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Photothermal measurement of the thermal conductivity of supercooled water

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Résumé. — La diffusivité thermique de l'eau surfondu a été mesurée entre + 40 et - 23 degrés centigrade par une méthode sans contact, dans laquelle la source de chaleur, modulée ou pulsee, est créée optiquement tandis que le champ de température est analysé par la déviation d'un faisceau sonde. La valeur de la conductivité thermique, λ, déduite de ces mesures décroit de manière monotone avec l'abaissement de la température. L'analyse de λ suivant l'expression classique et en terme de loi critique ainsi que le rôle de la structure du réseau de liaison hydrogène sont aussi discutés. On constate que les équations classiques reliant λ et la vitesse du son, c, sont bien vérifiées. On conclut que le réseau de liaisons hydrogène a la même influence sur λ et c.

Abstract. — Thermal diffusivity measurements of supercooled water have been performed between + 40 °C and - 23 °C, using both optically induced periodic and pulsed heat source in two separate experiments. The resulting temperature field is analysed by monitoring the deflection of a He-Ne laser beam. The thermal conductivity, λ, as deduced from the experiments, decreases continuously with decreasing temperature. The analysis of λ is also discussed both in terms of the classical expression and in terms of a critical law. The influence of the hydrogen bond network structure is discussed, as well. It is verified that the classical relations between λ and the sound velocity, c, are respected, and consequently that the hydrogen bond network structure has the same influence over both λ and c.

1. Introduction.

There has been a resurgence of interest in the study of supercooled water in the last few years because its anomalous properties are enhanced at low temperatures [1]. Theoretical models cannot yet describe the full behaviour of water, in spite of the progress made by computer molecular dynamic simulations [2]. Consequently, there is a need for experimental data, sufficiently accurate to allow comparison with the predictions of the different theoretical approaches. The temperature dependence of the thermal conductivity is particularly important because it is related to both molecular dynamics and molecular structure. It is interesting, for example, to determine to what extent a classical theory is sufficient to describe the data or if the enhanced hydrogen-bond structure induces additional effects.

Experiments on supercooled water are difficult because nucleation is difficult to avoid. In order to reduce the probability of nucleation, one must use relatively small samples. With water volumes of the order of 1 cm³, it is possible to reach - 25 °C without nucleation occurring. Below this temperature, emulsions have been shown to be easier to use [3]. In an emulsion, water droplets are isolated in a continuous oil phase, and stabilization is achieved through a surfactant. Measurements have also been performed by suspending a single small drop of supercooled water [4]. However, these last techniques restrict the number and the accuracy of the possible experimental measurements.

By using various experimental schemes, many of the most important properties of supercooled water have been measured [1]. However, the thermal conduc-
tivity of water is known only for temperatures above 0 °C, probably because of the incompatibility of the usual techniques with both the small value requirements and the high degree of cleanliness necessary to supercool the sample. In this paper, we use an original technique to determine the thermal diffusivity of water and subsequently obtain, from the known specific heat [5], the thermal conductivity of pure water down to -23 °C.

2. Experimental.

We measure the modulated or pulsed temperature gradients generated in a homogeneous liquid by optical excitation. The detection is made using the deflection of a probe laser beam.

2.1 MODULATED TEMPERATURE. — When absorption of an intensity modulated heat source (excitation beam) creates a plane « thermal wave » propagating in the x-direction, as illustrated in figure 1, the probe laser (assumed to be parallel to the plane of the thermal wave) will be deflected by a small angle, $\phi$, (typically $10^{-7}$-$10^{-6}$ rad) as given by [6]:

$$\phi = \frac{e}{n} \frac{\partial n}{\partial x} = \frac{e}{n} \frac{\partial n}{\partial T} \frac{2 T_0}{\mu} \exp\left(-\frac{x}{\mu}\right) \times \cos\left(\omega t - \frac{x}{\mu} + \frac{\pi}{4}\right) \quad (1)$$

where $e$ is the length over which the beam interacts with the heated region, $n$ is the refractive index of water, $T_0$ is the temperature at the origin ($x = 0$), $\omega/2 \pi$ is the modulation frequency, and $\mu$ is the thermal diffusion length. The thermal diffusion length is given by:

$$\mu = \left(\frac{2 \lambda}{\rho C_p \omega}\right)^{1/2} \quad (2)$$

where $\lambda$ is the thermal conductivity, $\rho$ is the mass density, and $C_p$ is the specific heat of the liquid. The quantity to be measured, $\mu$, may be obtained either from measurements of the amplitude or the phase of the signal, made as a function of the distance $x$. In the first experiment (modulated temperature), we used a glass cell of square shape, $1 \times 1$ mm$^2$. One wall of this cell was made to absorb the modulated power of a 1 mW He-Ne laser (Fig. 1). For this wavelength, the absorption of water is negligible. A position-sensitive detector was used to measure the deflection of the probe beam. The signal from the detector was fed into a lock-in amplifier referenced at the modulation frequency of the heat source $\omega$. We thus obtain both the amplitude and the phase of the signal as a function of the distance between the probe laser beam and the heated surface (Eq. (1)). Unfortunately, we were not able to reach temperatures below -16 °C without freezing with this experimental set-up (a problem which we attribute to the shape of the cell which prevents a very careful cleaning).

2.2 PULSED TEMPERATURE. — When heating is induced by a pulsed laser having a Gaussian spatial distribution (TEM$_{00}$ mode), as illustrated in figures 2a and 2b,
the time dependence, $t$, of the temperature gradient is given by:

$$\frac{\partial T}{\partial r}(t) = \frac{4 E_0 \alpha}{\pi \rho C_p} \frac{2 r}{(a^2 + 8 D t)^2} \exp\left(- \frac{2 r^2}{a^2 + 8 D t}\right)$$

(3)

where $\alpha$ is the absorption coefficient, $E_0$ is the pulse energy, $a$ is the Gaussian width (at the $1/e^2$ points), $D$ is the thermal diffusivity ($\lambda / \rho C_p$) and $r$ is the distance between the two beams, which are assumed to be parallel. In order to obtain this expression, the laser pulse duration is neglected; the experimental measurement is done by analysing the time dependence of the recorded signal. This optical technique is fully described in reference [7].

For this second set of experiments (Fig. 2a), we use a small amount of light from a Nd$^{3+}$ YAG laser (100 mJ, 15 ns, 1.06 μm). At this wavelength, the absorption coefficient of water is approximately $10^{-1}$ cm$^{-1}$. The two beams are not actually parallel: the probe beam (He-Ne laser) is shifted by a distance $x$ from, and forms an angle $\theta$ with, the pump beam (pulsed laser) (Fig. 2b). In this geometry, the time dependence of the deflection is given by:

$$\phi(t) = \frac{2 \alpha E_0}{\rho C_p \sin \theta} \left(\frac{\pi}{2}\right)^{1/2} \frac{\partial n}{\partial T} \frac{2 x}{(a^2 + 8 D t)^{3/2}} \times$$

$$\exp\left(- \frac{2 x^2}{(a^2 + 8 D t)}\right).$$

(4)

The signal from the position sensitive detector is averaged using a multichannel analyser. In spite of the low heating power, the signal to noise ratio is good. In figure 3, we show a typical signal obtained for a local temperature $T = -22 \, ^\circ C$, after having averaged over 128 pulses.

For the pulsed temperature measurements, two different water samples were studied. We first used quartz capillaries (0.8 or 1 mm) filled with distilled, deionized water, and reached $-21 \, ^\circ C$ before freezing occurred. We used commercial samples of distilled water prepared for medical purposes by Lab. Angellini SPA and by Lab. Meram and obtained at a temperature of $-23 \, ^\circ C$ before freezing occurred. The thermal stability of the sample was maintained by cooling a copper block in thermal contact with the sample with two Peltier devices. Measurements between 5 and $-5 \, ^\circ C$ were not possible because in this temperature range the refractive index of water is almost temperature independent (actually, $n$ exhibits a maximum around 0 °C [8]).

3. Experimental results and discussion.

Figures 4 and 5 show respectively the temperature dependence of the experimentally determined thermal diffusivity, $D$, and thermal conductivity, $\lambda$, between room temperature and $-23 \, ^\circ C$. For the evaluation of $\lambda$ from the experimental value of $D$, we used the
density data of Zheleznyi [4] and the specific heat data of Angell and co-workers [5]. The values of $\lambda/\rho C_p$ as obtained from equation (4) differ from the literature data by less than 10%. Variations may be due to geometrical parameters (such as the beam waist and the beam profile) which are not known with a good accuracy. The relative accuracy is high (± 1.6%) because, as seen from equation (4), all the curves normalized to an identical value, are related to each other by a simple time dilatation.

Figure 5 shows clearly that $\lambda$ exhibits a monotonic dependence with temperature in the measured temperature range.

The interpretation of the experimental data may be made using the classical theory [10], which relates $\lambda$ with other properties based on simple assumptions derived from the kinetic theory of gases and consideration of free volume. The classical expression for $\lambda$, for polyatomic liquids, is:

$$\lambda = 2.8 K_B \rho^{2/3} \gamma^{1/2} c$$

(5)

where $\rho$ is the density, $c$ is the sound velocity, and $\gamma(= C_p/C_v)$ is the ratio between the specific heat at constant pressure $C_p$, and at constant volume, $C_v$, and $K_B$ is the Boltzmann constant. Values for these quantities can be found in the literature [4, 5, 9, 11]. In figure 5 we show the plot of equation (5) versus temperature together with our experimental data. We note that the agreement between experiment and theory is good. This result is not surprising because the different transport mechanisms in water are related to each other in a classical way [12] in spite of their anomalous temperature dependence.

The increasing number of hydrogen bonds with decreasing temperature is the origin of an amplification mechanism which causes dramatic changes of the transport properties in the supercooled region. However, it has been shown [13] for the case of hydrogen bonds that the dynamic properties have a classical temperature dependence [14].

Measurements of the thermal conductivity at elevated pressures were recently performed by Dietz et al. [15]. These authors predict a minimum in $\lambda$ at a temperature near $-18^\circ$C. Our results do not confirm their extrapolations. The anomalous decrease of the thermal conductivity with decreasing temperature continues at least as far as $-23^\circ$C. Measurements of sound velocity [16] might, however, give a minimum, but at lower temperatures.

It is interesting to analyse our data with the critical exponents which give a good fit of the data for all the properties of water at low temperatures. This method of analysis was first suggested by Speedy and Angell [17] and, in spite of eventual controversial interpretation as a manifestation of critical behaviour, remains the best way to describe the data at low temperature.

Because the classical expression (Eq. (5)) applies, it is possible to use the published data for $\rho$ [9], $C_v$ [5] and $c$ [11] to predict that the critical exponent of $\lambda$ is 0.18. This value is nearly equal to the critical exponent of the sound velocity, the variation of the other parameters of formula (5) with temperature being small down to $-23^\circ$C. Nevertheless, this value is too small to be a good test of the theory, because in the temperature range studied, the variation of $\lambda$ is small. It must be pointed out, however, that this approach is at least compatible with our experimental results.

In conclusion, our measurements are consistent with the anomalous temperature dependence of other thermodynamic and transport properties of water. It is worth noting that the temperature dependence of the sound velocity controls the behaviour of the thermal conductivity. Indeed the critical exponent found from our results is very close to that of the sound velocity. Since the thermal conductivity is completely determined by the molecular dynamics, one can conclude that the hydrogen bound structure has the same influence over both $\lambda$ and $C$.
References