On the primacy of the hydrogen bond in paper mechanics

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ABSTRACT *In 1957, a theory was proposed that connected Young's modulus of paper to the characteristics and density of the hydrogen bonds within and between cellulosic fibers. Since then, the theory has been improved and extended. Recently, a new, rigorous derivation has been developed that discards the arbitrary assumptions and parameters used previously. The theory is founded on four axioms. Each axiom is examined for its validity.*

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Paper physics

In 1957, a two-part paper appeared in the Transactions of the Faraday Society (*1*) in which was discussed the contribution of the hydrogen bond to Young's modulus of paper. Since then, several other attempts at improving and extending the theory were made (*2, 3*). More recently, a rigorous derivation of the basic equation was made in which previously used arbitrary assumptions and parameters were dropped, and new falsifiability tests for the theory were offered (*4*). Also, it became possible to unify this molecular-scale theory with structural theories of paper, which are based on the larger scale of a fiber, with the development of a hydrogen-bond and percolation theory (*5–7*).

In brief, the primary statement of the H-bond theory is given by

$$E = \langle k_R \rangle n^{1/3} = (\partial^2 U/\partial R^2) n^{1/3} = (18.4 \pm 3) n^{1/3} Pa \quad (1)$$

where

E = Young's modulus for an ideal isotropic paper (i.e., wholly made of cellulose)

$\langle k_R \rangle$ = an average force constant for stretching the H bond

U = the potential for the bond in terms of R, the O—O distance of the O—H—O bond)

n = a predictable fraction of the total, or stoichiometric, number of intermolecular H-bonds per unit volume of the ideal paper.

The use of this equation leads to a falsifiability test of the theory in the form of a new relationship:

$$\partial \ln E/\partial T = (1/\langle k_R \rangle)(\partial^3 U/\partial R^3)(\partial R/\partial T) - \lambda \quad (2)$$

where

T = temperature

λ = the linear coefficient of thermal expansion.

The use of spectroscopic and statistical mechanical values for U and R for cellulose in Eq. 2 yields a value of $-2.4 \times 10^{-3} °C^{-1}$ for $\partial \ln E/\partial T$. This value has been checked against observed values and has been found to be valid.

When the ERCO Summer Fellowship prescribed a lecture on some aspect of this 30-year stretch of research, it became apparent that a critical review of the theory was in order. There, both assumptions and principal findings were reviewed. Since the findings are already published in the relevant literature, only the assumptions will be scrutinized here.

In the H-bond theory, four assumptions are made, each of which requires justification:

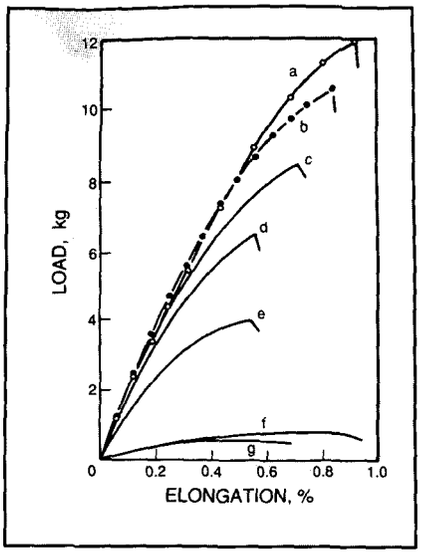
1. There is a class of solids which may be designated "H-bond-dominated-solids."
2. Paper belongs to the class of H-bond-dominated solids.
3. Although as many as ten parameters have been incorporated into the mathematical description of the H-bond, it is possible to describe the contribution of the H-bond to the elasticity of paper with one, or perhaps two, parameters.

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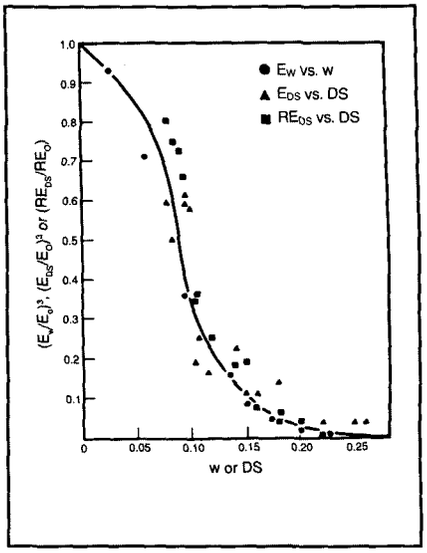
1. Elastic constants of ice, GPa

Constant	Calculated value (8)	Experimental value (9)
C_{11}	13.71	13.96 ± 0.06
C_{12}	6.63	7.15 ± 0.05
C_{13}	5.95	5.77 ± 0.03
C_{33}	14.39	15.01 ± 0.07
C_{44}	3.19	3.02 ± 0.02

1. Load-elongation curves for paper samples immersed in different fluids: (a) control in air, (b) benzene, (c) vinyl acetate, (d) nitromethane, (e) ethanol, (f) formamide, (g) water



2. The dependence of modulus E on water-cellulose ratio w and on the degree of substitution of hydroxyl groups by acetylation, DS, and of rupture energy RE on DS



4. Although the distribution of H-bonds is unknown and probably unknowable even in an ideal, isotropic paper, the statistical method of the theory is valid in computing Young's modulus from the "averaged" parameters of the H-bonds present and the bond density in the solid.

We shall endeavor to justify each of these assumptions separately.

Examination of the axioms

1. Is there a class of materials that may be designated as "H-bond-dominated solids?"

All solids are affected by intra- and intermolecular potentials as well as by changes in entropy upon deformation. The complexity of all the factors is such that it is the accepted method to select for any one solid under study only those factors considered to be of dominant importance and to ignore the others. The most remarkable of such treatments for its simplicity and success is that which treats natural rubber as a solid dominated by the entropy changes induced in it upon deformation, while ignoring all primary and secondary valence forces within and between the molecules. We could designate such a solid as an "entropy-dominated solid."

Similarly, we call a solid "H-bond-dominated" if the contribution of the H-bonds to the resistance of deformation dominates other effects from primary or other secondary valence forces and entropy changes. To affirm that such a class of solids exists, it is necessary to demonstrate the existence of only one such solid.

The prime example of an H-bond-dominated solid is ice. Haas (*8*) has calculated from first principles all five elastic constants of the Ice I crystal. His calculations agree well with experimental values, as shown in **Table I**.

What is interesting about Haas's calculations is that they are based solely on the H bonds that exist between the water molecules in ice. Haas completely ignores the primary valence forces (covalent, ionic, etc.) within the molecules in ice. Haas's assertion, that "the forces which hold the water molecules in an ice crystal together must be ascribed predominantly to hydrogen bonding," is verified by the excellent agreement between his calculations and the experimentally observed values. Thus, Ice I meets the definition of an H-bond-dominated solid, thereby establishing the class of H-bond-dominated solids.

2. Is paper an H-bond-dominated solid?

That all hydroxyl groups in paper participate in H-bond formation is beyond doubt, since spectroscopic studies of paper and cellulose show no absorption at the free hydroxyl stretching frequency of 3600 cm^{-1}. But do the H-bonds dominate the mechanical properties of paper?

In 1964, Robertson (*10*) published the effects of various saturants on the Young's modulus of paper. These effects are shown in **Fig. 1**, where it is seen that immersing paper in water destroys the mechanical integrity of the paper. Other liquids also reduce the value of E.

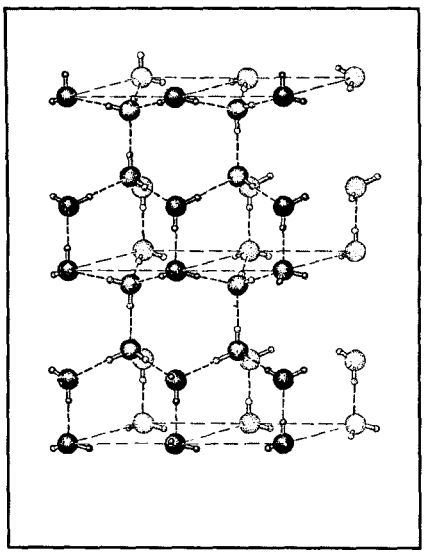
There are two possible explanations for these phenomena. First, as the polarities of the saturants increase, so do their abilities to break intermolecular H bonds in the cellulose matrix. By breaking H bonds, the liquids reduce n in Eq. 1 and hence E. Second, these saturants have progressively increasing dielectric constants. If the bonds in paper are ionic, then the strengths of the bonds are reduced as the dielectric constant of the saturant increases.

This second point is worth considering. Even though we have no evidence that the cellulosic hydroxyl groups are ionized, we must consider the possibility that the strong carboxylic acid groups (COOH) known to exist in paper (since paper is a weak ion-exchange medium) could be the primary bonding force between fibers, fibrils, or molecules in paper. Thus, according to the second explanation, the diminution in E is directly attributable to the dielectric constant of the saturant.

Which answer is correct? **Figure 2** gives us the answer: the loss in E is due to the breaking of intermolecular H bonds in paper.

Figure 2 shows three sets of data from two experiments by Higgins (*3, 11*). In one experiment, pulp was *first* beaten and then acetylated to different degrees. Standard handsheets

3. The arrangement of molecules in the ice crystal (*16*)



then were made from the pulp, and both E and rupture energy RE were measured. [Note: The beating was done prior to acetylation in these experiments to eliminate the effects of acetylation on beating as an unknown. This is distinctly different from a previous series of experiments performed by McKenzie and Higgins (*12*), in which the pulp was acetylated prior to beating.] In a second experiment, standard paper handsheets were humidified to various water-cellulose ratios w, and then Young's modulus was measured. The results from both experiments give only one curve. Thus, w and the degree of acetylation both have the same effect on E. Since the change in E on acetylation cannot be attributed to a change in the dielectric constant of the saturant, it is unlikely that the diminution in E is a result of the dielectric constant of the saturant. However, the acetylation of hydroxyl groups in cellulose does eliminate sites for H bonding. Thus, Occam's razor requires that we accept the proposition that both acetylation and w reduce E by diminishing the number of H bonds per unit volume.

Figure 2 shows that the reduction in E due to the breaking of H bonds by w approaches 95% at $w = 0.22$. Such a large effect is clearly a dominant one. Thus, we declare cellulose and paper to be members, with ice, of the class of H-bond-dominated solids. This allows us to relate E, as a first approximation, to the density and characteristics of H bonds, while ignoring all secondary factors (such as entropy, ionic character, and covalent contributions).

3. H-bonds have extremely complicated functions for their potentials. How many parameters are essential to a theory connecting E to H-bond characteristics?

Quantum mechanical models for the hydrogen bond generally contain at least four contributors to its energy: electrostatic, delocalization (or resonance), repulsive overlap (of charge clouds on nonbonded atoms), and dispersion (London) forces (*13*). Lippincott and Schroeder (*14*) use a semi-empirical model with quantum mechanical origins that includes ten parameters. Fortunately, these parameters are interrelated. Once any one of these parameters is determined experimentally (such as the potential energy at equilibrium or the equilibrium O—O distance, R), all others become calculable. Thus, the effect of the H bond may be related to a single observational parameter (such as U or R) for a particular type of H bond (e.g., O—H—O, as opposed to, say, F—H—F).

Haas has demonstrated (*8*) that two parameters are sufficient to calculate all five fundamental elastic constants of a crystal of Ice I. The parameters he used were k_R and k_θ, the force constants for stretching and bending the O—H—O bond, respectively. Ice I has a special structure in which four H bonds are centered on each oxygen atom, so that there is no possibility of stretching any one H bond without bending other hydrogen bonds. This geometry does not exist with cellulose, where the intermolecular H bonds are separated by a comparatively rigid cellulose backbone. Thus, in cellulose, only one parameter—the force constant of stretching, k_R—is sufficient for the calculation of E. This force constant of stretching is derived readily from the Lippincott-Schroeder potential function (*4*).

4. Can the proposed statistical method be used to calculate E from the average values of the parameters and the density of the H-bonds?

To demonstrate the efficacy of the statistical averaging method that we developed for paper, we apply it to a system in which the H-bond distribution is better known than in the case of paper. That system is Ice I.

As mentioned, Haas has calculated the five independent elastic constants for Ice I using a two-parameter potential function, with these elastic constants in good agreement with experimentally determined values. Using Haas's values for these five constants, we can calculate the two principal moduli E_1 and E_3:

$$E_1 = 9.7 \text{ GPa} \quad (3A)$$

$$E_3 = 10.9 \text{ GPa} \quad (3B)$$

Thus for polycrystalline ice, E is

$$E = (2E_1+E_3)/3 = 10.1 \text{ GPa} \quad (3C)$$

These calculated values agree well with the experimentally determined values for polycrystalline ice reported elsewhere (*15*). The average of all these reported values is $E = 9.9$ GPa. The standard deviation for all reported measurements is 0.8 GPa. For the experimental data reported in Table I, we have $E_1 = 9.67$ GPa, $E_3 = 11.86$ GPa, and $E = 10.4$ GPa.

We now apply the statistical averaging method to Ice I. If the method is good, it will result in a value for E of approximately 10 GPa.

In the statistical averaging method, we begin by assuming a random distribution of hydrogen bonds in the solid. In other words, the solid is treated as isotropic, as regards the orientation of H bonds within it. Thus, the hexagonal crystal structure of ice (**Fig. 3**) is replaced with the random distribution of **Fig. 4**. Using the spherical coordinate system, we see that the number of bonds dN' at the angle θ contained within a circular hoop on the surface of the sphere in Fig. 4 (with radius R) is

$$dN'/N' = 2\pi R \sin\theta R d\theta / 4\pi R^2 = \sin\theta d\theta/2 \quad (4)$$

If a force f_x is applied in the positive x direction, the force on a bond within the system is given by $f_x \cos\theta$. The energy stored in the bond due to stretching will be

$$U = (f_x \cos\theta)^2 / 2k_R \quad (5)$$

where

k_R = the Hookean force constant.

The total energy stored in all the bonds in the circular hoop is

$$U_\theta = UdN'$$
$$= N' (f_x \cos\theta)^2 \sin\theta \, d\theta / 4k_R \quad (6)$$

Integration yields the total energy stored in all the bonds:

$$U' = 2\int_0^{\pi/2} UdN'$$
$$= N' f_x^2 / 6k_R \quad (7)$$

Now consider a system with N bonds all oriented along the x axis. If such a system is subjected to a force f_x, the energy stored in the system is given by

$$U = N f_x^2 / 2k_R \quad (8)$$

If this model is equivalent to the isotropic model, then

$$U' = U \quad (9)$$

and

$$N = N' / 3 \quad (10)$$

In other words, for stretching modes of H bonds, an isotropic, randomly oriented network of H bonds is mathematically equivalent to one with a third of the bonds oriented along each of the three, orthogonal, principal axes. This holds true only for infinitesimal strains, when the energy functions are quadratic with respect to strain.

We now calculate the effect of bending in H bonds by using the same approach. A force acting on the bond at the angle θ will have a component $f_x \sin\theta$ acting at a right angle to the bond. The moment will be $f_x \sin\theta \, R$, and the bond deflection will be

$$\delta\theta = f_x \sin\theta \, R / k_\theta \quad (11)$$

The energy stored in the bond due to bending is

$$U = (f_x \sin\theta R)^2 / 2k_\theta \quad (12)$$

The total bending energy stored in all the bonds in the circular hoop is

$$U_\theta = N'$$
$$(f_x \sin\theta R)^2 \sin\theta \, d\theta / 4k_\theta \quad (13)$$

Integrating Eq. 13 yields the total bending energy per unit volume stored in the system:

$$U' = 2N' f_x^2 R^2 / 6k_\theta \quad (14)$$

Now consider a system with N bonds all oriented at right angles to the x axis. If such a system is subjected to a force f_x, the bending energy stored in the system will be

$$U' = N' f_x^2 R^2 / 2k_\theta \quad (15)$$

If this model is equivalent to the isotropic model, then

$$U = U' \quad (16)$$

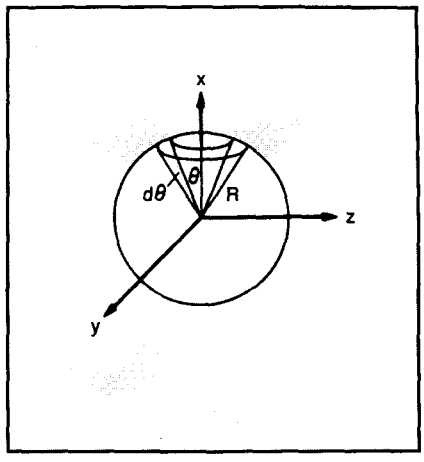
and

$$N = 2N' / 3 \quad (17)$$

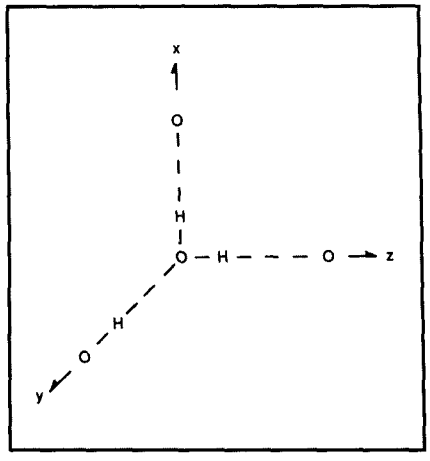
In other words, for bending modes of H bonds, an isotropic, randomly oriented network of H bonds is mathematically equivalent to one with two-thirds of the total bonds oriented at right angles to the direction of the force.

An examination of Fig. 3 confirms that each water molecule in the ice crystal is fully engaged in hydrogen-bonding. Thus, the statistical method as applied to ice results in the model shown in **Fig. 5**, in which one third of the H-bonds are aligned along the direction of the force, and two thirds are aligned along the two remaining orthogonal principal axes.

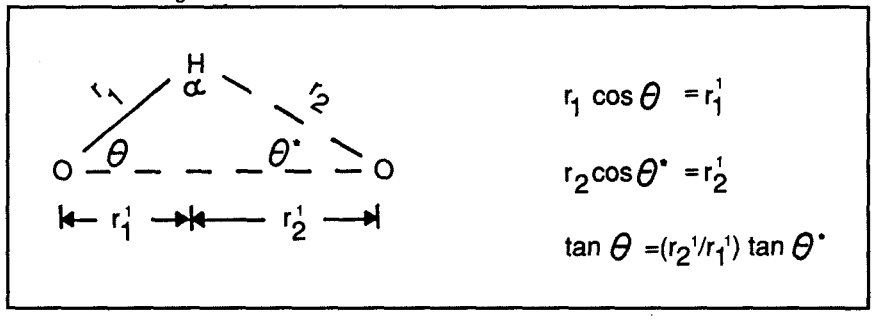
4. Directional distribution of hydrogen-bond orientation in an isotropic H-bonded solid at an angle θ to the x axis



5. Statistical model of the ice crystal



6. Definition of angles



If a force f is applied along the positive x axis of Fig. 5, the H bond along that axis will stretch by an amount δR (*stretch*). The two perpendicular bonds will also stretch, but this stretching will be mixed with bending. The total deformation along the x axis from force f is

$$\delta = \delta R\,(stretch) + \delta R\,(bend) \quad (18)$$

The value of δR (*stretch*) is simply f/k_R. The value of δR (*bend*) is

$$(fR_0^2/2)(1/k_\theta + 1/k_\alpha + 1/k_\theta)$$

where the k values are force constants for the angles defined in **Fig. 6**. Haas has taken $k_\theta = k_\alpha = k_\theta$. This yields for δR (*bend*) the value of $3fR_0^2/2k_\theta$. Thus, Eq. 18 becomes

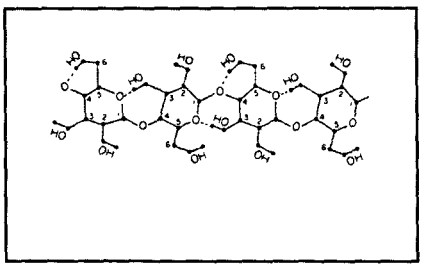
$$\delta = (f/k_R)[1 + (3/2)(R_0^2 k_R / k_\theta)] \quad (19)$$

Now, in a cube of unit sides containing n bonds per unit volume there are $n^{2/3}$ bonds in parallel. This gives for the stress σ

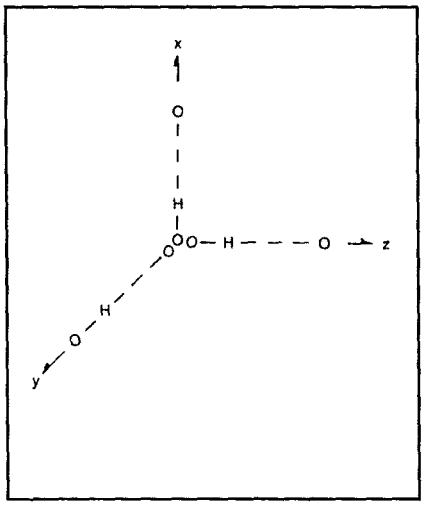
$$\sigma = f n^{2/3} \quad (20)$$

Likewise, the total strain is

7. The cellulose molecule



8. Statistical model of cellulose



$$\epsilon = \delta n^{1/3} \quad (21)$$

From this, we obtain Young's modulus:

$$E = \sigma/\epsilon = \langle k_R \rangle n^{1/3} \quad (22)$$

where $\langle k_R \rangle$ is the averaged force constant and is given by

$$\langle k_R \rangle = k_R [1 + (3/2) R_0^2 k_R / k_\theta]^{-1} \quad (23)$$

Using the values that Haas derived for k_R, k_θ, and R_0, we have

$$\langle k_R \rangle = 3.5\ N/m \quad (24)$$

The calculation of n, the number of H bonds per unit volume, follows Eq. 25:

$$n = (2Na\rho)/(3 \times 18) \quad (25)$$

where

Na = Avogadro's number

ρ = the density of ice.

In Eq. 25, 18 is the molecular weight of water, and the 3 in the denominator is from Eq. 10. The 2 in the numerator is in recognition that there are four H bonds per water molecule and that all the H-bonds are shared with other water molecules. This leaves an effective number of 2 H bonds per water molecule. The value of n from Eq. 25 is

$$n = 2.04 \times 10^{28} m^{-3} \quad (26)$$

From Eqs. 22, 24, and 26, we calculate E for polycrystalline ice, from the statistical method:

$$E = 9.6\ \text{GPa} \quad (27)$$

As stated previously, the average of all experimentally determined E values reported by Northwood (*15*) is E = 9.9 GPa, with a standard deviation of 0.8 GPa. The statistically determined value of E for ice differs from the average of experimental values by 3% and is clearly well within a standard deviation. It differs from the more recent measurements in Table I by less than 8%. Thus, the statistical method is valid in the computation of Young's modulus from the "averaged" parameters of the H bonds in the solid.

Applying the statistical method to cellulose yields similar results. We find that Eqs. 10 and 17 apply (*3*). In other words, H-bonded cellulose may be represented mathematically as a continuum of H bonds, one third of which are oriented along each of the three principal orthogonal axes.

A comparison of **Figs. 3 and 7**, however, points to one major difference between ice and cellulose. In ice, each water molecule is fully engaged in hydrogen bonding, so that each oxygen atom participates in the formation of four H bonds. Exertion of a force in any one direction causes bending of H bonds in the two other directions. Thus the statistical model for ice is that shown in Fig. 5, where the oxygen at the origin is involved in more than one H bond. For cellulose, the H bonds are widely separated by cellulose chains, which are assumed to be "infinitely" rigid when compared to the H bond. Applying a force in any one direction causes extension of H bonds in that direction but no bending in the two remaining directions. Thus, the statistical model for H bonds in cellulose is shown in **Fig. 8**. The difference between this model and the model for ice is simply that the three H bonds forming the unit cell are not connected to each other.

Note that this model does not imply that, for paper, there is no connection between a force in one direction and deformation in the two other directions. It does imply that, on a molecular scale, the extension of an H bond in one direction does not induce bending of H bonds in the other directions.

In keeping with the preceding analysis, we have for cellulose:

$$E = \sigma/\epsilon = f n^{2/3}/\delta n^{1/3} \quad (28)$$

$$E = \langle k_R \rangle n^{1/3} \quad (29)$$

where

$$\langle k_R \rangle = k_R \quad (30)$$

In other words, the averaged force constant for H bonds in cellulose is just the force constant of stretching. This has been derived previously for H bonds in cellulose from the Lippincott-Schroeder potential function (*4*):

$$k_R = 18.4\ \text{N/m} \quad (31)$$

The experimental determination of $\langle k_R \rangle$ in cellulose (*4*) from hysteresis loop studies in the plastic regime yield a value of 18.4 N/m ± 2.3 N/m. Again, the statistical method shows good agreement with experimental results.

Summary

We have critically examined the four fundamental axioms of the hydrogen bond theory. The axioms have been found to apply not only to ice, the classic H-bond-dominated solid, but also to paper. The results of the theory show good agreement with experimental data, both for paper and ice.

We conclude that, fundamentally, paper mechanics must be governed by the density and characteristics of the hydrogen bond, and no theory can be complete that is not based on this fact.□

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