SUMMING UP

A. H. NISSAN, Westvaco, N.Y., U.S.A.

I BELIEVE that the most difficult and complex area in the fibre science of paper-making is precisely the theme of the present conference. This is because the subjects we have addressed owe their existence to the interaction of a trinity of complex entities: (1) water, (2) cellulose, and (3) the structure of fibres and paper.

Water is a deceptively simple looking triatomic molecule which is the dihydride of oxygen, with a relatively low molecular weight of 18. But compare it by any measure you will with other hydrides—HCl, H_2S, NH_3 or CH_4 for example—or other triatomic molecules—CO_2, SO_2, NO_2—and you will find it anomalous in all respects. All these compounds are gases at temperatures below the boiling- and some even below the melting-points of water. All expand on melting; water contracts. It continues to contract for a rise of 4° when it changes course and begins to expand. Anomalously, other properties of water do not show maxima or minima at the temperature of its maximum density. For example, the heat capacity shows a flat minimum around 34–35° C. The surface tension, dielectric constant and other properties are also anomalously high. The rate of change of viscosity with temperature is higher for water than for any other self-respecting liquid of comparable molecular weight, size or shape.

A clue to these anomalies lies in the very high values of the heats of fusion and evaporation of water. It takes more energy to extract a molecule of water from its neighbours in the condensed state than is necessary with the other liquids. And this, of course, is due to the extra and unique bond—the hydrogen bond—which acts so strongly in water in addition to the electrostatic van der Waals' bonds aggregating other molecules into liquids and solids.

The second entity, cellulose, is a polyhydric alcohol, the composition of which is now well established. But once we move away from chemical to physical structure, complexities set in. Cellulose has crystallites, but the length of the molecule exceeds the length of the crystallite. Does the molecule

fold upon itself, or does it merely wander from one crystallite into another with a slightly chaotic interlude? The Meyer and Misch unit cell of native cellulose is very well authenticated, but until recently we thought the molecules were anti-parallel; today, majority of opinion veers to the parallel conformation. There are evidences of structure in multiples of the unit cell, but we are not sure. Ideally, cellulose has no branche or other active moities besides the hydroxyl groups, except at its ends, in practice, cellulose has base exchange capacities indicating other groups. The crystal forms of native cellulose are different from those of regenerated cellulose. Cellulose has several types of hydrogen bonds, each of a different strength. Some are intra-molecular acting simply as stiffeners for the molecule, while others are inter-molecular bonds, essential to the integrity of the crystal and amorphous portions alike. Talking of stiffeners, cellulose is always considered as a stiff, somewhat inflexible molecule, yet it exhibits transitions at temperatures as low as $-40°$ C and even in the range of -70 to $-100°$ C, attributed to the flip-flopping of portions of the molecules and rotations around the ether bonds.

It is not surprising, then, that cellulose–water interaction is so much more complex than, say, that of water and nylon (which is also hydrogen-bonded). Just one example of this difference: cellulose–water complexes exhibit hysteresis; nylon–water do not.

The third complex entity is, of course, the infinitely various, richly textured and ever fascinating composition, morphology and microscopic structures of fibres and paper. The composition is complicated by the presence of hemi-celluloses and lignin in fibres—ignoring many minor organic and inorganic components. The microscopic structure of cellulose fibres is a hymn of praise to the indescribable wisdom and patience of its architect—but it is a tremendous burden to the fallible and impatient scientist. The disposition and interconnections of the various units that make up fibres and paper—from crystallites to microfibrils and lamellae and macrofibrils, to fibres to flocs and finally to paper—provide mazes of almost impenetrable difficulties.

Each member of this trinity of complex entities is sufficient to frighten the faint-hearted. The combination of all three into the theme of this conference offers the most challenging invitation to its participants. You will not be surprised when I tell you that when I first heard that the Committee on these quadrennial conferences had chosen this particular theme, I went all biblical and muttered to myself: Verily, verily, the courage of man far exceedeth his wisdom!

Well, how have we done? I believe reasonably well. Our speakers waded right into battle like gladiators and acquitted themselves with courage and honour.

My thesis is best illustrated by the proceedings of the first day of our conference. By midmorning of the first session, the fire bed of a raging controversy had already been laid by my two friends Goring and Caulfield. Simply put, Goring maintains that water in the vicinity of cellulose has less structure than water in bulk. He says, 'Cellulose destructures water.' Caulfield, on the opposite side, maintains that water in the vicinity of cellulose is fully structured. He states 'Cellulose structures water.' All good controversies have accurate and valid data to support both sides, and both Goring and Caulfield adduced the evidence of careful experiments and logical deductions to support their contradictory arguments. But I believe that the most important aspects of the Goring–Caulfield debate were three. First, they were both looking at the foundations of our subject. Unless we understand the properties and interactions in material science—including, of course, paper science—in terms of molecular and thermodynamic parameters, we cannot understand our materials fully. Second, both Goring and Caulfield were probably, though paradoxically, right in their views of the interaction of water and cellulose surfaces. Thirdly, they only gave us a partial description of reality. The exciting full description is yet to come.

The word 'structure' as applied to water is complex and somewhat ambiguous. As a matter of fact, two major schools exist concerning the inner composition and structures of water. One school will only acknowledge a continuum of geometries and H-bond strengths in water and will not speak of 'structures'. The other school thinks of water as a mixture of bonded and unbonded entities.

I believe that much of the controversy between Goring and Caulfield could be resolved if the word 'structure' were explicitly defined in the two different contexts. The domains of water which are fully hydrogen-bonded—i.e. with four half-bonds per water molecule on average—are probably closed ring structures while the less hydrogen-bonded smaller groups with only three, two, one or no half-bonds per molecule may form either strained rings, open or branched chains, or stars. Thus, those fully bonded can be termed more 'structured' since they have lesser degrees of freedom to assume different configurations. In that sense, they are more ordered and, relatively, fixed in their internal pattern than the less hydrogen-bonded domains. They do not have to be tridymitic in their configurations as ice I is; they have to be, simply, fully bonded. I believe David Goring uses 'structure' in this sense. On the other hand, these domains are more open, or porous, and of lower density than the less-bonded domains. These latter, partially-bonded and unbonded, pack into closer groups and occupy space more efficiently. Since Van der Waals' forces are ubiquitous, these small, less-hydrogen-bonded clusters do

interact and the shorter distances between them compensate, though not fully, for the smaller energy of interaction compared to that of the hydrogen bond. Thus, the compact dense patterns of these less-hydrogen-bonded domains will transmit mechanical stress more efficiently than the more open, loosely held fully-hydrogen-bonded domains even in bulk water. Remember that we are not dealing with bulk water but with the water layers next to the cellulose surfaces. As both our protagonists have taught us, these small clusters are all anchored through hydrogen bonding to the cellulose. Consequently, a sort of structure—not necessarily the Meyer–Misch crystal structure of cellulose nor the tridymitic structure of ice I—is imposed on the basic layer. The other layers are densely packed and interact via polarisation and London dispersion forces and must conform to this basic structure. Thus, even though they are on average less hydrogen-bonded to each other, Dan Caulfield is entitled to view them as 'structured' but possessed of a different structure than that of the fully bonded domains. Personally, I do not consider it necessary to invoke a tridymitic structure of ice I for these layers, but this is a very minor disagreement.

Thus, I think Goring is correct in stating that water in the vicinity of sugars and cellulose is hydrogen-bonded to a lesser degree than bulk water at the same temperature. In that sense it loses structure—the transient structure of the flickering clusters of molecules and not necessarily the tridymitic crystal structure of ice. Evidence by Némethy and Scheraga on the specific heats of water containing hydrophilic and hydrophobic solutes support him and corroborate the predictions of Frank and Wen who laid the foundation stone of the flickering cluster theory of water structures in 1957. Thus, I believe Goring is correct in stating that cellulose destructures water in its immediate vicinity. But Caulfield, too, was correct in his observations and interpretation. When paper is wetted, its Young's modulus appears to behave as if the water surrounding the cellulose is structured, but not necessarily in the structure mode of bulk water. In this sense, I believe Caulfield is probably correct in telling us that the cellulose imposes a structure on the water layers.

Thus, the two meanings of the word 'structure' are different as used by Goring and by Caulfield; though both, once defined, are acceptable. But we have to define the word when we use it.

Add to all this the electrical layer effects and the difficulties in understanding them which were brought out so clearly in the afternoon of the same session on Monday by Overbeek, Hardman and Corte, and we begin to appreciate the complexity of our theme. But what is more interesting than the complexity is its recognition and the appearance of theories and methods to resolve it. Reality is complex beyond measure but is of no interest to the

blind mind. Intellectual excitement comes with recognition of the complexity and the formulation of ideas to resolve the complex into simple understanding.

Personally, I find the challenge and promise in this particular field of paper science of enduring fascination and of great potential value. Were I twenty years younger, I would gladly make them my chosen field of battle in research. But then a serious question would arise: Would I, as a director of industrial paper research, feel entitled to devote full time to resolve these questions? Or would I relegate such research entirely to weekends, vacations, and other free time, for another twenty years as I have done during the last twenty, because I could not justify expenditure of money and man-hours to research at the molecular and thermodynamic levels of paper science? The sad answer appears to me that these important questions may not be receiving their due share of research in these days of complete preoccupation with relevancy in research and the demand for instant profits.

There is, fortunately, more but only a little more interest in the third entity of our complex problem, that of fibre and paper structures than in the first two of water and cellulose. The first two papers of Monday's first session, given by Scallan and by Gray respectively, illustrated the richness and exquisite structures of fibres when studied in sufficient depth.

Graminski's contribution on Friday afternoon on image analysis promises well for the future in this area.

Over the years, Scallan's work, in its emphasis on interlamellar voids as being of critical significance in the structure of fibres and paper, has indirectly pointed to the lamella as the structural unit of paper. Even if we do not go to lower levels than the scale of the lamella—e.g., to the microfibril—the lamella as the ultimate structural unit of paper forces us to revise our views of paper mechanics so far advanced by structuralists. Lamellae in fibres exist in three-dimensional spirals. Therefore, despite the often quoted fact that paper, made on a fourdrinier and its multiple drainage elements, delaminates in layers, all theories which consider paper as two-dimensional networks of fibres must be viewed as gross approximations ignoring the 'forgotten dimension' of thickness. Well bonded paper has three-dimensional integrity, not only two. The paper by Alf de Ruvo on Friday morning, dealing with acetylation of fibres for recycling, is a testimonial to this idea that the building block for paper is the lamella of possibly the microfibril rather than the fibre.

I have already mentioned some of the papers of the second session of Monday. The electrodynamics of colloidal systems with ion-rich liquids are not easy to understand. A scientist who contributed greatly to elucidating

these systems is Dr Overbeek, whose book on lyophobic stability, published in 1948, proved to be a classic in his own lifetime. In his talk, he gave us an enlightening lecture on the pitfalls of oversimplifications in this mine field. His warnings were reinforced, even though opposed, by the two discourses of Hardman and Corte, illustrating the difficulties inherent in the double layer concept when applied to polyelectrolytes such as cellulose fibres.

Both Hardman and Corte emphasised some of the difficulties in interpretation of electrophoretic measurements. They calculated the net electric charges, found them sparse and expressed dissatisfaction with the concept of the electric double layer. Later in the afternoon, Dr Bianchin pointed out that a zeta potential of zero is not always synonymous with maximum retention. On the other hand, Dr Horn, Dr Goff and Dr Sack appeared comfortable in basing their observations and interpretations on different aspects of the double layer. Finally, the importance of the ionic atmosphere of the fibre was stressed by Mr Leask. What do we make of it all, particularly when we remember that our speakers receive support from observations by other scientists in other fields of colloidal studies?

I must confess that I am less comfortable with the controversy between Overbeek versus Hardman and Corte than I am with the controversy between Goring and Caulfield. In the latter, there were two diametrically opposed statements, each of which attempted to interpret a set of phenomena in its own distinctive but positive way. It was, therefore, possible to synthesise the two statements and resolve the controversy. In the debate between Overbeek and his two opponents, we face a different situation which is far more difficult to resolve. In his paper, Dr Overbeek explained the necessity of considering the retarding effects of the diffuse layer of counter ions on the motion of a charged particle in an electric field. Corte finds the magnitude of the factor too large for his liking. Literally, Corte does not like this interpretation.

Now, it is one of the essential freedoms of science and a necessary step in its paradigm for a scientist to reject a concept for any reason whatsoever, including simple dislike for the concept. It is not even obligatory for a scientist to put forward an alternative when he rejects a concept widely accepted by the scientific community, because he does not like it. But until he does put one forward, the rest of us have only two options. The first is to continue holding onto what science has forged so far, imperfect as it may be, and use it to the best of our abilities and its capabilities until a better one is produced. The second is to refuse it and join the sceptic in the wilderness of disbelief where sustained ambiguity may lead to a flash of creativity. Until Corte comes forward with an explanation which resolves more problems than Overbeek's system can, or resolves them more elegantly, more simply or more

accurately, I recommend with all due respect that we bear in mind his distaste for the concept elucidated by Overbeek, but accept it as the best we have so far. I hope Corte continues to challenge the double layer concept and in time gives us a positive alternative.

Dr Hardman went into greater thermodynamic depths and came back with the admonition that strict adherence to thermodynamic criteria is not being observed in the discussion and use of the electrostatics of the double layer. I am not sufficiently qualified in thermodynamics to be able to judge the validity of these strictures, but they do appear sound in considering electrostatics. What I find difficult to understand fully is whether we are free to apply the principles of classical thermodynamics of equilibria in reversible processes, to electrophoresis and other phenomena of electrodynamics where dissipative processes, characterised by the viscous transport of momentum, predominate. If these principles are not applicable and the use of thermodynamics of irreversible processes is called for, where the growth of entropy introduces new and complicated concepts, then until these are used, Dr Hardman's arguments against the use of the double layer once again, like Dr Corte's, distil into the single element of surprise at the large retarding effect calculated by Dr Oberbeek's methods. Here, too, I would submit that we have the options of accepting the double layer as workable or rejecting it and waiting for something new. Again, I would, personally, take the first option. Thus, while unhappily I cannot resolve the second controversy of Monday's session, I confess that I accept the double layer concept.

There is, however, one general fact that all three—Overbeek, Hardman and Corte—emphasised. It is this: No single parameter can explain in its entirety the disperson or coagulation of colloids in an ionic atmosphere. We may try to explain colloidal interactions among ionogenic particles like cellulosics in an ion-rich acqueous suspension through single parameters like the zeta potential. But we cannot do it. Other factors must also be considered. One example is the effect of an entropy barrier to flocculation when a polymer is adsorbed on a colloidal particle preventing flocculation even in an electrically neutral atmosphere. In an electrically active situation, the zeta potential is simply one factor in repulsion or attraction, being a net result of the interactions of the charge at the base of the Stern layer, the number, valency and sign of the charge of the ions surrounding it and the degree of interpenetration of some of these ions into the Stern layer. We shall not disperse the fog from what Ostwald called the cloudy science of colloids by ever thinking that the zeta potential, or any other single parameter, could explain by itself, and independently of the presence of other factors, the phenomena observed in the wet-end of the paper machine. On the other hand, I know of no alterna-

tive to a careful analysis in depth of these phenomena in terms of electro-dynamics and adsorption if we are ever to hope for a full understanding and control of wet-end systems.

I think you will agree that the afternoon of Monday was a worthy successor to its morning in both defining the complexity of our theme and in giving us some understanding of our observations.

The discussion which followed emphasised the jungle of problems we entered when we began to pop additives into the wet-end systems of our paper machines. We face two problems there. The first is to understand the inner workings of our colloidal suspensions and solutions. The second is to devise measuring and control instruments, strategies and methods. These problems received several suggestions for their solutions in the papers sub-mitted by the discussion leaders.

It is now a tradition of these Fundamental Research Symposia to ask central figures in the field of fibre science for an authoritative, critical and creative overview of their field of speciality. On the second day of this con-ference, we were favoured not by one but by two such reviews. The first was by Dr Moller on the hydrodynamics of fibre suspensions and the second by Dr Atack on grinding and refining. I am certain these two papers will be authoritative references to their respective fields for many years to come.

The second day of our conference saw us move to more open and familiar grounds for discussion. We left the invisible phenomena of molecules and electrons to view the visible flows of fibre-in-water suspensions. I could almost hear a sigh of relief from the more practical and down to earth scientists and engineers, as our authors and audience looked at suspension fluid-dynamics, fibre beating, wet pressing and web drying on Tuesday.

But it was not long before Dr Moller reminded us that network structures build up at surprisingly low concentrations of fibres in suspension. The strengths and other properties of these networks arise from the same pheno-mena we laboured to understand on our first day. But lacking exact formula-tions and even direct measurements of the strength of a network, Dr Moller demonstrated the power of statistical methods to elucidate the hydro-dynamics of these systems and the breakdown of networks by turbulence. I was interested in Dr Moller's search for the appropriate level, or fundamental unit, for the fluid mechanics of paper-making syspensions. He moved successively from the empirical level (i.e., a pipe diameter) through the smaller network level down to the fibre level. Unfortunately, so far not much work has been done at this smallest scale level. I believe the fact that the hydro-dynamic specific surface and so-called specific volume of fibres are powerful determinants of drainage resistance of fibre mats means that ultimately we

will have to go down to the fibril and microfibrils to understand the hydrodynamics of fibre suspensions. This is exactly the same situation as the one I discussed in the solid mechanics of paper when reviewing Scallan's contribution and for exactly the same reasons.

Dr Luner then followed with an explanation of flocculation of cellulosics by polymeric additives and shear. The wet end as well as stock preparation systems are profoundly affected by these phenomena.

Dr Atack brought us up to date on the developments in what I have always considered as the central process of papermaking, namely the refining art and technology during the last twenty years. He dealt clearly and extensively with the mechanism of beating both from the viewpoint of the fibre and of the machine. It was remarkable how many of the early insights of twenty years ago by Emerton proved correct by later microscopic and solute-exclusion studies on beaten and unbeaten fibres. The interior delamination of the secondary wall and the creation and the central significance of voids on beating are now well established. I believe beating and/or refining have moved a long way from the mysterious and unknowable art of former years to a near-science today. Atack's own contributions to the fundamentals of tribological phenomena in grinding and refining were of great significance in this direction, but many workers deserve our thanks. What is particularly gratifying is that many of them are still working towards the elucidation of this central process of papermaking, which uniquely affects both the speed of production and the quality of our major products.

A neglected aspect of refining is the physico–chemical interactions produced in our systems. Dr Levlin pointed out the substantial material losses which may occur in the refining of high yield pulp. Aside from the loss of profitable materials, this fact adds to our troubles in increasing BOD and COD of effluents from our mills. These observations were reinforced by a study on the solubility of cellulose as affected by beating as reported by Dr Borruso. These are neglected fields which may repay more study.

Drainage studies were reported by Arnevik. Then, Ionides related drainage factors to wet web strength, particularly on newsprint machines.

We spent Tuesday afternoon discussing the removal of water from the web by wet pressing and drying. Lindström considered water as a distinct phase being held in voids within a cellulose gel. His work echoed previous studies by Scallan. Short contributions by Nelson and Oliver emphasised the mechanical aspects of sheet and felt respectively in wet pressing. They were followed by Waterhouse who was interested in saturating webs with polymeric suspensions and reported on the significance of pressing parameters on saturation.

Through drying of tissues reported by Schlünder once again brought into emphatic prominence the role of the size distribution of pores and voids.

An excursion from the conventional studies of water–fibre interactions was made by Lars Nordman in his studies of wet web adhesion of fibre mats to hot metallic surfaces in the dry creeping process. An intermediate organic adhesive layer was pursued and analysed to reveal differences among adhesive propensities of different pulps to metallic surfaces.

The session was closed with a paper on drying stresses by Htun. Combining Kubát's technique for measuring internally frozen stresses in a sheet of paper with measurements of drying stresses, the two were found equal to each other suggesting cause and effect.

The four papers of the next session on Wednesday morning by Stannett, Haynes, Schubert and Hoyland brought us right back to fundamentals and reminded us that there are still new worlds to conquer. Professor Stannett dealt specifically with capillary-free transport of water in polymers by the solution–diffusion mechanism. His paper served to remind us that paper is a man-connected natural polymer, and to understand its interactions with water, we would do well to understand the kinetics and thermodynamics of adsorption and desorption, of permeability and of diffusivity of liquids and vapours into and out of polymers. Stannett found Zimm's thermodynamics of the clustering of water on cellulose derivatives of direct use in explaining otherwise unexplainable observations on diffusivities, and so have I in my paper on the effect of water on Young's modulus of hydrogen-bond dominated solids. Thus, paper and high polymers, like islands in an ocean, may appear far apart from each other, but, again like the islands, they are assuredly connected at their bases in the fundamental science of polymers.

Dr Haynes used a classical approach to capillary imbibition utilising the Washburn equation for calculating diameters but warned us that the original equation was derived for rigid, fixed-diameter pores and cannot be extrapolated to paper where the fibres are flexible and, through swelling, the pores vary in shape and size on contact with water. The difficulties emphasised by Dr Haynes are not the only ones we encounter in studies of imbibition of liquids by porous solids since Dr Schubert followed Haynes by a paper in which he discussed difficulties of analysis of even non-swelling, rigid, fixed-diameter pores in which imbibition takes place.

Dr Schubert broke new ground in attacking the problem of high-speed imbibition of liquids in porous systems. His equation (8) is a general solution to the fundamental equation (7) for a constant value of P_c, the static capillary pressure. If I may interject a personal note, I was a little disappointed that the modification which made it a pragmatically better tool depends on the

use of a variable P_c, linearly varying with the rate of imbibition v_p. This relationship, is or appears to me to be, a purely empirical adjustment to what was before an elegant analytical equation based on good physics. So while the final equation developed by Professor Schubert is evidently an improvement, I do hope he will persist and give us an equation free from *ad hoc* adjustments. As I said, Schubert is breaking new ground, and I wish him success in his endeavours. His paper will be a standard reference for many years to come because it provides both an authoritative review of the field and creative contributions to solving some difficult problems.

Dr Hoyland brought us back to paper swelling and permeability. He found paper to be indeed a three-dimensional network, with the thickness playing an important part. Most importantly, he discovered that the observed deviations from the Lucas–Washburn equation when water penetrates paper can be explained by the swelling observed in the thickness of the sheet. This is controlled by a diffusion mechanism which he successfully managed to quantify.

I believe it is fair to point out a contrast between the first day and the sessions of the following one and a half days. It seems to me that in the earlier sessions we were thrusting into the edges of the unknown and testing our strengths against the baffling power of Nature to hide her secrets in molecular electronic puzzles. On the following day and a half we were mostly consolidating previous gains and building on foundations laid down in the last twenty years, even though here and there we tried to break new ground. Both types of research are essential to our progress.

The treatments presented in the Sessions of Thursday were somewhat in between those of the first and second days. Some of the papers went back to fundamentals while the majority concentrated on pragmatic and empirical studies.

Mr de Yong and Dr Higgins demonstrated the effects of moisture content on physical properties of fibres and sheets. They related macroscopic properties of the sheet to microcompression and the twist characteristics of the fibres. Since these characteristics are determined by the properties of the fibrils—or even microfibrils—and their geometries, they brought us once again to focus at the fibril and microfibril as the elementary unit in the solid mechanics of paper.

Besides the two major controversies of Monday, there was another one yesterday in connection with my theory of the mechanical properties of paper at low strains. There appeared to be two camps. The first was led by those whose mighty labours in the past laid the foundations of paper rheology along structural theories, and who, for twenty years, have opposed a continuum

view of well bonded paper. The second was composed of those who are in the field of moduli and who keep adding to the experimental evidence. Salmén and Back showed a curve covering a temperature range of some 250° C and announced it fitted the predictions of the theory. Marchessault made one-dimensional paper from super fibres and stated it fitted the predictions of the theory. Caulfield demonstrates that in a large number of experiments a relationship predicted by the theory connecting the modulus to a function of the surface was valid. So what do we make of it all?

Of course, others will have to resolve this debate. My view is the following.

As I mentioned in a discussion on Wednesday it is impossible to prove a theory is valid, it is only possible to disprove it by contradictory evidence. So far opponents have not brought up contradictory evidence. They have simply dwelt on the discontinuous nature of paper. But all matter is discontinuous. We can only treat matter as a continuum if the scale of the discontinuities is small relative to an appropriate natural scale. I submit that the natural scale for paper can be derived from the speed with which a crack propagates to give failure. This speed is—for brittle materials—one half the speed of sound; for ductile materials somewhat smaller. The speed of sound for paper is in excess of 1 000 m/s. For a frequency in the upper reaches of sound, say, 10 kilohertz, the wavelength is of the order of a few centimetres. This, I believe, is the natural scale for paper and hence paper acts, mostly, as a continuum when stress is propagated through its microfibrils, fibrils and fibres even under dymanic tests.

A thoroughly practical approach to calendering was given by Dr Lyne. He introduced us to the quantitative understanding of moisture content gradients, not merely the average content on calendering. These gradients had direct influence on the printing qualities produced in the calendered sheets.

Kadoya, Usuda and Kimura reported the discovery that the effect of moisture on rapid rupture mechanisms shows an abrupt change at 70 per cent to 80 per cent relative humidity. They point to the greater degrees of slippage of fibres on failure of paper and under shock loads above 80 per cent relative humidity. This may contribute to this peculiar phenomenon, but the fact that cellophane, too, shows a maximum at 80 per cent r.h. suggests a more profound reason at the molecular level. It is an interesting observation worthy of further research.

Dr Salmén analysed the softening of paper by water. He used equations derived for the plasticisation of polymers based on the lowering of glass transition temperatures to calculate the effects of water on pulp and other cellulosics. The agreement with experimental results was gratifying. It also taught us once again the necessity to dig deep down to molecular levels if

we are to unearth the fundamental mechanisms governing such mundane and gross effects as the fluting of corrugating medium by wetting and heating the sheet under pressure.

Dr Lengyel reported on his work with pressing of paper on external and internal pores of paper. He then discussed the absorption of water and other liquids in paper and effects on the optical properties of the saturated paper.

Dr de Ruvo changed the effects of water on paper by forcing fundamental changes on the substrate either by grafting an oleophilic polymer onto it or by dissolving some of the crystallites. Thus, he produced radical changes in paper properties. Dr Caulfield then demonstrated that if the cellulose is chemically crosslinked or if it is wet strengthened by a resin, the enhanced wet strength is mostly due to a reduction in the amount of water the modified or protected cellulose is now able to imbibe. Dr Allan's contribution was a beautiful example of how viewing paper as a hydrogen-bond dominated continuum, when coupled with stereochemistry of cellulose and with an understanding of hydrogen-, ionic, and covalent-bond parameters, can yield usable predictions concerning the ideal properties of a wet strength additive. Allan listed such properties and determined that chitosan, an aminated version of cellulose which occurs naturally, fulfilled these requirements almost ideally. Experiments gratifyingly validated his predictions. Supply of chitosan on an industrial scale is not a fact of life as yet, but in a conference dedicated to fundamentals the gain in understanding is fully a cause for satisfaction. The arts of economics and of engineering must next be used to render fundamental understanding into profitable practice. In any case, Professor Allan may get help in meeting the supply problem from an unexpected source: A group of M.I.T. researchers have proposed that many marine plants be constructed to extract chitin and chitosan from sea shells for use as film-forming polymers for food wraps and dialysis membranes and as complexing agents for removing heavy metals from water streams.

Finally, Professor Marchessault developed another mechanism for wet strengthening of paper by encapsulation with microporous polyethylene layers. He explained how polymers can immobilise water in one of five different ways. The intriguing superswelling, modified cellulose fibres were used as bases for understanding the interaction of water with cellulose at the elementary fibrillar and molecular level. A so-called one-dimensional paper was made by extruding and drying a water suspension of these exotic fibres. He also made such fibres from native cellulose microcrystals. The polymerisation of nascent ethylene onto such one-dimensional fibres after partial freeze-drying showed that wet strength could be maintained by the polyethylene

excluding access of water to intermolecular hydrogen bonds. This conclusion is in line with Caulfield's ideas.

Combining the many studies so far presented, it appears, in brief, that the reduction in mechanical properties of paper on wetting is brought about by the breaking up of hydrogen bonds. Critical concentrations of water, when exceeded, bring about a sudden increase in the breakdown. Sometimes, these effects are put to good use as when we use the moisture, or moisture gradients, to enhance calendering or to render paper or board more flexible. Mostly, however, we seek to reduce the effects of moisture by some means of wet strengthening. Although different methods were described and different explanations given, it appears that a common factor resides in all of them: If we can prevent the water molecule from being adsorbed onto the cellulose, the paper sheet will not suffer a mechanical loss.

This morning's session on recycling is too close in our memory to need a reminder from me of what was said. But I cannot leave the session on recycling without a comment about an important new aspect of the subject. Of course, recycling is not new. Indeed, it may be said that Ts'ai Lun's invention of A.D. 105 was concerned with the recycling of textile fibres into paper. However, recycled fibres have always been discussed defensively and in cookbook style in the past. But today, almost for the first time, the recycled fibre was proudly exposed to study as a raw material in its own right. The physics, chemistry and physical chemistry of recycling were treated with the same critical scrutiny as that given to virgin fibres and to first-time made paper on our first and subsequent days.

At previous conferences of this series, foundation stones were laid in the crafts and sciences of fibres, of web formation and consolidation and of properties of paper. This conference has, I believe, succeeded in laying a firm base for the science and technology of recycling fibres in the paper industry. We shall do well to study carefully Dr Göttsching's analysis of the needs for research into recycling paper.

FINAL WORDS

I would like to close with a comment or two on the conference as a whole.

The first question is: 'Have we dealt with fundamental issues as the title of the symposium promises?' I believe the answer is 'yes'. The very existence, integrity and most uses of paper depend on the interaction of water with its various components.

A second, perhaps more important question is: 'Have we dealt with our issues in fundamental terms?' Again, I believe it is fair to say that we have. The interaction of water and cellulose has been investigated at the molecular

scale and in thermodynamic terms. The treatment of process and property parameters was often more empircal and occasionally *ad hoc*, but there, too, attempts were made to reach a deeper understanding and I am persuaded that, at least in part, the use of the term fundamental is justified.

A final question: 'Have we dealt with all fundamental issues concerning water–paper interactions?' Clearly, we must say 'No, we could not.'

Let me give you a few examples which may intrigue our organisers enough to mount another conference on the theme in the future. I choose, at random, three fields for illustration. Consider electrical conductivity. For paper, electrical conductivity varies with an extremely high power, no less than 9·3, of the water content. Since the conductivity is ionic, this implies a possible cooperative action among nine to ten protons on average, necessitating that many protons work as a unit before they could make an effective unit jump in carrying electric charges down a potential gradient. This fact has always seemed most intriguing to me. Why are so many ions needed? Why this particular number? How are they distributed in the bound water? This last question brings us back to the question: 'How is water distributed on cellulose?'

A second example is the creep of paper under constant load in humid atmospheres. Under constant load, a strip of paper creeps less at 30 per cent relative humidity than under 90 per cent. This fact we are just beginning to understand. But why does it creep even more if the humidity is cycled many times between 30 per cent and 90 per cent than if it is kept at 90 per cent? Some explanations have been given in terms of bond breaking on the drying limb of the cycle, but I am not fully happy with this explanation since wood shows the same phenomenon. An explanation in fundamental terms would be a satisfying experience.

I will choose my third example from our basic processes. Almost any process in pulping and paper making which uses water could be a candidate. Let me take beating or refining. Presence of ions in the water, including protons and hydroxyls, has profound effects on the rate ar.d extent of beating in terms of strength or slowness development. I do not believe we have a fundamental understanding of these phenomena.

In short, we have not covered *all* fundamental issues. How could we in the space of a week? But the selection of fundamental issues was judicious, and for this I believe the organisers and speakers should be congratulated.

Thus, I conclude that those of us present, who have had the privilege of participating in this symposium, and those less fortunate but who will be reading these papers, owe the committee of organisers a debt of deep gratitude. I think it proper to register our thanks to them.