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Sliding plastics on ice: fluorescence spectroscopic studies on interfacial water layers in the µm thickness regime

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Abstract. At a contact pressure characteristic of skiing conditions, assuming that the whole dissipated frictional energy is used for melting the ice in the case of hydrophobic plastics sliding on it, a liquid film with a thickness in the µm range should appear. By means of a fluorescence spectroscopic method we investigated the thickness of such an interfacial liquid film. However, no liquid film with a thickness ≥ 50 nm (detection limit of the setup) could be detected. Obviously heat emerges during the sliding process in an ice layer. However, the quantity of heat produced is only sufficient to raise the temperature of that ice volume. The measured friction coefficient of 0.03 corresponds to the usual value in the case of hydrophobic plastics sliding on ice. Evidently no lubricating liquid film of thichness ≥ 50 nm is necessary for such a small friction coefficient.

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In the case of a ski sliding on snow the energy corresponding to the frictional force between the running base of the ski and the snow is converted to heat near the ski–snow interface. This amount of heat is often assumed to cause a thin liquid film in the µm range between the running base and the snow [1–4]. However, it can be imagined that the heat is dissipated in a layer of greater thickness, for example, by irreversible compression of snow. This process would cause only an ignorable increase in the temperature of the snow without any melting.

We investigated the sliding of hydrophobic plastic on ice as a model system for skiing. The existence (and thickness) of a possible water film emerging was probed with the help of a fluorescence spectroscopic method [5]. Furthermore, we investigated whether the comparatively small coefficient of sliding friction of 0.03 valid for modern running bases is correlated to the existence of such a film or not.

The spatial distribution of the contact pressure between the running base of a ski and snow is extraordinarily inhomogeneous [1, 2, 6]. Areas of real contact (permanently changing when sliding) add up to only approximately 0.001 of the overall area of the running base. Those small surface elements in contact with ice (“sliding points”), however, are responsible for the true sliding process. The local pressure in these sliding points is correspondingly high and amounts typically to $5 \times 10^6\,\mathrm{N/m^2}$. Therefore the snow is strongly compressed in the sliding layer, allowing us to use ice as a model substance for snow in our investigations.

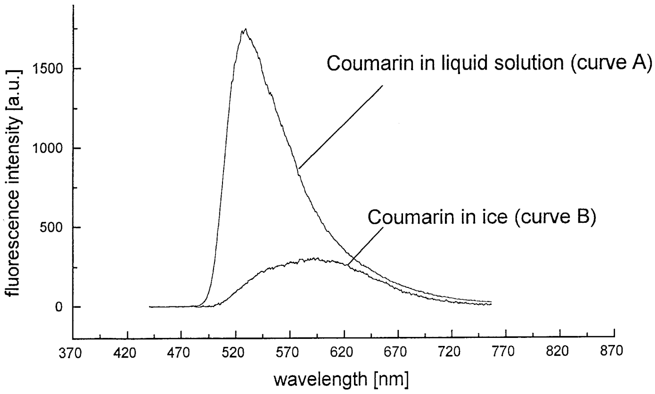

Fig. 1. Fluorescence spectra of a 3×10^{-4} moles/liter coumarine dye solution in water: (A) liquid phase, (B) ice phase

In our model system 1 cm × 1 cm polymere samples are pressed onto a rotating ice disc with a contact pressure between a sliding point of the running base and ice of $5 \times 10^6\,\mathrm{N/m^2}$ corresponding to that of skiing. A fluorescence spectroscopic method was used to determine the thickness of the interfacial water layer. The fluorescence spectrum of the coumarin dye 7-(N-Diethylamino)-3-[2-(5-methyl-7-sulfonatobenzoxazolyl)] is strongly influenced by the surrounding matrix. The spectral position of the fluorescence maximum shifts reversibly when the aqueous dye solution undergoes a phase transition between liquid and solid (Fig. 1). By analysing the fluorescence spectrum obtained (containing water and ice components as well), very small amounts of water can be detected and quantified.

1 Experimental

The experimental setup is shown in Fig. 2. The radiation of an Ar^+ laser ($\lambda = 458$nm, 4 mW, TEM_{00}) is coupled into the optical pathway of a conventional microscope through a spectrally selective beamsplitter and focused onto a section of the ice/sample interface. The sample is mounted on the objective and optical contact is by means of immersion oil. The exact adjustment of the focus position onto the plastics–ice interface is done with an additional collecting lens L_3 ($f = 250$ mm) inserted in the optical pathway. The fluorescence excited in the focus region is collected by the objective lens L_1 ($f = 6.9$ mm) and imaged to the aperture of an optical fiber by the ocular lens L_2, and finally transferred to the spectrometer. The diameter of the aperture at the entrance of the optical fiber is chosen as 100 µm in order to ensure that only fluorescence coming from the focal section of the excitation radiation is analysed by the spectrometer for the chosen magnification of the microscope (confocal microscope [7, 8]). Thus, only fluorescence coming from the interface region can enter the detector and no light from deeper ice layers or from the plastic layers above can come into play. So the intensity of the "ice peak" (curve B in Fig. 1) is minimized and the detection limit of the liquid phase (curve A in Fig. 1) maximized. For the detection of the fluorescence spectrum we used a CCD camera with a Peltier cooling unit and image amplifier. So it was possible to obtain an adequate signal-to-noise ratio providing an integration time of 4 s with a laser power of 4 mW. In order to avoid harmful warming-up of the sample an increase in laser power was not allowed. After several minutes, no melting of the motionless ice disc at a temperature of −2 °C could be observed with the chosen laser power of 4 mW.

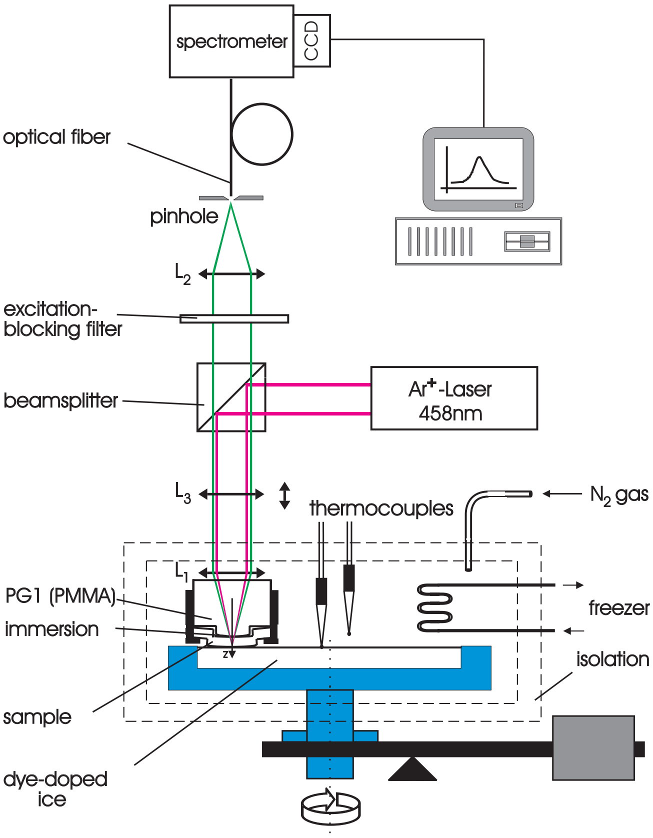

Fig. 2. Experimental setup

Polymer samples (PMMA) with a polished sliding surface of optical quality, and practically applied ski running bases, consisting of optically transparent material (Fischer GesmbH, Austria [9]) with the usual grooved surface structure were investigated. The cross section of the grooves in the running bases corresponds approximately to an isosceles triangle, with a groove depth of 30 µm. The 1 cm × 1 cm samples were mounted on the transparent piece of PMMA(PG1) as shown in Fig. 2 so that there was a convex curvature of the ski running base. In this way mechanical contact to the rotating disc in the section of the focus was ensured. The force pressing the ice disc on the sample could be chosen from within the range of 1 to 10 N. When ice and sample touch in this manner, an effective contact area is generated after 60 s (30 rotations of the disc) because of "rubbing-in" deformation (Fig. 3) and a constant pressure of approximately 5×10^6 N/m^2. Such contact presssure corresponds to that at the sliding points in the case of sliding in skiing.

The ice disc was made by inserting a teflon receptacle filled with an aqueous solution of the coumarin dye [10] in liquid nitrogen. By this shock freezing of the solution, a separation of dye and matrix was avoided, thus guaranteeing a homogenous distribution of dye in the ice volume. The dye concentration was chosen as 3×10^{-4} moles/liter, so that no concentration quenching of the fluorescence appeared and no effect of the coumarin dye on the melting conditions (melting point) of the ice could be observed. After the ice disc was attached to the rotation shaft inside the refrigerator box flooded with dry N_2 gas the uppermost layer of ice was removed mechanically by means of a scraping tool. This produced the appropriate smoothness for the measurement, and removed condensation of non-dye-containing water.

The formation of a water film as a result of melting after the freezer was switched off is shown by the spectra

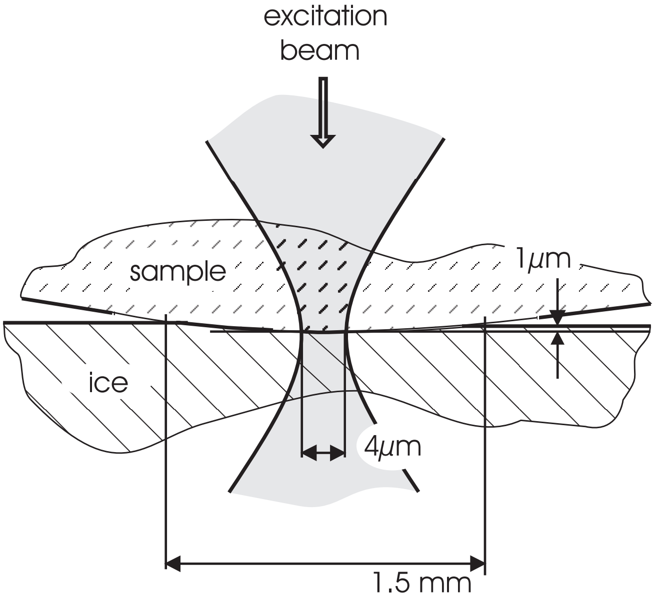

Fig. 3. Contact area of sample and ice ("sliding point"). The deformation of the ice surface by the samples "rubbing-in" is shown schematically

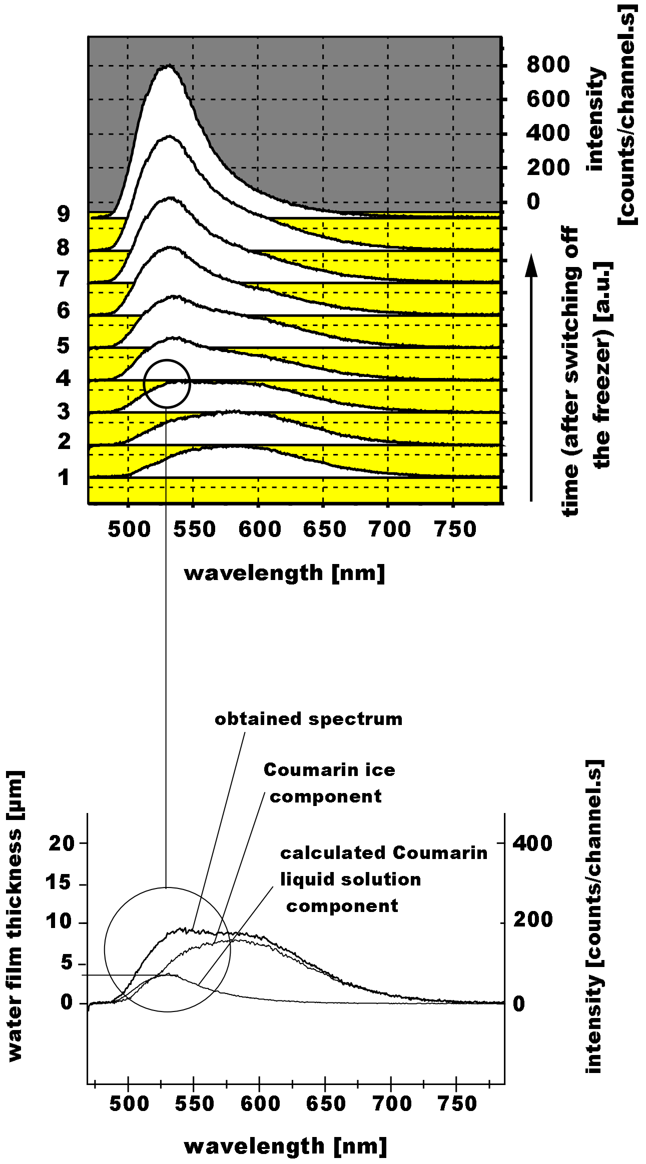

Fig. 4. Evolution of the fluorescence spectra after the freezer is switched off. The insert shows how to quantify the liquid phase by fitting the ice- and liquid-phase spectra to the measured spectra

recorded (motionless disc, PMMA sample) in Fig. 4. One recognizes the increasing intensity of the "liquid phase peak" at $\lambda = 530$ nm. The intensity of the liquid phase peak is proportional to the liquid layer thickness d as long as d is smaller than the z response of the confocal setup (3 µm). In this case it is possible to determine d from the intensity of the fluorescence peak, which is characteristic for the liquid solution ("liquid phase peak"). For calibration of the liquid phase peak, the ice disc was replaced by a glass plate with a film of the dye solution used for producing the ice disc. Then the intensity of the liquid phase peak was measured (at room temperature) at a 250-nm optical-film thickness determined by the interference of laser radiation reflected from the sample and the glass plate as well (Newton method). The insert in Fig. 4 shows the analysis of the fluorescence spectra for one of the curves as an example. With the pure ice signal subtracted (curve 1 in Fig. 4 corresponding to curve B in Fig. 1) the result is a liquid phase curve with line shape in good agreement with the shape of curve A shown in Fig. 1. Clearly, the sum of the liquid phase spectrum and the ice spectrum fits the obtained fluorescence spectra. From the peak intensity of the liquid-phase curve obtained by this fitting procedure the film thickness can be deduced by the calibration method described. The detection limit for the liquid film thickness achieved by this method is about 50 nm for PMMA samples and 250 nm for practically applied running bases of skis. The greater light scattering losses of the latter generally cause smaller signal intensities.

2 Results and discussion

PMMA samples and the practically applied running bases of skis were investigated at sliding velocities between 0.005 and 0.1 m/s and at a temperature of −2 °C (surrounding gas, ice, and sample). Under these conditions *no liquid film* between sample and ice could be detected. We can therefore conclude that in the case of PMMA samples the thickness of any liquid film generated must be smaller than 50 nm, and for real, grooved running bases smaller than 250 nm. Only at a sample temperature of > 0 °C could a liquid layer be detected. From this result, if any heat originating from the sliding process is used for melting the ice it is at best a very small percentage. An appropriate calculation for our model-experiment conditions results in the fact that using the total heat originating from the friction in the sliding process to 100% should have caused an easily detectable water film with a thickness in the range of 200–600 nm (200 nm at 1 N contact force, 600 nm at 10 N). Thus one can suppose that the heat produced by sliding friction emerges in a comparatively thick ice layer and not in an extremely thin interfacial layer between the running base of the ski and ice. If we assume that energy-dissipative compression of ice is the dominating mechanism causing the production of "friction heat" and, further, that this process takes place over an ice depth of 0.1–1 times the sliding point diameter, which correspondents in our case to an ice depth of 100 µm, the emerging heat caused by friction is only sufficient to increase the temperature of this ice volume by about 0.1–1 °C. This means that at the working temperature of −2 °C even the melting point cannot be obtained.

Measurements of the friction between ice and PMMA and running bases result in a coefficient of friction of 0.03 for the investigations made at −2 °C. This value corresponds to real skiing condition. So the conclusion is that in case of hydrophobic plastics surfaces sliding on ice *no liquid film* [11] with a thickness of > 50 nm working as a "lubrication" film is necessary for friction coefficients of 0.03 [1, 2, 6, 12], which is well known from practice. If there is an influence on the dynamics of the sliding process, by liquid or liquidlike ice layers, it is caused by layers of thickness smaller than 50 nm. This supports some suggestions in the literature, in which the interface is described as either "a liquidlike layer being several hundred molecules thick" [3, 4] or as "a dynamic outermost layer of water molecules" [13, 14].

We have demonstrated, by using a micro-fluorescence spectroscopic technique, that no liquid films with a thickness exceeding 50 nm appear when hydrophobic plastic surfaces slide on ice and that such films are obviously not necessary to obtain a typical coefficient of friction of 0.03 for this sliding process.

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References

1. F.P. Bowden: Endeavour **16**, 5 (1957)
2. B. Mayr: *Elektronische Messung des Wasserfilms beim Gleitvorgang*, dissertation (Universität Innsbruck 1979)
3. H.H.G. Jellinek: J. Colloid Sci. **14**, 268 (1959)
4. H.H.G. Jellinek: J. Colloid Interface Sci. **25**, 192 (1967)
5. H. Strausky, J.R. Krenn, A. Leitner, F.R. Aussenegg: Appl. Opt. **35**, 198 (1996)
6. J. Stroi, Fischer Gesellschaft mbH Austria: private communications (1997)
7. T. Wilson: *Confocal Microscopy* (Academic Press, London 1990) p. 7
8. K. Carlsson, P.E. Danielsson, R. Renz, A. Liljeborg, L. Majlöf, N. Åslund: Opt. Lett. **10**, 53 (1985)
9. Manufacturer material data sheet, Fischer Gesellschaft mbH Austria
10. Manufacturer material data sheet, Lambda Fluoreszenztechnologie E. Koller
11. J. Krim: Sci. Am. **275**, 48 (1996)
12. S. Haake: Phys. World **9**, 40 (1996)
13. C. Seife: Science **274**, 12 (1996)
14. J. Allen: Phys. World **10**, 17 (1997)