GENERAL PRINCIPLES OF ADHESION

WITH PARTICULAR REFERENCE TO THE HYDROGEN BOND

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Synopsis

A study of the morphology and energetics of fracture can shed some light on adhesion. Two approaches are made and both lead to the same general conclusions. In the first, the fracture of liquids of increasing viscosities—or their cavitation—leads to the ideas that fracture of polymers is governed by flaws or imperfections, not by molecular parameters. The second approach is that of Griffith, who postulated his now famous 'crack theory'. The fracture of materials is again seen as a statistically controlled process dependent on the presence of flaws. Qualitatively, it is known that fracture of paper is explicable by stochastic considerations, too; however, quantitatively, the crack or flow theory fails.

In order to explain the mechanical failure of paper, it becomes necessary to apply the statistical approach to the bonds between the molecules. These are the hydrogen bonds joining cellulose molecules together. It is found that, if a variance is assumed to exist around the mean value of the bond energy, the rupture energy of paper can be related to its content of hydrogen bonds. Thus, the adhesion of the elements of paper is quantitatively explicable in terms of characteristics of this bond.

Les principes généraux de l'adhesion et le rôle special du pont hydrogène

Le phénomène de l'adhésion est en partie expliqué par les résultats d'une étude de la morphologie et de l'énergie de rupture des corps fracturés.

L'auteur aborde le sujet de deux angles différents. Premièrement on remarque, en étudiant la fracture ou la cavitation de colonnes de liquides polymériques de viscosités croissantes, que la fracture est déterminée, non pas par des paramètres moléculaires, mais par la présence d'imperfections ou de discontinuités dans le liquide. Le deuxième point de vue est celui de Griffiths, dont la théorie déjà bien connue postule une distribution au hazard de fêlures qui initient la fracture. On sait que la rupture du papier peut en partie s'expliquer d'une façon qualitative par des considérations stochastiques. Cependant, la théorie de Griffiths ne se soutient plus dans le cas du papier lors d'un examen quantitatif.

Pour expliquer la rupture du papier il faut appliquer des méthodes statistiques à l'étude des liaisons moléculaires. Ces liaisons sont les ponts hydrogène existant entre les molécules de la cellulose. A condition d'admettre une variation statistique de l'énergie de liaison autour d'une valeur moyenne, un rapport peut être établi entre l'énergie de rupture du papier et son contenu en ponts hydrogène.

Ainsi les propriétés de ce genre de liaison servent à expliquer d'une façon quantitative l'adhésion entre les éléments de la feuille.

Allgemeine Prinzipien der Adhäsion mit besonderer Berücksichtigung der Wasserstoffbrücken

Das Studium der Morphologie und der Energetik von Brüchen kann gewisse Hinweise für die Adhäsion geben. So wurden zwei Näherungen vollzogen, die beide zu den gleichen allgemeinen Ergebnissen führten. Einerseits gestattet das Brechen von Flüssigkeiten zunehmender Viskosität bzw. ihre Kavitation die Vermutung, daß das Brechen von Polymeren bestimmt wird durch Risse oder Defekte und nicht auf molekularer Ebene vor sich geht. Die zweite Näherung beruht auf der nunmehr berühmten 'Bruchtheorie' von Griffith, bei welcher wiederum das Brechen von Materialien als ein statistisch kontrollierter Vorgang in Abhängigkeit von der Anwesenheit von Rissen angesehen wird. Bekanntlich ist das Reissen von Papier qualitativ auch mit Hilfe von Wahrscheinlichkeitsrechnungen zu

erklären, während quantitativ die von Brüchen oder Rissen abgeleiteten Theorien nicht zutreffen.

Um die mechanische Zerstörung von Papier zu erklären, ist es notwendig, die statistische Näherung gegen die Bindungen zwischen den Molekülen anzuwenden, wobei es sich um Wasserstoffbrücken handelt, die die Cellulosemoleküle zusammenhalten. Unter der Annahme, daß für den Mittelwert der Bindeenergie ein gewisser Variationsbereich besteht, kann die Bruchenergie des Papiers auf dessen Gehalt an Wasserstoffbrücken bezogen werden. Dies bedeutet, daß die Adhäsion der im Papier vorhandenen Elemente quantitativ durch die Eigenschaften der Brücken erklärt werden kann.

Introduction

ADHESION of one material to another must, ultimately, be due to interactions between the two at the molecular level. This is because, except for magnetic or electrostatic fields of force of macroscopic dimensions purposely impressed on the body, the fields of forces acting between surfaces die out very rapidly, so that they become negligible at distances of a few Ångstrom units (1 Å = 10^{-8} cm). Therefore, to understand adhesion, one must logically study the inter- and intra-molecular interactions directly. There are grave theoretical and experimental difficulties, which make such direct attack on the problem only rarely successful.

Instead, studies made on the behaviour of the macroscopic body itself are used to deduce indirectly what takes place at the seat of adhesion. In general, ideas about adhesion—and cohesion—are formed from a study of the energy, force or other parameters found critical in causing a coherent body to come apart. Thus, a study of the mechanism and morphology of *fracture* is indirectly a study of cohesion and adhesion. This is not an ideal approach, since fracture is (or may be) the end result of many independent processes. None the less, a study of fracture of materials does afford an insight into several interesting facets of the problem of adhesion. We shall, therefore, look briefly into this very important, though somewhat neglected, property of materials. We shall find that there are certain general features of fracture that correlate behaviour of liquids, glasses, amorphous polymers of a certain type and polycrystalline metals. These features appear qualitatively in the behaviour of paper, too, but significantly they do not fit the picture quantitatively. Certain quantitative deviations occur also with elastomeric polymers, even though qualitatively elastomers would not appear to differ from other polymers. A critical series of experiments performed by

Higgins[1] in Australia shows a definite relationship between the rupture energy and the number of hydrogen bonds per unit volume of paper. This naturally leads us to a study of this particular bond and its contribution to the adhesion of fibres.

Fracture

WHEN a material is fractured, energy is required for several purposes. In order that we may gain clear and definite ideas, we shall deliberately choose a very simple system and idealise it to the extreme. Even though it appears far removed from fibrous structure, we shall try to move step by step to these structures—occasionally leapfrogging over wide chasms of ignorance. The system we choose is the fracture of a column of liquid under tensile stress.

Here, we have a well-defined law. For a small bubble of radius r cm to grow in a liquid of surface energy γ erg/cm^2, the excess pressure P_c inside the bubble must be given by —

$$P_c \geq 2\,\gamma/r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For water, γ may be taken as 72 erg/cm^2. If we further assume that r is a cavity of molecular dimensions—say 10Å, then P will be of the order 1.4×10^9 dyn/cm^2 or in excess of 1 000 atm.[2]

Experiments show that water and other liquids can indeed withstand very great tensions and these theoretical calculations are partly justified. However, instead of 1 000 atm and more, ordinary water will cavitate under a tension of no more than 20 atm. It follows, therefore, that r, the radius of the cavity, is not of order 10 Å, but more likely of order 500 Å. This is a large cavity, as a bubble 1 000 Å across will pack several million molecules of water. Thus, we are led to the idea that fracture of liquids must be at sites of pre-existing bubbles (of air) and not across homogeneous faces of the material. These bubbles have indeed been detected and their influence fully confirmed—for example, progressively de-aerated water can withstand increasingly higher tensions.

There are two paths by which we can progress from water to solid polymers—of which latter group paper is but a subclass of natural polymers. The first line of attack is through liquids of increasing viscosities. Kolsky[3] reports a series of experiments by T. H. Bull on liquids of increasing viscosities. It was found that P_c, the critical cavitation tension, increased as $\eta^{0.2}$ where η = viscosity of the liquid. Thus, whilst water cavitated under a tension of 250 lb/in^2, syrup of 400 poise could sustain 2 000 lb/in^2. These facts led these workers to postulate that materials of higher viscosity would

also fracture by a process similar to cavitation with one significant difference. For liquids, the relaxation time—given by Maxwell's criterion η/G, where G is the shear modulus—is of the order of μ sec. Thus, the stress dies too quickly to form running cracks. A polymer like 2'-hydroxy-2:4:4:6:5'-pentamethyl flavan with $\eta = 3 \times 10^7$ poise has a relaxation time of about 0.01 sec and therefore running cracks could be induced under shock stresses. These cracks completely healed in 5 hr. Thus, by moving along the path of increasing viscosity, we arrive at the mechanism of fracture of solids— (*1*) fracture is initiated at local sites of weakness; (*2*) these sites have a stress concentration at the edges that exceeds the *local* strength, even though the average stress across the body is far too low to break it; (*3*) running cracks are produced that finally result in fracture.

A second path, starting from another position, leads us to the same qualitative conclusions, though with more precise and somewhat different quantitative formulations. Calculations on the inherent strength of glass— and later on several other materials, for example, metals—predict much higher values to be expected from atomic forces than are realised experimentally. This discrepancy led Griffith[4] to his now famous *crack theory*. Although later Poncelet[5] postulated that the cracks need not be pre-existent, as Griffith postulates, both theories yield essentially similar conclusions in so far as our studies are concerned; we shall, therefore, confine our remarks to Griffith's ideas. With remarkable insight, Griffith postulated that microscopic cracks of length c_o existed as the sites of weakness causing premature fracture of glass at a critical stress σ_c, which is lower than the ultimate stress demanded by calculations of atomic forces and is given by —

$$\sigma_c = \left(\frac{2\,\gamma\,E}{\pi\,C_o} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This formula has withstood the test of time and proved valid for glass, brittle fracture of metals, brittle polymers and other solids and, with appropriate though significant modifications, also for ductile fracture of metals and for both static and dynamic fatigue.[3] It is for this reason of apparent universal applicability of this criterion that it forces itself upon our attention in our studies of the adhesion and rupture of paper. Qualitatively, this criterion fits the behaviour of paper admirably, too. For example, since the critical breaking stress depends on the largest crack available, it follows that the breaking stress will decrease as the size of the sample increases. This is because the probability of finding a crack of a given size increases with the size of the sample. It is well known that paper behaves in this manner.

Secondly, Griffith's criterion predicts a lowering of breaking stress as the rate of stressing is decreased, since small cracks are given time to grow and cause a break. This, too, is observed with paper. Besides, by analogy with the action of humidity on glass, these considerations would lead us to expect a lowering of breaking stress with increasing humidity. Finally, the exact formula informs us that the breaking stress should increase as the modulus of the paper increases; again a known fact.

These many correct qualitative predictions notwithstanding, it behoves us to look more closely at this criterion before we pronounce it applicable to paper. For one thing, in its derivation, there are certain definite restrictions—for example, it deals with cracks in which elastic energy is stored without dissipation except through surface formation and kinetic energy of the advancing crack. Whilst it is a moot point whether the assumptions in its derivation apply to paper or not, there is another reason that we should be warned. Whilst the Griffith crack theory applies to a vast number of rigid and ductile materials—and qualitatively appears to apply to all polymers—it was found by Bueche and Berry[6] *not* to apply quantitatively to elastomeric polymers. It is found that, for elastomers, the breaking stress varies not with the half power of E nor with the inverse half power of C_o, but with the first power of E and, inversely, with the first power of C_o. Bueche[7] explains the ultimate properties of elastomers by applying the theory of absolute reaction rates of bond breaking to the kinetic theory of rubber elasticity that controls the behaviour of such materials. These facts suggest—(*1*) in order to be certain that the Griffith crack theory applies to paper, we must test it quantitatively; (*2*) despite its apparent universality, there is at least one other mechanism applicable to elastomers that appears to explain fracture. Indeed, the fracture of these special materials has also received an alternative explanation by F. Bueche.[8]

A critical test of the theory is to find whether the breaking stress varies with $E^{\frac{1}{2}}$ for constant C_o and with $C_o^{-\frac{1}{2}}$ for constant $E^{\frac{1}{2}}$. Such experiments are extremely difficult to perform for paper, where the control of all factors applied independently of one another, particularly of *crack length*, would be virtually impossible, since E is usually varied by, say, beating or pressing—processes that automatically vary C_o. There are, however, two sets of very carefully conducted experiments that suggest that the breaking stress varies with a higher power of E than $\frac{1}{2}$. Furthermore, the two sets, which were carried out independently on different fibres and by different techniques for varying E, give remarkably similar results. Higgins and his colleagues[9] acetylated beaten pulp and thereby blocked different amounts of OH groups. They then made paper by identical processes and measured their properties.

[See Table VII of their paper. This table is particularly useful, as acetylation was *after* beating. Thus, the degree of beating, fibrillation, etc. is identical for all pulps. Other tables relate to chemical treatment *before* beating; the pulps may not be in the same state of fibrillation.] In Table 1, we have an extract of pertinent data.

TABLE 1

Tenacity, 10^5 dyn	Thickness, cm	$A = \dfrac{Tenacity}{Thickness}$	Young's modulus E, 10^9 dyn/cm²
17.3	0.0121	1 430	11.6
36.5	0.0101	3 610	25.4
64.3	0.0090	7 120	39.5
20.3	0.0130	1 560	10.6
48.4	0.0122	3 960	23.9
69.6	0.0102	6 840	36.6
7.18	0.0166	433	3.6
16.0	0.0147	1 090	11.3
18.2	0.0146	1 250	10.2
21.2	0.0129	1 632	12.1
27.2	0.0124	2 190	14.9
26.7	0.0143	1 870	12.6
24.8	0.0171	1 450	10.7

The value A in Table 1 is proportional to the breaking stress. A plot of $\log A/\log E$ was made and the slope of the line was found to be 1.225 instead of $\frac{1}{2}$ demanded by Griffith's crack theory.

Another source of accurate data is the work by Andersson and Berkyto.[10] These workers determined the stress/strain characteristics of a very large number of samples. They found a correlation giving the breaking strength and Young's modulus at different temperatures. Table 2 gives their results for 0°C.

TABLE 2

Paper	Young's modulus (arbitrary units)	Breaking 'stress' (arbitrary units)
Newsprint		
Machine-direction ..	3.59	2.34
Cross-direction ..	1.41	1.23
Kraft		
Machine-direction ..	6.36	6.56
Cross-direction ..	3.27	3.04

A plot of these values on logarithmic scale shows the inevitable scatter, but the slope is 1.2—a surprisingly close value to that determined from Higgins' results.

Thus, it may be concluded that most probably Griffith's crack theory does *not* apply to paper and an alternative approach should be made. This conclusion, though negative, is not without merit; it encourages us to *look* into other directions.

What then shall we say of the *qualitative* agreement between the predictions of this theory and paper behaviour? Griffith's crack theory is not unique in giving these qualitative predictions. Any theory based on the weakest link concept would give the same results. As summarised and co-ordinated by Epstein,[11] the work of several workers over the years has produced a number of statistical theories of fracture all yielding results that show a decrease of breaking stress with increase of sample size, with a decrease in loading rate, with humidity, etc. Thus, these qualitative predictions are not enough to explain the inner mechanism; what is required is quantitative congruence between theory and observation. Thus, we find that the route to the understanding of the inner adhesion of paper via macroscopic and statistical considerations alone, which has proved successful for other materials, is particularly thorny for arriving at definite quantitative conclusions for paper. Coleman's[12] treatment of the creep failure of polymeric filaments by the theory of absolute reaction rates and Cumberbirch and Mack's[13] theory of the tenacity and breaking extension of wet, regenerated cellulose monofilaments should be mentioned here as other types of approach; these, too, unfortunately, do not apply to paper.

Let us then take the other and usually more difficult route—that is, let us look at the forces between the molecules of cellulose to see if we can deduce useful conclusions. Fortunately, this proves more useful, because of a very special feature of paper. Completely wet paper has very little adhesion to speak of; as it dries, fibres adhere together more tenaciously through hydrogen bonding. Can we idealise the situation by saying that, to a first approximation, *only* the hydrogen bonds contribute to the adhesion between fibres? Clearly, this is a gross oversimplification; but, if we can make it, we may have some hope of getting a glimmer of light on our subject. The critical experiments in the Australian laboratories of C.S.I.R.O. performed by Higgins and his colleagues[9] suggest that we may indeed do so. Higgins and Nissan[1] found a unique relationship between the loss of rupture energy of the paper so produced and the degree of substitution of the hydroxyl groups. Thus, by preventing hydrogen bonding, the rupture energy of the paper was systematically destroyed. What is more conclusive is that a theory based on

the assumption that, to a first approximation, the hydrogen bond was the sole agent of adhesion, predicted a relationship between the rupture energy and the cube of Young's modulus, that is, E^3. This prediction was validated.[14] Thus, it will be instructive to look at this particular bond. Our task will be to combine what we learn from this bond with the fact that a statistical treatment does predict correctly paper behaviour.

The hydrogen bond

THE hydrogen bond is only one of several types of bond that bind atoms together to give molecules or to cause molecules to adhere to one another. As Bernal[20] shows, however, there are three attractive energies that control most of the properties and particularly the mechanical properties of macromolecules. The strongest of these represents the homopolar bonds between the atoms constituting the molecule. They are formed by two atoms sharing an electron. They vary in strength, but are generally greater than, say, 60 kcal/mol. Equilibrium distances between the atoms joined by such energies are small; from less than, say, 1 Å unit (10^{-8} cm) to not more than 2 Å. The high energies of covalent bonds are responsible for the atoms of the cellulose chain holding their places with respect to one another. Only when chains of macromolecules like cellulose are cross-linked to other chains by side-chains through covalent bonds (or the weaker ionic bonds of 10 to 20 kcal/mol) do such bonds contribute to the 'adhesion' of chains to one another. This happens, for example, in branched chains of hemicelluloses and of starches, which can give a three-dimensional network, probably in lignin-cellulose junctions in native fibres and in artificially substituting reactive side chains for some of the hydroxyl groups on the cellulose. Pure cellulose has no side chains.

The second type is the attractive energy of the hydrogen bond. These bonds are formed by two electronegative atoms like oxygen sharing a proton. They are much weaker—only 4.5 kcal/mol in cellulose—than the electron-sharing homopolar bonds, but their significance to polymer structures and properties cannot be overemphasised. Probably, the evolution of the whole of living matter in all of its infinite variations on this planet was controlled and directed by this bond to at least as great an extent as by any other single factor. Its origin and main features may be studied in Pauling's[15] book, while details of its physical and chemical manifestations may be followed in the excellent book by Pimentel and McClellan.[16] The strength of this bond varies from less than 1 kcal/mol up to some 10 kcal/mol depending on the nature of the atoms that the hydrogen is bridging and on the presence

of other atoms or groups nearby. Similarly, the equilibrium distances between the atoms that are bonded by the intermediate hydrogen range about 2.4–3.5 Å; the smaller distances are associated with larger energies. In cellulose, the mean energy value is 4.5 kcal/mol and the distance between the centres of the oxygen atoms of the O - - - H–O structure is approximately 2.7 Å.

The third and weakest attractive energies are the ubiquitous van der Waals' energies, which bind all types of molecule together. They are rarely more than 1 or 2 kcal/mol and they act at distances of 3–5 Å. They contribute to the energy of cohesion even when such 'inert' groups as CH_2 and CH_3 come together. Thus, they contribute to the cohesion between elements of the cellulose chain molecules that come sufficiently near each other even when all other types of bonds are absent.

Thus, the hydrogen bonds are intermediate in strength between the strong covalent bonds and the secondary weak van der Waals' bonds. It is important also to realise that they do not have a single value. The hydrogen bonds joining OH groups in primary alcohols are between 5 and 6 kcal/mol, whereas those connecting carboxylic acids of similar molecular weights are between 7 and 8. This finds its counterpart in paper. Oxidised cellulose will yield stronger (though more brittle) paper.

There is conclusive evidence that in dry cellulose there are no free hydroxyl groups. [See, for example, Marinan and Mann.[17]] When water enters cellulose it breaks some of the bonds; but, since it attaches itself to cellulose through hydrogen bonds, there will still be no free hydroxyl groups; all groups are linked to each other or to water.

Bearing in mind the structure of cellulose—a polymer of cellobiose with two primary OH and four secondary OH groups to each unit—the following may be visualised as a simplified and idealised picture. The molecules, being very long and slender (length to 'diameter' ratio exceeding 1 000), are flexible. Certain segments will form crystallites through hydrogen bonds. These crystallites are rigid and strong rodlets. The reason for this great strength and rigidity lies in their perfection. To remove one molecule from them, the energy required is the sum total of the whole number of hydrogen bonds connecting this molecule to the crystallite times the strength of a hydrogen bond. This is clearly the case if they were all to be broken together. What is unexpected, but still true, is that, even if the molecule were to be peeled off by breaking the bonds *sequentially*, Longuet-Higgins[18] has shown from thermodynamics that it would still be necessary to supply at once the total energy required by *all* the bonds being broken. This situation, by a strange combination of circumstances, only applies in full to bonds with

energies equal to those of hydrogen bonds. The unique contributions of hydrogen bonds to cellulose adhesion would have merited study for this single fact alone: because of the relatively low energy of the hydrogen bonds, the crystallite can be formed from deposition of cellulose in the water medium of plant and animal cells at ordinary temperature; once having formed a crystallite, these same bonds will resist the attack of mechanical or even chemical forces to disrupt them. However, their contribution to the amorphous region is equally worthy of detailed study.

The segments of the molecules that are not aligned strictly parallel with each other are still hydrogen-bonded. They do not have the restriction of the crystallites, which demands their simultaneous break (or the equivalent sequential rupture). Thus, they give cellulose its relative flexibility and yielding. By assuming the Morse function to apply to the hydrogen bond energy, Nissan[19] has formulated a theory that describes the stress/strain behaviour of cellulose at vanishing strains. It appears that, to a first approximation, the assumption that the hydrogen bond controls the mechanical behaviour of cellulose sheets is valid.

Fibre adhesion

IT is now necessary to synthesise our studies of fracture principles in general and of the hydrogen bond in particular in order to understand inter- and intra-fibre adhesion in paper. We have considered three facts —

1. A statistical approach to strength of paper correctly predicts its behaviour at rupture.

2. The almost universal Griffith crack theory does not apply to paper.

3. The mechanical properties of paper (and this implies the adhesion properties) depend in the first instance on the hydrogen bond.

Thus, it appears that the statistical approach must be applied to the hydrogen bond. There is a clue in the fact that, whilst a hydrogen bond in cellulose has a mean value of 4.5 kcal/mol, there is a variance around this mean. Thus, by assuming a statistical distribution for the bond energy, Nissan[19] has propounded a theory of strength that appears to fit the facts. In brief, this theory postulates that all connections for cellulosic fibres (both inter- and intra-fibre bonds) are made through the hydrogen bond. These bonds appear to have a variance of about 15 per cent of the mean. Thus, when paper is stressed, the weakest of these bonds break. When the sample fails, the total rupture energy so consumed is only a fraction of the total possible, if all bonds were of uniform strength. This ratio—called the

efficiency of loading to rupture—is less for stronger papers than for weak ones and less also for larger than for small samples.

Further estimates are made that show that for weak papers van der Waals' bonds may contribute an appreciable proportion of the rupture energy. Even for strong paper, their contribution is not strictly negligible.

Conclusion

THE adhesion of cellulosic fibres invokes the forces that bind atoms together. Whilst a great deal is yet to be learnt, combining statistical techniques found useful in elucidating fracture of gross bodies with the laws of atomic and molecular physics promises to provide the means for understanding this difficult subject.

Acknowledgement

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DISCUSSION

PROF. B. G. RÅNBY: You say that the strength of the materials here were related to secondary forces, not to primary valency forces—can you qualify this statement? Does this relate to the tensile strength when the material breaks or only to the modulus on extending up to the limit of elastic deformation? Which one?

How would you explain that fibres break when the paper is strained so far that the sheet ruptures? How could these fibres break without breaking many cellulose chains—that is, without breaking many primary valency bonds?

PROF. A. H. NISSAN: In common with other polymers (except those forming rigid 3-dimensional networks by covalent cross-links at close intervals), I think the mechanical properties are due basically to secondary bonds. You are asking me how do I explain that fibres break without breaking primary bonds: I believe that it is breaking mostly secondary bonds, unless you have evidence to show that, for example, the molecular weight of the cellulose is reduced by breaking the fibre. The important point is this: if you assume a system in which you ascribe the ruptured energy to the number of secondary bonds that you calculate by this method times the energy per bond (that is, 4·5 kcal/mol), it gives you a figure that is reasonable. Of course, this does not prove that the assumptions are right, but it is in line with that and, until evidence is against it, one accepts it. Other strong evidence is given by Fig. 3 for my joint paper with Sternstein (p. 333).

MR. H. G. HIGGINS: With reference to the first question, it is of interest that the tensile strength of wood fibres is related to the angle of microfibrillar orientation in the layer S2: this has been shown by Wardrop. With a flatter spiral, the secondary forces between the microfibrils would presumably participate to a greater extent in rupture than they would in the case of a steeper spiral. Failure between microfibrils would lead to stress concentrations on the covalent bond structure.

PROF. NISSAN: Cumberbirch and Mack of the Shirley Institute have a theory of tensile strength of wet regenerated cellulose. They go to one extreme: the cellulose is wetted so that the hydrogen bond effect can be reduced as much as possible. At the other extreme of completely dry paper or cellulose,

it would be material mostly controlled by secondary bonds. You can move from one to the other and you modify the theory in accordance with observations.

PROF. RÅNBY: We know that very large amounts of energy are involved in the drying and wetting of cellulose and I believe, though I do not know, that most of the energy is really involved in the breaking of hydrogen bonds; some primary valency bonds are broken, too. As a piece of evidence, I mention the following experiments. By repeatedly wetting and drying cellulose, just ordinary filter paper, Dr. Fred Smith has shown that you do break primary valency bonds every time you wet and dry. The evidence is that, in the cyclic wetting and drying, lower molecular weight material is formed and can be isolated. These low molecular weight compounds are presumably broken off the cellulose fibres in the sheets. In addition, Sharples has shown that the repeated wetting and drying of cellulose give such forces by inner tension that easily hydrolysed acetal bonds ('weak links') are formed. We should be grateful for the beautiful work Nissan has described, but, of course, we would like to know the whole story, certainly not entirely exclude the rather obvious possibility that there is a high proportion of chain breaks when a cellulose structure is strained.

DR. F. L. HUDSON: With regard to Nissan's statement that van der Waals' forces act at distances of 3–5 Å, it is known that the potential between two *molecules* due to dispersion forces varies inversely as the sixth power of the distance between them and the force inversely as the seventh power. It has often been assumed that the forces between particles and between fibres behave in the same way. According, however, to Verwey and Overbeek,[1] if one considers two large parallel plates (which, in the case of fibres, may be regarded as infinite in width and thickness), the potential varies only inversely as the *square* of the distance between the plates. In order to explain colloidal behaviour, these authors consider that dispersion forces must act over much greater distances than 5 Å. The affinity of direct dyestuffs for cellulose may now be better explained by van der Waals' force than by hydrogen bonds[2] and this suggests that they might be considered more than they are at present in the theory of paper bonding.

PROF. NISSAN: I think any impression we might have of exclusiveness must be wrong—that is to say, any impression that, in rupture, only van der

[1] *Theory of the Stability of Lyophobic Colloids* (Elsevier, 1948), chapter VI, 98 *et seq.*
[2] Peters, R. H., and A. N. Derbyshire, *J. Soc. Dyers Col.*, 1955, **71**, 530–536.

Waals' forces or only hydrogen bonds or only main chain forces are involved must inevitably be wrong: all these things do come in, they do apply. As a matter of fact, in the particular theory that my colleagues and I have developed, a correction is introduced for the influence of the covalent bonds. Even then, approximately 25 per cent (again it is an estimate) of the ruptured energy should be ascribed to van der Waals' forces. In other words, there are clearly contributions from both homopolar and van der Waals' bonds: however, they come into the results as second approximations.

This is quite often done. Start, say, with $PV = RT$ for a gas: true for a very narrow range. Then plot it for a wider range and you find PV is not equal to RT, so you improve the relationship by introducing other parameters. We are at the stage before improvement, so any idea that we have an exclusive system of bonds is wrong. The appearance of exclusiveness comes in, because the mathematical model would be too complicated to deal with, that is all.

There is one thing I want to stress: until experiments—and only experiments, not what we think nor what we would like to have—show that the graph Higgins and I have published is wrong (showing that the percentage loss in ruptured energy and the percentage loss in E^3 are simple functions of the loss of hydrogen bonds*), then we have to accept the postulates of the theory that predicted these facts. There it is—a fact you cannot get away from. There is a spread in the plot, however, which shows our ignorance of other factors coming in. There are many important things in this graph—for example, the ruptured energy dies away to zero when only some 20 per cent of the hydrogen bonds have been blocked. Obviously, the picture is more complicated than our limited theory would allow us to see now. I hope I am giving a balanced view, but it looks to me as if the hydrogen bond, until the picture given by Higgins' critical experiment is disproved experimentally, is the primary independent variable.

PROF. B. STEENBERG: Is not your statement that there is a spread in the energy of the hydrogen bond around the 4·5 figure precisely a summing up of the question, not knowing exactly what the spread is? It may be all the way up into the bond and it may be all the way down into the van der Waals' region. It is only by knowing the complete distribution curve that we really know the details. Until then, it is possible to say that the chance of it being around 4·5 (which happens to be in the hydrogen bond) is just pure luck. I think luck is on your side.

* *Nature*, 1959, **184** (4697), 1477–8, reproduced as Fig. 3 by Sternstein and Nissan, this vol., 333.

PROF. NISSAN: An attempt was made to calculate the standard deviation of the mean of the hydrogen bond energy that will cover up the ruptured energy for paper with moduli in excess of 2.5×10^{10} dyn/cm^2. The statistics are not mine; they were postulated on the basis of the weak link theory. If you apply the statistics to the chain, then a coefficient of variation of not less than perhaps 10 per cent and not more than 20 per cent of the mean bond energy will cover the range of experimental results. Although the hydrogen bond has a variance, if we allow three times the coefficient of variation as being reasonable limits, then this means that we are dealing with ± 60 per cent of 4 500—that is, say, ± 2 700 kcal/mol. That takes us down the upper end of the van der Waals' forces—from, say, 2 000 kcal/mol to perhaps 7 000 kcal/mol—but it does not take us to regions of ionic bonds (greater than, say, 15 000) or covalent bonds (greater than 60 000). This is indirect evidence, it is a statistical calculation; but it shows that we are working within a reasonably narrow range of energy levels. It becomes unreasonable to ascribe such concordance between theory and observation entirely to luck.