

Title: An interesting deep eutectic solvent system: ChCl and Urea with changes in the radial distribution function of related to the hydrogen bonding at different temperatures, 295 K, 305 K and 315 K.

1. Background

A deep eutectic solvent (DES) is a type of ionic liquid formed by the combination of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). These solvents typically have a eutectic point, a temperature at which the mixture undergoes a sharp melting transition to form a liquid phase. Deep eutectic solvents have gained attention as environmentally friendly alternatives to traditional solvents due to their low toxicity, low volatility, and ease of preparation. One common example of a deep eutectic solvent is the Choline Chloride (ChCl) and Urea system. Choline chloride is the hydrogen bond acceptor, and urea is the hydrogen bond donor in this case. The mixture forms a eutectic mixture with unique properties.

The radial distribution function (RDF) is a useful tool in molecular simulation to analyze the structure of a system. In the context of DES, studying the RDF for hydrogen bonds at different temperatures can provide valuable insights into the temperature-dependent behavior of hydrogen bonding networks within the system.

As we change the temperature of a system, it can significantly influence the strength and prevalence of hydrogen bonds. At higher temperatures, the thermal energy can disrupt hydrogen bonding networks, leading to a decrease in the number and stability of hydrogen bonds. Studying RDF at different temperatures helps in understanding how the temperature affects the distribution and dynamics of hydrogen bonds in DES.

In summary, studying the hydrogen bond RDF at different temperatures in a deep eutectic solvent helps researchers understand the temperature-dependent behavior of hydrogen bonds. This information is crucial for designing and optimizing DES systems for specific applications, as the performance and properties of DES can vary with temperature.

2. Method

2.1 System preparation

All-atom MD simulations were performed using GRO-MACS/2016.5. The OPLS-DES force-field parameters were used for other molecules, including choline chloride and three hydrogen bond donors (HBD) proposed in a newly published paper by the Doherty group { Doherty B, Acevedo O. OPLS force field for choline chloride-based deep eutectic solvents[J]. The Journal of Physical Chemistry B, 2018, 122(43): 9982-9993. }. This nonpolarizable force field, OPLS-DES, gave near quantitative agreement at multiple temperatures for experimental densities, viscosities, heat capacities, and surface tensions.

2.2 Molecule dynamics

The DES system firstly was relaxed through a process called Energy minimization (EM) and used the steepest descent for 200000 steps and 20000 steps. Secondly, the three systems used the V-rescale thermostat to heated up to their respective temperatures for 200 ps. using the isothermal-isobaric (NPT)

ensemble for 8 ns to get the equilibrated box at 1 bar pressure used the V-rescale thermostat and Berendsen barostat. In the next step, the system was equilibrated in an isothermal-isovolumic (NVT) ensemble for 6 ns using different generate velocities according to a Maxwell distribution at temperature. Finally, the three systems were equilibrated in an isovolumetric (NVE) ensemble for 2 ns at their respective temperatures and equilibrated pressure. Then the three DES systems are all ensembled for 10 ns for production run. The equations of motion for each atom were solved using the leap-frog algorithm with a time step of 2 fs. Electrostatic interactions were evaluated using the particle-mesh-Ewald (PME) summation technique where the cutoff was 1.5 nm.

3. Results

3.1 MD results

This is a example temperature ($T=295$ K) MD steps results.

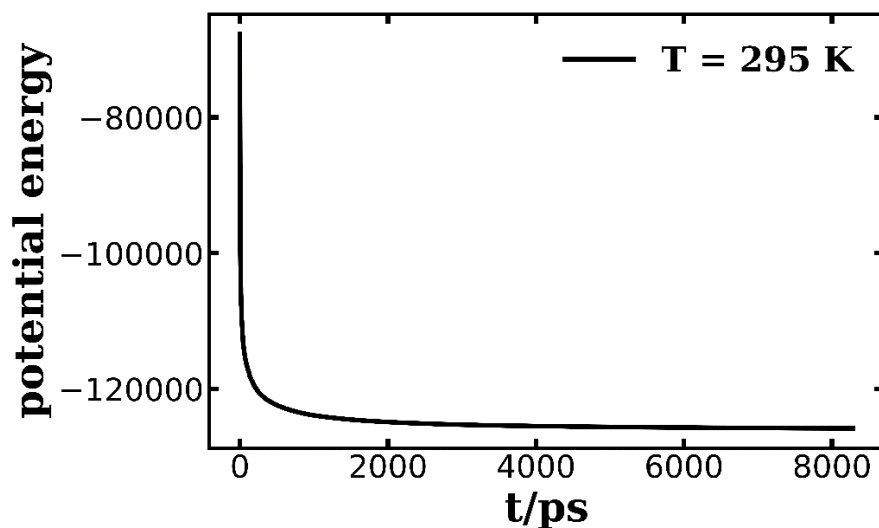


Figure1. Energy minimization 1

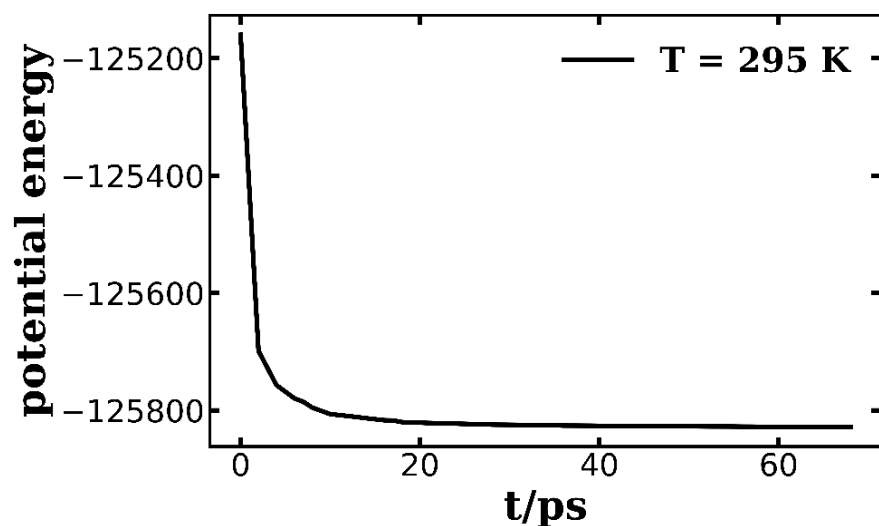


Figure2. Energy minimization 2

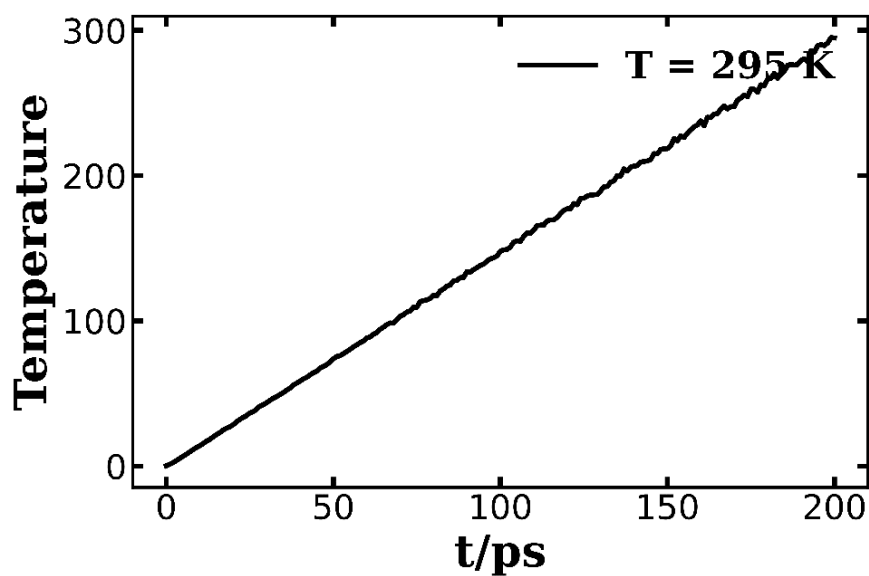


Figure3. Heat

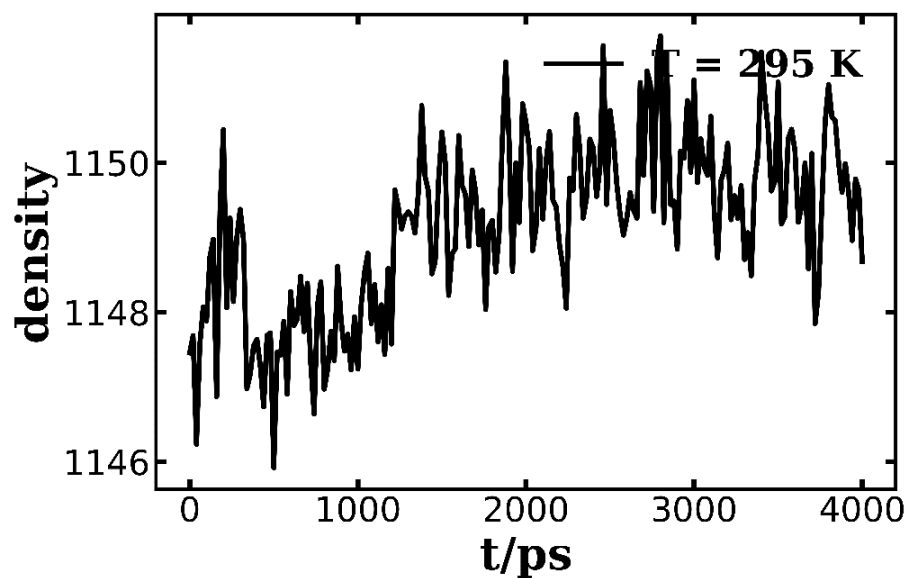
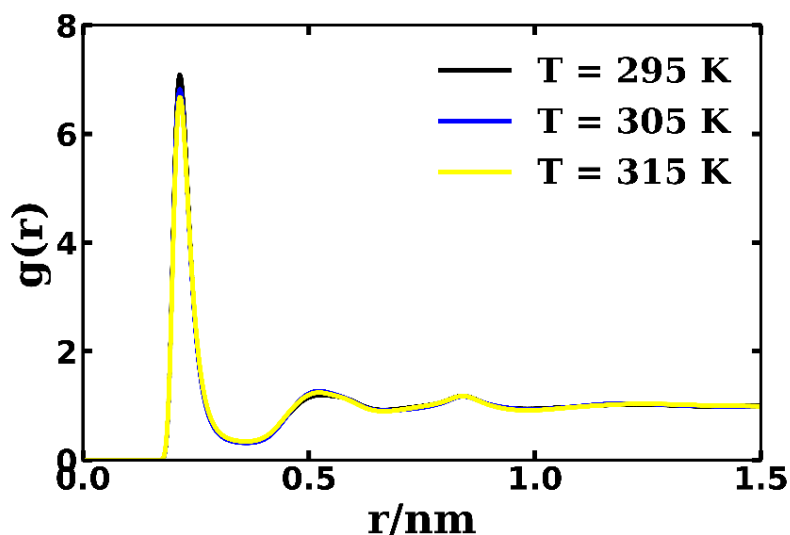


Figure4. isothermal-isobaric (NPT)

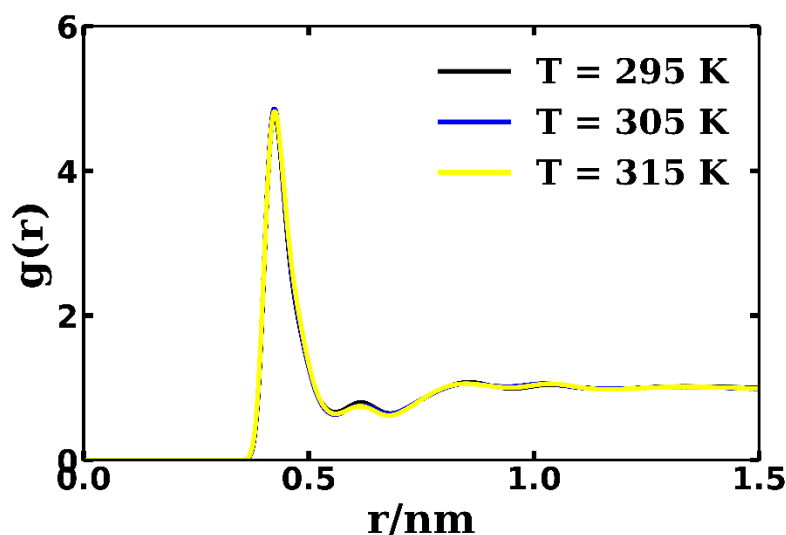
3.2 RDF result

In the system of choline chloride and urea, there are two special hydrogen bonds, one is the Cl anion and the hydrogen atom on urea, and the other is the Cl anion and the Na cation. So I mainly looked at how the radial distribution function between these two different types of atoms changes with temperature.

3.2.1 Cl-HY



3.2.2 Cl-NA



4. Summary

In summary, due to the temperature increase, the H-bonds part $g(r)$ would become lower. It indicates a weakening or disruption of the hydrogen bonding network. There are some reasons to explain this result. The first is the weakening of Hydrogen Bonds: a decrease in $g(r)$ suggests that the probability of finding hydrogen bonds at a certain distance is reduced. This could be indicative of weakened interactions between hydrogen bond donor and acceptor groups in the DES. At higher temperatures, thermal energy disrupts the hydrogen bonding network, making it easier for hydrogen bonds to break. The second is the decreased structural order. The reduction in $g(r)$ implies a decrease in the structural order associated with hydrogen bonds. This is consistent with the idea that increased temperature leads to more disorder in the system. Hydrogen bonds play a crucial role in maintaining the structure and organization of DES. A decrease in $g(r)$ signifies a loss of this structural order.