

# A MOLECULAR THEORY OF THE VISCO-ELASTICITY OF A THREE-DIMENSIONAL HYDROGEN-BONDED NETWORK

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## *Synopsis*

*A stress/strain law is derived for a hydrogen-bonded network that is isotropic for all strains. The calculus of variations is used in conjunction with the Principle of Least Work to obtain the distribution of strain among the hydrogen bonds of the system as a function of their orientation. In addition to unidirectional applied stress, the theory can be used to predict the effects of two- and three-dimensional tension. The solution for unidirectional strain is compared with a modified form of the original treatment of the theory by Nissan and experimental evidence is used to corroborate the postulate that these two solutions 'bracket' the stress/strain behaviour for anisotropic (oriented) systems.*

## ***Théorie moléculaire de la visco-élasticité d'un réseau tri-dimensionnel à ponts hydrogène***

*Une relation contrainte-déformation est donnée dans le cas d'un réseau à ponts hydrogène isotropique vis-à-vis de toutes les déformations. Le calcul des variations est utilisé en liaison avec le Principe du Moindre Travail pour établir la distribution des déformations parmi les ponts hydrogène du système en fonction de leur orientation. La théorie s'applique aux tensions unidirectionnelles et permet aussi de prévoir les effets des tensions bi- et tri-dimensionnelles.*

*La solution pour les déformations unidirectionnelles est comparée à une forme modifiée de la théorie initiale de Nissan. Les auteurs*

*prouvent expérimentalement que ces deux solutions servent chacune à expliquer en partie les relations effort-allongement des systèmes anisotropiques (c'est à dire, orientés).*

***Eine molekulare Theorie über die Viskoelastizität eines dreidimensionalen, durch Wasserstoffbrücken gebundenen Netzwerkes***

*Für ein durch Wasserstoffbrücken gebundenes Netzwerk, das für alle Dehnungsbeanspruchungen isotrop ist, wurde ein Spannungs/Dehnungsgesetz abgeleitet. Zur Beschreibung der Dehnungsbeanspruchungen auf die Wasserstoffbrücken des Systems als Funktion ihrer Orientierung wurde der Kalkül der Variationen zusammen mit dem Prinzip der geringsten Energie verwendet. Zusammen mit der in einer Richtung wirkenden Spannung kann die Theorie zur Voraussage der Wirkungen von zwei- und dreidimensionalen Zugbeanspruchungen herangezogen werden. Die Lösung für die in einer Richtung wirkenden Spannung wurde mit einer modifizierten Form der ursprünglichen Form der Theorie von Nissan verglichen und mit Hilfe experimenteller Beweise versucht, die Voraussetzung zu bestätigen, dass diese beiden Lösungen das Spannungs/Dehnungsverhalten von anisotropen (orientierten) Systemen vollständig beschreiben.*

***Introduction***

**P**APER consists of fibres bonded together at junctions that are loosely called 'bonded areas'. We wish to look deeper at these areas and see not only what constitutes the bonds, but in what way they are different from the bonded areas within the fibres that give coherence to the fibres themselves.

Looking microscopically at the bonded areas, we find a picture that repeats itself at each successive magnification. Firstly, large bundles of slender fibrillar elements appear to join at lower levels of dimensional measures and form smaller bonded areas, with spaces between these areas in which there is no bonding. Next, at a higher magnification, we find small single fibrils joined at still smaller bonded areas with empty spaces in between. Going to the electron microscope, we find these areas themselves consisting of still smaller bonded areas with empty spaces between microfibrils. Finally, we reach the molecular level, at which we still find long slender molecules of cellulose with bonded areas and non-bonded regions intervening. The bonded areas here are the hydrogen bonds interconnecting adjoining glucosidic groups.

In the process of increasing our magnifications, a significant absence of a distinction must not be allowed to escape our notice. At the level of the microfibril, we cannot tell whether we are looking at junctions *between* fibres or at those *within* fibres. Thus, for our purposes, we shall not distinguish between *inter-* and *intra-*fibre 'bonds'. (For other macroscopic purposes, there is a very distinct difference between these two types of junction.) Furthermore, to give clarity and precision to the present discussion, we shall use the words *bonds* and *bonded areas* only at the molecular level and refer to the hydrogen bonds acting between cellulosic molecules. Paper is not made entirely of cellulose, but we shall simplify our model by assuming it to be made of a network of cellulose—or other equivalent hydrogen-bonded molecules—joined together by randomly oriented, uniformly distributed hydrogen bonds.

Extension of cellulosic and other hydrogen-bonded materials is resisted by forces arising from several microscopic deformations that are conveniently classified as—(1) intermolecular deformation and (2) intramolecular deformation. The intramolecular forces are caused by bond angle deformation, straining of covalent bonds and changes in the statistical configuration of the cellulose chains. This last effect is a direct consequence of the ability of adjacent glucose units to rotate about the glucosidic link. The intermolecular forces arise from the separation of macromolecules that are joined by covalent links, ionic bonds, hydrogen bonds and van der Waals' forces.

Owing to the abundance of hydrogen bonds in cellulosic materials, the glucose units are effectively prohibited from rotating about the glucosidic links; however, wet cellulose should be capable of such rotations, since the intermolecular hydrogen bonds within the amorphous regions are destroyed by the adsorption of water on the sites capable of forming hydrogen bonds between molecules. It is plausible to expect wet cellulose to exhibit mechanical properties that are of a rubber type (or entropy) origin. Thus, it may be expected that completely wet cellulose may follow a set of laws regulating its mechanical properties different from those controlling the properties of dry cellulose. The tenacity of wet, regenerated cellulose has been considered from the entropy viewpoint by Cumberbirch and Mack,<sup>(1)</sup> who assumed the hydrogen-bond contributions to be of little consequence in the completely wet state.

We, on the other hand, consider the other extreme condition and postulate that rotational (or backbone) effects in *dry* cellulose can be neglected when compared to the weaker, more extensible hydrogen bonds, which tend to prohibit rotation. The two views are not contradictory; they are complementary. For small strains, the covalent bond, having a decomposition energy of about 100 kcal/mol, can be considered inextensible compared with

the hydrogen bond, which has a decomposition energy of about 5 kcal/mol. Thus, to a first approximation, small extensions in dry cellulose can be considered as arising from hydrogen-bond deformations with negligible covalent, rotational or van der Waals' effects. Presumably, at high relative humidities, cellulose will exhibit a complex behaviour subject to the combined actions of both entropy and hydrogen-bond effects.

As stated, no distinction will be made between intra- and interfibre hydrogen bonds, which is doubtless a simplification of the macroscopic structure; however, such an assumption is not as restrictive as it might at first appear to be. In the theory to be presented, it will be shown that the visco-elastic properties of hydrogen-bonded materials can be predicted and correlated by the results derived from the simplified model, after having defined suitably an equivalent structure for the material in question. The results are found to be applicable to single fibres and to 'well-knit' multi-fibre materials, such as paper, possessing a Young's modulus exceeding  $2-3 \times 10^{10}$  dyn/cm<sup>2</sup>—that is, to any material capable of being represented by the molecular model used in the derivation; 'loosely knit' structures such as very weak papers could not be represented in such a manner.

To summarise, several of the visco-elastic properties of paper can be accounted for by the theory to be presented, which is based on a three-dimensional network of hydrogen bonds attached to approximately rigid rods of 'backbone' material. The theory contains several parameters that can be evaluated by other than mechanical measurements, thus reducing the final results to a one parameter problem. The phenomena of creep, relaxation and regain effects are suitably explained by combination of the theory with the laws of chemical kinetics; application of the theory to ice, for which all of the required molecular constants are known, predicts a modulus of elasticity in good agreement with the experimental value, thus giving additional confirmation to the model used.

### *Review*

BEFORE considering the three-dimensional theory, it will be instructive to review the one-dimensional hydrogen bond theory previously published by one of the authors.<sup>(2)</sup> It can be shown (*see* Appendix 1) that, for infinitesimal strains, an isotropic, randomly oriented network of hydrogen bonds is mathematically equivalent to one with one third the number of bonds oriented along each of three orthogonal, principal axes. Therefore, we shall consider a rectangular parallelepiped that is constructed from cubes of volume  $l^3$ , each cube containing three orthogonal hydrogen bonds oriented along the three principal axes of the body. The length  $l$  can be considered as

the *average* repeat distance for a hydrogen bond in any direction, since the body is assumed to be isotropic. Let us also assume that perpendicular bonds are independent of each other—that is, it is possible to strain a single hydrogen bond without deformation of the two orthogonal bonds in the same unit cube (the cube of volume  $l^3$ ). The Morse function will be chosen to represent the potential energy of a hydrogen bond, namely—

$$U = U_0[1 - \exp(-b)(r - r_e)]^2 \quad \dots \quad (1)$$

where  $U_0$  is the bond dissociation energy,  $r_e$  is the equilibrium bond separation and  $b$  is a constant derivable from spectroscopic data.

The force ( $F$ ) required to separate the hydrogen bond a distance  $r$  is given by—

$$F = dU/dr \quad \dots \quad (2a)$$

$$F = 2bU_0[1 - \exp(-b)(r - r_e)][\exp(-b)(r - r_e)] \quad \dots \quad (2b)$$

If the hydrogen bond is in series with an essentially rigid rod of length  $x_e$ , then it is possible to relate the total elongation of the unit cube to the deformation of the hydrogen bond—

$$\begin{aligned} l &= x_e + r_e \\ \Delta l &= \Delta x + \Delta r = (x - x_e) + (r - r_e) \\ F &= k_1 \Delta x = k_2 \Delta r \\ \Delta l &= (1 + k_2/k_1)\Delta r = k \Delta r \\ e &= \Delta l/l = k \Delta r/l = \text{strain} \quad \dots \quad (3) \end{aligned}$$

In deriving equation (3), it has been assumed that the force constants  $k_1$  and  $k_2$  of the nearly rigid rod and hydrogen bond, respectively, are constant. Clearly, this is inconsistent with a Morse function for the potential energy expression; however, if the hydrogen bond is highly extensible compared with the cellulose backbone, then  $k_1 > k_2$  and the value of  $k$  in equation (3) is nearly unity, with little error introduced by a small variation in  $k_2$  or  $k_1$  with strain.

The term  $(b)(r - r_e)$  in equation (2b) can be combined with equation (3) to give—

$$(b)(r - r_e) = b \Delta r = ale/r_0 \quad \dots \quad (4)$$

where

$$a = br_e \quad \dots \quad (4a)$$

$$r_0 = r_e(1 + k_2/k_1) = r_e k \quad \dots \quad (4b)$$

$$e = \Delta l/l = \text{strain} \quad \dots \quad (4c)$$

The constant  $a$  is a dimensionless Morse constant. The group  $ale/r_0$  also is dimensionless and will be referred to hereafter as the *strain number*. The force ( $F$ ), given by equation (2b), acts on an area  $l^2$ ; thus the normal stress

( $\sigma$ ) is  $F/l^2$ , which, when substituted in equation (2b) and with the use of equation (4), yields upon rearrangement—

$$\frac{Nr_e l^2 \sigma}{2a \Delta H} = [1 - \exp(-ale/r_0)] [\exp(-ale/r_0)] \quad \dots \quad (5)$$

where  $\Delta H = NU_0$  is the molar heat of dissociation for the hydrogen bond and  $N$  is Avogadro's number. The left side of equation (5) is dimensionless and will be referred to as the *stress number*. It is easily shown that the right side of equation (5) approaches  $(ale/r_0)$  for vanishing strain ( $e$ ), thus giving for the initial modulus of elasticity ( $E$ ) the value—

$$E = \lim_{e \rightarrow 0} (\sigma/e) = \frac{2a^2 \Delta H}{Nr_e r_0 l} \quad \dots \quad (5a)$$

Besides a minor change in nomenclature,\* equation (5a) differs slightly from the value of the initial modulus presented in the original derivation of this theory; the original derivation was based upon an assumption that the macroscopic body as well as the hydrogen bond obeyed the Morse function, whilst the derivation given here is based upon the assumption that only the hydrogen bond itself obeys the Morse function, a more justifiable assumption. The effect of this change is to replace the term  $r_0^2$  appearing in the original derivation by the term  $r_e r_0$  appearing in equation (5a), the difference being negligible if  $k_1$  of equation (4b) is large compared to  $k_2$ .

Equation (5) predicts a universal stress/strain curve for hydrogen-bonded materials, which is shown in Fig 1; the implications of equation (5) and its application to visco-elastic phenomena and humidity effects will be discussed after the derivation of the three-dimensional theory when equations of greater applicability and of more rigorous derivation will be substituted for equation (5).

Within the framework of our assumption that paper and other cellulosic materials, when in the dry state, are three-dimensional networks of hydrogen bonds with the major portion of all deformations occurring within these bonds, there are three serious limitations on the applicability of equation (5)—

1. The assumption of orthogonal, non-interacting sets of hydrogen bonds is true for infinitesimal strains; it may not be true for higher strains.
2. The isotropy of the macroscopic body.
3. The failure to account for possible reorientation of bonds during the straining process.

\* The reader will note two changes in nomenclature from that originally used by Nissan; the  $a$  in the original paper corresponds to the group  $al/r_0$  used here and the  $a_2$  of the original article corresponds to the  $a$  used here. The changes in nomenclature for stress, strain, force, etc. are obvious.

The first assumption shall be considered in the theory section of this paper, in which the orthogonal sets of non-interacting bonds will be replaced by a randomly distributed hydrogen-bond network with interaction (for example, induced contraction in directions transverse to the direction of strain) among the bonds. In addition to unidirectional strain, the derived

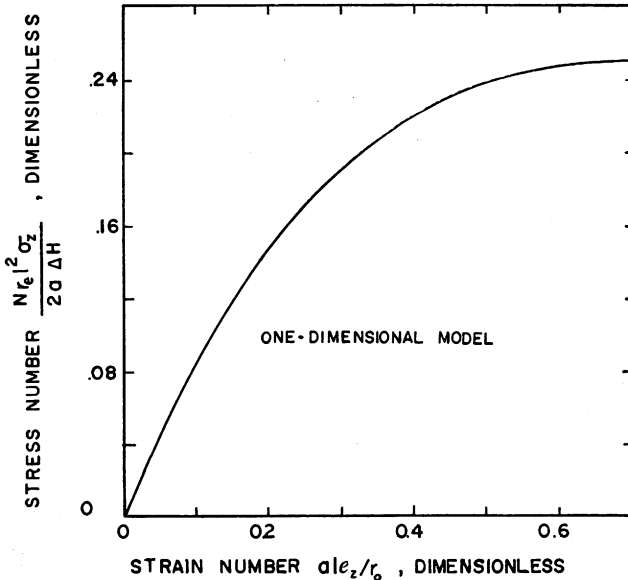


Fig. 1

equations are applicable to two- and three-dimensional tension and compression. Assumptions 2 and 3 are subjects for future investigation.

### Theory

In Appendix 2 is given a detailed derivation of the theory dealing with a three-dimensional network of hydrogen bonds. Here, a summary will be given delineating the main features of the theory; the mathematical equations derived in Appendix 2 will be explained, but not derived.

When a hydrogen-bonded material is stretched, it contracts along the axes transverse to the direction of elongation. It is logical to assume that a certain portion of the reversible strain energy required to elongate the sample is stored in hydrogen bonds, which are in compression owing to their orientation in the solid. Thus, the existence of a distribution of forces or the

corresponding extensions (positive and negative) that are due to various orientations of hydrogen bonds in the macroscopic body is to be expected on a phenomenological basis.

We shall assume, in this initial treatment of a three-dimensional, interacting hydrogen-bond network, that the hydrogen bonds are randomly oriented throughout the body and that the orientation of the bonds is maintained during the straining process. The fraction of the total number of hydrogen bonds in the system that exist at any arbitrarily chosen direction with respect to the three orthogonal axes that define the macroscopic body (a rectangular parallelepiped) is obtained, for convenience, in spherical coordinates. It is the invariance of this functional relationship for bond distribution with respect to strain that limits the theory to an isotropic, randomly oriented bond system.

The isotropic body is hypothetically subdivided into small cubes that contain, on the average, one randomly oriented hydrogen bond. The force acting on any particular hydrogen bond is then resolved into its components along the three body axes. These force components are summed with the aid of the bond distribution function and, with due consideration of equilibrium requirements, to obtain the normal stresses acting on the faces of the macroscopic body.

The problem is made tractable by performing the force summation on an 'unrestricted network' of hydrogen bonds; such a network is defined as one in which the force acting on any particular bond is solely a function of the bond's orientation in the macroscopic body for any given set of normal stresses acting on the body. The summation so obtained is related to what would be obtained on a 'restricted network' of hydrogen bonds by a co-ordination factor ( $\alpha$ ). A restricted network is defined as one in which the force acting on any particular hydrogen bond is a function both of the orientation of the bond being considered and of the bonds connected to it. The co-ordination factor is evaluated by comparison, at vanishing strain, with the earlier one-dimensional model proposed by Nissan and presented in the review section of this paper.

The energy stored in any particular bond is described by a potential function and the force acting on the bond by the space derivative of the potential function. Since the assumption has already been made that no reorientation occurs, we may choose a potential function that is only a function of the extension (or contraction) of the bond. As discussed in the introduction, we may, to a first approximation, consider all strain energy to be stored in the hydrogen bond. Thus, the potential function chosen must describe reasonably well the energy-extension characteristics of the hydrogen bond. We shall



find it instructive and useful to solve the problem for two specific potential functions, namely, the Morse function and a parabolic function.

The total strain energy stored in all hydrogen bonds of the system is obtained by summing, with the aid of the bond distribution function, the individual bond contributions. The integral equations obtained by the energy summation and the force summations, described earlier, form a *constrained minimum* problem, which can be solved by the calculus of variations. This may be demonstrated by considering the strain energy summation in greater detail. We have already hypothesised the existence of a distribution of forces (or strains) on a phenomenological basis. Thus, if we are describing the energy of an individual bond by a potential function that is a function of the extension (or compression) of the bond, it is possible to obtain the total strain energy stored in all hydrogen bonds of the system only after we have determined the variation of the extension of each hydrogen bond with its orientation in the body; however, it is to be expected that the extension of any particular hydrogen bond will vary also with the normal stresses applied to the macroscopic body. Furthermore, for a state of equilibrium to exist, the strain energy stored in the hydrogen bonds of the body should be a minimum—that is, the Principle of Least Work is applicable. Thus, the variation of extension (or compression) of the hydrogen bonds in the system with respect to their orientation must be such that it minimises the strain energy summation subject to the boundary conditions (or constraints) imposed upon this variation by the macroscopically applied normal stresses. The variation of strain with respect to orientation that minimises the strain energy will be referred to as an extremal and is obtained by solution of the Euler equation for the chosen potential function. The boundary conditions (that is, normal stress equations discussed earlier) are introduced into the solution by the use of Lagrange—or undetermined—multipliers.

In summary, the solution to the problem when a Morse function is used as the potential function for the hydrogen bond is as follows.

The boundary conditions, in stress number form, are—

$$\frac{Nr_e l^2 \sigma_x}{2a \Delta H} = \frac{2}{\pi} (3)^{2/3} \alpha \Gamma_x \dots \dots \dots (6)$$

$$\frac{Nr_e l^2 \sigma_y}{2a \Delta H} = \frac{2}{\pi} (3)^{2/3} \alpha \Gamma_y \dots \dots \dots (7)$$

$$\frac{Nr_e l^2 \sigma_z}{2a \Delta H} = \frac{2}{\pi} (3)^{2/3} \alpha \Gamma_z \dots \dots \dots (8)$$

where  $\Gamma_x = \int_0^{\pi/2} \int_0^{\pi/2} \frac{(\psi)(\psi-1)}{(1-2\psi)^2} \sin^2 \phi \cos \theta \, d\phi d\theta \dots (6a)$

$\Gamma_y = \int_0^{\pi/2} \int_0^{\pi/2} \frac{(\psi)(\psi-1)}{(1-2\psi)^2} \sin^2 \phi \sin \theta \, d\phi d\theta \dots (7a)$

$\Gamma_z = \int_0^{\pi/2} \int_0^{\pi/2} \frac{(\psi)(\psi-1)}{(1-2\psi)^2} \sin \phi \cos \phi \, d\phi d\theta \dots (8a)$

$\psi = \lambda_1 \sin \phi \cos \theta + \lambda_2 \sin \phi \sin \theta + \lambda_3 \cos \phi \dots (9)$

and  $\lambda_1, \lambda_2,$  and  $\lambda_3$  are Lagrange multipliers for the  $x, y$  and  $z$  directions, respectively. The symbols  $\phi$  and  $\theta$  are angles in the spherical co-ordinates used to describe the orientation of bonds in the macroscopic body and the other symbols have the same meaning as in the review section ( $\sigma$  still refers to normal stress and the subscripts  $x, y$  and  $z$  denote the axes of the rectangular parallelepiped along which the stresses act).

The total energy stored in the macroscopic body by the straining process ( $E_t$ ) is given by—

$$NE_t/n_t \Delta H = N\bar{E}/\Delta H = \frac{2}{\pi} \Gamma_E \dots (10)$$

where  $\Gamma_E = \int_0^{\pi/2} \int_0^{\pi/2} \left(\frac{\psi}{1-2\psi}\right)^2 \sin \phi \, d\phi d\theta \dots (10a)$

and  $n_t$  is the total number of effective hydrogen bonds in the system. The function ( $\psi$ ) is defined in equation (9).

We shall now consider the solution obtained for *unidirectional stress* in the  $z$  direction. We shall state without proof the fact that two stress numbers are equal if—and only if—the corresponding Lagrange multipliers are equal. Thus, it can be shown that for  $\lambda_1 = \lambda_2$  the numerical results given by equations (6) and (7) are equal regardless of the value of  $\lambda_3$ . Hence, for the unidirectional stress problem, we shall accordingly set  $\lambda_1 = \lambda_2$  and consider only equations (7) and (8). Using a trial and error procedure and a high speed computer, the parameter  $\lambda_1$  is determined as a function of  $\lambda_3$  such that any particular value of  $\lambda_1$  when used with the corresponding value of  $\lambda_3$  will reduce equation (7) and hence equation (6) to zero. Values of equations (8) and (10) are then tabulated as functions of  $\lambda_3$  by evaluating equations (8a) and (10a) only for those values of ( $\lambda_1, \lambda_3$ ) that reduce equation (7) to zero. For unidirectional tension in the  $z$  direction, the range of each parameter is found to be restricted as follows—

$$\lambda_3 < 0 \dots (11a)$$

$$0 < \lambda_1 < 0.35 \dots (11b)$$

A macroscopic energy balance leads to the following equation for the strain number—

$$\frac{al}{r_0} e_z = \frac{(3)^{1/3}}{2\alpha} \int_0^{\Gamma_E} \frac{d\Gamma_E}{\Gamma_z} \dots \dots \dots (12)$$

This equation is valid only for the unidirectional stress problem and can be evaluated graphically by use of the tabulated values obtained for equations (8) and (10). Thus, provided the co-ordination factor ( $\alpha$ ) can be evaluated, it is possible to calculate the stress number/strain number relationship for the unidirectional stress problem by the solution of equations (6–12), inclusive, as outlined above.

The co-ordination factor ( $\alpha$ ) is most accurately determined by obtaining the limiting forms of equations (8) and (12) as the strain on all hydrogen bonds in the system approaches zero. For infinitesimal strains, the hydrogen bond can be considered Hookean in nature, both for compression and extension. This leads to a parabolic potential function as the correct energy function to use for vanishing strains in a system that exhibits a stable equilibrium. We choose for the bond force constant the value  $2b^2U_0$  to correspond to the value predicted by the Morse function at vanishing strain. Thus, the potential function can be written as—

$$U(r) = b^2U_0(r - r_e)^2 \dots \dots \dots (13)$$

Solution of the Euler equation, using equation (13) in place of the Morse function, leads to the following equations in place of equations (8) and (12)—

$$\frac{Nr_e l^2 \sigma_z}{2a \Delta H} = -\frac{2}{\pi} (3)^{2/3} \alpha \lambda_3 C \dots \dots \dots (14)$$

$$\frac{al}{r_0} e_z = -\frac{(3)^{1/3}}{\alpha} \lambda_3 \dots \dots \dots (15)$$

where

$$C = \frac{(\pi - 2)(\pi + 4)}{6(\pi + 2)}$$

(The equations for zero stress in the  $x$  and  $y$  directions have been used to eliminate  $\lambda_1$  and  $\lambda_2$  from the solution.) Combining equations (14) and (15), we obtain—

$$\frac{\sigma_z}{Ee_z} = \frac{Nr_e r_0 l \sigma_z}{2a^2 \Delta H e_z} = \frac{2}{\pi} (3)^{1/3} C \alpha^2 \dots \dots \dots (16)$$

Equation (16) is valid at vanishing strains only, for which the Hookean approximation is valid. It is shown in Appendix 1 that the one-dimensional

model is correct for unidirectional, infinitesimal stress; thus, on comparing equations (16) and (5a), we obtain—

$$\frac{2}{\pi} (3)^{1/3} C\alpha^2 = \text{unity} \quad . . . . . (17)$$

or  $\alpha = 2.03 \quad . . . . . (17a)$

The use of this value of  $\alpha$ , obtained for vanishing strains, for finite strains implies the invariance of orientation of bonds with the state of strain. This assumption has already been explicitly stated and is therefore allowable. In real bodies, orientation does change at sufficiently high strains. The results of the stress number/strain number calculations are tabulated in Table 1 and

TABLE 1

| Strain number<br>$\frac{al}{r_0} e_z$ | Stress number<br>$\frac{Nr_e l^2 \sigma_z}{2a \Delta H}$ |                            |
|---------------------------------------|--|----------------------------|
|                                       | Three-dimen-<br>sional model                             | One-dimen-<br>sional model |
| 0                                     | 0  | 0                          |
| 0.05                                  | 0.046  | 0.046                      |
| 0.10                                  | 0.091  | 0.086                      |
| 0.15                                  | 0.132  | 0.120                      |
| 0.20                                  | 0.169  | 0.148                      |
| 0.25                                  | 0.204  | 0.172                      |
| 0.30                                  | 0.235  | 0.192                      |
| 0.40                                  | 0.292  | 0.221                      |
| 0.50                                  | 0.339  | 0.239                      |
| 0.60                                  | 0.378  | 0.248                      |
| 0.70                                  | 0.412  | 0.250                      |
| 0.80                                  | 0.441  | 0.247                      |
| 0.90                                  | 0.465  | 0.241                      |

plotted in Fig. 2 along with the one-dimensional results as predicted by equation (5). It is expected that these curves will describe the behaviour of real hydrogen-bonded solids at 'small' strains. At higher strains, orientation effects and the influence of covalent forces coming into play, as well as entropy contributions and the kinetics of bond breaking will all combine to cause increasing deviations between this theory and practice.

### Confrontation with experiment

THE effects of the various molecular constants on the initial modulus of elasticity are identical for the one- and three-dimensional theories, since

equations (16) and (5a) have been equated to evaluate the co-ordination factor ( $\alpha$ ). Thus, both theories indicate that the initial modulus of elasticity should vary with the cube root of the effective hydrogen bond density. The parameter  $l$  is defined in the one-dimensional model as the *average* repeat distance for a hydrogen bond. In the three-dimensional theory,  $l$  has a stoichiometric interpretation only. Thus,  $l^3$  is defined as the volume of the solid divided by one third the number of effective hydrogen bonds—that is, the volume occupied by three hydrogen bonds (the reciprocal of  $l^3$  is accordingly a hydrogen bond density); the orthogonality and non-interaction

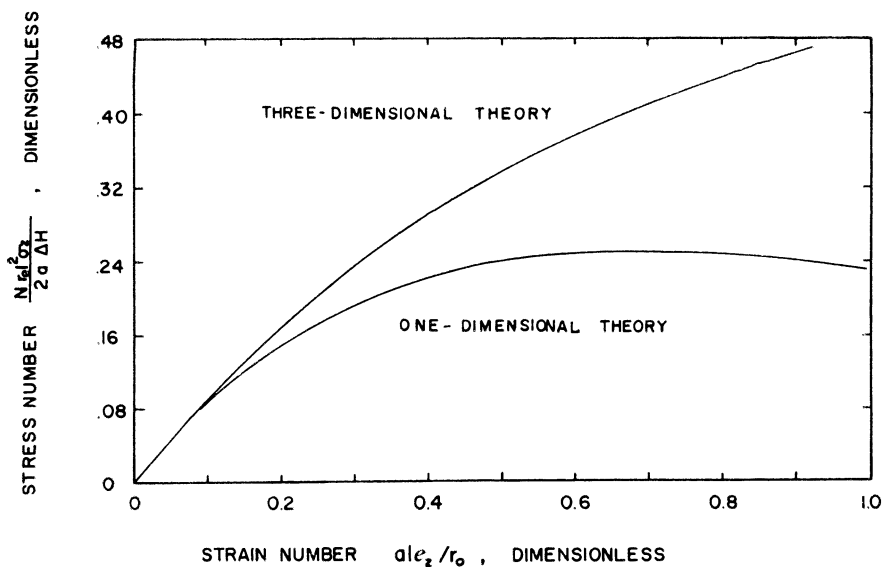


Fig. 2

conditions on these bonds have been *removed* in the three-dimensional derivation. The only difference in the results obtained by the two derivations is the stress number/strain number relationship indicated in Fig. 2. Thus, several of the experimental results cited by Nissan<sup>(2)</sup> as verification of the one-dimensional theory are applicable also to the three-dimensional theory—

1. Using equation (5a) or equation (16), we may calculate the modulus of elasticity ( $E$ ) for ice as  $1.5 \times 10^{11}$  dyn/cm<sup>2</sup>, if  $\Delta H = 4.5$  kcal/mol as given by Pauling<sup>(3)</sup> or  $1.1 \times 10^{11}$  dyn/cm<sup>2</sup>, if  $\Delta H = 3.4$  kcal/mol as given by Grunberg<sup>(11)</sup> and Nissan.<sup>(4)</sup> Experimental values fall in a narrow band around  $1.0 \times 10^{11}$  dyn/cm<sup>2</sup>.

2. By the use of further simplifying assumptions, it is shown that  $-d \ln E / dt$ , where  $t$  = temperature °C, should be between  $2.1 \times 10^{-3}$  and  $6.3 \times 10^{-3}$  for cellulose. Observations on paper yield average values of  $(2.0-2.6) \times 10^{-3}$  and on dry rayons of various types (4.43, 5.4, 3.0, 2.4 and  $1.8) \times 10^{-3}$ , respectively.

3. Taking into account previous observations on the interaction of water with dry cellulose, it is found that according to the theory, the effect of water adsorption by dry cellulose should be given by  $\log_e E_w / E_0 = -w$ , where  $E_w$  and  $E_0$  are the Young's moduli at water to solid ratios of  $w$  and 0, respectively. This relationship should hold until one third of the hydrogen bonds of the amorphous region are broken. Available data appear to support these predictions.

4. The effect of the beating process on the mechanical properties of cellulose sheets is suitably explained by the theory.<sup>(5)</sup> Thus, using equation (5a), the change in the number of hydrogen bonds (in the amorphous region) per cubic centimeter ( $\Delta n$ ) is related to the theoretical change in modulus ( $\Delta E$ ) by the equation  $\Delta n / (\Delta E)^3 = 2.92 \times 10^{-12}$ . The bonded area in sheets made from pulp beaten for various times was obtained by measurement of the coefficient of light scattering (Lars Nordman, Centrallaboratorium Ab., Helsinki, Finland, by private communication to Nissan). The moduli of elasticity of these sheets were measured and the number of hydrogen bonds per unit volume calculated from the optically measured bonded areas. Thus, an experimental value of  $\Delta n / (\Delta E)^3 = 3.08 \times 10^{-12}$  is obtained, which is in good agreement with the theoretical value. The theory explains the increase of modulus obtained when the pulp is beaten as a consequence of 1. rearrangement of bonds from within fibres to bonds between them and 2. an increase in the density of the amorphous regions, thereby increasing the effective hydrogen bond density in these regions.

5. A direct verification of the theory is obtained by investigating the effect of hydrogen-bond substitution on the modulus of elasticity ( $E$ ).<sup>(6)</sup> A cellulose pulp was acetylated to various extents and the moduli of the resultant sheets measured for various degrees of (OH) substitution. If  $E_0$  is the modulus for the virgin pulp, then equation (5a) predicts a unique relationship between  $100(1 - E/E_0)$  and the degree of substitution (owing to changes in  $l$ ). The lower curve of Fig. 3 indicates that in fact this is so; however, since  $l$  is proportional to the cube root of the hydrogen bond density, the relationship between  $100(1 - E^3/E_0^3)$  and degree of substitution is of primary interest. Half of the points on the upper curve of Fig. 3 represent a plot of these quantities.

The area under the stress/strain curve is the rupture energy (R.E.), which should be proportional, to a first approximation, to  $nU_0$ , where  $n$  is the number of effective hydrogen bonds per unit volume and  $U_0$  is the bond dissociation energy. Thus, a plot of  $100 [1 - \text{R.E.}/(\text{R.E.})_0]$  against degree of substitution should give the same curve as that given by  $100 (1 - E^3/E_0^3)$ . The other half of the points on the upper curve of Fig. 3 confirm this fact.

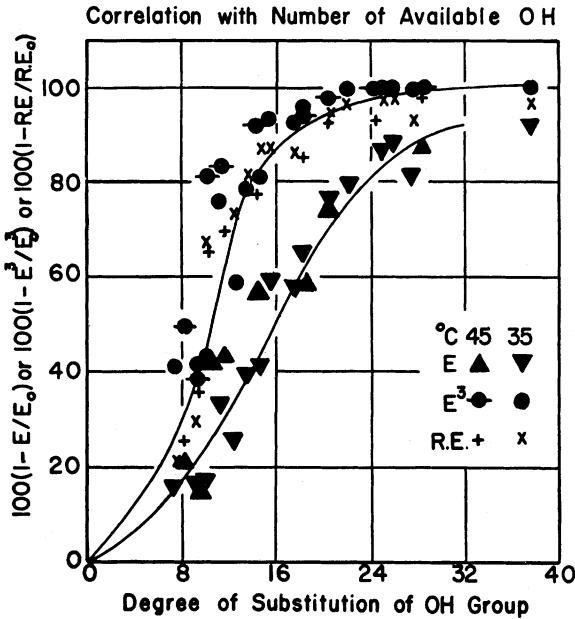


Fig. 3

The upper curve is not linear and this is probably due to the ‘opening up’ of the structure caused by the acetyl substitution, thus allowing additional hydrogen bonds to come into play. It will also be noted that not all chemically accessible OH groups are ‘effective’ mechanically.

We shall now investigate the validity of the stress/strain relationships predicted by both theories and plotted in Fig. 2 in dimensionless form. For convenience, we shall refer to the molecular constants appearing in the stress number as  $(I/A)$  and the constants appearing in the strain number as  $(B)$ ; thus—

$$\text{Stress number} = \frac{Nr_e l^2 \sigma_z}{2a \Delta H} = \frac{\sigma_z}{A} \dots \dots \dots (18)$$

$$\text{Strain number} = \frac{ale_z}{r_0} = Be_z \quad . \quad . \quad . \quad . \quad . \quad (19)$$

From equations (16) and (17), we find that the *initial* modulus of elasticity ( $E$ ) is given by—

$$E = \frac{2a^2 \Delta H}{Nr_e r_0 l} = AB \quad . \quad . \quad . \quad . \quad . \quad (20)$$

For paper, all of the molecular constants, except  $l$ , appearing in equations (18) and (19) are known from data on cellulose. However, we shall treat all molecular constants as unknowns and consider  $A$  and  $B$  as empirical constants, for reasons to be discussed below.

We shall consider the extensive and reliable data of Andersson and Berkyto,<sup>(7)</sup> already considered by Nissan<sup>(2)</sup> from a different point of view than that to be used in this paper. As a result of a large number of determinations, Andersson and Berkyto concluded that the following empirical equation correlated the data sufficiently well—

$$S = (C_1 + C_2 t)e' + (C_3 + C_4 t)(e')^2 \quad . \quad . \quad . \quad (21)$$

where  $S$  is load in kg,  $t$  is temperature °C and  $e'$  is percentage elongation. The constants ( $C$ ) are given in Table 2 for various types of paper.

TABLE 2

| Paper             | $C_1$ | $C_2$    | $C_3$  | $C_4$   |
|-------------------|-------|----------|--------|---------|
| Newsprint—        |       |          |        |         |
| Machine-direction | 3.59  | -0.0102  | -0.912 | 0.00278 |
| Cross-direction   | 1.41  | -0.00377 | -0.390 | 0.00139 |
| Kraft—            |       |          |        |         |
| Machine-direction | 6.36  | -0.0128  | -1.28  | 0.00291 |
| Cross-direction   | 3.27  | -0.00695 | -0.932 | 0.00158 |

Since the cross-sectional areas are not given, we shall indicate a method of treatment of the data that does not require an estimate of these areas. From equation (21), we note that the *initial* 'modulus' is given by—

$$E^* = (C_1 + C_2 t) \quad . \quad . \quad . \quad . \quad (22)$$

where  $E^*$  = modulus  $\times$  area.

We now assume a value of  $B$ , calculate  $A$  by use of equations (22) and (20) and transform equation (21) into dimensionless form by use of equations (18)



and (19). We note that the cross-sectional area is not required, since it is included in the value of  $A$ , calculated from  $B$  and equation (22). (For this purpose, equation (18) can be written as  $S/A$ , where  $S$  is load.) Various values of  $B$  are assumed until a 'best fit' to the three-dimensional curve of Fig. 2 is obtained. The points so calculated, for a temperature of 50°C, are plotted in Fig. 4. The values of  $B$  given in Fig. 4 are corrected by a factor of 100 so that they are consistent with equation (19) when  $e$  is strain (not percentage strain). We note that, for  $B=39$  and a Morse constant of  $a=2$ ,  $l/r_0$  is 19.5 and  $l$  is calculated to be 35Å, if  $r_0$  is taken as 1.8Å, approximately, for the hydrogen

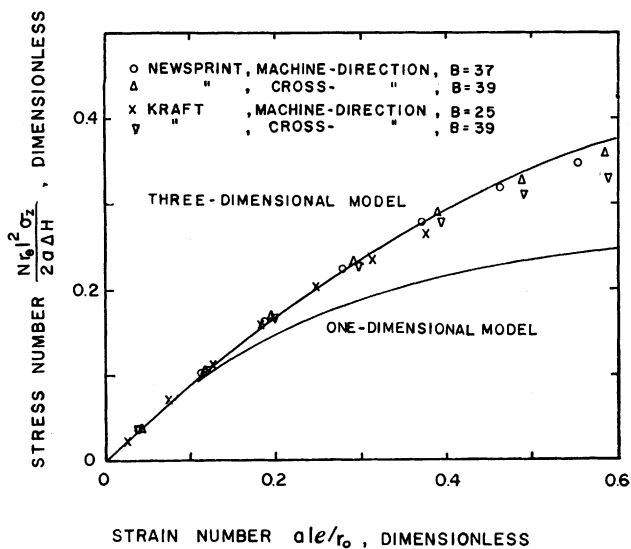


Fig. 4

bond in cellulose. This value of  $l$  is high when compared to the values calculated by Nissan<sup>(2)</sup> from the initial modulus and molecular parameters by use of equation (5a).

The above treatment does not allow a critical evaluation of the stress/strain laws predicted by the one- and three-dimensional models. By a suitable choice of  $B$ , the experimental points plotted in Fig. 4 could be shifted sufficiently so as to fall on the one-dimensional curve. A critical evaluation of the two models with actual stress/strain behaviour is to be found in the 'chord modulus' test. If we examine the ratio of stress number to strain number,  $(\sigma_z/A)/(Be_z)$ , we see that this ratio can be rearranged with the aid of equation (20) to give  $\sigma_z/Ee_z$ , where  $E$  is the initial modulus. This ratio is unity only when

the stress/strain curve is linear; for all stress/strain relationships, the group  $\sigma_z/Ee_z$  represents the ratio of the 'chord modulus'—that is, the ratio  $\sigma_z/e_z$ —to the *initial slope* modulus ( $E$ ). Using Fig. 2, it is possible to construct a plot of  $(1 - \sigma_z/Ee_z)$  against  $Be_z$ , and the results obtained for the one- and three-dimensional models are plotted in Fig. 5. For brevity, we shall refer to the presentation of data in the same form as Fig. 5 as a *chord modulus test*.

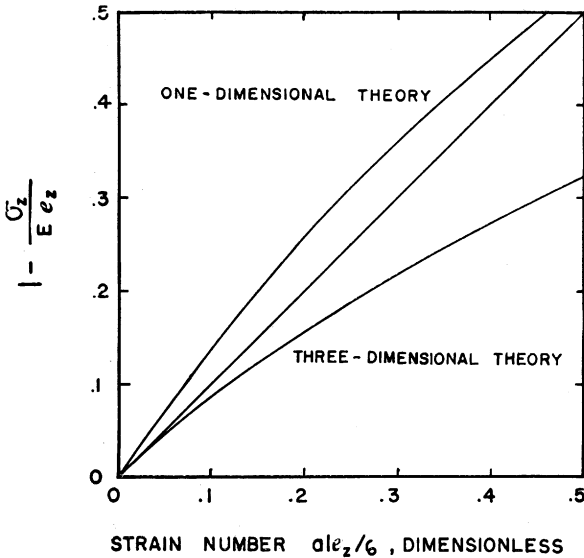


Fig. 5

Rearrangement of equation (21) yields the following equation—

$$(1 - S/E^*e') = -Be' \quad . . . . . (23)$$

where  $B = (C_3 + C_4)/(C_1 + C_2t)$ . Equation (23) is in chord modulus test form and is represented in Fig. 5 by a line of *unit slope*. Therefore, any second order stress/strain law, of the form indicated by equation (21), is represented by the unit slope line in Fig. 5. The one- and three-dimensional stress/strain laws bracket the empirical relationship proposed by Andersson and Berkyto when compared in chord modulus test form.

We postulate that this 'bracketing' effect is in reality a requirement of the one- and three-dimensional models when applied to non-isotropic materials. The one-dimensional model has been shown to be applicable to isotropic, randomly oriented bond systems at *vanishing* strains (see Appendix 1 and the

review section); however, within the framework of the proposed molecular behaviour for hydrogen-bonded materials, as given in the introduction, the one-dimensional theory is applicable at *all* strains to solids that have *complete* orientation of the bonds in the direction of strain. On the other hand, the three-dimensional model is strictly applicable to those systems that *remain* isotropic and randomly oriented throughout the strain cycle. Thus, the bracketing effect observed in Fig. 5 substantiates the validity of the one- and three-dimensional models as limiting cases. Real materials should always exhibit a behaviour that is bracketed by the two models, when compared by the chord modulus test. We conclude that the one- and three-dimensional models are valid representations of the behaviour of hydrogen-bonded systems and that these theories are compatible and complementary.

### *Extension of the theory*

THE major contribution of the present theory is that it relates the mechanical behaviour of hydrogen-bonded solids to the effective number of such bonds per unit volume of material. The problem of visco-elasticity, according to this view, is then *not* a problem of separate viscous and elastic elements, but one of an integrated unit—that is, the hydrogen bond—that on reversible straining yields elastic parameters and on breaking and reforming exhibits ‘viscous’ or ‘flow’ characteristics. Thus, such flows as seen in ‘creep’, ‘relaxation’, ‘rheodestruction with humidity’ become amenable to study by classical methods of chemical kinetics.<sup>(2)</sup>

### *Acknowledgements*

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### REFERENCES

1. Cumberbirch, R. J. E. and Mack, C., *Shirley Inst. Memoirs*, 1960, **33** (4), 25–50
2. Nissan, A. H., *Trans. Faraday Soc.*, 1957, **53** (5), 700–721
3. Pauling, *The Nature of the Chemical Bond* (Cornell, 1940)
4. Grunberg, L. and Nissan, A. H., *Trans. Faraday Soc.*, 1949, **45** (2), 125–137
5. Nissan, A. H., *Tappi*, 1958, **41** (3), 131–134
6. Nissan, A. H. and Higgins, H. G., *Nature*, 1959, **184** (4697), 1477–1478
7. Andersson, O. and Berkyto, E., *Svensk Papperstidn.*, 1951, **54** (13), 437–444
8. Courant, *Calculus of Variations* (N.Y. Univ. Inst. of Math. Sciences, 1957)
9. Bliss, *Lectures on the Calculus of Variations* (Univ. of Chicago Press, 1945)
10. Forsythe (1926), *Calculus of Variations* (Dover Publications, New York, 1960)

### Appendix 1

CONSIDER a randomly distributed hydrogen bond system subjected to an infinitesimal normal stress ( $f_x$ ) on one of the rectangular faces of the macroscopic body, which is taken to be a rectangular parallelepiped for convenience. Since we are considering the limiting case of infinitesimal stress and strain, the hydrogen bonds shall be considered Hookean in their behaviour, an assumption that is consistent with the Morse function at vanishing strain. Owing to

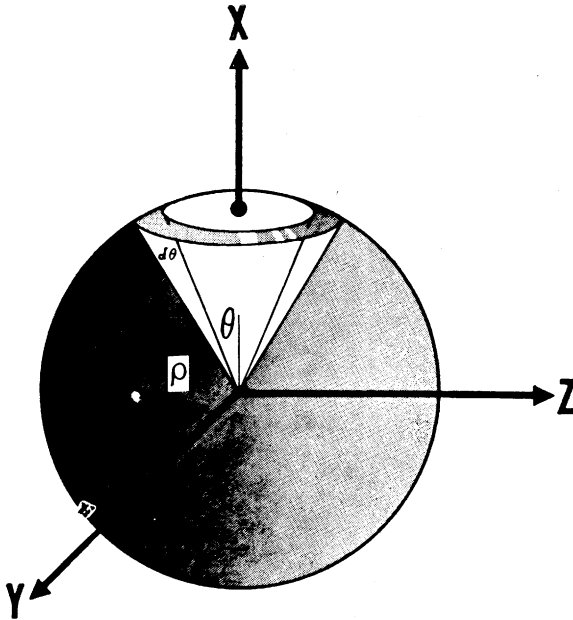


Fig. 6

our assumption of isotropy, the hydrogen bond distribution is a spherical surface. Consider the number of bonds oriented at the angle  $\theta$  taken with respect to the  $x$  axis (the direction in which the external stress is applied). The number of bonds ( $dn$ ) at the angle  $\theta$  contained within a circular hoop, of radius  $\rho$  (see Fig. 6), having the  $x$  axis as the central normal to the plane of the hoop, is given by—

$$\frac{dn}{n} = \frac{(2\pi\rho \sin \theta)\rho d\theta}{4\pi\rho^2} = \frac{\sin \theta d\theta}{2} \quad \dots \dots (I-1)$$

where  $n_t$  is the total number of effective hydrogen bonds in the system. It is easily shown that equation (I-1) is normalised, that is—

$$\frac{1}{n_t} \int_0^{n_t} dn = \frac{n_t}{n_t} = 1 = 2 \int_0^{\pi/2} \frac{\sin \theta d\theta}{2} = 1.$$

The factor 2 was introduced in the above equation to account for the fact that there are eight identical octants given by the distribution function equation (I-1) and only four of these octants are accounted for by integrating from 0 to  $\pi/2$ .

The stress on a bond at angle  $\theta$  is given by  $f_x \cos \theta$ , that is, the projection of  $f_x$  on the bond's line of action. The bond is assumed to be irrotational, hence allowing us to neglect the bending force ( $f_x \sin \theta$ ). The energy stored in the bond due to elongation is given by—

$$U = \frac{1}{2} \cdot \frac{(f_x \cos \theta)^2}{k'} \quad \dots \dots \dots (I-2)$$

where  $k'$  is the Hookean force constant for a hydrogen bond. The total energy stored in all bonds contained within the circular hoop is given by—

$$U_\theta = U dn$$

or

$$U_\theta = \frac{n_t}{2} \cdot \frac{(f_x \cos \theta)^2 \sin \theta d\theta}{k' \cdot 2} \quad \dots \dots \dots (I-3)$$

The total energy stored in all bonds is obtained by integrating equation (I-3) from 0 to  $\pi/2$  and multiplying the resultant integral by 2 (for the same reason stated earlier)—

$$U_t = \frac{n_t}{2} \cdot \frac{(f_x)^2}{k'} \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta$$

or

$$U_t = \frac{n_t}{6} \cdot \frac{(f_x)^2}{k'} \quad \dots \dots \dots (I-4)$$

Now consider a system with  $n'$  hydrogen bonds all oriented along the  $x$  axis. If the system is subjected to the stress  $f_x$ , then the energy stored in the system is given by—

$$U'_t = \frac{n'(f_x)^2}{2k'} \quad \dots \dots \dots (I-5)$$

However, both models are being used to describe the same system, hence  $U'_t = U_t$ , so we obtain, on equating equation (I-5) to equation (I-4), the following result—

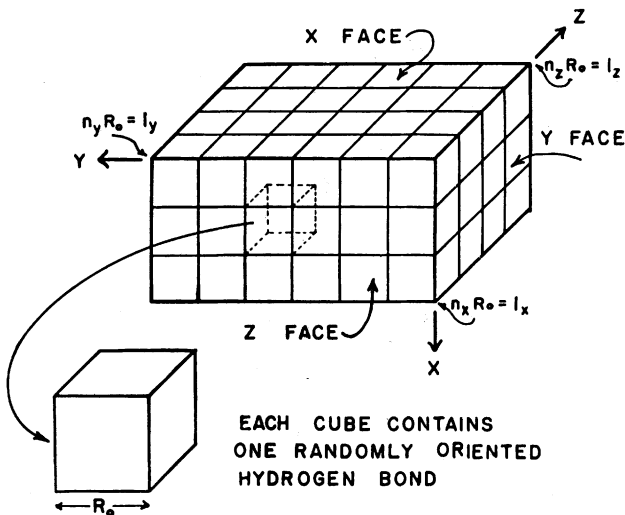
$$n' = n/3 \quad \text{Q.E.D.} \quad \dots \dots \dots (I-6)$$

**Appendix 2**

LET the macroscopic body be a rectangular parallelepiped of dimensions  $l_x$ ,  $l_y$  and  $l_z$  and let the body contain  $n_t$  randomly oriented effective hydrogen bonds that are attached to essentially rigid rods of backbone material as discussed in the introduction. If  $V$  is the volume of the body and  $R_0^3$  is defined as the *average* volume occupied by a single, randomly oriented hydrogen bond, then—

$$l_x l_y l_z = V = n_t R_0^3 \quad \dots \quad (II-1)$$

If we now consider  $n_x$ ,  $n_y$ , and  $n_z$  to be the number of unit cubes (cubes of side  $R_0$ , which contain a single hydrogen bond) bordering along the  $x$ ,  $y$  and  $z$



*Fig. 7*

axes, respectively, which define the macroscopic body (refer to Fig. 7), then we may write—

$$l_x = n_x R_0, \quad l_y = n_y R_0, \quad l_z = n_z R_0$$

$$V = l_x l_y l_z = n_x n_y n_z R_0^3 = n_t R_0^3$$

Therefore,  $n_t = n_x n_y n_z \quad \dots \quad (II-2)$

The hydrogen bond in any unit cube may have any particular orientation with respect to the axes  $x$ ,  $y$  and  $z$ , but the macroscopic body is assumed to be

sufficiently large so that all bonds taken together will form a random array with respect to orientation, thus forming an isotropic body. In the derivation that follows, it will be assumed that no reorientation occurs, that is, all bonds maintain their orientation in space before and after straining. The orientation of each hydrogen bond will be described by spherical co-ordinates (see Fig. 8) with respect to the axis system  $x$ ,  $y$  and  $z$ . Considering any bond in the system stretched (or compressed) to some length  $r$  by a force  $F$ , we obtain for the components of the force  $F$  along each of the co-ordinate axes  $x$ ,  $y$  and  $z$  the values—

$$F_x = F \sin \phi \cos \theta \quad \dots \dots \dots (II-3a)$$

$$F_y = F \sin \phi \sin \theta \quad \dots \dots \dots (II-3b)$$

$$F_z = F \cos \phi \quad \dots \dots \dots (II-3c)$$

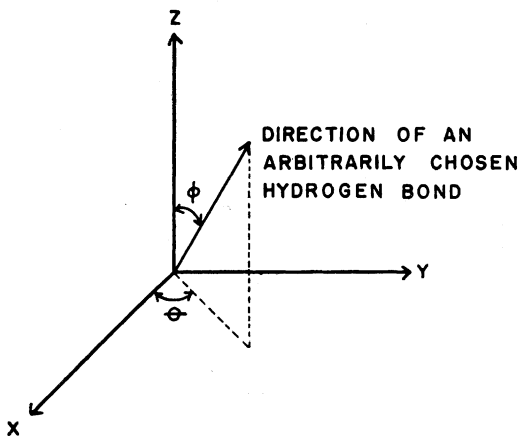


Fig. 8

Equation (2a) can be used in equations (II-3) to relate the force  $F$  to the derivative of the potential energy function  $U(r)$ —

$$F_x = \frac{dU}{dr} \sin \phi \cos \theta \quad \dots \dots \dots (II-4a)$$

$$F_y = \frac{dU}{dr} \sin \phi \sin \theta \quad \dots \dots \dots (II-4b)$$

$$F_z = \frac{dU}{dr} \cos \phi \quad \dots \dots \dots (II-4c)$$

The energy stored in the hydrogen bond is given by  $U(r)$ , since we shall assign a value of zero to the energy in the unstrained state, in accordance with equation (I)—

$$E' = U(r) \quad . \quad . \quad . \quad . \quad . \quad . \quad (II-5)$$

Let the length of a hydrogen bond and the essentially rigid rod to which it is attached be  $\rho$ . Since the bond distribution is isotropic, a spherical surface is the correct distribution to use when relating the number of bonds ( $dn$ ) at any orientation ( $\phi, \theta$ ) to the total number of bonds in the system ( $n_t$ )—

$$\frac{dn}{n_t} = \frac{(\rho \sin \phi d\theta)(\rho d\phi)}{4\pi\rho^2} = \frac{\sin \phi d\phi d\theta}{4\pi} \quad . \quad . \quad . \quad (II-6)$$

Equation (II-6) is strictly valid only for an isotropic system with no reorientation effects.

Referring to Fig. 7, we see that there are  $n_z$  slabs parallel to the  $xy$  plane, each slab containing  $n_x n_y$  cubes. Since these slabs are in equilibrium, the total force in the  $z$  direction must be the same for each slab. If equation (II-4c) is multiplied by  $dn$  from equation (II-6) and then integrated over all  $\phi$  and  $\theta$ , we would obtain the total  $z$  component of all hydrogen bonds in the system; however, the required normal force in the  $z$  direction is  $n_x n_y / n_t$  times the total summation, since there are  $n_z$  slabs in parallel. For convenience, we shall only consider  $\phi$  and  $\theta$  as varying from 0 to  $\pi/2$  and multiply the resultant integral by eight (8) to account for the eight identical octants that exist when the distribution function, equation (II-6), is considered for all  $\phi$  between 0 and  $\pi$  and all  $\theta$  between 0 and  $2\pi$ .

In combining equations (II-4c) and (II-6) according to the arguments presented above, it would be implicitly assumed that the force acting on a bond (or its elongation) is only a function of orientation, that is,  $F = F(\phi, \theta)$ ; however, there is another variable that influences the force exerted on any particular hydrogen bond, namely, the orientation of all the bonds connected to the hydrogen bond under consideration. We shall account for this effect by multiplying the force summation integral by a co-ordination factor ( $\alpha$ ), then consider the force ( $F$ ) to be only a function of orientation, that is,  $F = F(\phi, \theta)$ . Using the above arguments and equations (II-4c) and (II-6), we obtain for the normal force in the  $z$  direction ( $F'_z$ ) the equation—

$$F'_z = \frac{n_t}{4\pi} (8) \frac{n_x n_y}{n_t} \alpha \int_0^{\pi/2} \int_0^{\pi/2} \frac{dU(r)}{dr} \sin \phi \cos \phi d\phi d\theta. \quad (II-7)$$

The normal force ( $F'_z$ ) acts on a face of area ( $n_x n_y R_0^2$ ) and can be related to



the average normal stress ( $\sigma_z$ ) by the equation  $\sigma_z = F'_z/n_x n_y R_0^2$ , which can be substituted in equation (II-7) to yield, after rearrangement, the equation—

$$\frac{\pi}{2} R_0^2 \sigma_z = \alpha \int_0^{\pi/2} \int_0^{\pi/2} \frac{dU(r)}{dr} \sin \phi \cos \phi \, d\phi \, d\theta \quad \dots \quad (II-8c)$$

Similar equations can be derived for the  $x$  and  $y$  directions—

$$\frac{\pi}{2} R_0^2 \sigma_x = \alpha \int_0^{\pi/2} \int_0^{\pi/2} \frac{dU(r)}{dr} \sin^2 \phi \cos \theta \, d\phi \, d\theta \quad \dots \quad (II-8a)$$

$$\frac{\pi}{2} R_0^2 \sigma_y = \alpha \int_0^{\pi/2} \int_0^{\pi/2} \frac{dU(r)}{dr} \sin^2 \phi \sin \theta \, d\phi \, d\theta \quad \dots \quad (II-8b)$$

The assumption of isotropy allows us to use the same co-ordination factor ( $\alpha$ ) in each of equations (II-8).

The total strain energy ( $E_t$ ) stored in all the hydrogen bonds of the system is obtained by combining equations (II-5) and (II-6) and integrating over all bonds in the system, which yields, on rearrangement, the equation—

$$\frac{\pi}{2} \bar{E} = \int_0^{\pi/2} \int_0^{\pi/2} U(r) \sin \phi \, d\phi \, d\theta \quad \dots \quad (II-9)$$

where  $\bar{E} \equiv E_t/n_t$ . Equation (II-9) should be written with a co-ordination factor (say,  $\beta$ ) to be strictly correct; however, if the derivation is carried out with the term  $\beta$  included, it is found that only the factor ( $\alpha/\beta$ ) appears in the final result. Hence, we shall not use a co-ordination factor in equation (II-9) and we shall consider the factor  $\alpha$ , introduced in equations (II-8), already divided by the factor  $\beta$ .

To integrate equations (II-8) and (II-9), we must first choose a suitable expression for the representation of the potential energy of a hydrogen bond with strain; the Morse function, equation (I), will be quite adequate for this purpose. It is necessary to relate the extension (or compression) of a hydrogen bond—that is,  $r$ —to the orientation of the hydrogen bond within the body, namely, as a function of  $\phi$  and  $\theta$ . We shall now consider the macroscopic body to be loaded with a set of normal stresses, thus determining to within a factor  $R_0^2$  the left sides of equations (II-8), equations (II-8) being referred to as the boundary conditions. If the system is in equilibrium, it is reasonable to expect that the strain energy, given by equation (II-9), will be a minimum, subject to the given boundary conditions; hence, we must determine  $r = r(\phi, \theta)$  such that equation (II-9) is minimised—that is,  $r(\phi, \theta)$  must be an extremal that also satisfies the boundary conditions. This is a problem that is capable of solution by the calculus of variations and we shall accordingly make use of

the Euler condition, which must be satisfied if  $r(\phi, \theta)$  is to be an extremal (Courant,<sup>(8)</sup> Bliss,<sup>(9)</sup> Forsyth<sup>(10)</sup>). We note that the Euler equation is a necessary, but not sufficient, condition for the existence of an extremal and we shall rely on the physics of the problem, in the form of the Principle of Least Work, to ensure the existence of an extremal, that is,  $r(\phi, \theta)$ , which *minimises* the strain energy equation.

Denoting the integrands of equations (II-8a), (II-8b), (II-8c) and (II-9) by  $I_1, I_2, I_3$  and  $I$ , respectively, we have

$$I_1 = U'(r) \sin^2 \phi \cos \theta \quad \dots \dots \dots \quad (II-10a)$$

$$I_2 = U'(r) \sin^2 \phi \sin \theta \quad \dots \dots \dots \quad (II-10b)$$

$$I_3 = U'(r) \sin \phi \cos \phi \quad \dots \dots \dots \quad (II-10c)$$

$$I = U(r) \sin \phi \quad \dots \dots \dots \quad (II-10d)$$

The Euler condition for the extremal  $r(\phi, \theta)$  required to minimise equation (II-9), subject to the given restraints (that is, boundary conditions), is—

$$\frac{\partial M}{\partial r} = \frac{\partial}{\partial \theta} \cdot \frac{\partial M}{\partial r_\theta} + \frac{\partial}{\partial \phi} \cdot \frac{\partial M}{\partial r_\phi} \quad \dots \dots \dots \quad (II-11)$$

where

$$M \equiv I + \gamma_1 I_1 + \gamma_2 I_2 + \gamma_3 I_3 \quad \dots \dots \dots \quad (II-12)$$

and where  $r_\theta$  and  $r_\phi$  are the partial derivatives of  $r$  with respect to  $\theta$  and  $\phi$ , respectively; each to be considered as an independent variable in the variation of  $M$ —that is,  $M = M(\theta, \phi, r, r_\theta, r_\phi)$  and  $\gamma_1, \gamma_2$  and  $\gamma_3$  are Lagrange multipliers to be determined so that the boundary (restraining) conditions given by equations (II-8) are satisfied.

Upon inspection of equations (II-10) and (II-12), we note that  $M$  is not a function of any derivatives of  $r$ , thus reducing the right side of equation (II-11) to zero, giving—

$$\frac{\partial M}{\partial r} = 0 \quad \dots \dots \dots \quad (II-11a)$$

Combining equations (II-11a), (II-12) and (II-10), performing the required differentiation and dividing by the constant factor  $\sin \phi$ , we obtain—

$$U'(r) + [(\gamma_1 \cos \theta + \gamma_2 \sin \theta) \sin \phi + \gamma_3 \cos \phi] U''(r) = 0 \quad \dots \dots \dots \quad (II-11b)$$

Making use of the Morse function, equation (I), we have—

$$U(r) = U_0 [1 - \exp(-b)(r - r_e)]^2 \quad \dots \dots \dots \quad (I)$$

$$U'(r) = 2bU_0 [1 - \exp(-b)(r - r_e)] [\exp(-b)(r - r_e)] \quad \dots \dots \dots \quad (II-12a)$$

$$U''(r) = 2b^2 U_0 [2 \exp(-b)(r - r_e) - 1] [\exp(-b)(r - r_e)] \quad \dots \dots \dots \quad (II-12b)$$

Substituting equations (II-12) into equation (II-11b) and solving for  $\exp(-b)(r-r_e)$ , we have—

$$\exp(-b)(r-r_e) = \frac{1-\psi}{1-2\psi} \dots \dots \dots (II-13a)$$

or 
$$b(r-r_e) = \ln \frac{1-2\psi}{1-\psi} \dots \dots \dots (II-13b)$$

where 
$$\psi \equiv \lambda_1 \sin \phi \cos \theta + \lambda_2 \sin \phi \sin \theta + \lambda_3 \cos \phi \dots \dots (II-14)$$

and  $\lambda_1, \lambda_2,$  and  $\lambda_3$  are Lagrange multipliers with the Morse constant ( $b$ ) included—

$$\lambda_1 = b\gamma_1; \quad \lambda_2 = b\gamma_2; \quad \lambda_3 = b\gamma_3$$

(Since  $\gamma$  always occurs multiplied by  $b$ , the term  $\lambda$  has been defined for convenience.)

Substitution of equation (II-13a) into equations (I) and (II-12a) yields—

$$U(r) = U_0 \left( \frac{\psi}{1-2\psi} \right)^2 \dots \dots \dots (II-15a)$$

$$U'(r) = 2bU_0 \frac{(\psi)(\psi-1)}{(1-2\psi)^2} \dots \dots \dots (II-15b)$$

Substituting equation (II-15b) into equation (II-8c), rearranging and denoting the integral involved by  $\Gamma_z$  results in the following equation—

$$\frac{R_0^2 \sigma_z}{2bU_0} = \frac{2}{\pi} \alpha \Gamma_z \dots \dots \dots (II-16)$$

where 
$$\Gamma_z \equiv \int_0^{\pi/2} \int_0^{\pi/2} \frac{(\psi)(\psi-1)}{(1-2\psi)^2} \sin \phi \cos \phi \, d\phi \, d\theta$$

From a stoichiometric point of view, the parameter  $I^3$  (which has been discussed in the review section) is the volume occupied by three effective hydrogen bonds, while  $R_0^3$  is the volume occupied by one effective hydrogen bond, thus we are able to relate the two parameters as follows—

$$I^3 = 3R_0^3 \dots \dots \dots (II-17)$$

The following constants have been previously defined—

$$a = br_e \dots \dots \dots (4a)$$

$$\Delta H = NIJ_0 \dots \dots \dots (4d)$$

where  $N$  is Avogadro's number.

Substituting equations (II-17), (4a) and (4d) into equation (II-16) and rearranging so that the left side of the equation is in stress number form gives the following result—

$$\frac{Nr_e l^2 \sigma_z}{2a \Delta H} = \frac{2}{\pi} (3)^{2/3} \alpha \Gamma_z \dots \dots \dots (II-18c)$$

A similar treatment for the x and y directions yields the following equations—

$$\frac{Nr_e l^2 \sigma_x}{2a \Delta H} = \frac{2}{\pi} (3)^{2/3} \alpha \Gamma_x \dots \dots \dots (II-18a)$$

where 
$$\Gamma_x \equiv \int_0^{\pi/2} \int_0^{\pi/2} \frac{(\psi)(\psi-1)}{(1-2\psi)^2} \sin^2 \phi \cos \theta \, d\phi \, d\theta$$

$$\frac{Nr_e l^2 \sigma_y}{2a \Delta H} = \frac{2}{\pi} (3)^{2/3} \alpha \Gamma_y \dots \dots \dots (II-18b)$$

where 
$$\Gamma_y \equiv \int_0^{\pi/2} \int_0^{\pi/2} \frac{(\psi)(\psi-1)}{(1-2\psi)^2} \sin^2 \phi \sin \theta \, d\phi \, d\theta$$

Equations (II-9) and (II-15a), when combined and rearranged, give the following equation for the strain energy—

$$\frac{\bar{E}}{U_0} = \frac{2}{\pi} \Gamma_E \dots \dots \dots (II-19)$$

where 
$$\Gamma_E \equiv \int_0^{\pi/2} \int_0^{\pi/2} \left( \frac{\psi}{1-2\psi} \right)^2 \sin \phi \, d\phi \, d\theta$$

and 
$$\bar{E} = E_i/n_i.$$

The strain corresponding to the set of stresses given by equations (II-18) and to the strain energy given by equation (II-19) is obtained by a macroscopic energy balance. The work done on straining the body by differential strains  $de_x$ ,  $de_y$ , and  $de_z$  will be denoted by  $dW$  and is equal to the product of the forces involved and the differential elongations produced, namely—

$$dW = (l_x l_y \sigma_z)(l_z de_z) + (l_y l_z \sigma_x)(l_x de_x) + (l_x l_z \sigma_y)(l_y de_y)$$

or 
$$dW = V[\sigma_z de_z + \sigma_x de_x + \sigma_y de_y] \dots \dots \dots (II-20)$$

since  $V = l_x l_y l_z$ . To obtain the strain energy stored in the hydrogen bonds, we can, to a first approximation, divide each of the strains in equation (II-20) by the factor  $k$ , defined in equation (4b), to obtain the elongation produced in the hydrogen bonds, hence the energy stored in the hydrogen bond, that is,

$dW/k = dE_t$ . Thus, combining equations (II-20) and (II-1) gives the following result, after rearrangement—

$$\frac{dW}{n_t k} = \frac{dE_t}{n_t} = d\bar{E} = \frac{R_0^3}{k} [\sigma_z d\epsilon_z + \sigma_x d\epsilon_x + \sigma_y d\epsilon_y] \quad \text{. . . . . (II-21)}$$

It has been assumed that the strain energy is stored reversibly in the hydrogen bonds.

For the case of unidirectional stress in the  $z$  direction,  $\sigma_x = \sigma_y = 0$  and equation (II-21) becomes, after rearrangement and integration—

$$\frac{R_0^3}{k} e_z = \int_0^{\bar{E}} \frac{d\bar{E}}{\sigma_z} \quad \text{. . . . . (II-22)}$$

Combining equations (II-22), (II-18c), (II-17), (4a), and (4b), rearranging in strain number form gives—

$$\frac{al}{r_0} e_z = \frac{(3)^{1/3}}{2\alpha} \int_0^{\Gamma_E} \frac{d\Gamma_E}{\Gamma_z} \quad \text{. . . . . (II-23)}$$

For hydrostatic compression,  $\sigma_x = \sigma_y = \sigma_z = P$  and equation (II-21) becomes, after integration—

$$\frac{3R_0^3}{k} e = \int_0^{\bar{E}} \frac{d\bar{E}}{P}$$

We note that the volume change,  $(\Delta V)/V$ , for small strains is given by—

$$\frac{\Delta V}{V} = (1 + e)^3 - 1 \doteq 3e$$

Hence, we may write—

$$\frac{R_0^3 \Delta V/V}{k} = \int_0^{\bar{E}} \frac{d\bar{E}}{P} \quad \text{. . . . . (II-24)}$$

Finally, combination of equations (II-24), (II-18) and (II-17) yields—

$$\frac{al(\Delta V/V)}{r_0} = \frac{(3)^{1/3}}{2\alpha} \int_0^{\Gamma_E} \frac{d\Gamma_E}{\Gamma_z} \quad \text{. . . . . (II-25)}$$

where  $\Gamma_z = \Gamma_x = \Gamma_y$ .

The interpretation of the integrals in equations (II-23) and (II-25) is not obvious and is discussed in the theory section of this paper.

**Terms used**

- $1/A$  = molecular constants in the stress number (empirical)  
 $a, b$  = Morse constants (dimensionless),  $a = br_e$   
 $B$  = constants in the strain number (empirical)  
 $b$  = constant derivable from spectroscopic data  
 $C$  = constants  $C_1, C_2, C_3$  and  $C_4$   
 $E$  = initial Young's modulus of elasticity  
 $E'$  =  $U(r)$ , the energy stored in the hydrogen bond  
 $E_0$  = Young's modulus of cellulose at a water to solid ratio of 0 (virgin pulp)  
 $E_t$  = total energy stored in the macroscopic body by the straining process  
 $E_w$  = Young's modulus of cellulose at a water to solid ratio of  $w$   
 $E^*$  = initial modulus  $\times$  area  
 $e$  = strain  
 $e'$  = percentage elongation  
 $\left. \begin{matrix} de_x \\ de_y \\ de_z \end{matrix} \right\}$  = differential strains  
 $F$  = force required to separate (or compress) the equilibrium bond a distance  $r$   
 $F'_z$  = normal force in  $z$  direction  
 $\Delta H$  =  $NU_0$ , the molar heat of dissociation for the hydrogen bond  
 $k_1$  = force constant of a nearly rigid rod of length  $x_e$   
 $k_2$  = force constant of the hydrogen bond  
 $l$  = *average* repeat distance for a hydrogen bond in any direction  
 $M$  *see* equation (II-12)  
 $N$  = Avogadro's number  
 $n$  = number of effective hydrogen bonds per unit volume  
 $n_t$  = total number of effective hydrogen bonds in the system  
 $R_0^3$  = *average* volume occupied by a single, randomly oriented hydrogen bond  
 $r_e$  = equilibrium bond separation  
 $R.E.$  = rupture energy  
 $S$  = load (kg)  
 $t$  = temperature ( $^{\circ}C$ )  
 $U$  = potential energy of a hydrogen bond  
 $U_0$  = hydrogen bond dissociation energy  
 $V$  = volume of the body  
 $dW$  = work done in straining the body  
 $ale/r_0$  = strain number, where  $r_o = r_e (1 + k_2/k_1)$   
 $\frac{Nr_e l^2 \sigma}{2a\Delta H}$  = stress number (dimensionless)  
 $\alpha, \beta$  = co-ordination factors of a 'restricted network' of hydrogen bonds  
 $\left. \begin{matrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \end{matrix} \right\}$  = Lagrange multipliers in boundary (restraining) conditions

- $\lambda_1$  = Lagrange multiplier for the  $x$  direction  
 $\lambda_2$  = Lagrange multiplier for the  $y$  direction  
 $\lambda_3$  = Lagrange multiplier for the  $z$  direction  
 $\rho$  = circle radius  
 $\sigma$  = normal stress  
 $\phi$  } = angles in the spherical co-ordinates used to describe the orientation of bonds  
 $\theta$  } in the macroscopic body  
 $\psi$  see equation (II-14)

## Transcription of Discussion

### DISCUSSION

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DR. C. W. CARROLL: The simplifications in your initial model imply that it is basically a *steady state* model with regard to the least work principle. Building in dynamic features, which are important in reality, would increase the complexity of the model considerably. A mathematical approach that may be useful in solving such complex, constrained optimisation problems resulting from dynamic analysis of the hydrogen-bonded network is the method of *dynamic programming*. This method has been developed during the past few years principally by Richard Bellman of the Rand Corporation in the United States and has been successfully applied to certain complex problems falling in the realm of the calculus of variations. Dynamic programming, especially in conjunction with the digital computer programmes that are becoming available, could well be used to make possible complex dynamic analyses that would be impossible from a practical point of view, if one had no other recourse than to use the conventional calculus of variations technique in the classical fashion.