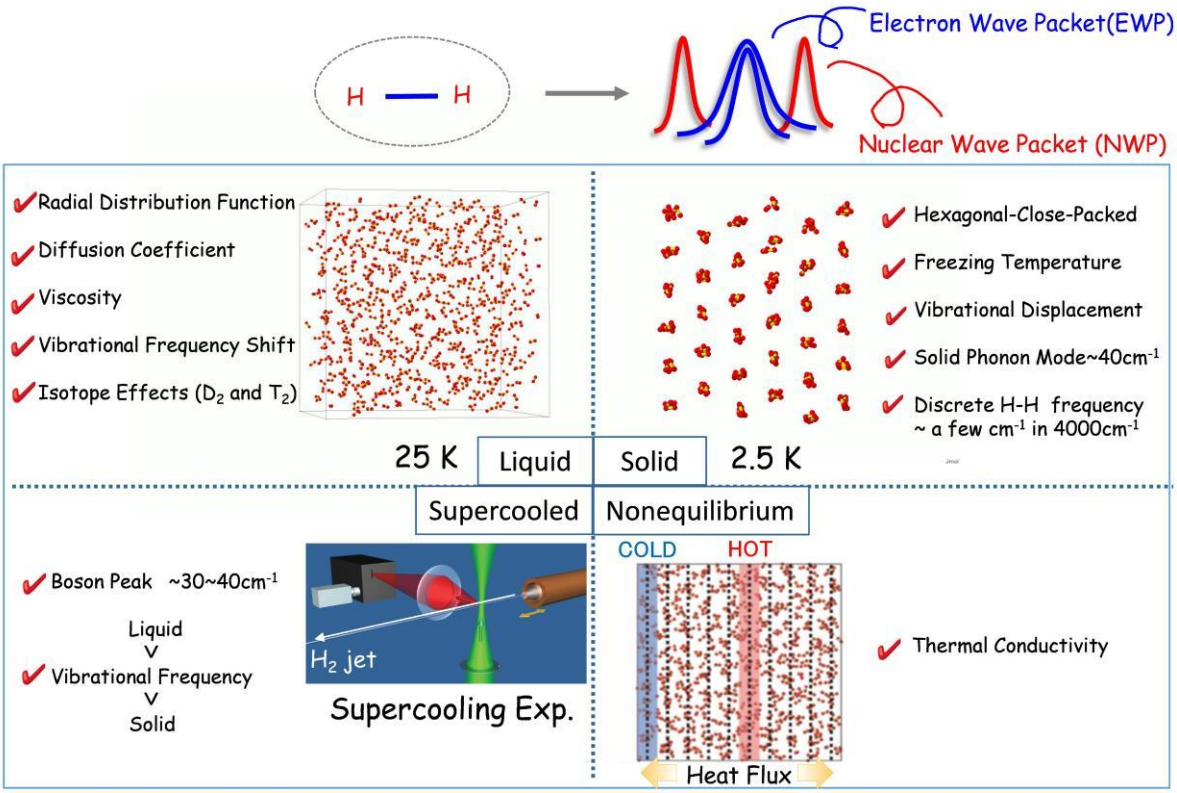

Figure 1: Far-different various phases and thermodynamic states of hydrogen molecules calculated by the NEWPMD method. The left-bottom figure was taken from Kuhnel et al., 2014, Phys. Rev. B 89, 180201.

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