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A SURVEY OF PAPER MECHANICS IN FUNDAMENTAL TERMS

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Synopsis The object of this survey is to review recent work on the mechanical properties of paper with particular reference to the role of fundamental parameters and to attempt an assessment of the current position. Precisely which parameters are to be distinguished as fundamental is of course still a major field for research, so it is hoped that a spirit of reasonableness will be perceived in the interpretations that are offered below.

As a preliminary to the survey, some physical and chemical properties of cellulose are collected together with associated properties of fibres and certain structural features of paper. In its end usage, the mechanical attributes of paper are influenced markedly by environmental factors such as temperature and the presence of moisture, but it still remains a problem to separate these effects in basic terms. Rheologically, paper has a long memory of its past history, but its structural heterogeneity makes this memory appear erratic to the experimenter and it often yields counterexamples to embarass theoretical developments. Nevertheless, there has accumulated a large body of data on the mechanical behaviour of paper and there has been considerable success in fitting this into a working patchwork of respectable theory that has served well in stimulating experimental discoveries, thereby providing for a continued regenerative development, which is the subject of this article.

The early work borrowed and developed rheological models from the textile industry and the subsequent avalanche of data needed to evaluate empirical parameters exposed an intricate interdependency of effects. This stimulated a retraction into the apparently safer realm of molecular theory by employing classical physical chemistry to exploit the accumulating data on hydrogen bonds. The reaction to the enthusiastic development of molecular models must have been dismay in many scientific papermakers, for valuable as they clearly were (and still are) these models said nothing about fibres, which manifestly distinguish paper from other materials. Accordingly, general attention was turned to models that appeared more faithful in a structural sense and might support a theory of fracture, which phenomenon of course was well known to be an eager accompaniment of any mechanical treatment. There emerged two principal developments, statistical geometry and linear network

Under the chairmanship of Prof. H. W. Giertz theories. Firstly, the former provided a clinically statistical treatment of fracture in open networks. Various refinements of the linear network theories were successful for well-behaved synthetic fibrous networks. Inevitably, they were not able to overcome the obstacle that physical properties of natural fibres depend on the structure and treatment of the sheet. So fitting factors of dubious heritage had to be used to fix the initial slope of predicted stress/strain curves and to represent fracture by a subsequent decay of that slope. Meanwhile, statistical geometry gave rise to a kind of statistical elasticity that acknowledged the fibrous structure and successfully derived from it a covariance with deformation of the network during straining. The same obstacle prevented absolute predictions (as had faced the linear theories) and fracture was not considered. On the other hand, two independent approaches to fracture that seemed to represent the mechanism in a phenomenological way depended on energy rather than geometrical considerations, but experiments show that—at least for thin sheets—the fracture process is governed by geometrical properties of the network.

As for the future of research on mechanical properties of paper, it is the view of the author that treatment of paper as a heterogeneous continuum will prevail while linear network theories will be recognised as being with little value for predicting the behaviour of real paper. There is clearly a rich field of research for organic and physical chemists both at the level of fibre-to-fibre bonds and in the treatment of bulk properties to answer the many questions that remain, about the role of hemicellulose and migration of water, about the interdependence of rheological and thermal effects and about the extent to which the molecular structure and disposition of fibrils can influence bonding and hygroexpansivity, to name but a few.

Introduction

WE SHALL begin with a general view of paper physics, giving a description of paper as a foil-like material in general terms and allowing for a subsequent refinement to accommodate details of particular attributes as side branches to the general theme. Thus, we shall put papers into a 'hyper-box', the sides of which are the ranges of apparently important properties; later, we shall consider the origin of some of these ranges.

The essential structural feature of paper is that it is a bonded fibrous network; it may contain nothing more than natural cellulose fibres, air and water. Accordingly, we follow our view of paper as a foil by a closer examination and we shall set out some properties of fibres, fibre-to-fibre bonds and cellulose. Most of the numerical values quoted in the next section are common currency among papermaking scientists. General references are Casey,(1) Pimentel & McClellan,(2) Algar,(3, 4) Page *et al.*,(5) Corte,(6) Dodson(7); others are mentioned in context.

The following section gives an historical survey of paper mechanics, separated into aspects of bonding, structure, the response to strain, partial and total fracture. The final section is a critical essay on the present position.

Paper as a heterogeneous foil

A general view

OUR material covers the range of flexibility and apparent thickness that we normally associate with foils; it is evidently non-uniform, but its properties over areas of a square centimetre or so are usually similar, to within a few per cent. Then thickness lies in the range 30–300 μm and areal density varies 1–30 mg cm^{-2}. The force that resists small tensile deformations ranges over two powers of ten, in linear proportion to areal density(8, 9) and, for any particular paper, displays anisotropy to the extent of a factor of about 2 to 1 in favour of the direction of manufacture.

As for local variability,(10) perhaps the most useful figures to bear in mind are those for the range 3–18 per cent for the coefficient of variation of areal density over areas of 1 mm^2. For a given type of paper, doubling this coefficient of variation can result in a drop of about 15 per cent in the resistance to small tensile extensions(8) and in final strength;(4) a similar drop is caused if the ambient temperature during testing is raised by about 1°C.(11, 12)

Three modes of fracture may be considered worth comparing as related dissipative processes. A convenient quantitative impression is given by the following orders of magnitude for the total fracture energy per unit nominal new area formed in each mode—

Zero-span tensile,(13, 14) 5×10^7 erg cm^{-2}
Tearing,(15) 5×10^6 erg cm^{-2}
Splitting,(16) 5×10^4 erg cm^{-2}

Paper displays a subfracture behaviour of rheological type common to many materials; typical examples are creep and the relaxation of tension at constant strain.

Upon saturation with water, paper typically expands some 0·3 per cent in machine-direction, 3 per cent in cross-direction and 30 per cent in thickness. A most useful range of expansions is that pertaining to a sudden change in ambient relative humidity at constant temperature. For such a change from 65 to 90 per cent relative humidity at 20° C, the expansions are typically one third to one half of the saturation values above; they are achieved in little more than one minute and they are in proportion to the absorbed mass of water.(17) Most strength properties decrease rapidly when this absorption exceeds 5–7 per cent; that is, when appreciable free water is present, for the first 3–4 per cent of water is bound to the cellulose and very difficult to remove.

Natural cellulose fibres

At the outset, we note that, whereas paper may consist almost entirely of fibrous material, other organic or inorganic fillers may be present, but most importantly there is often a large proportion of the cellulosic matter in the form of fibre debris. Furthermore, it is in the nature of the bonding process that cellulose fibres that do survive with a ribbon-like form in paper are likely to have markedly different physical properties from those fibres that are tested without being subjected to the constraints of bonding in a network.

Natural cellulose fibres are usually 10–50 per cent void, with a mean density when collapsed of about 1·5. The subfibre structure is fibre-like down through fibrils and microfibrils to the polymeric molecular form. A typical 'whole' fibre as used in paper is ribbon-like with dimensions 1mm by 25 μm by 5μm and with weight 2×10^{-7} g. Thus, if it is flattened out in a sheet, such a fibre contributes 0·5 mg cm^{-2} to the areal density of the sheet over its own area. Hence, thin sheets of paper are only a few fibres thick, whereas thick papers may be fifty fibres thick on average. The irregularity of the microfibrillar structure leads to high specific surface. The cellulose/air interface of fibrous material is of the order of 10^6 cm^2 g^{-1}, of which some 1 per cent is accessible externally. Under normal conditions, the surface is covered by water bound at high density to the cellulose.(1) The bound water amounts to a few per cent by weight of the cellulose. Further water can be accommodated in capillaries and cavities with an immediate softening and swelling effect on the host fibre. A subsequent removal of this free water by exposure to a drier environment may very well be considered as the cue for the fundamental drama of papermaking. This elementary process reflects at once the peculiar affinity of cellulose for water and its interaction with the anisotropy of fibres, whose fibrils are arranged more or less axially. Some 20 per cent shrinkage may occur laterally, giving rise to very large forces over short distances in small intervals of time. Such effects in a drying paper web are portrayed by brief local spasms of movement ending in a locking of distorted fibres into a coherent network.

The molecular interaction of cellulose and water is displayed in another role by fibres in aqueous suspension. They take up hydroxyl ions from the water and so become surrounded by a negatively charged layer. The subsequent envelopment by positive ions induces a zeta-potential, of some —10 mV, from the fibre surface to the outer regions of the positive envelope. An enrichment of the water with hydrogen ions decreases the preliminary collection of hydroxyl ions, hence reduces the potential until the isoelectric point is reached at a pH value of 2 or 3. The link between this ionic process and the role of fibres in paper is the not unexpected observation that greatest swelling of fibres occurs under conditions of greatest zeta-potential.(1, 18)

A single fibre without obvious flaws can be expected to support a tensile load of up to a few tens of grammes before fracturing; then the total work done is up to a few hundred ergs. Page *et al.*(5, 19) have surveyed the mechanics of fibres, so too have Reizin,(20) Petrovan & Diaconescu(21) and Harrington.(22)

Direct measurements have been reported of fibre stiffness(23) and transverse compressibility of fibres.(24)

Bonds between natural cellulose fibres

Two fibres overlapping at rightangles have a common projected area of about 25 μm × 25 μm = $6{\cdot}25 \times 10^{-6}$ cm^2. When bonding has occurred between two fibres in paper, it is found that typically 10 per cent or more of the interface is in optical contact: having a separation of less than about 10^{-5} cm.(25) When the bonded pair is in a thin sheet of paper or near the surface, it can be removed intact. Then, typically, it is capable of supporting a shear load of up to about 1 g before breaking with a total expenditure of a few ergs.(26, 27) Contrary to the views of Davison,(28) most would consider that fibre-to-fibre bonds are relatively strong in being able to support up to 10^6 times their own weight. Moreover, that author claimed that the measured strength of such bonds is much less than the calculated value; this is difficult to accept, since any measurement inevitably includes contributions from other dissipative processes within fibres.

The mechanism responsible for the strong interaction between fibres is that of hydrogen bridging between hydroxyl groups on sufficiently close cellulose molecules. In this context, sufficiently close means a separation of about 10^{-8} cm. This is achieved through the agency of surface tension, in evaporating water menisci between drying fibres. Water softens fibres by attacking hydrogen bridges of the microfibrillar structure. It gives rise to large surface tension forces in interstitial films that may also link across fibres. Finally, upon exposure to a drier atmosphere, water leaves the scene of action at a rate appropriate for balancing the maintenance of plasticity within fibres and links between fibres, to attain an eventual cohesion reflected in some 10 per cent of all interfaces being in optical contact and a specific strength commensurable with that of solids like glass.

Hydrogen bridges are amenable to indirect experimental determinations of their strength and profusion. In the context of papermaking, interest is centred on those formed between fibres rather than those unaltered or merely rearranged within fibres. It turns out that some 0·5–2 per cent of all hydroxyl groups are additionally hydrogen bridged in the manufacture of paper and these bridges have an average energy of about 4·5 kcal per mole OH.(29) We note for those who think of binding energy in other terms that this average energy amounts to about 3×10^{-13} erg or 0·2 eV per bridge. Now, kT is about 0·025 eV at room temperature, so we may expect a fraction e^{-8}, about $3{\cdot}3 \times 10^{-4}$, of all hydrogen bridges to have sufficient thermal energy to dissociate at any time.

Cellulose

Cellulose consists of a chain of 1, 4 β-glucosidoglucose units of molecular weight 162, with a degree of polymerisation of about 1 000 for woodpulp cellulose. The theoretical crystal structure has a unit cell 10·3 Å × 8·35 Å × 7·9 Å and yields a density 1·625 g cm^{-3} compared with experimental values of 1·56 g cm^{-3}.

As mentioned before, the first layer of water molecules is bound very strongly to cellulose. The heat of sorption is 250 cal g^{-1} compared with the latent heat of fusion of ice, 80 cal g^{-1}. Thus, whereas the binding energy of hydrogen bridges is about 0·2 eV between cellulose molecules, it is about 0·1 eV between cellulose and water and about 0·03 eV between water and ice.

A wide coverage of cellulose chemistry for papermaking is given by Casey.(1)

Some history

Bonding in paper

THE deuteration experiments of Corte & Schaschek(29) admitted their conclusion that some 1 per cent of the hydrogen bridges in paper are between fibres, moreover the energies involved are of the order of those required locally for mechanical fracture.(30, 31) Nissan (11, 32, 33) extrapolated plausible properties of hydrogen bridges in an approach to a thermodynamic basis for paper mechanics; little has been added since in the way of conceptual developments.

Page *et al.*(34–37) pioneered the study of fibre-to-fibre bonds with optical microscopes using polarised vertical illumination, which renders black any areas of optical contact between fibres. These workers were satisfied that their observations near the surface of paper were valid within its bulk. Page & Tydeman(35) showed that the optical scattering work of Nordman(38) correponded well with their observations of loss of areas of optical contact in paper during straining; similar effects of straining in machine and cross direction were found. Page & Tydeman(35) showed micrographs of axial microcompressions of fibres that had occurred at bond sites during drying, both in freely dried handsheets and in tracing paper. Stone(39) and Kallmes & Eckert(40) compared measurements of areas of optical contact with those for nitrogen adsorption. Finding that areas of optical contact were inaccessible to nitrogen, they agreed with Page & Tydeman that they were probably hydrogen bridged throughout. Further evidence was offered by Mayhood *et al.*,(26) who found a more or less constant value of 3 × 10^4 g cm^{-2} for the shear strength of fibre-to-fibre bonds referred to area of optical contact. In addition, Smith(41) correlated bonding with electrical conductivity.

The properties of fibres certainly influence the bonding in paper, though we have noted that these properties are themselves influenced by the constraints of drying in a network. Hartler(42) had observed that mechanical treatment of wet fibres caused local defects in their walls, which he called misaligned zones. Page & de Grace(43) recorded the delamination of cell walls in these zones and Hartler & Nyren(44) suggested that this effect could explain the halving of stiffness that is observed when the number of such zones increases to more than a few per fibre. Dumbleton(45) identified misaligned zones with disoriented fibrils arising from longitudinal compression of fibres and pointed out that they would be likely to cause stress concentrations upon subsequent loading. Hill(46) also found structural changes in fibres subjected to tension: the crystallite orientation increased without apparent change in the crystallinity of the cellulose. The concomitant effect on mechanical properties was similar to that observed by Spiegelberg(47) when fibres were dried under tension: their initial modulus increased. Kallmes & Perez,(48) however, found no increase in the tensile properties of fibres removed from sheets dried under tension. Furthermore, whereas beating increased the modulus of fibres in the wet state, the opposite effect was demonstrated when a comparison was made for fibres dried without tension. Iwasaki *et al.* (49) and Labosky & Martin(50) compared ultrasonically treated fibres with those beaten mechanically. It seems that the former process leaves fibres more resistant to collapse during drying. Petrovan & Diaconescu(21) in an extensive survey point out that beating or refining causes essential changes in the correlations between fibre characteristics and sheet properties. This is in contrast to the findings of Nordman *et al.*(51) that the bonding strength of paper made from bleached and unbleached low hemicellulose pulp was virtually independent of beating and wet pressing. Yet these authors did find an increase with beating for high hemicellulose pulps, then a decrease of strength with increased wet pressing. For a given increase in bonded area measured by optical scattering, beating is more effective than wet pressing in increasing paper strength. One explanation is that wet pressing may damage fibre walls and result in less entangled contact zones. It is now known(52) that in wet conditions fibres are susceptible to shear failure in the swollen fibre wall. Parsons (53) claimed that, for any given pulp, tearing strength attains a maximum within a narrow range of bonding strength. Malmberg(54) reported an increase of fibre-to-fibre bonding with increased wet pressing. Malmberg(55) had used the effects of different conditions of formation on paper properties to determine characteristics of bonding. He found on the one hand that strength properties indicate a saturation point in effective bonding as bulk density is increased; on the other hand, no such levelling off was observed in an optically bonded area or in an inactive area.

Turning to effects of a more direct chemical nature, we note that the term hemicellulose is used for any carbohydrate material, other than cellulose, that is present in woodpulp. Clark(56) has criticised the emphasis by some authors of the role of hemicellulose in bonding. Firstly, we note that McIntosh(57) found that the alkali extraction of hemicellulose reduces the breaking load of fibres, but not their breaking elongation. Jentzen *et al.*(58) were of the opinion that, rather than having a specific effect by contributing local strength, hemicellulose promoted an even stress distribution. Clark believes that fibrillation may be promoted by an easier disruption of fibres during beating, in the presence of hemicelluloses; having shorter chained molecules than cellulose, they offer more polar molecule ends per unit area and so induce more small-scale disruptions. Robertson(59) pursued chemical effects on interfibre and intrafibre bonds and on the swelling of fibres. He claimed some evidence of other bonding than by hydrogen bridges, but notes that the effects of organic liquids on cellulose fibres are determined *inter alia* by the hydrogen bridging properties of the liquids. Didwania(60, 61) used ethylene oxide to effect a hydroxyethylation of wood fibres and thereby increased by 40 per cent the extent of their bonding in paper and apparently also increased their specific bond strength between fibres by a factor of more than two. The chemical effect in this case seems to be one of plasticising. The fibres are made more responsive to surface tension forces at a given moisture content.

Experiments support the intuitive expectation that the incorporation of a filler like clay into a pulp will yield a weaker paper. The phenomenon has recently been studied in detail by Schott.(62) He showed that the adhesion between cellulose and clay is at least as strong as that of cellulose to itself. So any weakening effect is not due to a substitution of weaker molecular interactions, but to fewer or smaller effectively linked areas between fibres. Hemicelluloses form a weak boundary layer between clay particles and cellulose fibrils so reducing their adhesion, according to Schott. Another or perhaps complementary suggestion that he makes is that clay absorbs a small amount of hemicellulose from fibrillar surfaces, that is, from regions that would otherwise be most active in fibre-to-fibre bonding. Recalling Clark,(56) we note that such a phenomenon is consistent with the higher density of polar molecular ends for shorter chain hemicelluloses giving a facility to even out local stress distributions.

The structure of paper

This topic will be treated elsewhere and we shall require only a brief sketch of the history to provide some terminology for our discussion. Corte/Kallmes and their co-workers(63–68) formulated and developed a statistical description of superimposed random fibrous networks. This resembled a lamination of thin sheets of paper and could accommodate non-random constraints such as flocculation and a preferential orientation of fibres in real paper. The existence of a layered structure for real paper was proved by Radvan *et al.*,(69) who also explained this phenomenon in terms of the hydrodynamics of papermaking. Kallmes, Corte & Bernier(67) used the concept of relative bonded area (RBA) to characterise the bonding states of fibres in random models. It gave rise to a bonding state diagram, which seems also to represent the extent of bonding in non-random networks.(68) Microscopic and nitrogen adsorption measurements gave estimates of RBA that led Kallmes & Eckert(40) to conclude that the bonding state theory is reasonably applicable to real paper. Kallmes used statistical geometry directly in refining linear network theories of elastic behaviour.(48) Meanwhile, Corte developed the theory of pore structure in paper from its origins in statistical geometry.(70) The next development in the structural theory of paper provided a rigorous link between the point processes of statistical geometry and the observable averages of areal density over finite zones.(71) This link arises from the finite dimensions of fibres and subsequently admitted a description of small deformations in paper as a locally observable cross-correlation of areal density with strain over finite regions.(7, 72)

The response of paper to strain

Paper exhibits almost every known rheological phenomenon and a review of these effects by one of the principal contributors to the subject has appeared recently.(73)

Eyring's thermodynamics of rate processes(74) was the basis for the approach by Leaderman(75) and Halsey *et al.*(76) in model building for time-dependent deformational phenomena in textile materials. These methods were transferred to paper by Steenberg(77) and developed with extensive experimentation by Andersson *et al.*(12, 15, 78, 79) The outcome of these studies was in effect a phenomenological parametrisation of experimental results, without links to the known physical structure of paper and without a consideration of fracture. This was criticised by Rance,(80) who also argued that it is inappropriate to consider paper as being in equilibrium if it is supporting any finite tension. Thus, creep persists while a load is present, only the rate is reduced; similarly, stress relaxation continues until no tension remains.

Kubát(81) gave a theory for the relaxation of tension L in a strip of paper at fixed length as a function of time t; approximately $L = L_o - b \log(1+t)$ for some positive constant b. Such a relationship for paper was found by Kubát, also by Maynard,(82) Andersson & Sjöberg(79) and Craven(83). The relaxation rate b increases with initial tension L_o. This is not surprising; but of a more subtle nature is the increase of b with the rate of prior straining(79) and negative values for b after periods of partial destraining.(83) On average, Craven found a linear decrease of b with L_o and a decrease of b with drying tension, both effects independent of beating and fibre length. This was explained in terms of stress relaxation at fibre-to-fibre bonds with the influence of drying tension as the result of greater uniformity in the bond structure. Craven extrapolated to zero relaxation rate and interpreted the intercept value L_{oo} of initial load as the maximum for elastic behaviour; it corresponded to a strain of about 0·1 per cent below which value he inferred that bonds were not broken. Subsequent work of Johanson & Kubát(84) and Johanson *et al.*(85) showed that L_{oo} increased during the early stages of beating, then remained constant, as did the tensile strength of the samples. Some effects were also found of beating, fibre orientation and relative humidity, on the L_o/b relationship. There was a well-defined, non-zero, equilibrium tension L_∞ for paper undergoing stress relaxation at 85 per cent relative humidity. On the other hand, at 65 per cent relative humidity, the relaxation rate was much slower, with no evidence of an equilibrium tension, but with slightly increased relaxation rate after long periods of time. The parameter L_{oo} is increased by increasing drying tension and decreased by increased humidity during testing. Some interesting general results emerged from this study and were noted by authors. For paper tested at 85 per cent relative humidity—

1. Plots of b against $(L_o—L_\infty)$ were linear with slope $\simeq$ 0·1.
2. Plots of creep recovery rate against initial minus final extension were approximately linear with slope $\simeq$ 0·1.

This slope value of about 0·1 is found for other materials as well as paper. Kubát *et al.*(86) had investigated strain hardening by cycling paper between two tensions or two extensions. They found that W_n, the hysteresis loss after n cycles, was given by—

$$W_n = W_l - k \log n.$$

Significantly, k/W was about 0·12 for a wide range of papers, independently of relative humidity and anisotropy. This prompted the suggestion that similar rate processes were involved with stress relaxation, relaxation recovery, creep and creep recovery. Johanson & Kubát (87) rewetted and freely dried machine-made papers with only small changes in the anisotropy of their strength and modulus; no systematic relationship was found between L_{oo} and various mechanical properties.

Craven(88) performed tensile tests on paper samples dried under different tensions. The yield point strain was always in the range 0·5–1·0 per cent, unaffected by the drying tension or the length of fibres in the samples. While this transitional strain was not very well defined, Craven considered that it was a boundary between two mechanisms of deformation. The total strain D suffered during drying at constant tension was found to be an important factor. In particular, the breaking strain of paper decreased linearly with drying strain D over the range $-7\% \leqslant D \leqslant +2\%$. Borruso & Serra(89) found similar effects on the load elongation curve and relaxation rates. Retsler & Ostrikov(90) reported that an increase of beating promoted the tendency of paper to shrink and they investigated the kinetics of the developing shrinkage strains during drying. These strains seem to arise at about 15 per cent moisture content, pass through a definite maximum, then diminish at about 2 per cent moisture content. Such effects and the increase of drying to given moisture with beating were explained in terms of capillary contraction forces, which depend on the dimensions of pores and the latter decrease in size with beating.

The introduction of defects into paper by gamma-radiation of up to 1 megarad,(3, 91) had apparently negligible effects. Higher doses reduced strength and brightness, probably without changing the mechanisms, but perhaps initiating structural changes earlier in straining. Besides this, there were only small effects on the results of such irradiation from the presence of water, other swelling agents or content and type of hemicelluloses. Natural and accelerated ageing of paper, however, probably increase cross-linking or crystallinity to cause the observed enhancement in wet strength.(92)

Working with kraft liner board, Benson(93) investigated the effects of temperature (15·5°–48·9° C) and relative humidity (22–90 per cent rh) on the response to tensile strain. His results fell between those of Andersson & Berkyto,(12) who eliminated the effect of moisture leaving only a small temperature effect and those of Wink *et al.*,(74) who raised relative humidity with temperature to produce a maximum effect. The equilibrium moisture content c decreases linearly with temperature at any given relative humidity, more steeply at lower relative humidities. Both initial modulus and breaking strength decrease with c, in each case twice as quickly in the machine-direction as in the cross-direction. The energy dissipated in tensile failure was found to pass through a maximum at $c = 8$ per cent. Lapter/Ivanov(95–97) attempted to separate the contributions of the fibres to moisture effects on the deformation of paper from those of the sheet structure itself. They were persuaded that the effect of beating on bonding and on moisture expansion were similar and deduced that, at higher levels of beating, the effect of fibre swelling was transmitted to the entire sheet structure. According to Nierychlewski & Wincziakiewics,(98) who investigated step changes from 30 per cent to 80 per cent rh, there is little specific effect of mean areal density on expansion.

Brecht(99) has given a review of paper's dimensional stability and concludes that every humidity expansion depends on shrinkage during drying and that the most effective remedy for unwanted effects is by applying appropriate tension during drying. Setterholm & Kuenzi(100) agreed for stretch-dependent effects, but found that tensile strength was influenced more by fibre orientation. Niessner(101) pointed out that only machine-direction hygroexpansion is important to the control of register in offset printing; he favoured controlled conditioning before printing rather than quality control of paper hygroexpansivity during manufacture.

Paper exhibits also a thermal expansivity. The coefficient for dry paper is of order 10^{-5} °C^{-1}, being greater in the cross-direction than in the machine-direction by a factor of two or three.(73) This coefficient λ increased abruptly at 35°C and again at 65°C, in each case by 35–40 per cent. Barker (102) had found that the modulus of elasticity E for a variety of homogeneous and isotropic materials was proportional to λ^{-2}. For dry papers and boards at 25° C, however, Kubát and his co-workers found $E\lambda$ to be constant, independent of the alignment of sampling with respect to the direction of manufacture. This effect persisted in samples that were subjected to rewetting and stress-free drying to reduce internal stresses. In addition, the work of Back *et al.*(103) seems to indicate that the increases in λ at 35° C and 60° C are accompanied by decreases in E.

Turning attention now to theories of deformation relating behaviour to structure, we recall first the molecular model of Nissan.(11, 32, 33) That depended on the physical chemistry of hydrogen bridges. The subsequent elaboration to a three-dimensional system(104) may be of academic interest. The early network models of Le Cacheux,(105) Onogi & Sasaguri(106) and Litt(107) were welcomed for their resemblance, however rudimentary, to the fibrous structure of paper. They quickly led to the more sophisticated models of Kallmes & Bernier,(65, 108) Van den Akker(109) and Campbell.(110) Kallmes *et al.*(111) compared existing theories and concluded that the assumption of affine deformation gave most realistic predictions. Such a model was used successfully, even for representing fracture, by Hearle & Stevenson(112) for bonded non-woven textiles. We note that the constituent fibres in the latter case are relatively unaltered by the process of manufacture, in marked contrast to the situation in paper. Algar(3) had reported effects of non-uniformity in paper induced by forming at high consistencies. When these were increased from 0·19 to 0·76 g fibre per litre, strength properties were reduced by some 10–20 per cent, of the same order as those mentioned before.(18) In an attempt to relate variability in local structure to that in local deformations, Dodson(7) devised a theory of local correlation between observable averages of areal density and areal dilatation over finite zones of inspection.

The phenomenon of fracture in paper

Corte *et al.*(113) filmed the failure of individual bonds in thin paper sheets during tensile straining; each such failure was accompanied by an audible click and by a sharp drop in tension of up to 1 g. Similar sound recordings were obtained for any type of paper and in all cases bond failures apparently occurred almost from the first development of tension. This substantiated the point made by Rance(80) that fracture is commonplace in paper and the plastic part of a load/elongation curve is an expression of the diminishing strength of the network as a result of bond failure. Nordman and his co-workers(38, 51, 114, 115) correlated the optical scattering coefficient of paper with the dissipated energy during tensile straining. It is now generally agreed that the changes in scattering coefficient arise from changes in areas of optical contact between fibres.

Tydeman & Hiron(116) showed that the final line of fracture across a strip of paper tended to follow a locally weak path, from a weak spot on one edge across to the other edge. The progress of crack-fracture in paper was studied by Andersson & Falk(15) and Goldschmidt & Wahren.(31) They found that the gross energy consumed was of the order 10^5 erg per cm of crack and Griffith's creeping crack velocity was about 6×10^4 cm s^{-1} in tracing paper. Moreover, a favourable agreement was found with the work of Corte *et al.*,(30) who had inferred a value for the energy dissipated in fracture zones by extrapolating fracture energy to zero strip length of their samples. The latter work itself was in order of magnitude agreement with a plausible estimate of the number of hydrogen bridges that are dissociated. At the same time, a theory of energy conversion was offered for the processes that occur during drying. Corte *et al.*(30) argued that the potential work required to fracture a strip of paper is reduced by an amount proportional to the integral of drying tension over drying time. This was confirmed by experiments in which they varied the drying tension integral over one decade by altering the distance of samples from an infra-red lamp.

Only in the case of thin sheets are direct structural descriptions of fracture possible in terms of individual bond failures. Then, in random samples, Corte *et al.*(113) used extreme value statistics to predict the total number of bond failures. Noticing that in these experiments the succession of bond failures closely followed the strain energy, Dodson(117) gave a simple model for the dissipation. The differential equation involved admitted a simple solution—

$$\varepsilon B = W - F[1 - \exp(-W/F)]$$

where W is the area under the load/extension curve up to the stage when B bonds have broken at an average energy of ϵ per bond. A value of the constant

F of the order of the work done up to the initiation of the avalanche of bond failures was appropriate for a reasonable agreement with observations. No effect of rate of straining was found.

Both fibres and fibre-to-fibre bonds are broken in the fracture of normal papers. This was recognised by Kallmes & Perez,(118) who based on it a criterion for fracture, in their affine network models of paper.

The only complete description of fracture in terms of more or less observable parameters has been formulated by Page.(119) It is no accident that he had spent many years observing fibres and bonds and their behaviour in real paper. Applying general arguments, he gives the maximum tension T before tensile failure of strips of finite length in terms of zero-span strength Z and the shear strength b of bonds. We can write his equation in the form—

$$1/T = 1/\alpha Z + \gamma/\beta b$$

where the factor β is the average bonded area per fibre; α and γ are constants depending on the density and Poisson ratio for the sample and on the cross-sectional areas of fibres. Thus, the first term relates to the strength of fibres and the second term to the extent and strength of bonding between fibres. Page tested the equation with experimental data and found the required linear relation between $1/T$ and $1/\beta$. Since β is proportional to mean fibre length l, a linear relation is also expected between $1/T$ and $1/l$; this was found.

A critique on the present position

THE word rheology may fairly be said to mean all things to all material scientists. It is in the nature of matter to resist attempts to alter its shape. It is inevitable that primitive experiments display this effect initially in linear terms, partly because of imprecision in any real measurements and partly because our descriptions have roots in topology, that is, in the mathematical concept of continuity. That these two reasons are in mutual conflict, because we cannot make measurements at points and continuity requires the existence of limits at points, has been well recognised since Poincaré formulated the problem and it continues to be a subject of mathematical research.(120) It is also in the nature of matter to reveal successively more intricate phenomenology by way of reward for increasingly sophisticated experimentation. The common ground of those intricacies arising from the deformation of different materials is a useful characterisation of rheology. What (if anything) flows, depends on the particular material and the sophistication of the structural model that is used to display the revelations.

In the following paragraphs, an attempt is made to assess the present position of paper mechanics, whenever possible in fundamental terms. Necessarily, the views that are expressed reflect personal prejudices, but an effort has been made to retain objectivity through the required theme—the relevance to the end usage of paper.

Like any material that is subjected to scientific study, paper has continued to exhibit increasingly complex facets of its nature. Also like the studies of other materials, paper science has ranged from fundamental molecular interactions through chemical effects to macroscopic phenomena. Unlike other technological materials, however, paper has essential structural elements that can be pulled out and held between two finger nails; moreover, these elements owe their own coherence to a precisely similar bonding mechanism to what holds them in a sheet of paper. This dual role of hydrogen bridging between hydroxyl groups of cellulose molecules has assured the continuing importance of paper because of the basic simplicity it gives to the manufacturing process. On the other hand, the same dualism has so far confounded structurally based theories of its physical behaviour. At the moment, we have neither a theory of one fibre-to-fibre bond in terms of the molecular mechanics of hydrogen bridges nor a deep enough theory of paper in terms of fibre and bond mechanics. Even for idealised fibres, there are inherent mathematical difficulties in handling for the first case the thermal statistics of hydrogen bridges and for the second case the spatial statistics of fibrous networks. Supposing this were possible in probabilistic terms, there remains to be superimposed the hygrostatistics of interference by free water. Of necessity then, we must be pessimistic about a global theory of paper mechanics; but equally, in the face of such difficulty, we must temper our criticism of local efforts by promoting those developments that are firmly anchored to reality through treating observable parameters.

By way of illustrating the relevance of these remarks to current work, Perez(121) declared—

> 'Additional experimental work is now required to determine both actual bond strength and the curl distributions in the sheet. This can be accomplished by examining the shape of the stress/strain curve in the biaxial mode, since the second and third derivatives of the stress/strain curve have been shown to be related to the bond strength distribution. Once actual bond strength and curl distributions are determined, the theory must be tested further to determine how well actual stress/strain curves are predicted.'

Van den Akker in his review of structure and tensile properties(122) saw fit to present two pages of quadruply integrated trigonometric travesties of paper mechanics, then to criticise such diligence for lacking certain joint distributions and the accommodation of variability in fibrils. In contrast to that section in his review, Van den Akker(123) gave a highly realistic analysis of the Nordman bonding strength. There the useful concept of dissipative processes of local fracture being limited by the force required to break a bond was introduced and used to account for Nordman's correlation with optical changes.

The work of Nissan(11, 32, 33) must be considered as an important contribution to paper science in providing a unified approach to the physical chemistry of paper. The abundance and strength of hydrogen bridges in amorphous regions is such as to admit viscoelastic effects in terms of their dissociation and rearrangement, whether activated by strain or thermally. Similarly, free water offers a substitution of its hydroxyl groups for hydrogen bridging to cellulose in place of bridges across cellulose molecules. So a qualitative description of the effects of temperature, strain and moisture can be formulated by making these effects specific to the properties of a typical hydrogen bridge. We note that such an approach actually takes advantage of the similarity of interfibre and intrafibre bonding, a characteristic feature of paper, by ignoring the fibres and treating the cellulose. Accordingly, Nissan chose an acceptable model for a hydrogen bond, then attempted not to deduce the response of paper to strain, but to infer the effect of temperature on this response. His estimate for the effect on the modulus E at small strains was—

$$\frac{\mathrm{d}\log E}{\mathrm{d}T} \simeq -4\times 10^{-3}$$

in good agreement with the data of Andersson & Berkyto.(12) Continuing this thermodynamic approach, Nissan(11) found that a first order rate process for the substituting effect of water could describe the influence of relative humidity at low moisture levels. Similarly, some viscoelastic properties could be described by a kinetic description of the rearrangement of hydrogen bridges under strain. Clearly, Nissan's models are neither unique nor realistic in detail, since, for example, fibres as structural elements are ignored, whereas they are known to have a specific effect on mechanical properties. This notwithstanding, some such gross thermodynamic formalism is necessary as an anchor for paper science in physical chemistry just as, at the other extreme, statistical geometry is necessary for an idealised portrait of structural behaviour. It is the happy conjunction of these facets that is lacking. There is no competition between the two theoretical extremes, for they have no common ground.

It is of course well known where any process of convergence must have its limit: there stands the papermaker, his quality controller and the printer. They are very much aware that paper is of a fibrous nature, displaying significant reactions to commonplace constraints that are necessary in its handling and usage. Their attention is inevitably directed to quantitative changes in observable parameters. In the context of porosity properties for inert fluids, there has already been derived a firm link between statistical geometry and the interests of users of paper. In the context of paper mechanics, the observables of interest to users are total strength, its interaction with relative humidity and, increasingly, the local variability of any deformations from whatever cause. Of these, the former category will probably have to be dealt with for some time by the traditional usage of experience and families of charts, but the problems revealed by precision printers have added a new dimension of interest—local behaviour inextricably linked with actual local structure. This is where theoretical developments can make a valuable contribution. Some small progress has been made.

The present author was introduced to the problems of paper mechanics by Corte and Radvan at a time when the former had effectively linked abstract statistical geometry to the observables of pore structure and the latter was completing a similar link through the hydrodynamics of formation to give a quantitative description of the extent of layering in paper structure. The natural next step was to devise a statistical, structurally based link between areal density and patterns of small deformation in a locally observable relation. The preliminary requisite was the derivation, from statistical geometry, of the distribution of areal density in random networks not at points, but for averages over finite zones of inspection.(71, 72) From there, it was a short step to hypothesise the existence of an associated distribution for local averages of areal dilation in a network subjected to deformation. This new distribution would have a similar spatial covariance to areal density, since deformations in a network are inevitably propagated along fibres and across bonds. The same finite dimensions of fibres communicate sympathetic variations in average quantities for neighbouring finite zones of inspection, simply because some fibres lie partly in each zone. Just as the variability in areal density from zone to zone was evolved from considerations of the variability in numbers of fibres covering a point and their finite dimensions, so a similar process was applied to strain. The coverage by fibres at a point measures, mathematically, the resistance to deformation of the network at that point; its evolution to averages over finite zones yielded local covariations of areal dilatation and areal density in a natural way. The essence of this development being the treatment of finite zones, the spatial covariations of mass and strain are observable. Some such observations and an outline of the theory may be found in Dodson.(124) Here is not the place for details, but an approximate result from the theory is worth recording, since it is simple and explicit. Suppose the grammage distribution in a sheet of paper is measured over finite zones—one millimetre squares, for example —and a total mean $\bar{\beta}$ and variance $\mathrm{Var}(\tilde{\beta})$ is found. In a subsequent programme of small deformations, the areal dilatation (that is, change in area per unit area) also varies from zone to zone and has a total average $\bar{\Delta}$, say. Then the regression equation for predicting areal dilatation $\overset{\backsim}{\Delta}$ of a zone of areal density $\overset{\backsim}{\beta}$ is approximately—

$$\overset{\backsim}{\Delta} = \bar{\Delta} - \frac{\bar{\Delta}\ \bar{\beta}}{(\beta)^2 + \mathrm{Var}\ (\overset{\backsim}{\beta})}(\overset{\backsim}{\beta} - \bar{\beta})$$

for any paper, not necessarily random. In addition, the coefficients of variation—

$$d = \frac{\sqrt{\mathrm{Var}\ (\overset{\backsim}{\nabla})}}{\bar{\Delta}} \text{ and } b = \frac{\sqrt{\mathrm{Var}\ (\beta)}}{\bar{\beta}}$$

are related by $d = b/(1+b^2)$.
Now, typically for paper, we have $0{\cdot}03 \lessapprox \underline{b} \lessapprox 0{\cdot}18$, as given by Corte.(10) Hence, $1+b^2 \simeq 1$ and there obtains the result $d \simeq b$, which has some considerable significance for printers.

Relatively few local relations of this kind have been reported in the literature. On the experimental side, Page & Tydeman(35) observed micro-compressions at bond sites and reported that at least some of the permanent set in subsequent tensioning was seen to arise from straightening out. Tydeman & Hiron(116) found that the path of tensile failure in paper tended to run through locally weak regions, that is, through zones of lower areal density. Mathematical analysis showed that the phenomenon could be explained in terms of the fracture path hunting for weak regions over distances of 1–2 mm. Nordman *et al.*(115) observed local non-uniformity in the response of optical scattering to strain; changes were concentrated in the areas of lower areal density. Detailed local effects were not reported for other changes that accompany straining: increases in porosity(125) and increases in thickness.(126)

We know that the elementary fracture process in paper is the dissociation of a hydrogen bridge, costing about 0·2 eV. At a fibre-to-fibre bond in paper, there will be up to some 10^8 such bridges at most, since that figure corresponds to one bridge per 10Å × 10Å over an area of optical contact of 10^{-6} cm^2. The weight of evidence is in favour of such dense packing for a variety of reasons. Areas of optical contact between fibres are independent of wavelength of visible light and unaltered by small deformations of the fibres. Besides, they are inaccessible to molecules of nitrogen. Then the maximum energy density of hydrogen bridging in a fibre-to-fibre bond is about 0·2 eV per 100Å^2, that is, about 30 erg cm^{-2}. This figure can be compared with the range 45–70 erg cm^{-2} of free surface energy for the creation of cellulose vacuum interface.(127) From the known energy of one hydrogen bridge, it follows that a fraction, rather more than 10^{-4}, of all hydrogen bridges have enough thermal energy to dissociate at any time under normal conditions. It is significant that, whereas the fringe patterns round an area of optical contact between fibres indicate that the fibre surfaces diverge rapidly away from the bond, the predominant mode of loss of area of optical contact was by partial failures at bonds.(26) Evidently, the former observation is indicative of local rigidity in the configuration; the mere partial loss of bonded area suggests either some local flexibility attributable to thermal statistics or some blocking mechanism such as patterns of defects in the array of hydrogen bridges. Studies in this field would be valuable, since the phenomenon is pertinent to the regimes of deformation that commonly occur in handling and printing paper.

Still in the context of partial fracture, the correlation of optical behaviour and the dissipation of strain energy provides a valuable, albeit indirect monitor of structural changes. Fortuitously or otherwise, depending on one's valuation of controversy in advancing science, the natural choice of scattering coefficient increased linearly with the dissipation of strain energy and the rate of increase was independent of beating and wet pressing. Theories of the static optical behaviour of paper rely on models for powder-like media, Kubelka & Munk(128, 129) applied, for example, by Van den Akker,(130) Koller & Chapman(131) and Schlumbom.(132) It is evidently beyond their scope to determine for any given paper the absolute increase in scattering area that is associated with a given increase in a scattering coefficient, even if the notion of such an association is meaningful. The controversy arising from attempts to discern an association of this kind is analysed by Van den Akker.(123)

Proceeding to gross fracture, those theories that have attempted a link between fibrous structure and bond or fibre failure(118) can give at best only globally qualitative results for paper. Many differing criteria for local failure in a bonded network would yield similar analogues of the actual observations. Ignoring for the present the fibrous structure, the propagation of the path of fracture in reasonably dense paper is rather like that of crack propagation in any brittle material. As such, Griffith's theory is applicable under certain conditions.(133) Physically, local strain energy is delivered and concentrated by a brittle structure at the tip of an existing crack or flaw. When the energy density exceeds an appropriate local threshold value, the crack can grow. Under certain assumptions, the work done per unit new area opened up by a crack and the velocity of propagation can be related to the modulus of the material and the tension required to extend a crack of given size. As has been mentioned, some progress in implementing these ideas for paper has been made by the experiments of Andersson & Falk(15) and Goldschmidt & Wahren.(31) It must of course be remembered that the structural elements in paper, being fibres or parts thereof, have dimensions of the same order of size as natural defects, that is, incipient cracks. The problems of formulating a structurally based crack theory specific to paper are therefore very great; a frustration not unlike that in interpreting changes of scattering coefficient in terms of changes in actual bonded area.

The present review has given only limited coverage to chemical effects on paper mechanics. This is partly because few general patterns have emerged and partly because the reviewer sympathises with the opinion of Reizin.(20) This was that differences in the plasticity of fibres determined by the degree of lignification are considerably smaller than those caused by variations in moisture contents and the latter is of more direct significance to the end usage of paper. Taking up the last point, we shall conclude with some suggestions for an approach to a structurally based theory of relevant observable parameters. The obvious development would be to link the local areal dilatations caused by absorption of water via the local variability in areal density of the host paper. A starting point would seem to be the work of Barkas,(134, 135) who gave a thermodynamic analysis of the increase in water adsorption that accompanies deformations of paper. This effect was observed by Kubát & Nyborg.(86) The goal would be to correlate the various spatial distributions that alter during sorption and desorption of water by paper—that is, during drying in manufacture and during environmental changes in usage. Again, attempts to derive absolute values for parameters in paper must probably be abandoned. Instead, specific changes in observable relations are required to show how local variability in one parameter influences that of another.

It is not intended in the foregoing discussion to imply criticism of, on the one hand, experimental programmes that chart interrelated global properties of paper samples or, on the other hand, theoretical programmes seeking particular links between structural and mechanical properties. Such schemes of study have sustained the continuing growth of paper mechanics for a long time and will do so in the future. The only plea that we enter here is that we do not too often fail to see, on the one hand, the characteristics for their dependents or, on the other hand, the paper for the fibres.

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Discussion

Dr D. H. Page The question of the expansion of paper in thickness (Z-direction) is a very interesting one theoretically and the mechanism by which it occurs is something that I have thought about for some time. I think you have added much in experimental expertise, though I think you have still left open how exactly this thickness increase occurs. I have a possible suggestion for a mechanism.

If you take a single fibre and extend it, because it has a finite spiral angle, the fibre tends to take a more round form, a less flattened form. If the lumen is completely bonded, the fibre will not debond and you obtain no thickness increase; if the lumen is not totally bonded, a flattened fibre will tend to come to a more rounded form. Is it possible that the explanation for the thickness increase of the paper is related in this way to the thickness increase of the fibre itself?

Mr H. L. Baumgarten Yes, this may be one of the processes that take place during tensile elongation, but (as I tried to say) there are at least three different processes.

Dr Page This would be a process that would lead to plastic deformation later on in the load/elongation curve and I would expect it from the single fibre data—but does it occur?

Mr Baumgarten At the end of the load/elongation process, we sometimes found a plastic increase in thickness.

The Chairman During drying, the whole sheet is compacted by the Campbell forces and, when bonding takes place, dried-in stresses are created in the Z-direction. When the bonds partly break under loading, then the fibres will spring back again. This was shown by Ranger & Hopkins in their paper at the 1961 symposium.

Under the chairmanship of Prof. H. W. Giertz

Dr L. S. Nordman Have you made any measurements of thickness changes during relaxation or during creep experiments?

Mr Baumgarten We are doing these tests at present, but we have no results that we can give here.

Mr J. F. Waterhouse We have obtained some very similar results to yours on the permanent set characteristics of polymer-reinforced fibre networks. We found that the plastic deformation was unaffected by the type of polymer used, but was mainly controlled by the kind of fibre. Furthermore, the set characteristics were essentially the same for the machine-direction and cross-direction of the paper. These results indicate that the plastic deformation, which I think your results in part show, is almost solely controlled by the plastic behaviour of the fibre itself. Yet, in Fig. 9, your results do not seem to indicate that the plastic deformation depends on the kind of fibre.

Dr N. G. M. Tuck In your graphs, I assume that the thickness decrease shown as being negative is in fact a thickness increase—in effect, a double negative.

Mr Baumgarten That is correct.

Dr S. I. Cavlin Did you ever find that drying conditions, the restraint during drying and so on, were important? Many experimental facts in the current literature show that the shrinkage affects the strain, particularly the plastic strain, to break point.

Mr Baumgarten We have experimented, but it is very difficult to get handsheets dried in different ways without altering the surface properties of the sheet, so we made no thickness measurements on this handsheet.

Dr Cavlin It is possible to change the modulus of elasticity in one direction to at least 50 per cent. Theoretically, this implies that the Poisson ratio also can be changed by about 50 per cent just by restraining the web during its drying.

Mr Baumgarten The relationship between the plastic elongation and total elongation is unchanged by the method of drying.

Dr A. de Ruvo I would like to comment that, when we are investigating different modes of deformation for single fibres, our intention is not to put them into any network theory or any theory in which the characteristics of the fibre are introduced in some very complicated formula. We aim for the limiting strengths of the fibre, then to see which characteristics of paper are similar to the behaviour of the fibre. From that, we hope to evaluate what deformations prevail in the sheet—for example, in spite of the elastic property in tensile deformation of the fibre, it is not sensitive to humidity, although the shear modulus is sensitive to humidity in the same way as the elastic property of the sheet. This indicates to me that the main deformation during elastic strain is in the shear and bending of the fibres.

The Chairman Dr Dodson has presented his paper in a very clear way indeed and it is not the aim of this meeting to discuss the theoretical points in it. We have to discuss how paper behaves when it is used.