

# SUMMING UP

B. G. RÅNBY

STATE UNIVERSITY OF NEW YORK, COLLEGE OF FORESTRY,  
SYRACUSE, NEW YORK, U.S.A.\*

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IT is a privilege and an honour for me to have been asked by the organising committee to give the concluding summary to this symposium. Although I have been working on cellulose and cellulosic fibres off and on since graduate school, until now, I have not published a single paper in the field of paper structure and properties. This symposium has been a most informative and enlightening part of my education as a scientist. Because of my assignment, I have tried to understand and, if possible, assimilate the various contributions to the symposium. Needless to say, this has been a strenuous task. The hydrodynamic discussions have been difficult for me to follow. I have had to annoy both chairmen and speakers by asking questions in my attempts to get a more complete picture of the subject matters discussed: I am grateful for the answers. My situation has often reminded me of a story from the University of Uppsala, my Alma Mater. One of the physics professors was known to have an unusually detailed and comprehensive knowledge of both classical and modern physics. One of his colleagues asked him, out of curiosity, 'How did you acquire all this fabulous knowledge? You are, after all, a highly specialised physicist in atomic spectra.' 'Well, you see, I have to take many oral examinations. By a systematic questioning of the students, then comparing the answers from the bright ones, I have learned a lot in all branches of physics, without reading all the books,' was his reply. This is in fact what I have done here.

I have one point of criticism about some of the authors who have contributed to this symposium: not all have honoured *the virtue of brevity* in their preprinted papers. Everyone who has tried to read through these preprinted texts will agree with me. The long papers have, of course, their obvious value as sources of data, background knowledge and references. In addition, those who work in industry can tell your management that printing

\*Present address—Department of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden

these long papers and the numerous discussion remarks is good for the paper industry!

Now to the main question—what have we learned during the symposium? Its outstanding feature is that we have been given physical models for the structure of paper sheets based on micrographs in visible light, polarised light and interference light by Emerton, Page, Giertz and others, on electron micrographs of conventional specimens and replicas by Jayme, Hunger and the British groups and on results from application of the scanning electron microscope by Buchanan and his colleagues in Montreal. The lack of reference to treatments of the physical structure of paper in the present literature was pointed out by Rance in his introduction to the symposium. With this conference, especially with the planned publication of the new conference volumes, this deficiency in the literature is beginning to be filled. *From now on, paper has indeed a structure that can be defined in clear physical terms.*

Let us look at these physical models of a paper sheet. In a well-bonded sheet, which means a reasonably strong paper, the fibres are found to be very intimately bonded to one another along most of their length, but they do not coalesce—that is, the fibres retain their individuality and they can be observed as entities under suitable experimental conditions. Therefore, paper cannot be treated as a homogeneous material. The bonding is by no means a phenomenon related only to the surface of the fibres. When bonding occurs, two fibres are in intimate contact at a crossing point, usually resulting in a practically total collapse of the lumen in the bonded fibre at the cross-section as Mason clearly demonstrated for paper fibres of higher grades in one of his contributions. This gives rise to sharp bending, considerable shrinkage and creping of the fibres. Owing to the extensive bonding of collapsed fibres, the free, unbonded surface area of the fibres is quite limited. The bonding fibre crossings are so large ( $100\text{--}1\,000\ \mu^2$ ) and are so closely scattered along the fibres that the so-called *intercrossing distance* in the cases studied are about  $50\ \mu$ , about one fibre width. The concept *free fibre length*, used in earlier work, loses some of its importance and direct physical significance, because the *projected interbond distance* as defined this week has an average value close to zero and it varies from  $-50\ \mu$  to  $+(100\text{--}150)\ \mu$  in a well-bonded sheet.

From the studies of Emerton, Page and Tydeman, a *direct method to observe and microscopically investigate interfibre bonding* has been developed. Bonding occurs when two fibre surfaces are in direct physical contact, that is, when the surfaces are at most  $150\ \text{Å}$  apart. Straining a paper beyond the elastic regime is observed to give both partial and complete rupture of inter-

fibre bonds. Because of the intimate bonding, these ruptures are accompanied by deformation in the adjacent fibre network in the sheet. What we have been given here is a beautiful verification and further development of Nordman's pioneering work on the simple relationships between irreversible energy loss in deformation and increase in scattering coefficient of a paper sheet. These concepts were initiated by Rance, further developed in the 1950s and intensely discussed at the Cambridge symposium four years ago. It appears certain now that the Rance-Nordman interpretation was essentially correct quantitatively—that is, the energy consumed in the straining of paper is directly related to broken interfibre bonds. One difficulty we had four years ago is now largely resolved: the measured energy values per opened surface area ( $100\text{--}300 \times 10^3$  erg/cm<sup>2</sup> for a well-bonded paper) are about a thousand times larger than the energies calculated for the breaking of any possible type of molecular bond when two fibre surfaces are separated. We can now say that this huge excess of energy is irreversibly absorbed in the fibre network, owing to the extensive deformation that inevitably occurs when the interfibre bonds are opened.

These relationships refer to well-bonded paper with a closed and partly overlapping system of interfibre bonds. For loose interfibre bonding, the energies of fibre separation may approach the theoretically predicted values for clean breaks as Luner reported in one of the discussions. For weak bonding between two sheets, the peeling energy of separation was determined as 73–177 erg/cm<sup>2</sup>. The specific energy of straining one weak sheet was found to be 80–86 erg/cm<sup>2</sup>, which is in close agreement with theory. For stronger bonding between two sheets and for stronger sheets, the peeling and specific energy values respectively increase by a factor of 10–20, which may well be explained as an effect of more extensive fibre deformation in the bond-breaking process.

We shall now turn our attention to *the statistical geometry of the fibre network in a paper sheet*. As a result of the work of Corte and Kallmes, we have arrived at a mathematical treatment of the formation of a random fibre network by deposition of freely moving rod-like fibres. The result for a mono-layer of fibres is that the completely random network shows fluctuations in density that are conspicuous enough to be observed with the naked eye. Even if we pile up at random a number of such mono-layer networks to form a sheet of more normal thickness, these fluctuations are retained on an absolute scale to such an extent that many commercial paper sheets are indeed more homogeneous in density. This is a remarkable fact, which may lead you to conclude that the average papermaker is smarter than the paper scientists. Fortunately, this is not so. A commercial sheet of paper is *not*

formed as a random piling up of random mono-layers. As we have learned from Wrist and Andersson, the hydrodynamics of sheet formation on a papermachine wire causes fibres to be deposited more abundantly in the more open areas on the bottom of the sheet (the wire side). The net effect under favourable conditions is predicted to be more a homogeneous sheet than a random sheet. Even so, the theoretical work of Corte and Kallmes has its value by giving a standard for density fluctuations in a paper sheet. When the fluctuations in a real sheet are found to be smaller than those of a random sheet, hydrodynamic factors in the formation may be involved. When the density fluctuations are larger than random, we may have fibre flocculation in the paper stock, which could carry through to the finished paper. You must excuse me, but I found the discussion of flocculation at this symposium somewhat confusing.

The random mono-layer networks, both the mathematical and those prepared from fibre suspensions of extreme dilution, have been used for studies of paper properties. *Pore size distributions* have been calculated and measured, as well as the mechanical properties of paper. Very striking were the sound films of the straining and gradual breaking of the mono-layer paper networks. The application of stress beyond the elastic limit gave a sequence of sharp breaks of interfibre bonds in direct agreement with Rance's and Nordman's original concepts.

The calculations of the elastic properties for two-dimensional fibre networks and for ideal multi-planar sheets agree, according to Kallmes, fairly well with measured values in some of the cases studied. This supports the multi-planar model for paper sheets, but this approach has its limitations in attempts to use it for strong, well-bonded paper.

To the highlights of this symposium belong the two *theoretical contributions on the mechanical properties of paper* by Van den Akker and Hopkins and Ranger. Based on a realistic model, Van den Akker has managed to treat theoretically the mechanical stress deformation of a paper sheet both in the *elastic regime* (where the changes are reversible) and the *plastic regime* (where the changes are irreversible). The treatment of the elastic phenomena is fairly complete: Poisson's ratio and Young's modulus in two dimensions of a sheet and the modulus of rigidity are calculated and found to agree with experimental data. The stress/strain phenomena in the plastic regime are much more complex and the theoretical treatment is still incomplete. The stress applied tends to break interfibre bonds in two different ways—by *shearing forces* in fibre segments giving torque on the bonds and by *tension forces* in fibre segments giving stress on the bonds. Bond failures from torque and tension, caused respectively by anisotropic shrinkage (such as from drying)

and by applied stress, are predicted from the theory and a general shape of the plastic stress/strain curves is derived.

Hopkins and Ranger have worked closer to experimental data than has Van den Akker. They have shown that weak papers, when stressed, break by shear along single strain lines. Strong papers respond to stress by a general increase in opacity, increase in thickness, decrease in width and formation of short strain lines in the plane of the sheet, scattered in all directions. The ultimate failure of a strong paper sheet is related to the shear strength of interfibre bonds and to the tensile strength of individual fibres. The rupture of interfibre bonds during straining is, according to Hopkins and Ranger, to a large extent due to the buckling of the fibres that occurs when the paper contracts in the plane of the sheet at rightangles to the strain direction. All these effects are related to a basic structural model for paper sheets. The effects of strain on fibre orientation, permanent deformation, frozen-in stresses and the formation of strain lines in the sheet are treated as part of the theory for tensile behaviour.

These theories of Van den Akker on the one hand and Hopkins and Ranger on the other stand out as a culmination of previous developments by Steenberg and his group and by Rance during the 1940s and early 1950s. The present theories are both based on Nordman's quantitative interpretation of interfibre bond breakage in paper straining. The two theories are *formal*, however—they are not directly related to the underlying molecular phenomena involved in the paper deformation.

We know now that *the cohesive forces in the fibre-to-fibre bonds are largely hydrogen bonds* involving the two or three hydroxyl groups and the ring and glycosidic oxygen atoms on the monosaccharide units along the cellulose and hemicellulose chains. Other polar groups present in the fibre material can also take part in the hydrogen bonding. It is quite likely, for example, that the phenolic, hydroxyl, carbonyl and alkoxy groups in lignin are involved in bonding. These groups are of types known from model experiments with low molecular weight compounds to form hydrogen bonds of well-developed strength. The characteristic features of lignin in this respect are its irregular cross-linked macromolecular structure and its low content of polar groups compared with the wood polysaccharides. We discussed hydrogen bonds rather extensively at the Cambridge symposium. To preach the dominant influence of hydrogen bonds in paper structures is now becoming as ubiquitous as the bonds themselves. This is like the weather: everybody talks about it, but very few are trying to do anything about it. Among those few, we have one outstanding and active scientist, Alfred Nissan, who works on hydrogen bonds (not on the weather).

Before discussing Nissan's contributions to the symposium. I would like to outline the main properties of O—H—O hydrogen bonds—

- (a) They are all *weak bonds*, they have bond energies well below 10 kcal/mol; most of them are in the range 2–8 kcal/mol, which means that they are about 10 times weaker than most covalent bonds.
- (b) The hydrogen bonds are typical *dipole bonds*, the donor group —OH being the positive end and the acceptor group  $\text{O} \ltimes$  being the negative end.
- (c) The hydrogen bonds can easily be broken, for example, *by addition of a polar medium* like water, urea, dimethylsulphoxide, *by heating* to rather moderate temperatures (often 70–80°C is sufficient) and *by mechanical straining* not only in the plastic regime, but also in the elastic region.
- (d) The hydrogen bonds *break and re-form easily*, with very short relaxation times when the molecular substrate permits that.

Recognising the importance of the subject, we can agree that every effort should be made to formulate a quantitative theory for the mechanical properties of paper based on hydrogen bonds. The accepted method of approach is statistical mechanics. Nissan has used a particular type of function, the Morse function, to relate bond energy to bond length. Doing so, he has succeeded in calculating the mechanical properties of ice, which is a beautiful achievement. Nissan and his research group has courageously approached cellulose fibres, cellulose film and now paper, using the same tools. He assumes that (1) the deformation of these materials can be related to the stress/strain response in the isotropic, amorphous regions, (2) the crystallites are rigid and strong rodlets, (3) the hydrogen bonds obey a Morse function until they break and (4) the relaxation times for these changes are short compared with the rate of application of the stress. In spite of the fact that all these assumptions are open to criticism and even to objections when applied to our system, Nissan and Sternstein have calculated stress/strain relationships for a three-dimensional hydrogen-bonded network, which for very small deformations (vanishing strains) give acceptable values for the elastic modulus of paper. For larger deformations, the difficulties and discrepancies are piling up. In this situation, I humbly offer these suggestions—

- (a) A theory for mechanical properties of paper based on hydrogen bonds should account for both the opening and re-forming of the bonds.
- (b) Both amorphous and crystalline regions of the fibres should be considered (crystallites, too, are deformed by mechanical stress).
- (c) A physical model of paper structure, as we now see it, should be accepted.

- (d) Relaxation phenomena (time-dependence in the stress/strain response) should be considered and worked into the theory.\*
- (e) Other forms of energy dissipation than hydrogen bond processes should be considered—for example, rupture of covalent bonds, changes in chain conformation and energy.

With these suggestions, I am leaving the subject of hydrogen bonds in paper, wishing Nissan and his group all success in their future endeavours. Considering the difficulties, I am happy that a scientist of Nissan's capacity is working on these problems.

In research, some problems not only seem, but may well be too difficult to tackle at one particular time. This was pointed out to me by Professor Tiselius, when I was a graduate student at the University of Uppsala. Should this happen to you, when you are a graduate student, reconsider your situation: if you cannot change your thesis problem, you may have to change professors. I hope that the theories of the mechanical properties of paper based on hydrogen bonds do not belong to this type of problem.

At this symposium, we have heard three comprehensive lectures on some of the more *technical properties of paper* given by Brecht, Harrison and Gallay, respectively. Of considerable practical importance are the effects of water, oil and grease on paper, particularly the adsorption and penetration of these materials through the porous structure of commercial paper sheets, as described by Brecht. The optical properties of paper and their definition were well presented by Harrison, who also discussed presently accepted formal theories for the opacity of paper sheets. The attempts by Gallay to interpret the interdependence of paper properties were thought-provoking and presumably of direct interest to the practical papermaker. It seems clear that some paper properties have to be bought at the expense of other properties; the question is, however, to what extent. The strength of individual fibres was pointed out to be of utmost importance for the mechanical properties of well-bonded paper sheets and for the interdependence of paper properties.

The *influence of type of fibre, fibre dimensions, fibre separation methods and fibre treatments* (both chemical and mechanical) on the properties of paper sheets were outlined in a series of papers by Dadswell and Watson, Grant, Giertz, Higgins and de Yong, respectively. A wealth of information is available here and it is impossible in this short summary to give even a general abstract of these data and their interrelationships. The contribution by Groen on *filler distribution in paper* is interesting both as such and as a

\*A time-dependent breakdown of the stress-supporting hydrogen bonds has been considered by S. S. Sternstein in his Ph.D thesis on work done at Dr. Nissan's laboratories (August 1961).

model system for a study of the drainage characteristics of the wet paper web. An effective and simple method for delamination (sectioning) of paper was developed and applied in this investigation.

The last four papers of the symposium, dealing largely with *the hydrodynamics of fibre suspensions* and *the formation of wet fibre webs* on the paper-machine, are of great importance for further developments in papermaking. At this stage of the process, the paper sheet is formed and the characteristics acquired then will to a large extent be carried through to the finished product. The discussions here on fibre suspensions were at times difficult to follow. From reading the papers, however, the subject matter appears to be less controversial than were the discussions and a coherent picture of the rheological properties of fibre suspensions is beginning to emerge. Therefore, I have reason to recommend for further detailed study the four papers by Majewski, Andersson and Steen, Robertson and Mason and Wrist, respectively. We can look forward to learn more about fibre suspensions as related to wet web formation at forthcoming meetings on the structure of paper.

With these remarks, I have covered what I think are the main basic problems and advances in paper structure and properties as presented at this symposium. I know that many who have come here to learn specific things about different papers, different fibres, beating processes, fibre suspensions, formation, distribution of fillers, etc. have been well rewarded by reading the preprints and taking part in the discussions. I would like, however, to state my opinion in these matters. At the moment, we do not know enough to describe, in basic terms, the behaviour of different commercial fibres in the papermaking process and as paper. Eventually, we will have acquired such knowledge. As an example, I would like to remind you about our discussions of pulp fibres from springwood and summerwood, which is indeed a basic problem. In many cases, the questions asked about the papermaking properties of these fibres were answered with both yes and no. There are other examples, too. The differences between fibres from sulphite and kraft pulps, as discussed by Giertz, cannot yet be defined in clear physical terms. The same is true for many of the properties of cotton linters and rag fibres, as discussed by Grant. We have here a wide field for future basic research.

In connection with the discussions on *the basic structure of papermaking fibres from wood*, I should like to present briefly some new data on the accessibility of such fibre materials. These investigations are being carried out at the College of Forestry in Syracuse, N.Y., in co-operation with Drs. Y. Sumi, J. Mayer and Mr. R. Hale, with the support of a grant from TAPPI and are still in progress. Using deuterium exchange and infra-red analysis applied to freshly grown membranes of bacterial cellulose gels, we have



found that the native cellulose microfibrils (about 100 Å wide) are without doubt directly synthesised in crystalline form. The cellulose they contain is about 45 per cent accessible when deposited in its original state. Purification and drying can decrease the accessibility to a 30–35 per cent level. Native wood cellulose fibres, purified and dried, are 58 per cent accessible, according to measurements both with deuterium and with tritium exchange, in agreement with data reported by Mason and his group in Montreal. Because of experimental difficulties, we do not yet know how accessible the wood cellulose microfibrils are in their original native state. Measurements with tritium exchange of holocellulose from spruce wood have shown, however, that these fibres, containing about one third hemicellulose and two thirds cellulose, are also about 50 per cent accessible. If we assume that the hemicellulose in holocellulose is amorphous (according to X-ray data), we may expect it to be 100 per cent accessible. If we further assume that the cellulose microfibrils in holocellulose are 50 per cent accessible (this is a lower limit), a numerical calculation will give an expected accessibility of 67 per cent, which again is a lower limit. With these data, it is an inevitable conclusion that hemicellulose and cellulose microfibrils in holocellulose from wood are deposited together in such a way that about 50 per cent of the hydroxyl groups in the hemicellulose are inaccessible. This may be due to a well-ordered adsorption of hemicellulose chains on the cellulose microfibrils, involving regularly arranged hydrogen bonds, which would prevent exchange with tritium. Another possibility is that the hemicellulose fraction, without being X-ray crystalline, is internally hydrogen-bonded in a regular way to prevent accessibility. Whatever the correct interpretation may be, the accessibility data indicate some type of regular order in the cellulose-hemicellulose structure in wood. This interpretation is well in line with other observations such as the good retention of hemicellulose in holocellulose and the contributions of hemicellulose to the tensile strength of holocellulose fibres. A regular, native association of hemicellulose to cellulose microfibrils with hydrogen bonds would also explain the effect of mechanical treatments, say, in the refining of woodpulp fibres and in chip damage. The removal of hemicellulose from a pulp fibre by different methods is also expected to give cellulose fibres of different properties as experienced in the sulphite and kraft processes. We believe, therefore, that this new concept of a well-ordered hemicellulose fraction in wood fibres is constructive and useful in wood chemistry and paper technology.

In closing, I must congratulate the contributors to this symposium for their fine papers. What has been presented here has, indeed, advanced our knowledge of the structure and basic properties of paper. In particular, I

congratulate our British colleagues, who have contributed so beautifully in this field of research, which we previously did not think of as a speciality for this country. I would like to pay my respects also to the organising committee, which has made this symposium possible and planned it so well in every detail.