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Prepared discussion contribution

CAPILLAROGRAPHY: A NEW SURFACE PROBE

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PAPER is a porous structure containing two broad classes of pore: inter- and intra-fibre, and penetration of liquids such as water is determined by the geometries of the two classes. In this brief note we wish to describe a technique and present preliminary results on surface wetting and absorption into single fibres.

The equilibrium contact angle θ_0 of a liquid at a three-phase contact point is the most widely used measure of wetting, and is related to the interfacial tension γ by the classical Young-Dupré (surface thermodynamic) equation.

$$\gamma_{LV} \cos \theta_0 = \gamma_{SV} - \gamma_{SL}, \quad . \quad . \quad . \quad . \quad (1)$$

the subscript S, L, V designating solid, liquid and vapour phases respectively. This equation, however, is strictly valid only for an ideal solid with a smooth, homogeneous and isotropic solid surface. In real systems at least two 'equilibrium' contact angles are generally observed: one obtained as the liquid spreads and the other as it retracts. While the advancing contact angle θ_a is always greater than the receding angle θ_r, it has been taken by most workers as the experimental measure of θ_0; this cannot be correct as long as there is hysteresis, i.e. $\theta_a \neq \theta_r$. It has recently been shown[1, 2, 3] that roughness of the solid surface alone, apart from any heterogeneity and anisotropy in γ_{SV} and γ_{SL} can account for the hysteresis even when the scale of the surface asperities is very small, perhaps of the order of several nanometers, i.e. near atomic dimensions.

Conventional visual and photographic methods of measuring θ are time consuming, of low accuracy and, because of almost inevitable hysteresis, are of dubious thermodynamic significance.[2, 3] As an alternative we have

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developed a method which can record sensitively and automatically variations of contact angle as the liquid advances and recedes. The principle involved has long served as the basis of the Wilhelmy plate method for measuring liquid surface and interfacial tensions and monolayer surface pressures. At equilibrium, a solid sample experiences a capillary force F due to the deformed interface, which is given by

$$F = P\gamma_{LV} \cos \theta^* \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P is the periphery of the three-phase contact line and θ^* is the apparent contact angle (*2*). In practice a sample is suspended in a fixed position from a recording electromicrobalance, and the liquid container is moved up and down mechanically so that any variation in F (and hence θ^*) is recorded automatically. The method has been used to study dynamic wetting, spreading and contact-angle hysteresis with various solid surfaces by Guastalla,[4] with mica and platinum plates in various liquids by Bendure,[5] and with single synthetic fibres by Miller and Young.[6] Although sudden changes in the force measurement during wetting and dewetting have been noted and attributed to local surface roughness of the solid, the only attempt to correlate the stick-jump behaviour of the contact line with surface profile appears to have been in our laboratory by Oliver *et al.*[3]

We have developed instruments similar to those used by the previous investigators but with many improvements particularly in facilities for simultaneous viewing of the contact line and greatly increased sensitivity in measuring F and linear displacement of the contact line. They are designed essentially to characterise surface roughness by measuring variations in θ^* as the liquid advances and retracts. We call the technique 'Capillarography'.

Each apparatus (two of which have been constructed with different accessories) consists of a microelectrobalance (Cahn Model RG) and a hydraulic drive system. A sample is hung on one side of the balance arm and liquid is moved up and down by the hydraulic drive at the speeds of a few to several hundred μm per min. during which the force F on the sample is automatically recorded with resolution better than 1 μg. By using a hydraulic drive, the vibration normally associated with a mechanical drive system which can introduce a large noise signal into F, is eliminated. It is also equipped with a microscope so that the meniscus shape of the liquid and the profile of the solid surface in the region of three-phase contact can be seen directly and photographed on still or cine film, or monitored and tape-recorded by video methods.

Although we have tested various materials and liquids including single pulp fibres and paper strips the capability of the apparatus is best illustrated

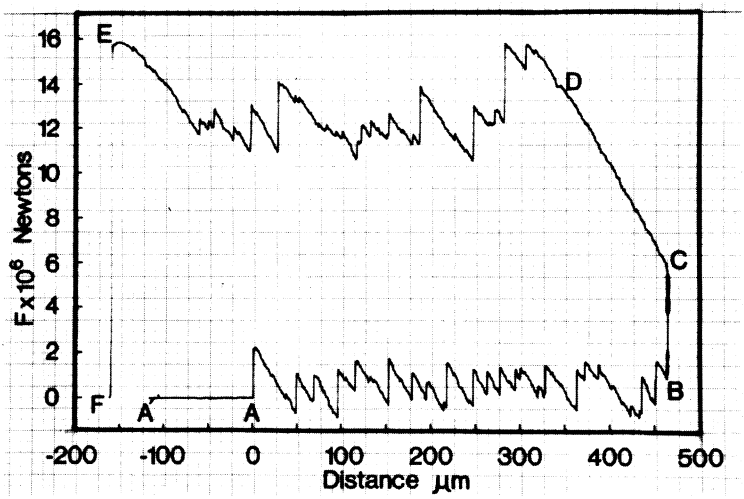

Fig. 1—Capillarogram of a human hair during a wetting–dewetting cycle in water. At A the hair touches the water and the distance measurement starts. From A to B, the water level advances at 8 μm/min. From B to C the water level is stationary for 1 h. From C through D to E, water level is lowered (recedes) at the same speed as from A to B. Note (1) the hysteresis between advancing (AB) and receding (CE) portions, (2) the fluctuations in F (regions AB and DE) and (3) the steady increase in F (region CD) believed due to relaxation (a decrease) in the apparent contact-angle θ^* when the water surface is stationary.

by immersing a human hair in water. Figure 1 shows one complete hysteresis cycle drawn on an X–Y recorder. Initially, the hair hangs freely so that there is no force change (A′ to A). When the rising water first touches it (point A) F increases suddenly after which it gradually decreases as the water level is raised at 8 μm/min. until another jump in F occurs. This stick-jump behaviour continues as the liquid advances. At B, the water level is kept stationary. The steady increase in F (B to C) is observed probably due to a relaxation i.e. a decrease of θ^* (cf. equation (*2*)). Upon lowering the water level, F increases steadily (C to D) until the contact line starts to move (point D), followed by a similar stick-jump behaviour of the contact line as in the advancing case. The difference in the mean F between advancing and receding indicates contact-angle hysteresis in the system. Detachment of water from the hair occurs at E where the force is reduced to point F which is the same value as A′ showing that no detectable water remains on the hair. Taking $\gamma_{LV} = 72 \times 10^{-3}$ N/M and $P = 3{\cdot}07 \times 10^{-4}$ m (dia = 97·6 μm), the apparent contact angle θ^* can be calculated from (*2*). For the advance A to B, the mean $\bar{\theta}_a$ obtained by averaging between maxima and minima is $\bar{\theta}_a = 88{\cdot}7°$ with a S.D. of 2·0°.

For the recession D to E, the mean $\bar{\theta}_r = 55{\cdot}6° \pm$ (S.D. 4·0°). The mean contact–angle hysteresis is thus $\Delta\bar{\theta} = \bar{\theta}_a - \bar{\theta}_r = 33{\cdot}1°$.

It is known that the outer shell of most animal hairs consists of cylindrical cuticle cells which overlap one another thus forming a scaly step-like structure. The mean step length between adjacent cells of the hair used in the experiment, measured from a scanning electron micrograph is 7·6 ± 2·6 μm. The periodic jumps in F observed for advancing is rather regular and the mean distance between them corresponds to displacement of the water level of 20·4 ± 7·7 (S.D.) μm, i.e. about 2·7 times the cell interval. The distance of sudden displacement in the contact line is determined rather by the height of each jump in F since it is equivalent to the height of capillary rise for different contact angles. This may be calculated as follows. From the value of F at each maximum and minimum, the corresponding θ*'s are calculated from equation (*2*). Then assuming that the contact is uniformly located around the periphery of the fibre (only approximately so, based on the visual observation of the contact line), the capillary rise around the cylindrical hair can be estimated using James' approximate solution[7] from the measured θ*. The difference in this capillary rise between maximum and minimum force values is equivalent to the slip distance of the contact line. This is estimated to be 12·3 ± 4·6 μm for the advancing case. Thus jumps occur over approximately 1·6 cuticle cells, i.e. much smaller than the average distance between jumps, the difference being due to the very small jumps or continuous movement of the contact line.

The resolution in capillarography is determined by that of (1) the electrobalance, (2) the displacement transducer, (3) the recorder and (4) the hydraulic drive system. In order to use the microelectrobalance to its full potential, it is essential to reduce vibration of the apparatus by means of an air or other suitable mount. At present for a fibre of 100 μm diameter immersed in water, the vibration-suppressing resolution in terms of γ_{LV} is 10^{-5} N/M and that in terms of θ* is 0·01° at $\theta^* = 30°$. If the liquid level moves at the speed of 100 nm/sec., depending upon recorder used, a resolution of 2 nm in linear dimension can be achieved; this is of the order of resolution of the electron microscope.

Capillarography can apply to any kind of fibrous material including woodpulp fibres (one of our main interests) and to a sheet such as paper. With a single fibre, considerable care is required to obtain the capillarogram since the fibre is so small that the maximum resolution is needed. With a paper strip, interesting complications arise from absorption of the liquid into the interior of the paper and eventual swelling of the fibres and the paper itself.

The absorption of water into single ramie fibres (natural, and bleach

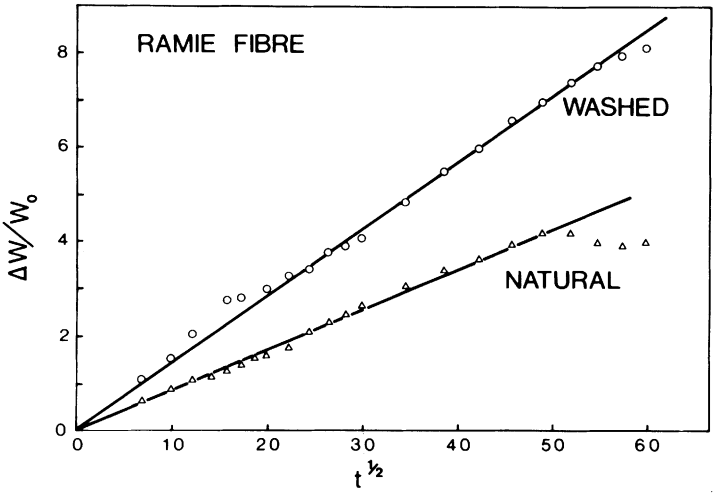

Fig. 2—The absorption of water (measured as the fractional increase in weight) into natural and washed ramie single fibres plotted against (time)$^{1/2}$, the straight line indicating that the absorption follows the Lucas–Washburn equation.

washed) measured from the increase in weight over 1 h is shown in Fig. 2. It is seen that the absorption is proportional to $t^{1/2}$ indicating it follows the Lucas–Washburn equation and that the washed fibre absorbs water 1·6 times as fast as the natural fibre. After absorption for 3 h the fibre width increased from 32·7 μm to 37·7 μm (5 μm increase or 15·3%) and 38·4 μm to 51·9 μm (13·5 μm increase or 35·2%) for washed and natural ramie respectively. Therefore the weight increase shown in Fig. 2 may not be due entirely to water absorption and may include an increment in F due to increase in P.

The capillarograms for advancing water obtained for the above two fibres immersed are shown in Fig. 3. It is obvious that natural ramie shows greater irregularity than the washed. This stick-jump behaviour reflects both the surface roughness and chemical heterogeneity although, of course, the two effects cannot be separated. A preliminary estimate of the mean advancing contact angle is $\bar{\theta}_a = 47{\cdot}0°$ and 42·0° for natural and washed ramie respectively.

Quantitative methods of statistically analysing the signals such as by autocorrelation functions and power spectra density, etc., on the measured variation in F are being examined in order to establish correlations with the surface structure of the solid. We believe that the method shows considerable promise in studying 1-, 2-, and 3-dimensional wetting[8] in single fibres and in consolidated porous media such as paper whether used at high or low

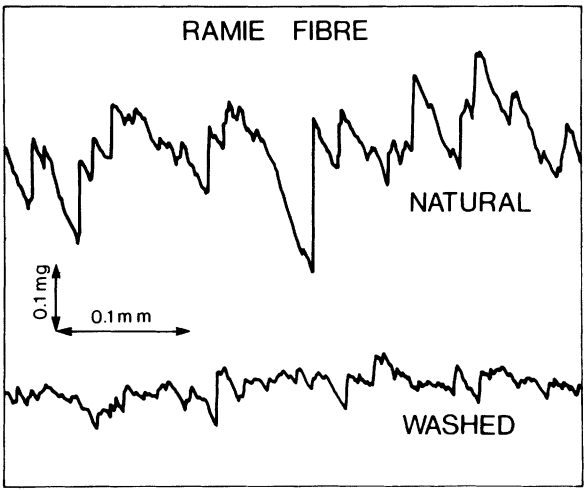

Fig. 3—Advancing capillarograms of natural and washed single ramie fibres in water.

capillary force–distance–line resolution, correcting, when necessary for buoyancy forces.

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