FT-IR Microscopy of Liquid Microjets

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Motivation

It is well known that the thermodynamic properties of liquid water show anomalous behavior in the deeply supercooled region of the phase diagram. Specifically, the density, heat capacity and isothermal compressibility all show rapid divergence at a singular temperature, $T_s = -45^oC$. In addition, the transport and relaxation properties show similar behavior as T_s is approached. Currently, two thermodynamic scenarios have been postulated to account for the divergent response functions observed in deeply supercooled water.

The Stability Limit Conjecture, proposed by Speedy and coworkers[1], attributes the low temperature behavior of supercooled water to the reentry of the liquid-gas (L-G) spinodal through the negative pressure region of the phase diagram. As a consequence, T_s is the point at which the free energy surface of the liquid terminates at a first order phase transition to crystalline ice. Adequate determination of the proposed L-G spinodal, at negative pressures, is severely complicated by the experimental difficulties in working with superstretched liquids.

Poole et al.[2] have suggested an alternative explanation—the Critical Point Hypothesis. At T_s there exists another critical point in the water phase diagram. At $T<T_s$ there is a line of first order phase transitions between two structurally distinct liquid phases. Mishima et al.[3] have offered indirect evidence for a liquid-liquid phase transition in the decompression induced melting of Ice IV.

Currently it is not been possible to distinguish between the two scenarios either by Molecular Dynamics simulations or direct experimental investigation. MD simulations are hampered by the slow relaxation processes inherent in supercooled liquids, while experiments have failed to penetrate the homogenous nucleation limit ($-40\ ^0$ C, 1 atm).

Preliminary Experimental Results

Liquid jets, technology pioneered by Faubel and coworkers[4], may provide a novel way to circumvent the many difficulties encountered in studying metastable liquids. Micron-sized liquid jets have been shown to produce deeply supercooled water ($-63\ ^0$ C) by large rates of evaporative cooling (10^5 K/sec).[4] We have endeavored to characterize these jets by Raman Spectroscopy, FT-IR microscopy, and X-Ray absorption in an effort to corroborate the low reported surface temperatures and to hopefully investigate the structure of deeply supercooled water. FT-IR microscopy was used to probe the temperature profile as well as the character of hydrogen bonding in these liquid microjets.

Preliminary experiments conducted on ALS beamline 1.4.3 (spring 1998), with Drs. Wayne McKinney and Michael Martin, have supported the low temperatures previously reported and have provided compelling evidence for a large temperature gradient within the liquid jet. Figure 1 shows the temperature gradient determined by the shift in the OH stretching frequency in a 5% H_2O/D_2O solution[1]. A "sheath" of supercooled water ($\sim-50^OC$), 3 microns from the edge of the jet, appears to surround a warmer core ($\sim25^OC$). Raman experiments, which give complimentary information, were conducted at UC Berkeley. However, these experiments lacked the spatial resolution of beamline 1.4.3 and therefore the 3 micron "sheath" of what appears to be supercooled water could not be detected. In this way, the spectromicroscopy facility's spatial as well as spectral resolution has been indispensable in the investigation of liquid microjets.

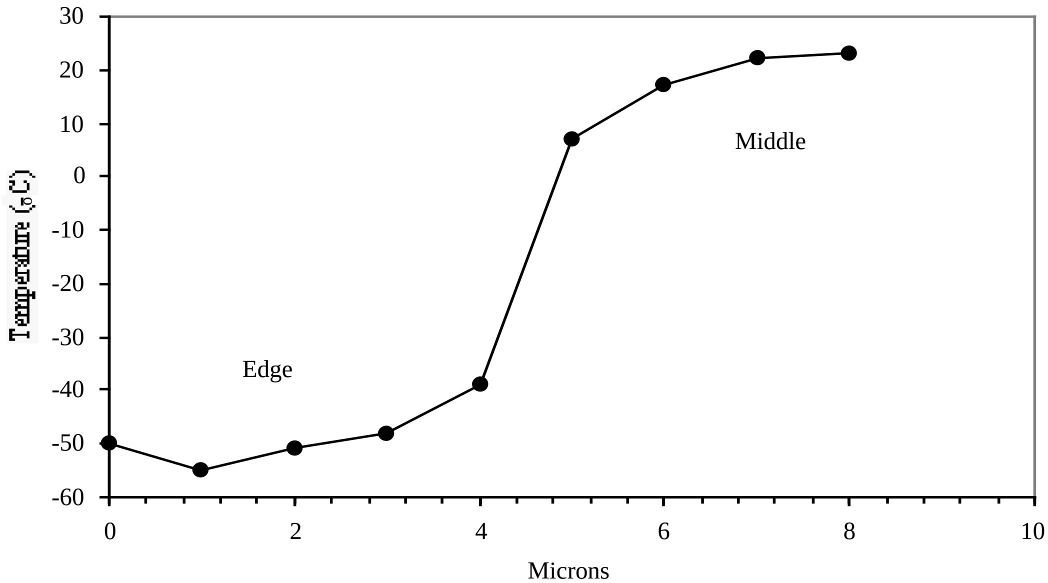

Fig. 1: Temperature vs. position in a 20 micron jet obtained by infrared absorption of 5% H_2O/D_2O (v/v).

In addition, we have examined the OH (OD) stretching and bending frequencies in pure H_2O (D_2O). The OH stretch region has been demonstrated to be a highly sensitive probe of hydrogen bonding.[2] The infrared spectrum taken in the middle of the jet is consistent with room temperature liquid water. In contrast, water within the 3-5 micron "sheath" show significant aspectral perturbations that may be due to enhanced hydrogen bonding. Specifically, the OH stretching frequencies, shown in Fig. 2, are dramatically red-shifted from the normal room temperature water that is observed in the middle of the jet. This shift may be consistent with the microscopic picture of cage-like structures theorized to be present in deeply supercooled water. In addition, the sharp peak observed around 3600 cm^{-1} is not observed in the room temperature liquid and may be a surface localized mode or perhaps a unique feature of the deeply supercooled state.

Future Directions

The experiments and data described above are still in the initial stages. Further experiments are needed to map out the temperature profile across as well as down the axis of the microjet. To better understand the cooling mechanism, a variety of jet sizes (5 to 30 microns in diameter) will be used. Furthermore, we would like to extend our studies to the intermolecular vibrational modes (<1000cm^{-1}) of both H_2O and D_2O, which are extremely sensitive probes of the hydrogen-bonding environment within the liquid.[6]

In general, liquid microjet technology coupled with the high spatial and spectral resolution of beamline 1.4.3 may provide a powerful new tool in the investigation of metastable liquids.

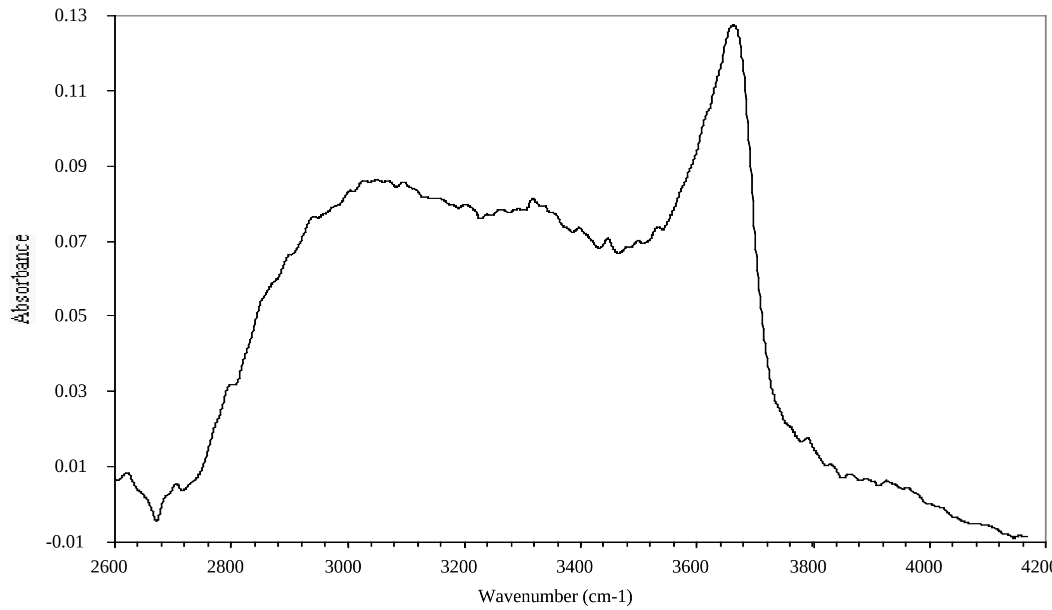

Fig. 2: The infrared OH stretch region of water measured near the edge of a 20 micron liquid microjet

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