Is Liquid Water a Hot Quantum Fluid?
Anomalies of Thin Liquid Film of Water and Biological Systems

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The properties and structure of water give very important information for understanding certain phenomenon of life. Water is a representative liquid, however it has many mysterious properties compared with simple liquids in bulk phase. Water exhibits anomalous behavior in thin liquid film too. Reports indicate that the viscosity of water between two quartz plates separated by several hundred angstroms shows a wave-like nature with peaks at every multiple of 15ºC [1]. The disjoining pressure of quartz plates has the inflections [2] and the diffusion coefficient of thiourea in water has the kinks at about the same temperatures [3]. These anomalies of thin film of liquid water seem to be related to the properties of water in small cells and therefore to the preferred temperatures of animals or plants [4]. In thin liquid film or when confined in a small space, the viscosity of water increases highly at temperatures that are approximately multiples of 15ºC and thus metabolites are not easily transported in cells at those temperatures, and this results in many other biochemical effects to cells.

Molecules in liquid phase display thermal motion in a relatively larger free space than in solid phase. This free volume is related directly to the entropy. At high temperature, when a molecule is in thermal motion, the thermal wavelength, λ, is defined and it is referred to as the effective size of the molecule, as follows,

$$\lambda = \frac{h}{\sqrt{2\pi mkT}} \quad . \tag{1}$$

The thermal wavelength of an ordinary molecule at room temperature is very small compared with the size of molecular free volume. Therefore molecules move, more or less, freely in the free space. However when the temperature is low and thus the thermal wavelength is long, or when the molecular free volume is relatively small even at high temperature, quantum effects take place due to the thermal wavelength.

The intermolecular interaction between water molecules is very strong. Therefore large holes or vacancies are not expected in the liquid phase of water. According to the calculation using the significant structure theory, the free volume of liquid water is very small [5]. And when the one dimensional molecular free volume ($l_f = (v_f)^{1/3}$), (where v_f is the free volume in molecular dimension) is divided by the thermal wavelength, the quantum numbers ($q = l_f/\lambda$) of approximate half integer appear at 15ºC (q=2.9), 30ºC(q=3.7), 45ºC(q=4.2), and 60ºC(q=4.8). Thus the q value is more like a half integer at temperatures that are multiples of 15ºC.

According to the free volume theory of Kirkood, the entropy, S, is expressed as follows,

$$\frac{S}{R} = C_0 + \ln\frac{v_f}{\lambda^3} \quad . \tag{2}$$

Using the experimental value for the entropy of water and q=3.0 at 15ºC, C_0=4.82 is obtained, that is very similar value of the entropy of ice at 0ºC, and the free volumes and quantum numbers are calculated. Here also appear the quantum numbers of the half integer at every multiple of around 15ºC. At the temperatures where the quantum numbers are a half integer, the nodes of thermal wavelength match the boundary of molecular free volume. Therefore molecular motions will be *stationary* at these temperatures and thus high viscosity is expected.

The toxicity of heavy water is widely reported. The toxicity might not be a chemical problem. Equation (2) is applied to heavy water with C_0=5.60, *i.e.*, the value of the entropy of D_2O ice. The results are (11, 3.0), (24, 3.5), (36, 4.0), (48, 4.5) in a set of (t(ºC), q). The temperatures 24 and 36ºC are the preferred ones for organisms however in the case of heavy water, the viscosity might be high at those temperatures and thus multicellular organisms are injurious at their preferred temperature.

In conclusion, water has a strong hydrogen bond interaction. Thus small free volume is included. In this small free space, the water molecule shows high-temperature quantum mechanical behavior. The anomalies in a thin liquid film of water are not associated with a *surface effect* that comes from the surface/volume ratio, but rather with a *wall effect* of boundary that causes quantum mechanical repulsions.

References

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