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THEORETICAL STRENGTH
OF
MATERIALS

RELEASABLE TO
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THEORETICAL STRENGTH
OF
MATERIALS

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FOREWORD

The wide difference in strength between what is presently realizable the materials of commerce and what is assumed to be theoretically poss is of continuing concern to materials specialists. A committee of the Materials Advisory Board, in report MAB-187-M, December 1962, ma an extensive study of the situation with respect to metals, and expresse the results in terms of the so-called metal gaps between the practically obtainable and the theoretically possible. The report aroused widesprea interest both as to technology and as a guide in supporting metallurgical programs.

The question arose as to whether a similar analysis could be applied materials generally, recognizing the difficulties presented by such dive substances as metals, ceramics, glasses, and polymers. In a letter Dr. Earl T. Hayes, Assistant Director (Materials) of the Office of Dir of Defense Research and Engineering to Dr. Frederick Seitz, President the National Academy of Sciences (Appendix), it was requested that a stu be conducted to summarize the procedures for estimating theoretical strength, together with discussion of assumptions and their limitations. and examples of calculations of maximum strength for different classes materials.

The project was assigned to the Materials Advisory Board which organized the Committee on Theoretical Properties of Materials, with membership as shown on page iii.

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ABSTRACT

This report is in six sections, i.e., Introduction, Theoretical Considerations for Ideal Solids, Cohesive Strength of Crystals, Strength o Inorganic Glassy Solids, Strength of Organic Polymers, and Examples Theoretical Strength Calculations. Equations suitable for engineering purposes are developed for each class, along with a discussion of th assumptions involved, and the limitations and uncertainties applicable to the expression of strength in terms of other properties which are measurable experimentally. The report sets forth the considerations upon which the concept of theoretical strength is based, the methods b which calculations can be made, the information required to make the calculations quantitative, the sources of such information, and the lev of confidence to be placed upon the results applicable to various types materials.

SECTION I - INTRODUCTION

The advances of present day technology are in large measure limited by the properties of the materials of which useful structures and devices are made. A limiting property of particular interest is strength and a tremendous effort is being devoted to a materials development program aimed at the improvement of the strength properties of known substances and the discovery of other substances, not now known, which will exhibit superior properties. In the prosecution of such a program it is only natural that attention should be given to the fundamental ultimate strength of a substance, a strength determined by the basic physical or chemical forces which hold the individual atoms together to form the solid. That such a strength is theoretical and cannot directly be measured must be obvious because neither a kindly nature nor the skill of man has provided us with substances in bulk form which are so perfect in structure that the basic interatomic forces can manifest themselves to their utmost.

Nevertheless, a knowledge of the theoretical strength of a substance would be very useful for a number of reasons. In the first place, it clearly indicates the ultimate potential of particular substances for particular applications in which the material acts as a structural element. Secondly, the theoretical strength provides an important index by means of which one may judge the progress being made in development programs directed toward the achievement of higher strengths in particular substances. And thirdly, in the search for new materials, the ability to predict the theoretical strength provides a powerful tool of great utility in the organization of an efficient and systematic exploration.

A general definition of theoretical strength may be stated in relatively simple terms. One can imagine a body of the ideal substance that is completely homogeneous and free from all defects. The surfaces of the body are so remote from the area of interest as to have no influence. The geometrical model of such an idealized substance presents no particular problem for crystalline substances but will involve some assumptions if the material is non-crystalline. Consider now a plane passing through the body and an external force applied such that a uniform uniaxial tensile stress acts normal to this plane, producing elastic deformation of the body. Across the plane, a separation of the atoms to distances greater than their normal spacing results. As the separation increases, the resultant of the interatomic forces, acting across the plane and opposing the applied stress, increases, at first rapidly and then more slowly, until a maximum is reached, after which the resultant stress decreases. If a stress less than the maximum is applied and then released, the body returns to its original configuration. If the applied stress reaches the maximum value, however, the body will fracture. The theoretical strength or cohesive strength, therefore, is the maximum value of the stress, resulting from the interaction of the atomic force fields, which opposes the separation of the atoms. A calculation of the theoretical strength would require not only an understanding of the interatomic forces themselves, but also a knowledge of the atomic configuration so that an appropriate summation of the forces could be carried out.

Tremendous progress has been made in the last quarter century in the understanding of the structures of all sorts of materials and a large collection of quantitative data on a variety of properties has become available. It should be possible, at least in principle, to calculate the theoretical strength of a substance on the basis of its known physical and chemical characteristics. If the results are to be quantitative, the required properties must be known quantitatively or must be measurable. It would be particularly advantageous if it could be shown that the theoretical strength could be expressed in terms of properties which are relatively insensitive to those aspects of structure which distinguish the real from the ideal substance, but to which the observed strength values of the real material itself are very sensitive. These measurements would provide the basis for a quantitative determination of the theoretical strength.

Because of the complexity of the problem on the one hand and present limitations of the theory on the other, it is inevitable that certain assumptions must be involved in the expression of strength in terms of other and more basic properties. In attempting to give quantitative answers to the problem, these assumptions must be examined with great care and a thorough assessment made as to their influence upon the reliability of the result.

It is the purpose of this report to set forth the considerations upon which the concept of theoretical strength is based, the methods by which calculations can be made, the information which is required to make the calculations quantitative, the sources of such information and to indicate the level of confidence which can be placed upon the results which apply to various types of material.

Before defining the theoretical cohesive strength of a solid in more specific terms or considering the controlling factors, it is useful to make a general classification of solid types since a somewhat different approach may be required, depending on the nature of the solid. Any such classification must be rather arbitrary because of the wide variety which is evident, but it is possible to make a grouping into three main categories if emphasis is placed upon those materials which have, or may have, engineering possibilities.

These categories are:

1. Crystalline solids
2. Glassy solids
3. Polymeric solids

The crystalline solids are in many ways the simplest and easiest to describe. The elements of the structure are atoms (or ions) and the distinguishing feature is the regularity of the arrangement. The structural elements are considered as occupying the points of a three-dimensional lattice which repeats itself at regular intervals in all directions throughout the crystal, however large or small it may be. The repeating pattern may be simple or very complex but the fundamental characteristic is a long-range order in the structure and consequently it is susceptible to an exact geometrical formulation. The environment in which each atom finds itself may be exactly specified. Examples of crystalline solids are the metals; the covalent crystals such as diamond, silicon and germanium; the ionic compounds typified by the alkali halides; the refractory oxides and silicates of ceramics; the hard and refractory compounds of the transition metals such as carbides, borides, and silicides; and of course many others.

Contrasted with the orderly atomic array in crystalline solids is the amorphous substance in which the atoms pack themselves in a disorderly fashion in which no regular repeating pattern can be recognized. Truly amorphous substances are rare, for nature has a strong inclination to be orderly in her ways. Occupying an intermediate position are the glassy solids which are characterized by order on a localized atomic scale but a lack of order on a long-range basis. Perhaps the simplest example is silica glass in which the basic structural elements are silicon atoms surrounded by four oxygen atoms at the corners of regular tetrahedra. The tetrahedral units are distinctive but they join up in the glass by sharing the oxygen atoms at their corners to form a structural network which is irregular in the sense that it does not show long-range order. The sharing is controlled primarily by the fact that a finite piece should contain twice as many oxygen atoms as silicon atoms. Important engineering glasses are more complex than this simple example but in recent years great progress has been made in understanding them. It is clear that in approaching the problem of strength, the case for the glassy solids will be somewhat different from that for crystalline solids.

Still another class of solids is composed of molecular groupings of atoms as the structural elements. In general, the forces that act within the molecules are similar to those in the simpler crystals, but the forces holding one molecule to another are of a somewhat different and usually much weaker nature. The molecular solids of engineering interest usually are those with very large molecules formed by the aggregation (polymerization) of simpler molecular units. The polymerized molecules may be in the form of linear chains, two-dimensional sheets, or three-dimensional networks and frequently contain a very large number of individual atoms.

Some polymeric substances are truly crystalline, as for instance when chain-like molecules are packed together in a regular repetitive fashion to produce a three-dimensional order capable of exact specification. Usually, however, the degree of order is quite low. Furthermore, complications are created by the existence of strong cross-links between molecules, or connections through branching chains. This makes an exact description of the structure extremely difficult and poses serious problems for one attempting to make theoretical calculations of the strength. These solids exhibit a wide variety of strength properties which are susceptible to modification and control in various ways. Consequently, considerations of theoretical strength are particularly pertinent for them.

The relations between theoretical strength estimates and the behavior of current engineering materials creates serious problems of judgement because of the complex structures of many materials. Consider, for example, the case of a high steel strength. Such a steel contains atoms of several elements in addition to iron and carbon. These atoms are grouped to form several distinct phases, each phase having its own internal structure. Furthermore, since the material is polyphase, it is also polycrystalline and the various crystals are packed together in a complex textural configuration. It becomes a matter of questionable judgement to choose what is to be considered to be the "basic substance." Should it be the matrix phase, in this case an iron-rich solid solution? Or should one arbitrarily decide that the basic substance is pure iron itself, even though in some temperature ranges the crystal structure of the solid solution and pure iron may be different? This dilemma point up the need for development, on theoretical grounds, of basic relationships between strength and other properties such as the elastic moduli or thermal expansion coefficients which are relatively structure-insensitive. Even though these relationships may be approximate ones, and provided the uncertainty involved is recognized, such measures of the theoretical strength should be valuable and useful concepts in the field of materials development.

SECTION II - THEORETICAL CONSIDERATIONS FOR IDEAL SOLIDS

A. CRYSTALLINE AND NON-CRYSTALLINE SOLIDS

When a piece of solid material is formed from its constituent atoms, the many possible arrangements can possess various degrees of regularity. The extent of the regularity can be described in terms of a set of vectors drawn from any particular atom or molecule to all other identical atoms or molecules in the specimen. At one extreme of organization, if each of these vectors can be expressed as a sum $n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$, where the n's are integers and the $\vec{a}$'s are not coplanar, then we say that the piece of material is perfectly crystalline. In more visual terms, in a perfectly crystalline material the same pattern of inter-atomic vectors is repeated throughout the entire region of space occupied by the material. This pattern is referred to as a crystal structure. At the other extreme of atomic organization—or, in this case, disorganization—there is no correlation at all between the various inter-atomic vectors, and we say that the material is amorphous. Thus, in an amorphous material, knowledge of the direction and distance from one atom to another identical atom tells us nothing about the locations of any other atoms.

Neither extreme is found in nature. Although most solids are—for energetic reasons—highly crystalline, none are perfect crystals. They may contain impurity atoms, vacant atomic sites, interstitial atoms, lines of crystal dislocation, and—especially at elevated temperatures—small transient vibrational displacements. Thus, for real crystals, the vector condition stated above holds only approximately—but sometimes to a very good approximation for most of the atoms. Similarly, few if any, solid materials are completely amorphous. They tend not to be because of the rather well-defined radii of atoms, plus the fact that the interatomic forces usually reduce the interatomic spacings to the sums of two radii, thereby ensuring a relatively small spread in the spacings between any atom or molecule and its nearest neighbors. Moreover, the stereogeometry of valence bonds, plus spatial limitations on how one sphere can be surrounded by many equivalent spheres, further tends to reduce the randomness. Thus, it is not surprising that even in materials which lack long-range crystalline order, considerable short-range order still exists around each atom. A gradual increase in the definition and range of such short-range order produces a gradual transition to the crystalline state. Therefore materials are found with structures that range over the whole spectrum of regularity between the perfectly crystalline and the completely amorphous states.

Since solids do not evaporate at low temperatures, there must be attractive forces between their atoms and molecules. These attractions can be expressed in terms of a binding energy. This binding energy of the solid may be measured relative to a gas of isolated atoms (as in the case of copper metal), a gas of isolated molecules (as for anthracene crystals), or a gas of positively charged metal ions and negatively charged nonmetallic ions (as for sodium chloride); the choice of reference state is a matter of convenience.

The most universal—and also the weakest—of the binding forces between two atoms or molecules results from interactions between electric dipole moments on each. Even if neither has a permanent dipole moment (as in the case with all atoms and with many molecules of high symmetry), such a force will still exist because of transient induced moments. That is, fluctuations in the electronic charge density on atom A will induce a dipole moment on B, and vice versa, giving rise to a net attraction. This attraction is known as the van der Waals interaction, and is the only source of binding in such materials as the solidified rare gases and many non-polar organic crystals such as naphthalene and anthracene. In these "van der Waals" crystals, the binding energy is very small, typically one or two tenths of an electron volt* per molecule. If the constituent molecules have, in

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*One electron volt (eV) = 1.6 x 10-19 joules; 1 eV/atom = 23 kcal/gm mole.

addition, a permanent electric dipole moment (due to an inequality in the affinities of the constituent atoms for valence electrons) or can form hydrogen bonds between strongly electronegative atoms such as oxygen, then the binding energy is somewhat larger—up to about half an electron volt per molecule. Thus, ice has a much higher melting point than does hydrogen sulfide because it has a larger dipole moment and forms stronger hydrogen bonds. Similarly, the extensive hydrogen bonding between fibrous protein chains gives the hard-boiled egg a greater mechanical strength than an unboiled one, in which proteins are globular. The binding in van der Waals crystals, however, is never very strong compared to typical chemical bonding. Thus, the formation of such a solid perturbs the electronic structure only slightly so that a crystal of anthracene, for example, has an optical absorption spectrum very like that of the isolated molecule.

If van der Waals forces were the only interactions producing solid-state binding, then the field of "strength of materials" would be better characterized as the "weakness of materials." Fortunately, however, for many materials there exist much stronger attractive forces. These forces are wave-mechanical in nature and have their origin in a decrease in the total energy of the outer, or valence, electrons upon bringing the atoms into close contact. We recall that electrons, as is the case with other particles, exhibit wave properties. For any particular state of the particle, these properties are determined by a "wave function," a function of the spatial coordinates which gives the probability of finding the electron in each region of space. The kinetic energy of an electron is proportional to the square of the momentum and hence, according to de Broglie's equation (momentum equals Planck's constant divided by the wavelength of the wave function), varies inversely as the square of the wavelength. The potential energy, on the other hand, depends on the average distances between the electron and the positive nuclei of the atoms involved, as well as on its proximity to other electrons. The potential energy will be algebraically small when the wave function describing the electron has large amplitude near nuclei. The nuclei, of course, are not fixed but vibrate relative to one another. This nuclear motion, however, is so slow relative to that of the electrons that at any given moment the electron "sees" the nuclei as essentially at rest. The study of binding forces is thus concerned with the way in which the proximity of other atoms can so distort the wavelengths and the shapes of the wave functions of the outer electrons that a large decrease in total energy is achieved. Increasing the wavelength of a valence electron decreases its kinetic energy, whereas distortion of shape of the wave function affects the potential energy, since the electron is mainly found in those regions where the amplitude of the wave function is large. These two factors form the basis of the covalent and the metallic bonds.

Just as the coupling of two identical pendulums results in a more complicated motion involving a superposition of two different frequencies, so the interaction between two atoms "splits" each original energy state or wave function into two new ones. In general, one of these new states will have a lower energy than the original value and the other will have a higher energy. This effect of interatomic interaction on the electronic wave function, together with the fact that no more than two electrons in a crystal can exist with a given wave function (as demanded by the Pauli exclusion principle), gives rise to the varied types of bonding found in solids.

In the case of hydrogen atoms, for example, a new low energy state is formed by placing two such atoms very near one another. This state can hold the two electrons supplied by the two atoms. Addition of a third atom, however, would not lower the energy of the original two electrons sufficiently to compensate for the resulting increase in energy of the last electron; a third atom cannot, therefore, bond to the others. Solidified hydrogen thus consists of a collection of diatomic molecules, held together only by van der Waals forces.

In the case of germanium or diamond, on the other hand, the electronic structure of the atom allows each one to form strong covalent or homopolar bonds with four others, rather than with just one other as for hydrogen. With four linkages per atom, one can build up a three-dimensional structure with no limitation on the number of atoms in this giant "molecule." Such a "molecule," as in the case of a crystal of germanium, is referred to as a covalent crystal. Because the atoms are bound to one another with chemical bond energies (of the order of ten electron volts), covalent crystals are generally very stable.

A metal might be thought of as a material which sets out to form a covalent crystal, but in which there are more low-energy states than there are valence electrons to fill them. The net effect of the resulting electronic freedom is that the electrons behave in many ways like a gas, giving rise to the familiar metallic conductivity and specular reflection. Each electron is distributed over the entire crystal, and the resulting increase in average wavelength (compare with the free atom, where the electron wavelength is of the order of the atomic radius) gives rise to a binding energy of a few electron volts for simple metals and up to about ten electron volts for transition metals (with unfilled inner shells). The excess of available low energy states makes the interatomic bonding much less directional than in the case of covalent crystals; hence, metals form crystals with high coordination number (8 or 12) and are typically quite plastic.

Consider now a covalent crystal made up of two types of atoms, say A and B. Suppose we could gradually increase the potential energy of a valence electron when near A and similarly decrease it when near B. In chemical terms, we are making A more electropositive and B more electronegative. The effect of this is to encourage the electrons to spend more time in the vicinity of B atoms than near A atoms; we have introduced ionic character into the bonding. An extreme case of ionic bonding would be that in which A and B existed in the crystal as A^{+n} and B^{-n}, where the charges shown are those exhibited by the same ions in aqueous solution. This model appears to be a rather good one for many alkali halides, such as NaCl, where the binding energy calculated on the basis of undistorted spherical ions is very close to that observed. This energy is of the order of 5 to 10 electron volts for crystals of monovalent ions, and is several times larger for crystals containing polyvalent ions. The ionic model is also useful for discussing cases intermediate between pure ionic and covalent, where the lack of complete ionic charge separation can be allowed for by the introduction of terms describing a deformation, or polarization, of the ions by one another.

Below is a table of typical binding energies for various types of solids. The binding energies are measured relative to the free molecules for van der Waals binding, to the free atoms for covalent and metallic binding, an to the free ions for ionic binding. Binding energies are given in electron volts (eV) per molecule or atom (multiplication by 23 converts these valu into kcal/gm mole).

Crystal Type	Binding Energy in eV
van der Waals (without permanent dipole moment)	$\sim$0.1
van der Waals (with permanent dipole moment or hydrogen bonding)	0.3 - 0.5
Covalent	8 - 15
Metallic (no partially filled d-shells)	1 - 5
Metallic (transition metals with partially filled d-shells)	4 - 10
Ionic (monovalent ions, such as alkali halides)	5 - 8
Ionic (divalent ions, such as alkaline earth oxides)	10 - 18

For comparison, the energy of the O-H bond in water is 5 eV and that for the single C-C bond in organic molecules is 2.5 eV.

These binding energies may be roughly correlated with cohesive strengt within a given type of solid (e.g., ionic, metallic, etc.). One cannot, however, compare different types of solids without additional information, suc as the distances over which interatomic forces act in the different types of bonding. This is evident from the fact that energy = force x distance; thus, the cohesive strength depends on the maximum slope, rather than depth, of the plot of energy vs. interatomic spacing. These concepts are treated more fully in the following sections.

B. USE OF POTENTIAL FUNCTIONS

If one considers a solid as an assembly of atoms and applies an external force, the potential energy of the assembly or a unit volume thereof will be changed as a result of the work done by the external force in producing a strain or a change in the relative positions of the atoms within the body. If it were possible from first principles to predict the potential energy both qualitatively and quantitatively as a function of the strain, it would be possible to calculate the theoretical strength of the material. Such a mathematical relationship between potential energy and strain is called a potential function.

From a qualitative point of view it is quite easy to predict the general form of the potential function from a simple consideration of the nature of interatomic forces. The very simplest example which illustrates the nature of the potential function is the one-dimensional crystal consisting of a linear chain of equally spaced identical atoms. Because of the interaction of the outer electrons of the atoms, attractive forces exist between them for otherwise the crystal would not be stable. At the same time repulsive forces must exist which effectively prevent two atoms from occupying the same space, forces which also result from electronic interaction. With no external force acting, the normal spacing of the atoms represents an equilibrium between attractive and repulsive forces and the structure has the lowest potential energy.

If a tensile force is applied along the axis of the chain, work must be done to separate the atoms against the attractive forces and the potential energy rises. Similarly if a compressive force is applied, work must be done to push the atoms together against the repulsive forces and again the energy rises. Using the convention that the potential energy of the system is zero when the atoms are separated to such large distances that they have no mutual interaction and using the interatomic spacing itself as a measure of the strain, the potential energy vs. strain curve would have the form shown in Figure II-1.

On this basis the potential energy curve will be negative over most of its range and have a minimum at the equilibrium atomic spacing χ_o. The curve rises steeply for spacings less than χ_o because the repulsive forces are short-range in character but rises more slowly at larger values of χ because the attractive forces are long range. The curve must have an inflection point at some value of χ greater than χ_o since it approaches zero asymptotically at very large values of χ.

A corresponding force curve can be derived from the potential curve which represents the resultant force acting between atoms at different values of χ and equals the external force which would have to be applied to produce a separation equal to χ. By definition, the force curve is the first derivative of the energy curve. Thus the force passes through zero at $\chi = \chi_o$ and rises to a maximum at a value of χ corresponding to the inflection point of the energy curve as shown in the lower half of Figure II-1. In principle, the value of χ at the force maximum would be the extension at which the crystal would break and the value of the force at the maximum would be the theoretical strength. Thus it can be seen that if a potential function can be established which truly describes the behavior of a substance, it provides a useful vehicle by means of which the various properties of the substance can be related. The development of relationships between properties which are capable of direct measurement on real materials and the theoretical strength which is not measurable directly constitutes the basis for a practical approach to the theoretical strength problem.

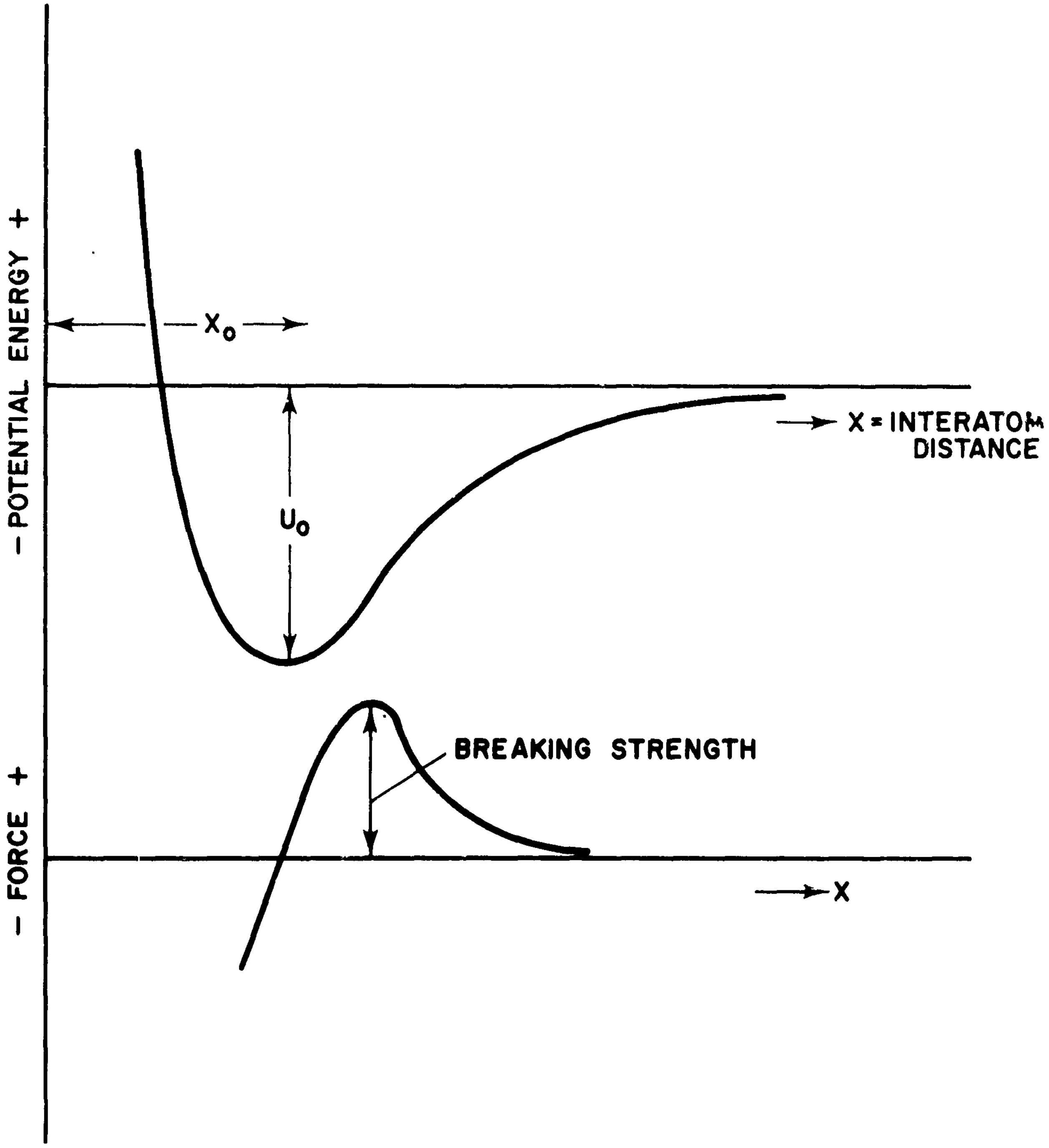

Figure II-1. Potential Function and Force Function for One-Dimensional Crystal.

The potential function for the hydrogen molecule and for a very few other substances has been computed by quantum mechanical methods. For most substances accurate quantum mechanical calculations are not feasible even with the highest-speed computers now available; hence, empirical functions fitted to various experimentally determined properties are employed instead. By empirical fitting of assumed potential functions to sets of observed data a satisfactory correlation of several properties has been achieved in some of the simpler types of solids (argon, alkali halides, etc.).

The recognition that the behavior of many solids is primarily controlled by a particular type of bonding has led to the employment of assumed potential functions having characteristic mathematical forms. Thus in the case of metallic and covalent bonding, the so-called Morse function is commonly used. For ionic crystals a function of the Born or Born-Mayer type has given good results. For crystals in which van der Waals forces play the primary role, the Lennard-Jones type of potential function has been extensively studied.

All of these potential functions* may indeed in a given case be applicable. However, there are real differences in the shape of the potential function for different classes of binding as illustrated in Figure II-2. Metallic and covalent bonding yield steeper and sharper potential functions than found for ionically bonded solids or van der Waals bonded solids.

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*The several potential functions may be expressed in their simplest form as follows:

Morse $U = D\left[1 - e^{-a(X - X_0)}\right]^2$

Born $U = -\frac{A}{X} + \frac{B}{X^n}$

Lennard-Jones $U = -\frac{A}{X^m} + \frac{B}{X^n}$

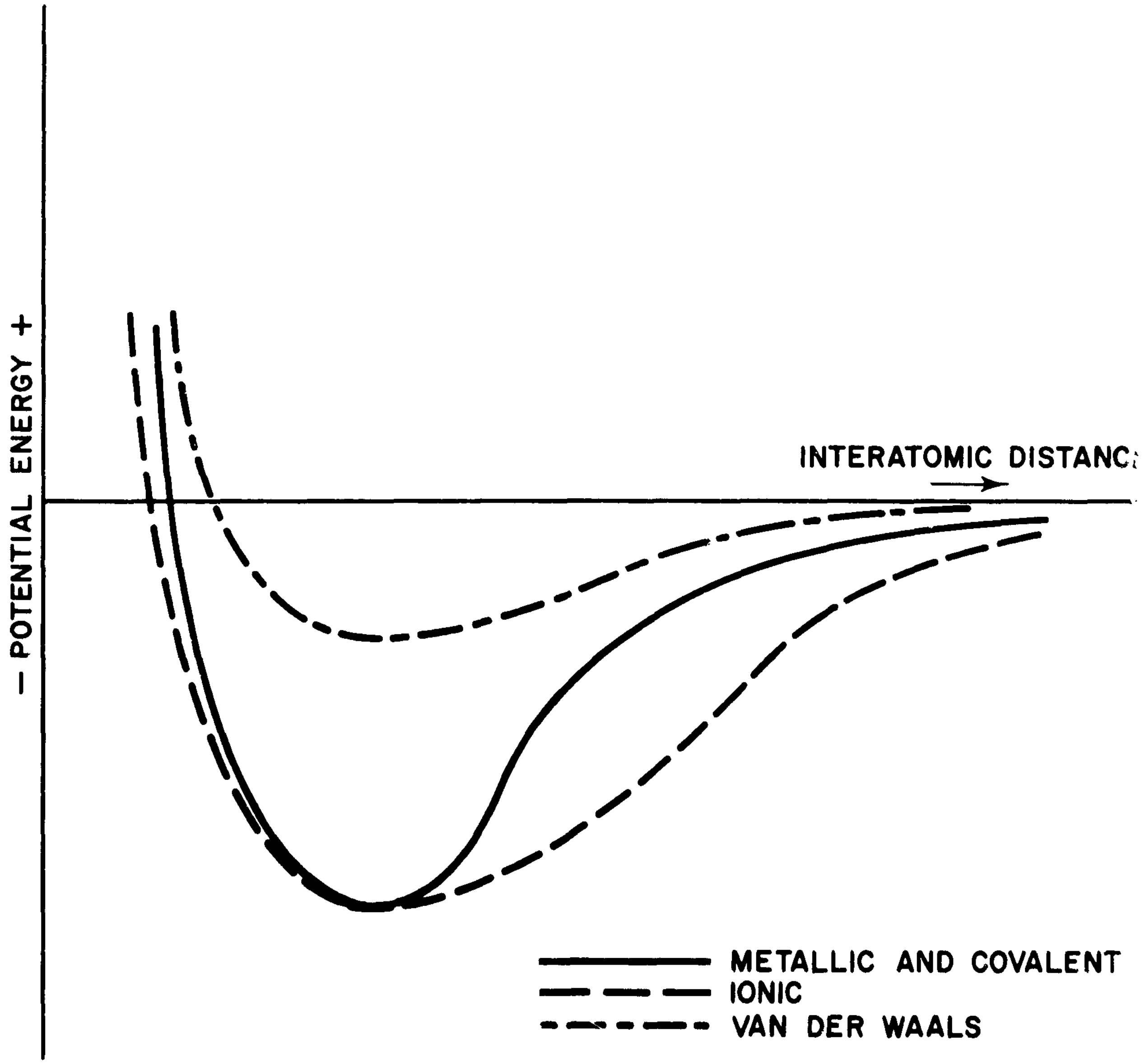

Figure II-2. Potential Functions of Different Bond Types.

The mathematical form of the potential function is rarely determined uniquely by empirical methods. The only exceptions are the potential functions for a few diatomic molecules for which very complete sets of accurate spectroscopic data are available. In these few cases, potential functions derived from experimental data deviate from all of the simpler potential functions, such as the Morse function, by amounts which would correspond to 25 to 100 per cent error in the calculated theoretical strength of a solid having interatomic force fields similar to those of the molecules.

Unlike the spectra of the few molecules mentioned above, the available experimental data on solids do not provide information sufficient to define the precise mathematical form of the potential function. In other words, there is no experimental means of determining completely the shape of the potential curve, although portions of the curve can be obtained readily. Elastic constants, which may be measured directly, and force constants (derived from optical spectra, neutron scattering and other data) give the curvature at the minimum in the potential energy function; X-ray data give the equilibrium atomic positions corresponding to the minimum; and the cohesive energy (derived from the thermodynamic data) is related to the depth of the potential well.

If one of the simpler types of functions (e.g., Morse function) is assumed, the above data for simple solids are sufficient to determine all of the adjustable parameters in the potential function. Other properties derivable from this potential function may be compared with experimental values. The greater the number of properties that can be treated satisfactorily, the more confidence one has in the utility of the potential function. The agreement often is remarkably good for several properties of substances like the alkali halides. However, the properties amenable to quantitative treatment in this manner are not sensitive to the part of the potential curve relevant to theoretical strength, that is, the region of the inflection point. Furthermore, significant deviations do occur in a sufficient number of cases to indicate inaccuracies in the form of functions assumed.

The single interatomic potential function usually employed in the treatment of highly symmetric solids, such as the alkali halides and the solid state of rare gases, neglects all directional effects in the force fields; i.e., central force fields are assumed. Although this is a fairly good approximation in the substances mentioned, the approximation is not consistent with all experimental observations, such as stability of different crystalline forms and the relationships between elastic constants. Theoretical studies also lead to the conclusion that small directional effects exist even in the rare gases and alkali halide solids. Furthermore, X-ray and neutron scattering data clearly indicate deviations from the additive central force fields usually assumed. The effects of such deviations on the calculated theoretical strength may be neglected in cubic solids but probably not for other close-packed solids. Neglect of directional effects is likely to introduce serious errors in other cases.

Nevertheless, with these limitations being acknowledged, the use of Morse functions, Born or Born-Mayer, and other similar functions is recommended in studies of theoretical strength. A formal statement of how they may be employed follows.

One or more potential functions may be selected to represent the various types of interatomic force fields considered appropriate to the type of chemical binding and to the structure of the crystal. In general, these functions will be related to changes of interatomic distances and angles (i.e., internal coordinates), combined in a manner corresponding to the crystal symmetry. The internal coordinates should also be related to the direction of the external force. The potential functions then are summed over the internal coordinates to obtain the potential energy of the solid. This corresponds to the energy of the solid at 0°K referred to free atoms (or ions). At other temperatures, entropy must be included so that the energy becomes the Helmholtz free energy in thermodynamic terminology.

Having constructed the potential energy function of the solid as a function of interatomic distances and angles, we now seek methods to transform the function to the external coordinate having the direction of the applied force. A relationship between a large number of internal coordinates and one external coordinate is required. Since the strain is uniform throughout the solid, one need consider only a small typical region of the solid. The size of this region is determined by the symmetry of the strained solid and by the number of different types of interatomic force fields relevant to the particular solid. The transformation becomes more tedious as the complexity of the solid increases. For small displacements, methods employed in the study of vibrations in solids and large molecules could be used. However, for large displacements corresponding to maximum elongation, iterative procedures may be required to determine the relationship between interatomic displacements and the external displacement.

The potential energy function of the solid may now be differentiated with respect to the appropriate external coordinate to obtain forces. The maximum force is the required theoretical strength. It occurs at an inflection point in the interatomic potential function in simple cases where a single force field gives an adequate representation of the properties of the solid.

Elastic constants for the 0°K temperature are derived in an analogous manner. The equations for the elastic constants, together with the condition equations for the cohesive energy and zero force in the normal atomic positions, may be used to evaluate some of the parameters in the potential energy function of the solid. Other properties, such as the vibrational frequency distribution, may also be correlated by appropriate extension of these methods. The application of lattice dynamics, in turn, leads to temperature dependent properties. Thus, in principle, many different properties are correlated with the solid potential energy function.

Examples of theoretical strength evaluations are treated in other sections of this report. A polymer, one of the more complex examples, is amenable to treatment. Other cases, such as graphite and silica, could be treated in a similar manner. The simpler solids such as cubic crystals are covered earlier.

The formal methods described above are applicable to any solid, but are likely to require an excessive effort in many of the more complex cases. The principles, if not detailed analysis, may be applied in other ways; e.g., to obtain approximate relationships between theoretical strength and other properties. The potential function concepts also provide a coherent basis for comparing the various methods for obtaining theoretical strength since all properties that are related to the dynamics of a crystal lattice and to interatomic forces are related formally through the potential treatment described above. Utilization of an ensemble of data on structure, elastic constants, thermodynamic properties, etc., in a manner consistent with the geometry of the solids and with concepts of interatomic forces should yield satisfactory estimates of theoretical strength.

Theoretical strength may be considered as being a product of several factors each of which may be appraised separately in light of our knowledge of the properties of chemical bonds and of interatomic forces in molecules and solids in order to estimate the reliability of the strength prediction.

The cohesive energy density is the product of the number of bonds per cubic centimeter multiplied by the bond energy when a single type of potential function is adequate or a sum of the latter, if more than one is required to represent the properties. In any case sufficient information is available either from experimentally determined thermodynamic and related properties or semiempirical correlations thereof to permit assignment of numerical values to the parameters with reliabilities varying from about one to ten per cent in most cases that are likely to be of interest. This is essentially an estimate of the availability and reliability of thermodynamic and structural data needed to evaluate two parameters in the potential function: position of the minimum and depth of the potential well (bond dissociation energy). In addition, one can obtain values for bond force constants or the equivalent elastic constants fairly readily but with somewhat less accuracy, say 5 to 25 per cent.

A second factor arises from the non-linear nature of the stress-strain function. This in turn may be considered to be the product of two factors. One is a shape parameter in the interatomic potential function (e.g., "a" in the Morse potential function); the other is a more complex transformation function which gives the relationship between the strain and the changes in interatomic distances and angles.

The former probably contributes from 25 to 100 per cent to the uncertainty in any evaluation of theoretical strength. This opinion is based upon consideration of the empirical nature of the functions and the paucity of experimental data relevant to the part of the potential function (inflection point) related to theoretical strength.

The other factor can be evaluated quantitatively only in those cases where a complete potential function treatment is feasible. It is obtained from a summation of components of the internal displacement and forces in the direction of the external displacements and forces. It has the value unity in the linear molecule with one type of bond and is near unity in planar structures similar to graphite. The mathematical relationships involved are similar to the transformation from interatomic force constants to the appropriate elastic modulus. The latter have been derived for some of the simpler solids. The difference arises from the difference between Hooke's law forces applicable to small displacements and the nonlinear forces occurring in large displacements (20 to 30 per cent elongation) relevant to theoretical strength. Errors arising from this factor probably can be neglected in cubic solids, and possibly in other close-packed solids as well, if the deformation is such that it does not lead to another stable crystalline form. In other cases, such as the crystalline polymethylene treated in Section V, errors arising from neglect of the transformation factor may be comparable to the other errors.

In those cases where structural data are not available the potential energy treatment cannot be applied. Furthermore, in such cases the simple approximation of strength, ~ 1/20 of the modulus may be subject to large errors. Elastomeric and glassy materials above their softening temperatures are excluded. (See sections on glasses and polymers.)

A general statement concerning reliability of estimates of theoretical strength is that for cubic solids, the estimate should be within a factor of about two. For more complex solids, this probably is too optimistic and a more reasonable figure is an error not greater than a factor of three with 95 per cent confidence.

A prediction of the upper limit of theoretical strength of any substance, known or unknown, may be appropriate. From considerations discussed above and from current understanding of the nature of the chemical bond, a maximum theoretical strength of greater than $1 - 3 \times 10^{12}$ dyne/cm^2 seems highly improbable. Few real substances are likely to approach this upper limit and later sections of this report give estimates for different solid types which may be compared with this ultimate value.

SECTION III - THE COHESIVE STRENGTH OF CRYSTALS

List of Symbols

α - constant in theoretical shear strength expression.

α_1 - vectorial thermal expansion coefficient.

a - constant = $(m+1)/(n+1)$.

A_o - atomic area.

b - constant = $n-m$; also magnitude of Burgers vector.

β - constant in theoretical cohesive strength expression.

C_{11}', C_{44}' - elastic constants in direction of interest.

C_{11}, C_{12}, C_{44} - elastic constants referred to cube axes.

D - equal to $(x-x_o)$ at the maximum force value in the variable lattice potential.

D' - D for the special case of the Morse potential function.

e - Napierian base of logarithms; also the charge on an electron.

γ_1 - vectorial surface energy.

H_s - heat of sublimation.

h - Planck constant.

k - Boltzmann constant.

m - exponent in Lennard-Jones potential function.

μ - shear modulus.

n - exponent in Lennard-Jones potential function.

N - Avogadro number.

r - interatomic spacing.

σ - tensile stress.

σ_{coh} - theoretical tensile cohesive stress.

σ_{frac} - theoretical stress for crack nucleation.

τ - shear stress.

τ_{max} - theoretical maximum resolved shear stress for shear failure.

T - absolute temperature.

U - potential energy.

U_o - vector binding energy per atom.

$\overline{U}$ - average value of U_o.

u - bond energy.

V - atomic volume.

x - displacement of atoms in a given direction.

x_o - equilibrium spacing of atom in a given direction.

x_{max} - displacement at energy maximum.

$\overline{x}$ - mean distance of thermal vibration.

ϕ - Lennard-Jones potential.

Φ - constant in theoretical cohesive stress calculation.

A. INTRODUCTION

Materials that are used specifically for their ability to resist high mechanical stresses are almost always built up from crystals. This is true for metallic, ceramic, and polymeric materials. There is a good reason for this: a solid is in its lowest possible energy state when its molecules are neatly arranged according to some simple periodic pattern. Because its energy is very low when it is crystalline, a solid endeavors to maintain its crystallinity when subjected to stresses that tend to deform or break it. This gives a special and relatively simple character to the modes of failure of crystalline solids. Failure in tension occurs by the formation and growth of planar cleavage cracks; failure by shear occurs by the formation and growth of dislocation loops.

In the continual search for materials of great strength, it is important to be aware that an upper limit of feasibility exists for crystalline solids, and to know what the magnitude of the upper limit is. Certain existing materials, such as steel, already have great strength and this strength approaches the upper feasible limit for iron-carbon alloys in polycrystalline form. Because the chemical bonds in diamond are the strongest ones known, the intrinsic strength of mono-crystalline diamond (or graphite) imposes an absolute upper limit that is only about 100 times the strength of steel. Thus it is unlikely that very strong substances will be found by pure chance. Because of defects in them, solid materials usually have strengths much weaker than their intrinsic cohesive strengths. This is especially true when they are first synthesized, so it is important to be able to estimate what strength could be expected of a substance if it had optimum form and structure.

In principle, theoretical strengths, both tensile and shear, can be calculated from the quantum theory of chemical binding. However, this is not a practical procedure for dealing with a large variety of materials for several reasons. One is that such calculations are very tedious. Another is that most of the background of such calculations is concerned with the isotropic property, cohesive *energy*, whereas the cohesive *stress* is an anisotropic property.

Semi-empirical force laws based on quantum mechanical principles are also difficult to apply to strength calculations, because in their simplest form they can only be applied to central force models in which the energy depends only on the distances between atoms, whereas crystal bonding in most cases involves directional bonding. When these laws are modified to take account of directional bonding, the resulting calculations again become tedious. The difficulties that arise because of directional bonding are more severe for calculations of the theoretical shear strength than for the tensile strength, because directional bonding is relatively more important in the former case.

Finally, one notes that existing theory has notoriously little predictive power, being mainly a kind of retrospective analysis.

The approach taken here is to find relations between readily-measured anisotropic physical properties and cohesive stresses, thereby making it possible to estimate cohesive stresses for various crystallographic directions. Anisotropy is not of prime importance for cubic metals, but it is quite important for such things as hexagonal metals, layered silicates, and fibrous high polymers.

Tensile cohesive strength will be related to: Elastic stiffness, thermal expansion, and surface energy, as well as roughly to cohesive energy and atomic diameter. An empirical atomic force law will be used for sample calculations throughout this treatment. The same method may be readily applied for any other force law, and the effect of changing the functional form of the force law will be indicated.

The term "tensile cohesive strength" is taken to mean an upper limit of tensile strength (in a given direction) under idealized conditions. Thus it is assumed that:

a) no allotropic changes occur as the solid is stretched.
b) the solid is infinite in extent so only one strain component is important.
c) the temperature is low so that thermally activated crack nucleation cannot occur.
d) no surface notches, inclusions, or other stress concentrators are present.
e) plastic flow does not occur.
f) no chemical reactions between the material and its environment occur.

The effect of thermal activation on the cohesive strength will be considered in a later section, as will chemical reactions.

For the design of new materials, it would be useful to be able to predict the cohesive strengths of unknown or poorly known substances. The only practical means for this at present is "intuitive chemistry;" that is, small extrapolation from known substances. This will be discussed briefly.

Finally, the theoretical shear strengths of crystals will be considered. The conditions under which shear failure or tensile failure should occur preferentially will be discussed.

B. RELATION OF STRENGTH TO OTHER ANISOTROPIC PROPERTIES

Consider a piece of solid that is being separated into two parts along a plane that passes between two planes of atoms. From Hooke's Law it is known that the initial resistance to deformation must depend linearly on the separation distance. Since solids fracture suddenly at small strains, it may also be concluded that the resistance to separation must rise quickly to a maximum value and then decrease. On the other hand, van der Waals attractive forces act at relatively large distances so that weak resistance to separation should extend quite far (that is, the binding stress should not suddenly drop to zero). Since the wave functions that describe the electronic structure decrease exponentially with distance, it is reasonable to expect that the condition expressed just above can be represented by forces that decrease exponentially with distances, for large separations.

a) Choice of a Binding Stress Law

The simplest stress law that combines all of the above properties is the following:

$$\sigma(x-x_o) = \left(\frac{U_o}{A_o D^2}\right)(x-x_o)\, e^{-(x-x_o)/D} \qquad (1)$$

where x_o is the initial separation distance, x is a larger distance, U_o is a constant that will be shown shortly to be the binding energy, A_o is the atomic area over which the forces act, and D is a constant that may be seen to be a "relaxation distance." The graphical form of this equation is shown in Figure III-1. It may be seen that it rises linearly at first, reaches a maximum at x_{max}, and then falls away exponentially in the required manner. Hooke's Law determines the initial coefficient in this equation quite critically so that only the distance D, is uncertain.

The present stress law is certainly not rigorously obeyed, as comparison with even a simple quantum theory such as that of the hydrogen molecule will show. However, its shape is qualitatively correct, and it will be shown

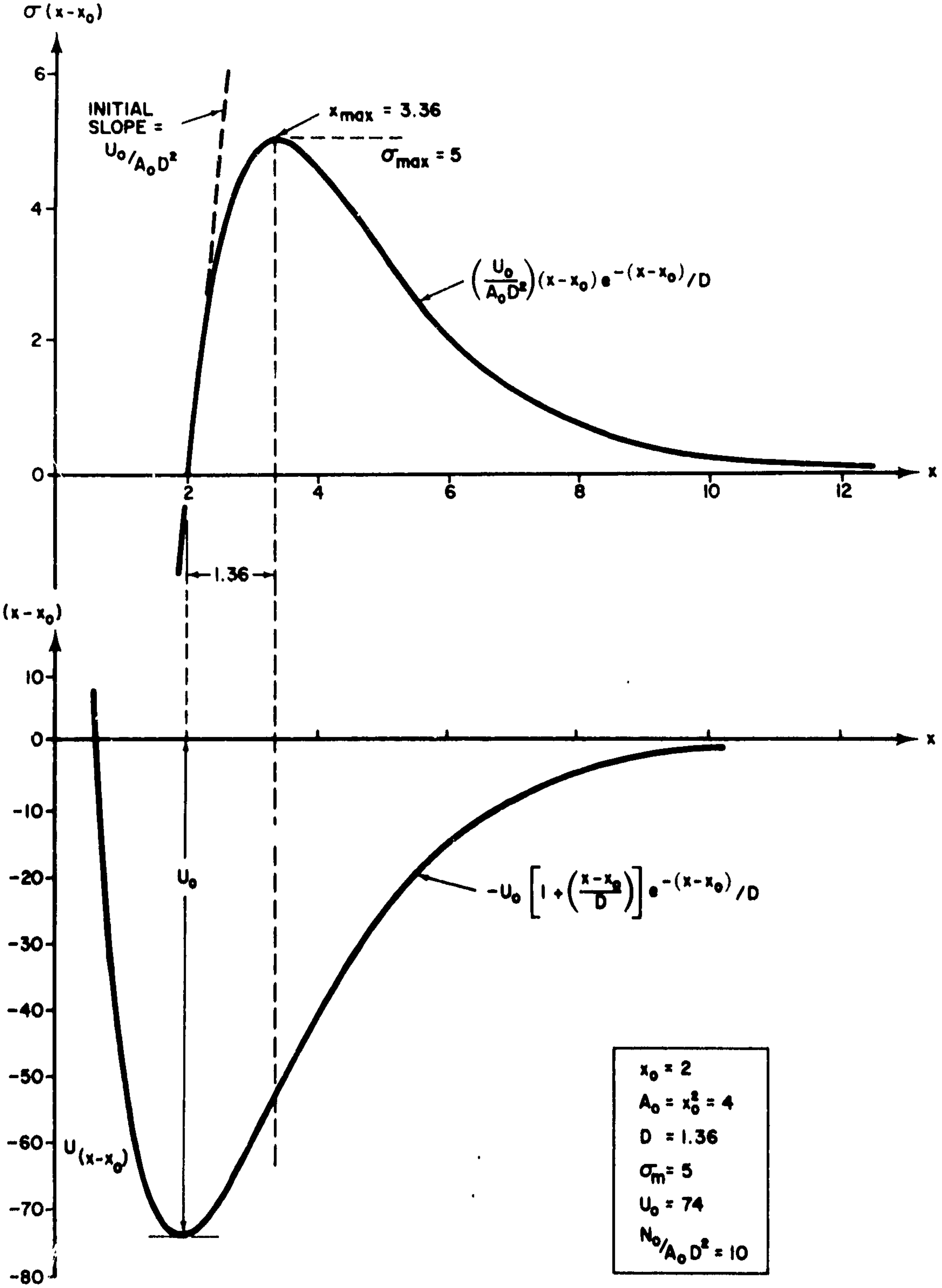

Figure III-1. Binding Stress Law and Corresponding Potential Function.

here that it gives reasonable relationships between a variety of physical properties. Also, it must be kept in mind that at the present time, little theory and few experiments exist that deal with the properties of a solid that is being subjected to large tensile strains. Therefore, it is necessary to extrapolate measurements from the small strain regime to large strains. Without a background of measurements made at large strains it is not realistic to try to develop any but the simplest of theoretical treatments. Details of the present treatment, using the force law of equation (1), are given in Appendix I, in order not to retard the pace of the main text. It is emphasized that the method outlined in Appendix I may be applied in general to any force law involving up to three force parameters.

b) Heat of Sublimation

Equation (3a) of Appendix I relates the tensile cohesive stress to the vector binding energy per atom U_o, the relaxation distance D, the area per atom A_o, and the numerical factor e = 2.72:

$$\sigma_{coh} = \frac{U_o}{eDA_o} \tag{2}$$

If U_o is averaged over all directions, and eDA_o is taken to be the atomic volume V, this becomes:

$$\sigma_{coh} \simeq \frac{\overline{U}}{V}$$

so, if H_s is the sublimation energy per unit volume, the cohesive stress is just approximately equal to it:

$$\sigma_{coh} \simeq H_s \tag{3}$$

After detailed and careful lattice theory calculations, Born and Furth [Proc. Camb. Phil. Soc. 36, 454 (1940)] concluded that the tensile cohesive stress for a face-centered-cubic structure, bonded by centrally acting forces between particles should be given by:

$$\sigma_{coh} = \left(\frac{nm}{n-m}\right)\frac{u}{4}$$

where u is the interaction energy between two particles and n, m are the exponents in the Lennard-Jones potential function.* The interaction energy u, is related to the heat of sublimation by:

$$u \simeq 0.094\ H_s$$

so the cohesive energy is related to H_s by:

$$\sigma_{coh} \simeq 0.024 \left(\frac{nm}{n-m}\right) H_s \tag{4}$$

This is certainly roughly true, and may be a good approximation for isotropic solids. For highly anisotropic solids it will be quite misleading. For example, graphite has a rather high heat of sublimation and is strong in the a-axis direction, but is exceedingly weak in the direction of its c-axis. This emphasizes one of the pitfalls of attempting to correlate vector properties with scalar properties, and it is believed that equation (4) should only be used with discretion.

Equation (4) provides a simple means for estimating the effect of bond type on the tensile cohesive stress. Table I (p. 61) gives values of (nm/n-m) for the range of n and m that seem to be observed in practice. The typical extremes are m, n = 1, 10 for a hard ionic crystal like MgO; and m, n = 6, 12 for a molecular crystal like solid CO_2. Metals and covalent crystals fall in between. It may be seen that the coefficient relating tensile cohesive stress and the heat of sublimation changes by a factor of ten between the extremes.

c) Thermal Expansion

A vector property that is useful for present purposes is the thermal expansion coefficient α_1, because it can be measured with bulk samples by

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*If u is the bond energy and n, m are exponents with n > m, this potential law is:

$$\phi(x) = u\left(\frac{nm}{n-m}\right)\left[-\frac{1}{m}\left(\frac{x_o}{x}\right)^m + \frac{1}{n}\left(\frac{x_o}{x}\right)^n\right]$$

dilatometry, or with small particles by means of X-ray diffraction. Equation (4a) of Appendix I shows how the cohesive stress is related to it:

$$\sigma_{coh} = \Phi/\alpha_1 V \tag{5}$$

where Φ is a constant [equal to (k/2e) for the law of equation (1)], V is the atomic volume, and α_1 is the thermal expansion coefficient in the direction of interest and measured above the Debye temperature where it is nearly independent of temperature.

Equation (5) is in accord with the general experience that soft solids expand rapidly with temperature while hard ones do not. Also, for an anisotropic crystal like zinc, α_1 is larger parallel to the c-axis (the mechanically weak direction) than it is perpendicular to the α-axis (the mechanically strong direction) . This expression also has the advantage that it does not depend on the relaxation distance, D. The relation must be used with some caution, however, when substances with complex structures are considered (fused silica and Invar being notable examples) because bulk expansion is not always simply related to the expansion of interatomic bonds.

d) Elastic Stiffness

Through the use of modern ultrasonic methods, elastic stiffnesses can be measured readily, making this property useful for estimating cohesive stresses. The measurements do require somewhat larger samples than thermal expansion measurements, but have the advantage of being more directly related to the cohesive stress. The equation relating stiffness and cohesion is (5a) of Appendix I:

$$\sigma_{coh} = \left(\frac{D}{x_o}\right)\frac{C_{11}'}{e} \tag{6}$$

where C_{11}' is the elastic stiffness in the direction of interest. Since (D/x_o) is expected to be nearly independent of material and direction because an increase in x_o will tend to be associated with an increase in D, this relation is often simplified to the "rule-of-thumb":

$$\sigma_{coh} = C_{11}'/\beta \qquad (7)$$

where β is a constant approximately equal to 10. If it were possible to measure D independently, equation (6) would certainly be more reliable than (7), but this is in fact not possible, so one is forced to be satisfied with (7). However, in dealing with the cohesion of polymers it may be desirable to make independent estimates of D and x_o so that equation (6) can be used.

The dependence of β on the type of binding can be estimated by using the Lennard-Jones Potential to express the binding between particles. Then the ratio between elastic stiffness C_{11}', and tensile cohesive stress σ_{coh}, becomes:

$$\frac{C_{11}'}{\sigma_{coh}} = \left[\frac{b}{a^{(m+1)/b} - a^{(n+1)/b}}\right] = \beta$$

where n, m = exponents in the potential law and:

$$a = \frac{m+1}{n+1} \qquad b = n - m$$

Table II (p. 61) lists various values of β, and it may be seen that the change in β between hard ionic crystals (m, n = 1, 9) and soft molecular crystals (m, n = 6, 12) is by a factor of only about two.* This supports the assertion that the elastic modulus is a good measure of cohesive strength for strong crystals and a conservative value of β is 20, whereas favorable circumstances might allow β to reach values as small as 10.

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*Estimates of values for (m, n) and β for various types of binding are:

	(m, n)	β
Ionic	(1, 9)	15.0
Covalent	(2, 12)	20.2
Alkali metals	(1, 2)	7.0
Noble metals	(3, 9)	18.4
Transition metals	(4, 9)	19.9
Molecular crystals	(6, 12)	28.2

e) Surface Energy

Most techniques for measuring surface energies yield an average value which may be quite different from the maximum and minimum vector values. However, the method of quantitative cleavage provides vector surface energies that can be applied to cohesive stress estimates, using equation (6a) of Appendix I:

$$\sigma_{coh} = \left[\frac{2\gamma_1 C_{11}'}{x_o e^2}\right]^{1/2} \tag{8}$$

where γ_1 is the specific surface energy of the plane across which the stress acts. Since γ_1 (measured at T = 0°K) is the work of decohesion per unit area, it should be closely related to σ_{coh}. Note that the range parameter D does not appear in this equation, making it somewhat more reliable than the other estimates.

f) Comparison of Estimates

Examples of the theoretical strength as estimated by equations (7) and (8) are listed in Table III (p. 62), along with the result of a detailed lattice calculation for NaCl by Zwicky.

C. THERMALLY ACTIVATED CRACK NUCLEATION

According to simple crack nucleation theory [J. C. Fisher, J. Appl. Phys. 19, 1062 (1948)] the fracture stress at a finite temperature T, should be:

$$\sigma_{frac} = \left[\frac{6.23\,\gamma_1^3 (C_{11}')^2}{k\,T \ln(NkT/h)}\right]^{1/4} \tag{9}$$

where γ_1 = specific surface energy, C_{11}' = elastic stiffness modulus in the appropriate direction, k = Boltzmann's constant, h = Planck's constant, N = Avogadro's number. Some calculations from this theory are presented in Table IV (p. 63) [data on glass from Fisher's paper; data on water from L.J Briggs, J. Appl. Phys. 24, 488 (1953)]. It may be concluded that the tensile cohesive stress is not reduced very much by thermal nucleation at room temperature.

D. PREDICTION OF COHESION FROM CHEMISTRY

In the search for stronger materials it is useful to be able to predict the strength properties of compounds for which physical property data may not be available. It is not possible to do this in any absolute sense, but study of elastic constant data shows that it can be done on a relative basis because of the systematic dependence of elastic stiffness on atomic size, valence electron concentration, and atomic polarizability.

Once quantum mechanics has given the electron distribution in a chemical bond, the bonding forces can be calculated from electrostatics, except for the relatively small dispersion forces. The electrostatic force between oppositely charged centers varies as e^2/r^2 where e is the magnitude of charge on each center and r is the distance between them. In a closely-packed crystal, r is simply the mean interatomic distance and the cross-sectional area per atom is proportional to r^2 so that the stress between atoms is proportional to e^2/r^4.

Elastic stiffness data for some 20 ionic crystals (Figure III-2) and for a number of b.c.c. metals (Figure III-3) and h.c.p. metals (Figure III-4) verify the proportionality of attractive stress and e^2/r^4, and in addition show a small increase in stiffness with decreasing atomic polarizability. Also covalent crystals with the zincblende (or diamond) structure nearly obey the r^{-4} relation (Figure III-5), but f.c.c. metals show an r^{-6} dependence (Figure III-6). The stiffnesses of the b.c.c. transition metals (Figure III-3) show very little dependence on atomic size, but a strong dependence on atomic number (valence). Therefore, it may be said that if other factors are equal, the cohesive strength of a substance will increase with:

(1) decreasing atomic volume
(2) increasing valence electron concentration
(3) decreasing atomic polarizability

For molecular crystals, where dispersion forces constitute most of the binding, the third rule is inverted.

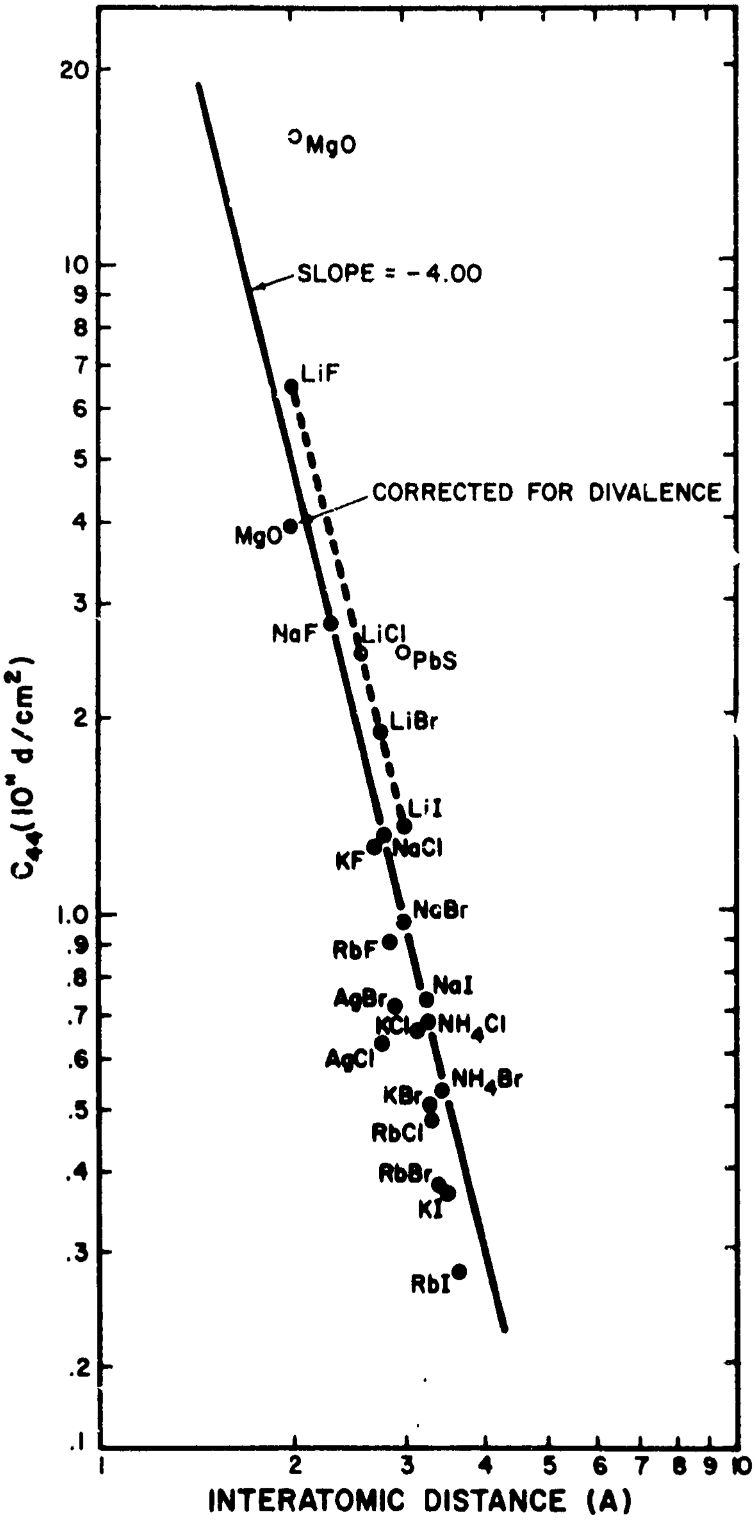

Figure III-2. Ionic Crystals with Rocksalt Structure.

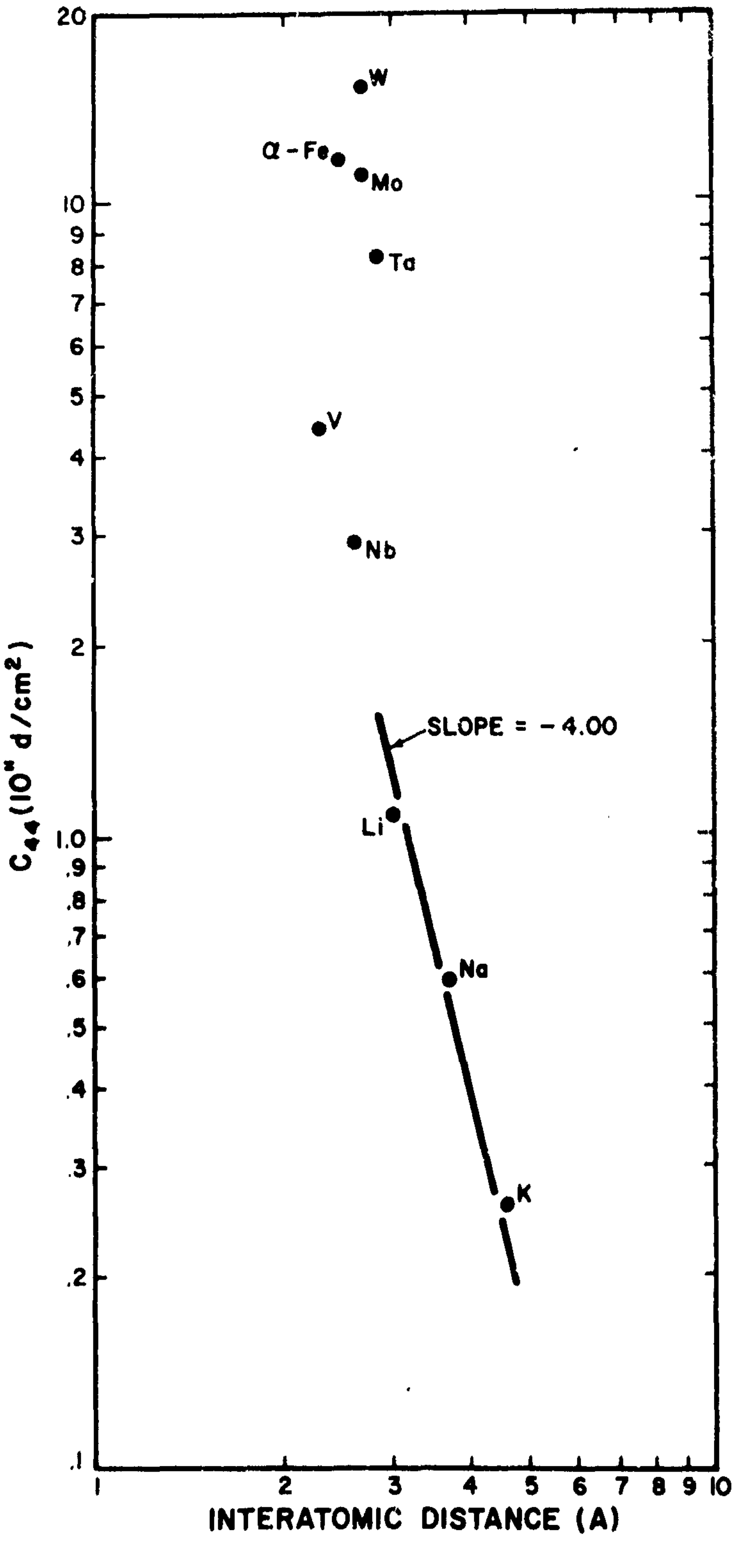

Figure III-3. Body-Centered Cubic Metals.

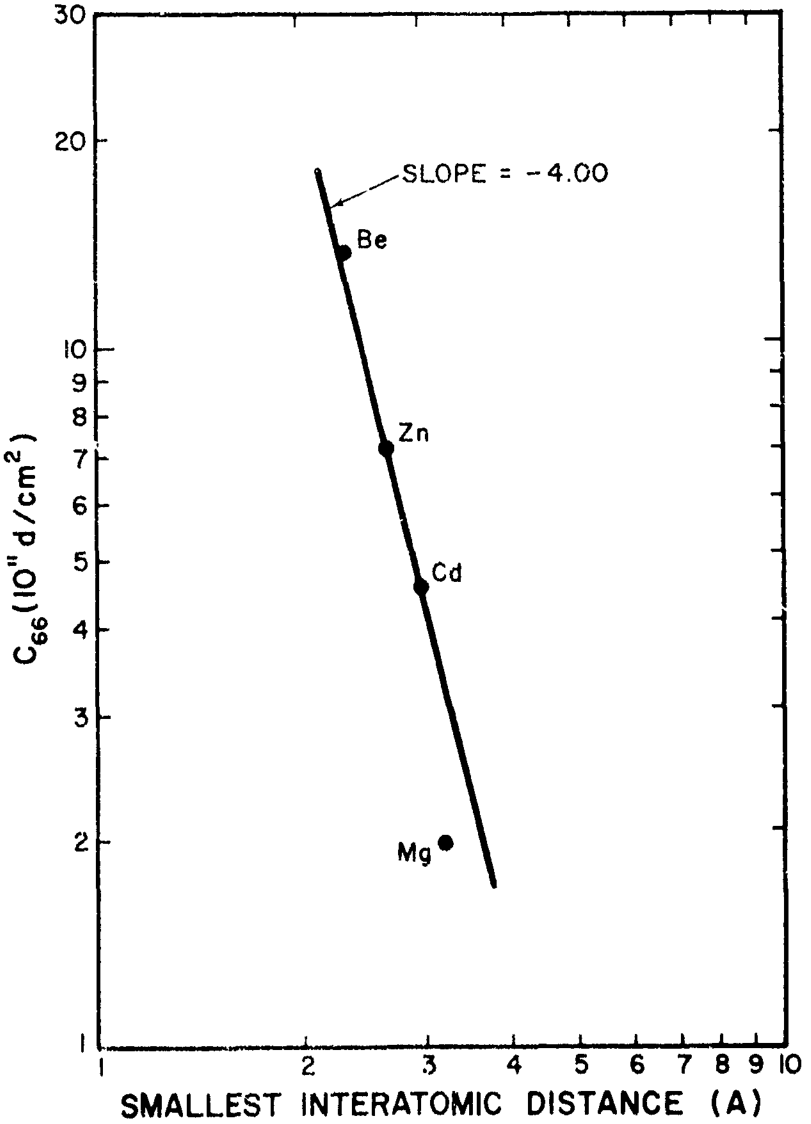

Figure III-4. Hexagonal Metals (Divalent).

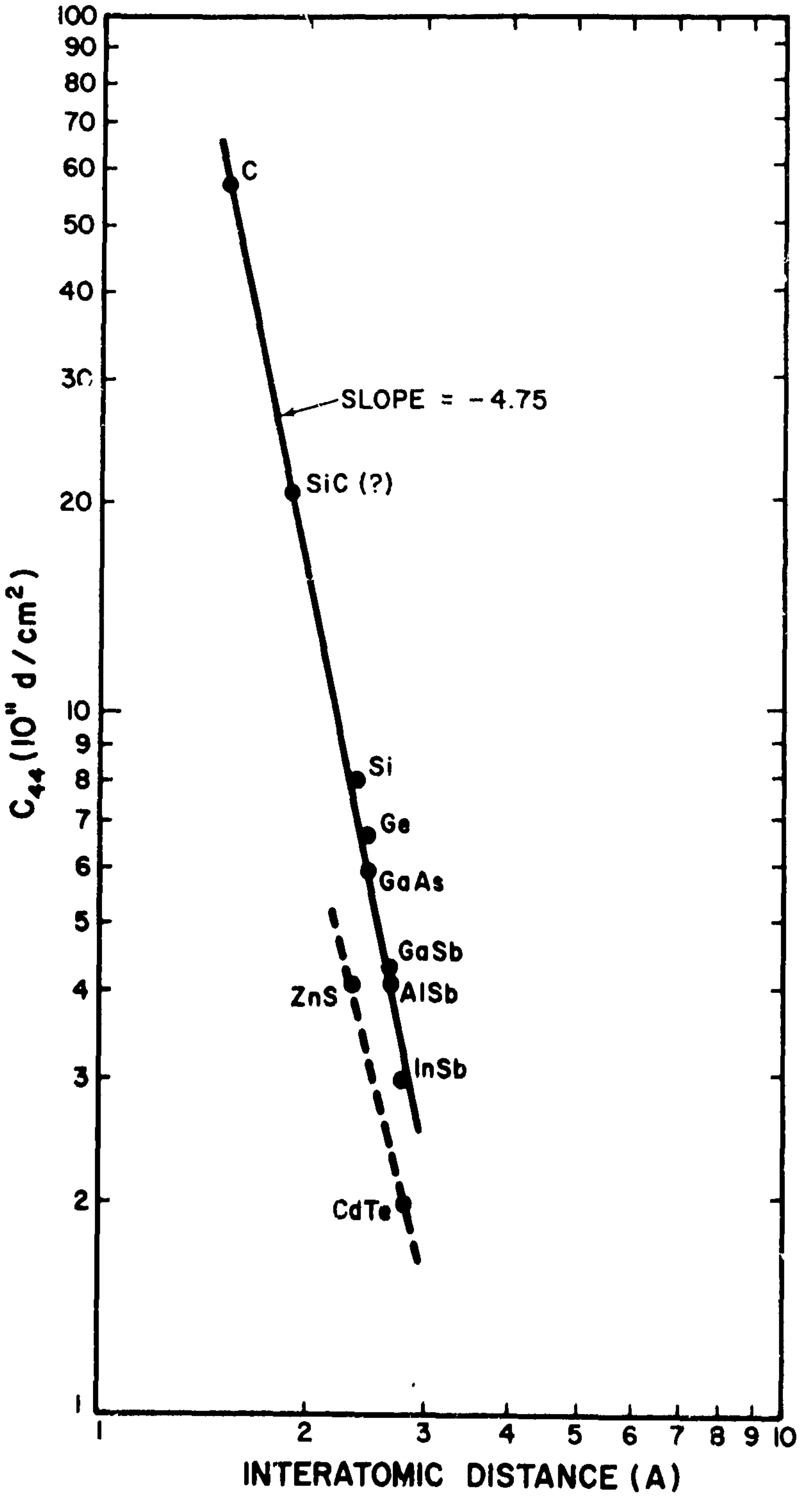

Figure III-5. Covalent Crystals with Zincblende Structure.

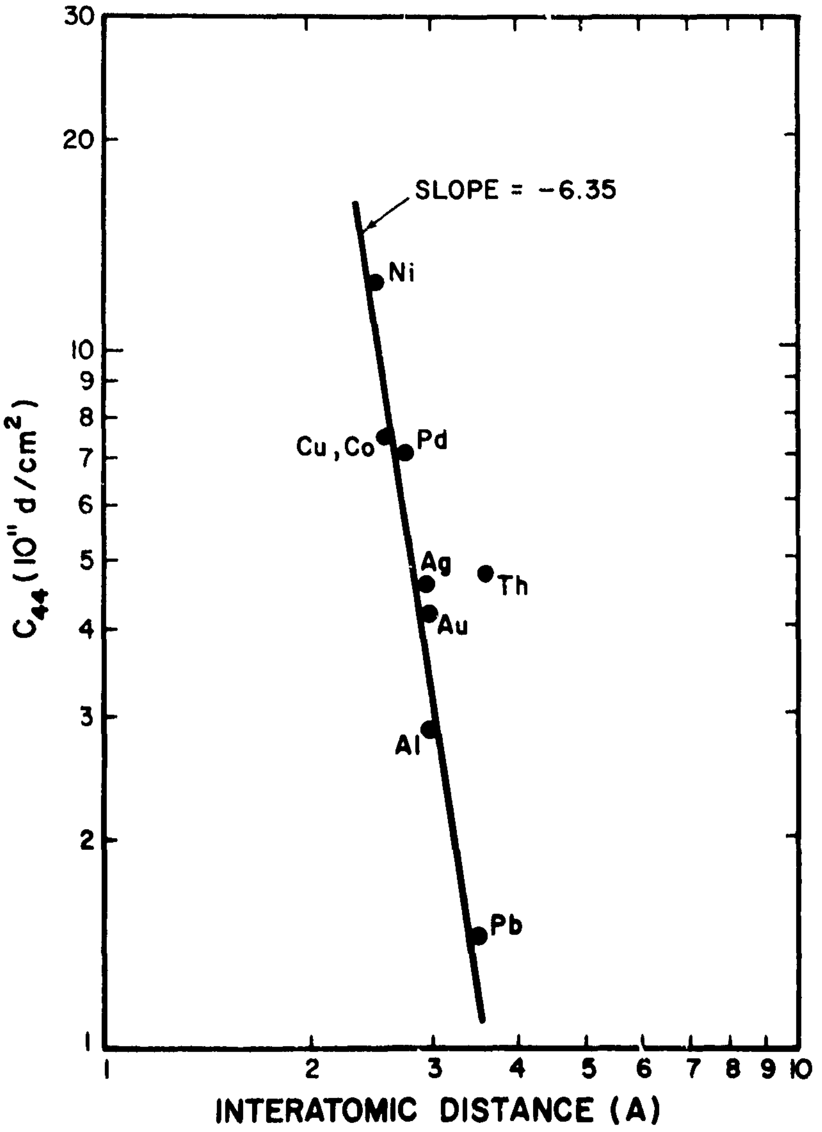

Figure III-6. Face-Centered-Cubic Metals.

0.3

E. THEORETICAL SHEAR STRENGTH

As noted at the outset, the semi-empirical force treatment of the theoretical shear strength is more tenuous than that for the cohesive strength because of the greater importance of directional bonding; i.e., variation of the force with bond angle, in the shear process. Nonetheless, based on the present state of knowledge, it appears that a reasonable estimate of the theoretical resolved-shear-stress required to cause a permanent shear displacement of one lattice period is given by

$$\tau_{max} = \alpha\mu/15 \tag{10}$$

where μ is the shear modulus and α is a numerical factor given by

$$2 \overset{\sim}{>} \alpha \overset{\sim}{>} 0.5 \tag{11}$$

Equation (10) is based on analysis of the shear strength of a perfect crystal, and of the nucleation of dislocations in crystals. These analyses are briefly reviewed below, together with some other considerations that bear on the accuracy of equation (10).

The theoretical shear strength was first treated by Frenkel [A. Phys. 37, 572 (1926)] who approximated the periodic force that is required to shear a perfect crystal by a sinusoidal function. His treatment is outlined in Appendix II. As shown there, by invoking the condition that the force law must reduce to Hooke's Law for small displacements, he found that the maximum force corresponded to a theoretical shear strength of $\tau_{max} = (\mu/2\pi)$. Mackenzie [thesis, Bristol University (1949)] noted that the use of a sinusoidal potential probably led to an overestimate of the theoretical strength, because the corresponding force increases more rapidly with displacement than would be the case for lattice potentials such as a Morse potential or a Lennard-Jones potential. For close-packed metal structures, Mackenzie used a central force model and obtained $\tau_{max} = (\mu/30)$ as a lower limit for the theoretical strength. The real strength must be somewhat greater because directional forces will also contribute to the shear resistance. Attempts (T. Jøssang, private communication) to calculate stacking fault energies (stacking faults are formed by large shears of the lattice) using central Morse forces have shown that much of the energy arises from the directional forces. This occurs even in the case of copper which has a more nearly spherical Fermi-surface than other f.c.c. metals, so that it should be most amenable to a central force analysis.

In the case of ionic crystals, the class whose binding is best approximated by central force laws, there remains the same problem of estimating the contribution due to directional forces, because the role of such forces is maximized during a shear displacement. Therefore, there is a large uncertainty in the theoretical strength, and it remains unresolved at this time. The actual value should be in the range $\mu/2\pi > \tau_{\max} > \mu/30$, however, so we choose $\mu/15$ as a rough average value, and this would suggest choosing $\alpha = 1$ in equation (10).

F. EFFECT OF DISLOCATION NUCLEATION ON THE THEORETICAL SHEAR STRENGTH

The stress at which plastic shear deformation would be started by homogeneous nucleation of dislocation loops inside a crystal has been considered by several authors.* In all cases that have been considered the room-temperature shear stresses at which the nucleation rate became appreciable were in the range $\tau_{\max} > \mu/15$. Therefore, such nucleation would not change the strength predicted above.

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*A. H. Cottrell, "Dislocations and Plastic Flow in Crystals," Oxford University Press, Oxford (1956).

F. C. Frank, in "Symposium on Plastic Deformation of Crystalline Solids," Carnegie Institute of Technology and Office of Naval Research, Pittsburgh (1950).

F. R. N. Nabarro, Advances in Phys. 1, 332 (1952).

J. P. Hirth, "Proceedings of the N. P. L. Conference on the Relation between Structure and Strength of Metals and Alloys," H. M. Stationery Office, London (1963), p. 217.

At free surfaces, on the other hand, image forces and the presence of surface ledges may lead to dislocation nucleation at lower stress levels (see Hirth's paper). The results in Table V (from Hirth's paper) indicate that for crystals with perfect surfaces such as the surfaces on some whiskers, the nucleation of dislocations at the surface occurs at about the same stress level as the theoretical strength noted above. However, for materials such as copper with low stacking energies (so that imperfect dislocations may form in them), nucleation occurs at lower stresses, particularly if surface imperfections (ledges) are present.

These considerations of nucleation suggest that the value $\alpha \sim 1$ should still be a rough approximation for materials in which only perfect dislocations may form, but that a value of $\alpha \sim 0.3$ would be a better approximation for materials in which imperfect, or partial, dislocations may form.

To the same order of accuracy as the above estimates, the temperature dependence of μ may be introduced into equation (10). In addition, however, the nucleation of dislocations occurs at lower ratios of $\tau_{\max}$ to μ at high temperatures so that α in equation (10) should also decrease with temperature. For example, the critical stress required to nucleate dislocations at a copper surface is $\tau_{\max} = \mu(1200^\circ\mathrm{K})/100$ at 1200°K versus $\tau_{\max} = \mu(300^\circ\mathrm{K})/50$ at room temperature. Again very roughly, one would expect α to decrease by a factor of about 2 from room temperature to the melting point.

Where data are available [see the review of H. B. Huntington, Solid State Physics, 7, 214 (1958)], the appropriate value of the anisotropic elastic constant C_{44}' should be used for the shear plane in question. For metals, in most cases the use of the average value $\mu = C_{44} - 1/5\,(2C_{44} + C_{12} - C_{11})$ should not lead to uncertainties greater than those already present in the above estimates for $\tau_{\max}$.

For non-metals, in many cases gross uncertainties would be introduced by the use of average modulus values, so that the value appropriate to the slip plane must be used. As an example, the shear modulus in the basal slip plane of graphite has a value one-tenth of that of the average shear modulus.

G. INTRINSIC RESISTANCE TO DISLOCATION MOTION

Even when dislocation nucleation is possible, dislocation motion must occur in order for shear failure to occur. In metals, both theory and experiment indicate that the intrinsic lattice stress that resists dislocation motion (often termed the Peierls stress) is less than the stress for homogeneous shear displacement or for dislocation nucleation. On the other hand, for ionically or covalently bonded crystals, the intrinsic lattice resistance is of the same order as the above theoretical shear strengths. This is clearly illustrated by Figure III-7 which compares the variation of hardness with elastic modulus for covalent and metallic crystals [J. J. Gilman, Mechanical Engineering, p. 55, September (1961)].

The upper line in Figure III-7 is drawn through the data for crystals with the zincblende structure which are insulators or semiconductors. The lower line correlates data for several face-centered-cubic metals. In both cases the hardness is proportional to the elastic modulus, but the proportionality constants differ by a factor of 500.

Hardness is a measure of the yield stress, or the ease with which dislocations move in a crystal. Thus for metals, in which dislocations move easily, the hardness value is a small fraction of the elastic modulus (about 5×10^{-3} for the data shown). In contrast, the hardnesses of covalent crystals are a much larger fraction of the moduli (about 10 per cent). Since this is close to what the cohesive shear strength is expected to be, it is concluded that dislocations have great difficulty in moving through covalent crystals. The reason for this is suggested by Figure III-8.

The solid circles in Figure III-8 are arranged as the atoms are along the direction of glide in the diamond (or zincblende) crystal structure. The central core of a dislocation line is shown at two positions of symmetry.

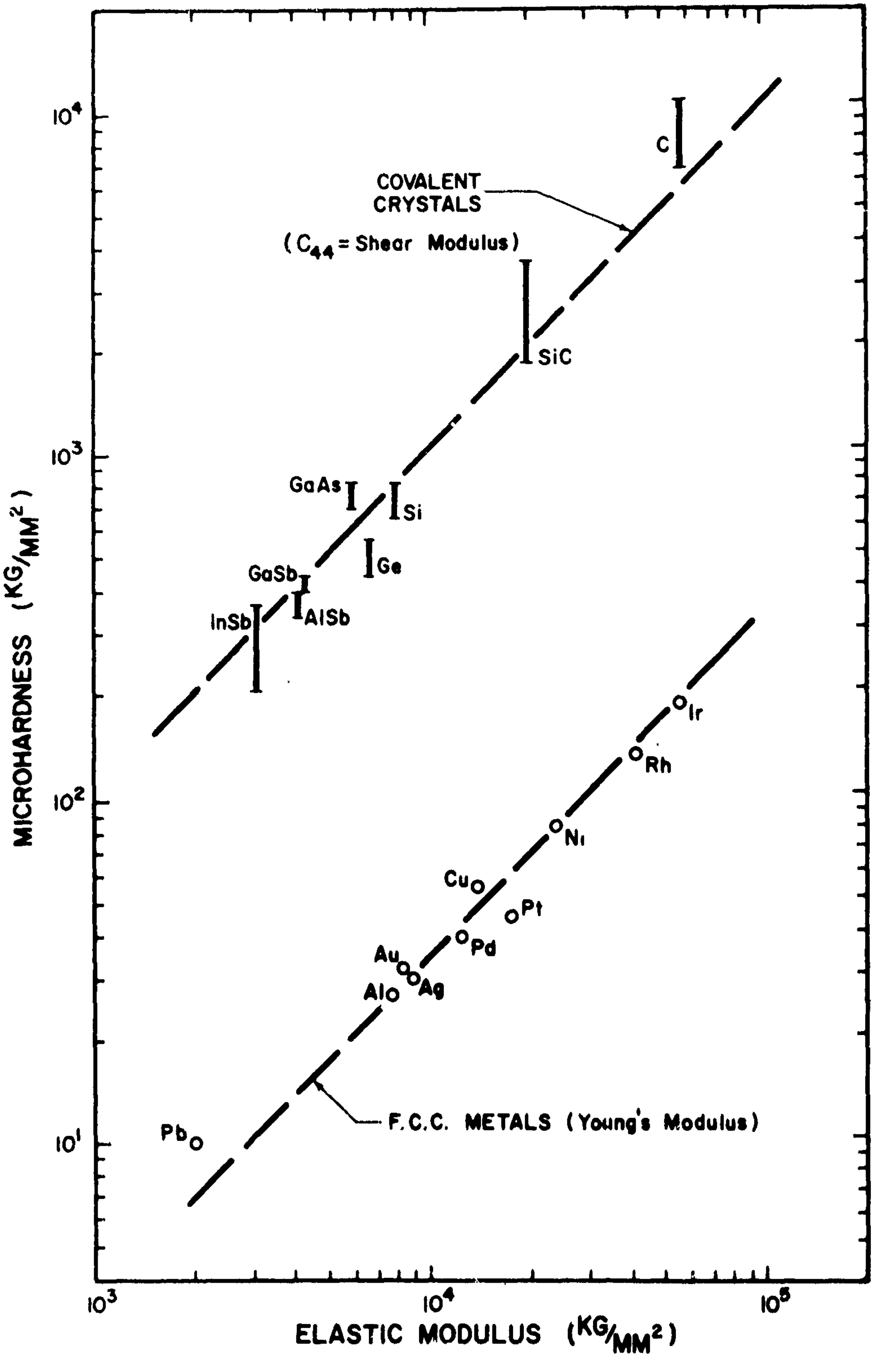

Figure III-7. Hardness vs. Elastic Modulus Compared for F.C.C. Metals and Covalent Crystals (ZnS structure).

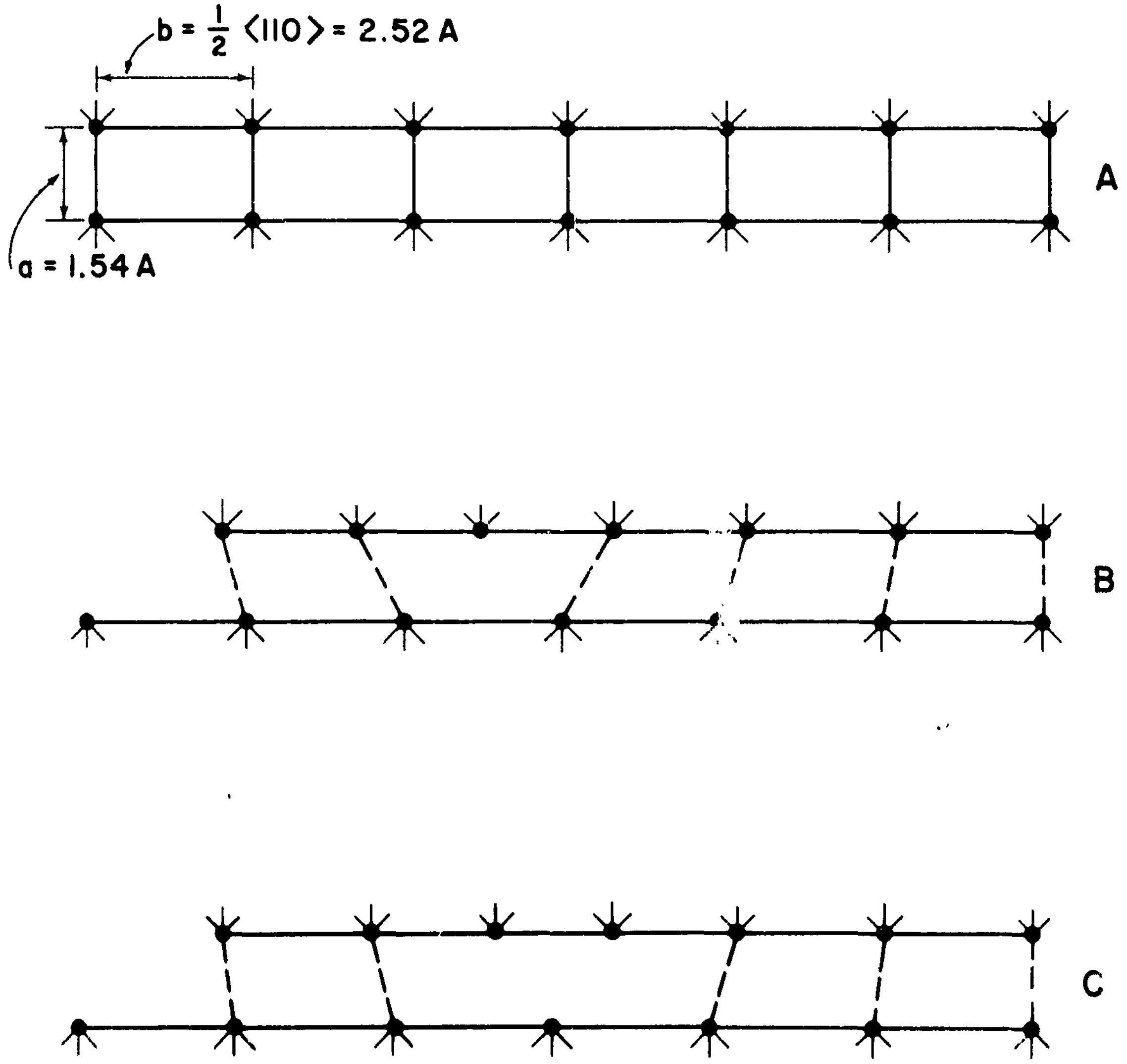

Figure III-8. Schematic Motion of the Core of an Edge Dislocation in the Diamond Crystal Structure. Each Atom has Four Bonds in the Lattice.

A) Strip of atoms lying along the glide plane in a ⟨110⟩ direction; {112} plane lies parallel to paper. No dislocation present.

B) Dislocation core in symmetric position.

C) Dislocation core moved to second symmetric position.

Only one atomic plane is shown, but the next one behind the one shown has the same geometric form; it is simply shifted by b/2 with respect to the ribbon shown. Since nearest neighbor interactions determine the behavior, only the one strip needs to be considered. According to the data of Table I, a covalent bond breaks at a strain of about 65 per cent. Therefore, the energy of the dislocation core changes markedly between the two configurations, B and C. In the configuration B, the equivalent of one bond is broken and at C, roughly two bonds are broken. As the dislocation move along then, its energy fluctuates by an amount equal to one C-C bond. The period of the fluctuations is b/2, and very little of the energy is conserved, most of it being converted directly into heat. Then, since the force that acts per atomic plane is approximately τb^2 (where τ is the applied shear stress), the work done per fluctuation is $\tau b^3/4$. This must equal the bond energy of 6.22×10^{12} ergs, so the required shear stress is $\sim 10^{12}$ d/cm^2 or about $C_{44}/10$ as suggested by Figure III-7.

The idea that nearest neighbor interactions control dislocation motions in covalent crystals is given further support by recent measurements of Chaudhuri, Patel, and Rubin [J. Appl. Phys. 33, 2732 (1962)]. They measured the velocities of individual dislocations in several crystals (Ge, Si, GaSb, and InSb) as a function of stress and temperature. They found that the temperature dependences of the dislocation velocities in these crystals can be described by Arrhenius equations. The activation energies that they determined from these equations are shown in Figure III to be proportional to the elastic shear stiffnesses of the crystals. Furthermore, it may be noted that the activation energies for dislocation glide are quite nearly equal to the energies of single bonds in Ge and Si as given by Pauling (1961). Thus the rate determining step for dislocation glide through these crystals is the breaking of individual chemical bonds.

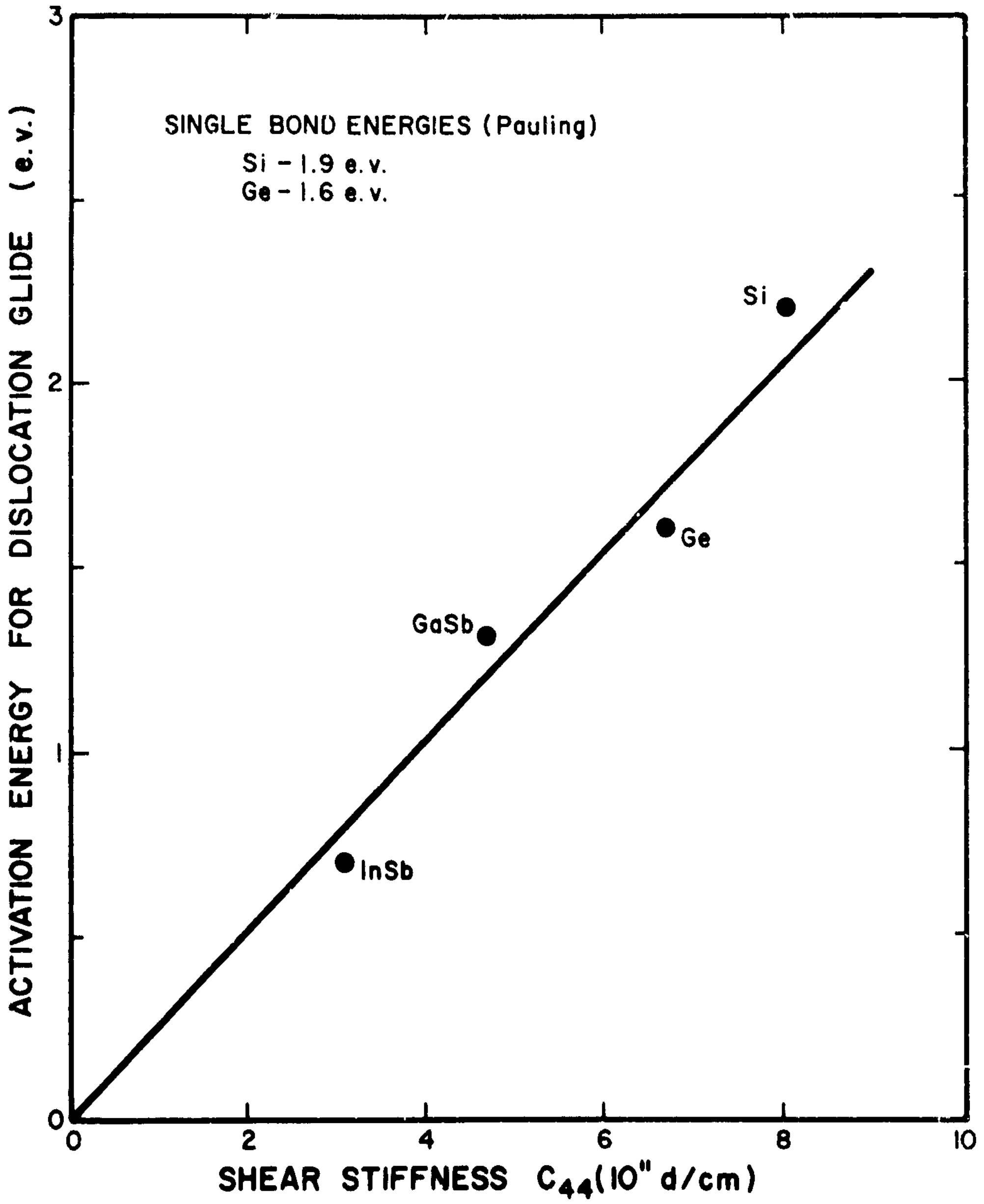

Figure III-9. Correlation between Activation Energies for Dislocation Motions and Elastic Stiffness (data from Chaudhuri, Patel, and Rubin).

H. TENSILE FAILURE VERSUS SHEAR FAILURE

In addition to considerations of the directional strength of crystals, the state of stress will influence the mode of failure of a crystal. For example, in a simple tensile test of a f.c.c. crystal, m = the ratio of the maximum resolved shear stress {111} ⟨110⟩ to the tensile stress, will be 0.5 for a tensile axis oriented in position ② in Figure III-10, and will be only 0.28 for a tensile axis oriented in position ①. In hydrostatic tension (triaxially balanced stresses) the resolved shear stress will always be zero. Thus in general, the state of stress will always tend to favor tensile failure because the maximum resolved normal stress will always exceed the maximum resolved shear stress by at least a factor of two. This factor approximately equals the ratio of Young's modulus to the shear modulus, making the tensile and shear strengths of isotropic crystals nearly equal in simple tension. Anisotropy of a crystal may often overcome the equalizing effect of the stress state, however.

Based on the above discussion, it is expected that, at room temperature, perfect metal crystals will fail by shear, whereas perfect crystals of ionically and covalently bonded crystals will fail by cleavage. Crystals of mixed bonding, which tend to be markedly anisotropic, may fail by either mechanism, depending mainly on the state of stress relative to the crystal axes. Thus one would expect a large perfect crystal of mica or kaolinite to fail by shear if stressed in simple shear parallel to the basal plane, but to fail by cleavage under a tensile stress applied either normal to or parallel to the basal plane.

At cryogenic temperatures, h.c.p. and b.c.c metals are likely to fail by cleavage below some critical temperature, because, in these metals, the resistance to dislocation motion increases rapidly with decreasing temperature.

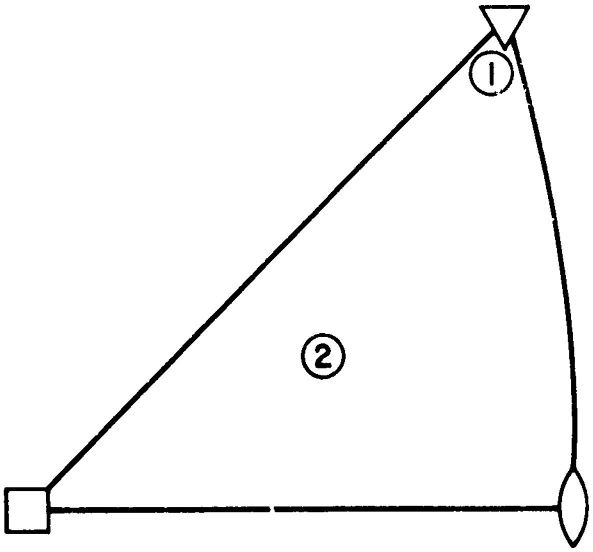

Figure III-10. Unit Stereographic Triangle with Two Stress Axes Indicated.

I. COMPARISON WITH EXPERIMENT

There are two lines of evidence indicating that the estimates of cohesive tensile stress and maximum shear stress made here are not grossly in error. The strongest evidence is provided by quantitative cleavage experiments. [J. J. Gilman, J. Appl. Phys. 31, 2208 (1960)] in which the stresses needed to cause cleavage are measured and the corresponding surface energies deduced. The results are consistent with the estimates given here.

Other evidence is provided by the highest values of strength that have been measured. Measurements have been made for a number of filamentary specimens (whiskers) and also for more massive specimens. The measurements indicate that: a) strengths nearly equal to theoretical estimates can be achieved experimentally, and b) observed strengths never exceed theoretical estimates.

Table VI lists the highest strengths attained by various filamentary crystals and their modes of failure. These slender crystals have very smooth surfaces, and perfect internal structures, and so approach the idealized forms that have been under discussion.

In agreement with expectations based on the above discussion, the ionically and covalently bonded materials failed by fracture, while the metals failed by shear. Also, in agreement with the rough trend noted in Tables III and V, the ratios of (μ/τ) are on the average larger than the ratios of (E/σ). Finally, it is noteworthy that in the case of the h.c.p. metal whiskers, zinc and cadmium, the mode of failure changed to cleavage at sub-zero temperatures (below 160°K for zinc, 80°K for cadmium).

Crystals need not be small in order to be strong. This is shown by data in Table VII for bulk specimen crystals that were tested with carefully prepared smooth surfaces. It may be seen that their strengths are comparable with the strengths of whiskers. Some data for polycrystalline steel and glassy silica are included in this table for comparison.

J. SUMMARY AND CONCLUSIONS

The ultimate theoretical strength of a crystal can be estimated in terms of measurable physical properties within a factor of about two, provided judgement is used to avoid pitfalls in special cases.

The mode of mechanical failure will depend on the state of stress, so this must be given. Then estimates of both the shear and tensile cohesive stresses must be compared with the given stress state to decide whether failure by crack formation or dislocation nucleation can be expected.

Loss of cohesion will occur at large strains where pertinent experimental data are not available. Therefore, it is necessary to extrapolate from the small strain regime and then justify the extrapolation by comparison with representative experiments.

Shear and tensile cohesion change with orientation in a crystal. Therefore, they have been related here to anisotropic physical properties in addition to the heat of sublimation. Using the simplest binding stress law that is consistent with elasticity and quantum mechanics, it is shown that the tensile cohesion in a given direction is proportional to:

a) elastic stiffness

b) inverse thermal expansion coefficient

c) square root of surface energy

Therefore, these properties can be used to rank the strengths of crystals and directions in a given crystal. It is also shown that strength of an isotropic crystal increases in proportion to its heat of sublimation and the reciprocal of its atomic or molecular volume.

The simplest procedure for estimating the magnitude of tensile cohesion is to divide the elastic stiffness constant for a given direction by a coefficient that is called β here. For various bonding types, approximate values for β are:

Ionic	15
Covalent	20
Alkali metals	7
Noble metals	18
Transition metals	20
Molecular crystals	28

It is shown that shear cohesive stresses tend to be about half as great as tensile ones. However, for simple stress states a given load yields only half as much applied shear stress as tension. Thus these two factors tend to cancel. Also, shear failure requires mobile dislocations and in many non-metallic crystals dislocations are highly immobile. All this makes it difficult to predict the mode of failure, but there seems to be a tendency for metals to fail via shear and for non-metals to fail by cracking.

Experimental measurements of both surface energies and strengths of carefully prepared specimens approximately confirm the theoretical discussion that is given.

The chemical factors that tend to increase the strength of a crystal are the following:

a) small atomic volumes
b) high valence electron concentration
c) small atomic polarizabilities (except for molecular crystals)

APPENDIX I

Derivations of Relations between Tensile Cohesive Stress and Other Properties

The potential energy function that corresponds to the stress function (Equation 1) is:

$$U(x-x_o) = -U_o\left[1+\frac{(x-x_o)}{D}\right]e^{-(x-x_o)/D} \qquad (1a)$$

The stress function is obtained from this by differentiation:

$$\sigma\,(x-x_o) = \frac{1}{A_o}\left(\frac{\partial U}{\partial x}\right) = \left[\frac{U_o}{A_oD^2}\right](x-x_o)\;e^{-(x-x_o)/D} \qquad (2a)$$

where A_o is the atomic area across which the forces act. The maximum value of the stress is found by setting the derivative of the stress equal to zero, solving for the value of $(x-x_o)$ at the maximum, and substituting this value back into the expression for the stress:

$$\frac{\partial\sigma}{\partial x} = \frac{1}{A_o}\left(\frac{\partial^2 U}{\partial x^2}\right) = \left[\frac{U_o}{A_oD^2}\right]e^{-(x-x_o)/D}\left[1-\frac{x-x_o}{D}\right] = 0$$

hence: $(x-x_o) = D$ at the maximum, and:

$$\sigma_{max} = \sigma(D) = \frac{U_o}{eDA_o} = \sigma_{coh} \qquad (3a)$$

Here we see immediately that the cohesive stress increases with the vector binding energy and decreases with the relaxation distance of the forces (i.e., localized bonds are strongest). This equation also indicates, since DA_oe is approximately an atomic volume, that the cohesive stress should be proportional to the cohesive energy per atom (or molecule) of the solid.

The third derivative of $U(x-x_o)$ will be needed shortly and so will be written down here:

$$\frac{\partial^3 U}{\partial x^3} = \left(\frac{U_o}{D^3}\right) e^{-(x-x_o)/D} \left[\frac{(x-x_o)}{D} - 2\right]$$

According to Hooke's Law a change in stress is given by:

$$d\sigma = C'_{11} \left(\frac{dx}{x_o}\right)$$

where C'_{11} is the elastic stiffness in the direction of interest (C_{11} is the elastic stiffness referred to crystallographic axes; C'_{11} will be related to C_{11} by a tensor transformation, J. F. Nye, "Physical Properties of Crystals," Oxford, 1957). Then:

$$C'_{11} = \frac{x_o}{A_o} \left(\frac{\partial^2 U}{\partial x^2}\right)_{x=x_o} = \frac{X_o U_o}{A_o D^2}$$

which is one relation between U_o, D, and known physical properties; another is needed to evaluate them separately. This is obtained by considering thermal expansion which is related to the first anharmonic term of the Taylor expansion of $U(x-x_o)$ about the point $x = x_o$. The potential function and its first three derivatives have the following values at $x = x_o$:

$$U(o) = -U_o$$

$$U'(o) = 0$$

$$U''(o) = U_o/D^2$$

$$U'''(o) = -2U_o/D^3$$

Therefore, the Taylor expansion about $x = x_o$ is:

$$U(x-x_o) = -U_o + C(x-x_o)^2 - G(x-x_o)^3 + \ldots\ldots$$

where $C = U_o/2D^2$

$G = U_o/3D^3$

and this represents an anharmonic oscillator whose average displacement during thermal excitation at high temperatures [C. Kittel, "Introduction to Solid State Physics," J. Wiley & Sons (1956), p. 152] is:

$$\bar{x} = \frac{3kTG}{4C^2} = \frac{kTD}{U_o}$$

where T is the absolute temperature and k is the Boltzmann's constant. From this, the thermal expansion coefficient normal to the plane of interest is:

$$\alpha_1 = \frac{2\bar{x}}{x_o T} = \frac{2Dk}{x_o U_o}$$

and using this second relation for U_o, D, and known physical properties, the tensile cohesive stress can be found:

$$\sigma_{coh} = \frac{U_o}{eDA_o} = \frac{k}{2\alpha_1 x_o eA_o}$$

but $x_o A_o = V$ = atomic volume; so:

$$\sigma_{coh} = \frac{k}{2\alpha_1 eV} \tag{4a}$$

and we see that the cohesive stress is inversely proportional to the expansion coefficient. This is in accord with empirical correlations.

Rearranging the relation for the elastic stiffness:

$$\frac{U_o}{DA_o} = \frac{D}{x_o} C'_{11}$$

and since:

$$\sigma_{coh} = \frac{1}{e}\left(\frac{U_o}{DA_o}\right)$$

the cohesive stress may be related to elastic stiffness:

$$\sigma_{coh} = \left(\frac{D}{x_o}\right) \frac{C'_{11}}{e} \tag{5a}$$

The ratio of the relaxation distance to the interplanar spacing (D/x_o) is not expected to vary much from one substance to another because they tend to both increase or decrease together. Therefore, this relation indicates that σ_{coh} is simply a constant fraction of the elastic stiffness.

Next, and finally, we seek to relate σ_{coh} to the surface energy of the solid for the specific surface formed by the fracture. This can be done because the energy required to separate the solid into two pieces and thereby create two new surfaces is just the area under the stress-distance curve. Since two surfaces are created, the work must be divided by two, and so the surface energy is given by:

$$\gamma_1 = \frac{1}{2}\int_0^\infty \sigma(x-x_0)\, d(x-x_0)$$

$$= \frac{U_o}{2A}$$

$$= \frac{eD\sigma_{coh}}{2}$$

but:

$$D = \frac{ex_o\sigma_{coh}}{C'_{11}}$$

so that:

$$\sigma_{coh} = \left[\frac{2\gamma_1 C'_{11}}{x_o e^2}\right]^{1/2} \qquad (6a)$$

It may be noted in passing that these equations yield a relation between surface energy and other properties that may be useful for estimating anisotropic surface energy values:

$$\gamma_1 = \frac{2x_o k^2 C'_{11}}{\alpha_1^{\,2} V} \qquad (7a)$$

In general, using the above relations involving the elastic stiffness, the thermal expansion coefficient, and the surface energy, force laws containing up to three unknown parameters may be expressed in terms of physical constants for the crystal in question. For example, if one used the well-known Morse potential function:

$$U(x-x_o) = U_o'\left[e^{-2(x-x_o)/D'} - 2e^{-(x-x_o)/D'}\right] \qquad (8a)$$

by the same procedure one would obtain:

$$\sigma_{coh} = \frac{U_o'}{2A_o D'} \tag{9a}$$

$$C_{11}' = \frac{2x_o U_o'}{A_o (D')^2} \tag{10a}$$

$$\sigma_{coh} = \frac{3k}{16\alpha_1 V} \tag{11a}$$

$$= \left(\frac{D'}{4x_o}\right) C_{11}' \tag{12a}$$

APPENDIX II

Derivations of the Theoretical Shear Cohesive Stress

Unlike the case of the tensile cohesive force, in failure by shear the crystal will be restored to essentially its original configuration (neglecting small surface steps) periodically as the crystal is sheared on a given plane. The period of the force (or energy) will be b, a distance related to the interatomic spacing in the shear plane. Frenkel [Z. Phys. 37, 572 (1926)] assumed that the periodic shear stress function was sinusoidal:

$$\tau = \tau_{max} \sin \left[\frac{2\pi(x-x_o)}{b}\right] \tag{16}$$

Here, as in Figure III-1, $(x-x_o)$ represents the displacement from the equilibrium position x_o. For small displacements, Hooke's Law holds, so that:

$$\tau = \frac{\mu(x-x_o)}{d} \qquad (x-x_o) \ll 1 \tag{26}$$

where d is the interplanar spacing normal to the shear plane. Equating (16) and (26) in the limit of small displacements, one finds

$$\tau_{\max} = \frac{\mu}{2\pi}\left(\frac{b}{d}\right) \simeq \mu/2\pi \tag{36}$$

Unlike the case of the tensile strength, the surface energy does not enter the shear process. Also, it is questionable whether one could associate the thermal expansion coefficient with the third order term in a Taylor's series expansion of the shear strain energy per atom as a function of x. Thus, rather than a three parameter fit of an empirical force law, one has only a one parameter fit as in equation (36). The use of other force laws, such as the Morse function, involves a detailed, and rather tedious, consideration of the displacements of the atoms in shear [Mackenzie, thesis, Bristol University (1949)]. Also, as discussed earlier, the use of such semi-empirical central force laws is questionable because of the importance of directional bonding in shear processes.

One may, of course, obtain a one parameter fit of such force laws. For example, assuming a law of the form of equation (8a) to hold up to $\tau_{\max}$, one calculates, c.f. equation (12a),

$$\tau_{\max} = \left(\frac{D'}{4x_o}\right)C'_{44} \tag{46}$$

TABLE I

Values of the Ratio $({}^{nm}/n-m)$ for Various n, m ($n>m$)

n	m 1	2	3	4	5	6
2	2.0	---	---	---	---	---
3	1.50	6	---	---	---	---
4	1.33	4	12	---	---	---
5	1.25	3.3	7.5	20	---	---
6	1.20	3	6	12	30	---
8	1.14	2.7	4.8	8	13	24
10	1.11	2.5	4.3	6.7	10	15
12	1.09	2.4	4	6	8.6	12

TABLE II

Values of the Coefficient β for Various n, m (with $n>m$)

n	m 1	2	3	4	5	6
2	7.1	---	---	---	---	---
4	9.4	10.6	12.2	---	---	---
6	10.8	13.2	14.5	16.2	17.3	---
8	13.9	15.6	17.2	18.7	20.2	21.8
10	16.0	17.9	19.6	21.2	22.8	24.2
12	18.2	20.2	22.0	23.6	26.4	28.2

TABLE III

Tensile Cohesive Stress Estimates

(stress unit = 10^{10} d/cm^2)

Expression for Cohesive Stress	Diamond		Sodium Chloride	
	σ_{coh}	β	σ_{coh}	β
C_{11}'/β	59	20	3.2	15
$\left[\dfrac{C_{11}'\gamma_1}{4x_o}\right]^{1/2}$	94	13	2.7	18
Zwicky (lattice theory)	--	--	2.0	24

References:

Diamond (111) plane normal

$C_{11}' = 1.2 \times 10^{13}$ d/cm^2

γ_1 = 5650 d/cm [W. D. Harkins, J. Chem. Phys. 10, 269 (1942)]

Sodium Chloride (100) plane normal

$C_{11}' = 4.9 \times 10^{11}$ d/cm^2

γ_1 = 155 d/cm [R. Shuttleworth, Proc. Phys. Soc. 62A, 167 (1949)]

Lattice theory [F. Zwicky, Physikal. Zeit. 24, 131 (1923)]

TABLE IV

Fracture Stresses for Glasses and Water at Room Temperature

Material	Surface Energy (d/cm)	C'_{11} (10^9 d/cm^2)	Fracture stress (10^9 d/cm^2) calc.	exp.	$C'_{11}/\sigma_{frac.}$
Soft Glass	150-300	400-500	30-38	34	13
Pyrex	250	610	55	120	11
Fused Silica	350	700	76	90	9
Water	75	500*	1.5	~ 1	500

*This is the compressibility since C'_{11} is not defined for water.

TABLE V

Effect of Surface Stress Concentrations on the Stress for Dislocation Nucleation

Crystal	Critical Stress Smooth Surface	Surface with Ledges
Copper		
Perfect dislocation	$\mu/15$	$\mu/25$
Imperfect dislocation	$\mu/25$	$\mu/30$
Aluminum		
Perfect dislocation	$\mu/15$	$\mu/20$
Iron		
Perfect dislocation	$\mu/10$	$\mu/15$

TABLE VI
Highest Observed Strengths of Various Filamentary Crystals at Room Temperature

Tensile Failures

Crystal	Strength (mpsi)	Young's Modulus (mpsi)	Modulus: Strength Ratio	Reference
BeO	2.8	49	17	Ryshkewitch
Al_2O_3	2.2	72	33	Brenner
Si	0.94	24	26	Evans
NaCl	0.16	6.3	40	Gyulai
S,C	3.0	70.0	23	Carborundum
AlN	1.0	50.0	50	Davies & Evans

Shear Failures

Crystal	Shear Strength (mpsi)	Shear Modulus (mpsi)	Modulus: Strength Ratio	Reference
Fe	0.71	12	17	Brenner
Cu	0.13	6	45	Brenner
Ag	0.13	4	30	Brenner
Zn	0.03	2.5	83	Coleman
Cd	0.02	1.4	71	Coleman

References

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E. Ryshkewitch, "Science and Technology" (February 1962)

A more recent and extensive table of the properties of reinforcing filaments is to be found in Table I of "Ceramics, Graphite Fibers and Whiskers," L. R. McCreight, H. W. Rauch, Jr., N. H. Sutton, Academic Press. In assessing the reported values, the reader should consult the original references.

TABLE VII

Highest Strengths Observed for Bulk Materials
(one mm or more in outside dimensions)

Material	Strength (mpsi)	Young's Modulus (mpsi)	Modulus: Strength Ratio	Reference
		Crystals		
Al_2O_3	1.03	72	70	Morley
TiC	0.08	70	87	Williams
Si	0.75	24	32	Pearson
Mica	0.43	--	--	Orowan
B	0.35	51	145	Talley
		Others		
Fused silica	1.90	14	7	Hillig
Ausformed steel	0.45	29	64	Shyne
Music wire	0.40	20	72	NBS

References

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SECTION IV - THE STRENGTH OF INORGANIC GLASSY SOLIDS

As stated previously, concepts of the strengths of solids imply a theoretical limiting strength derived from the forces required to separate atoms. In inquiring into the factors that control strength it is necessary to consider the binding and spatial arrangements of these atoms. Glasses may generally be considered to be composed of sub-units, each well ordered and each consisting of only a few atoms. Lack of order in the assembly of these units results in the amorphous characteristic of glasses. Since the most important technical glasses have compositions based on silica it is of advantage to use silica and silicate structures as the basis for a discussion of strength. In general, the results for glasses based on other compositions (phosphates, borates, aluminates, etc.) will differ only in degree rather than in kind.

The building blocks of most silicates are tetrahedra of oxygen atoms in which each of the oxygen atoms shares a partially covalent and relatively strong bond with a centrally enclosed silicon atom. Each of the tetrahedra has a strong tendency to join with others by sharing oxygen atoms and thus an excellent mechanism is set up for building chains of oxygen tetrahedra. In most crystalline silicate minerals the characteristic Si-O-Si angle between tetrahedra is around 145° and allows ordered and relatively close packings of individual units. Most of these minerals show characteristic chains which are oriented in special crystallographic directions. It is apparent that if, in the cooling of a molten silica mass, insufficient time is allowed or if the chains are insufficiently segmented because of other charged ions which compete for association with oxygen atoms, then great difficulty may be encountered in arranging silica chains in a definite pattern. In such a case the chains may become rigid in much the same degree of disorder as is exhibited in the melt,and the rigid, amorphous structure which results is termed a glass. The low densities of silicate glasses indicate inefficient packing of the tetrahedral building blocks.

A simple two-dimensional picture of a silica glass structure, pertinent to later discussion, is given in Figure IV-1. For purposes of illustration the silicon atoms in this figure are considered to be trivalent rather than quadrivalent. The simple mechanism by which a high degree of disorder may be introduced into a substance that readily forms chains is clearly evident. It is also clear why the glass technologist refers to such an arrangement of atoms as a "network structure" and why the oxygen atoms are referred to as "bridging." The network may be modified by the addition of bulky cations (alkali metal and alkaline earth ions) which associate, mainly ionically and therefore more weakly, to the oxygen atoms in the chains. Introduction of these cations, external to the chains, necessitates that some oxygen atoms no longer bridge between silicon atoms and the structural picture given in Figure IV-2 results. The particular oxygen atoms that associate external cations to the network are termed, again for obvious reasons, "non-bridging" or the cation—oxygen atom assemblies are referred to as "terminal structures."

With due allowance made for special glass compositions, in which other small and highly charged ions may substitute for silicon as network formers, the logical conclusions have been arrived at that the ratio of network structure to terminal structure in a glass might control many of the physical properties of such a glass—including its strength. This conclusion is substantiated by the fact that many glass properties, such as density, refractive index and dispersion, expansion, heat capacity, etc., can be calculated on an additivity basis with some degree of success. From the preceding discussion of glass constitution, it is apparent that the network structure provides cohesiveness and thus supplies the major resistance to an applied stress.

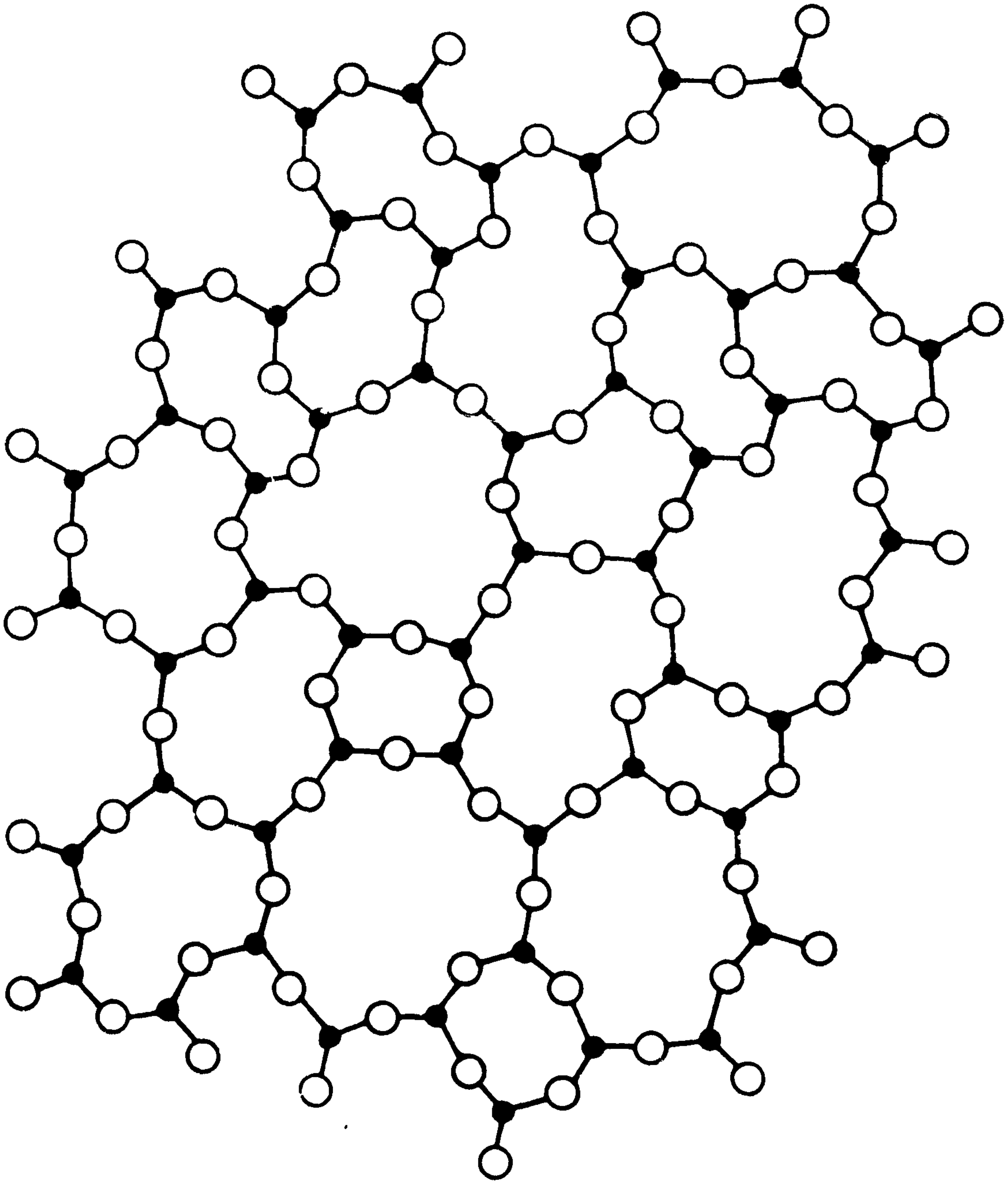


Figure IV-1. Schematic Two-Dimensional Representation of a Crystal and Glass A_2O_3 According to Zachariasen (A represents a network-former).

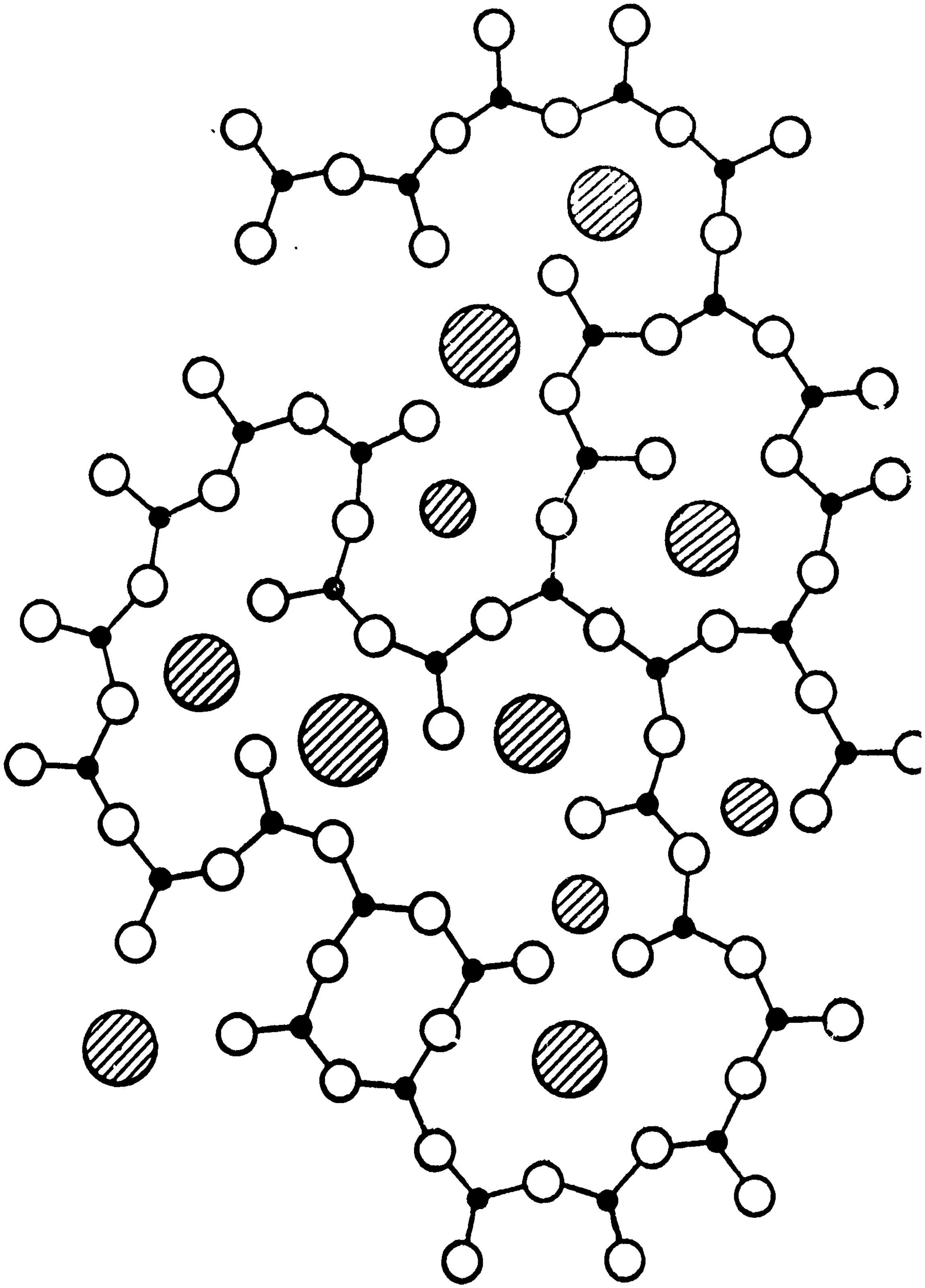


Figure IV-2. Schematic Two-Dimensional Representation of the Structur
of a Glass According to Biscoe and Warren.

Further, in the open network structures of glasses, it is evident that accommodation to tensile stresses will be not only by atom separation within individual ordered units but by alterations in the spatial interrelationships of the building blocks themselves (i.e., translations and rotations by shearing, flexing, and twisting). Given the characteristics of external forces applied to a macroscopic piece of glass one can specify the macroscopi : stress state within the glass but because of the network structure one cannot specify, with much degree of precision, the alterations in stress state between the atoms. For this reason the use of a very simple and approximate force-separation diagram is warranted for discussion of the expected ultimate strength of inorganic glasses.

A two-atom force-separation diagram can be applied to a block of glass of arbitrary dimensions and one can approximate the major portions of the separation curve by a half-cycle sine wave. Thus, with the parameters defined in Figure IV-3,

$$\sigma = \sigma_{th} \sin (2\pi X/\lambda) \tag{1}$$

At the equilibrium atom separation distance,

$$\frac{d\sigma}{dx} = \frac{E}{a} \tag{2}$$

where E is the Young's modulus of the material. Since, in this region

$$\cos \frac{2\pi X}{\lambda} \approx 1 \tag{3}$$

then

$$\frac{d\sigma}{dx} \approx \frac{2\pi\sigma_{th}}{\lambda} \approx E/a$$

and

$$\sigma_{th} \approx \frac{E\lambda}{2\pi a} \tag{4}$$

Even though no further derivation can be made without additional assumptions, equation (4) gives important information for glasses in which the main cohesiveness is supplied by the Si-O linkage. It would be expected

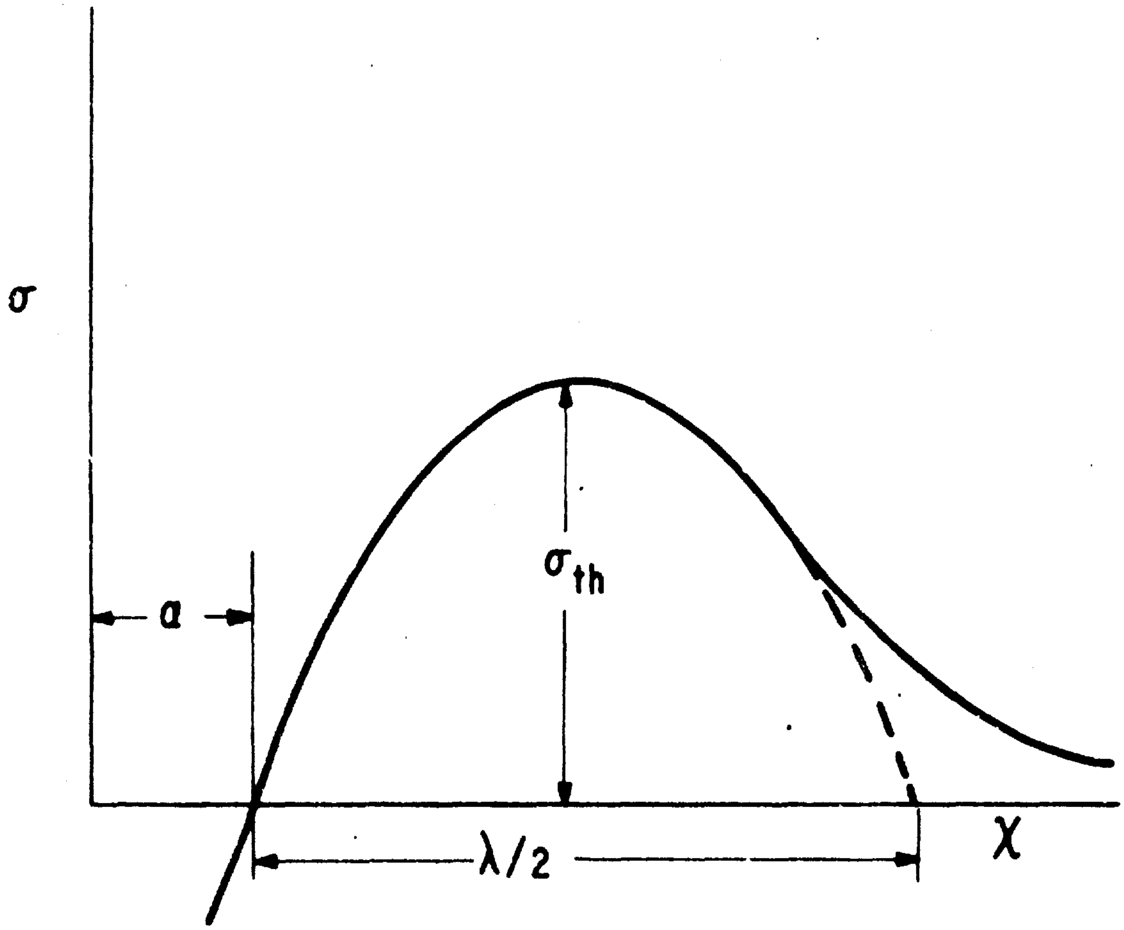


Figure IV-3. Interatomic Force as a Function of Spacing.

that λ/a be relatively constant, regardless of over-all composition, and thus the theoretical strength of a particular silicate glass would be expected to be proportional to its Young's modulus. For an order of magnitude estimate on glasses, a value of $\lambda/2$ equal to about the interatomic separation would not be unreasonable and, thus, for fused silica a theoretical strength of about 3 to 4 million lb/in^2 is obtained.

An energy balance of the separation process may be obtained, utilizing equation (1), for the work of fracture appears as the surface energy, 2S, of the new surfaces produced. Thus

$$2S = \int_0^{\lambda/2} \sigma dx = \frac{\lambda\sigma_{th}}{\pi} \qquad (5)$$

and from (2)

$$\lambda = \frac{2\pi\sigma_{th} a}{E} \qquad (6)$$

and

$$\sigma_{th} = \sqrt{\frac{SE}{a}} \qquad (7)$$

Existing thermochemical data and data on the gaseous species present in the Si-SiO$_2$ system at high temperature indicate that a reasonable value for the heat of vaporization of silica would be about 150 kcal/mol. Because of the low heat of melting of silica, the above value may be used as an approximate heat of sublimation and thus continue the estimate of the theoretical strength of silicate glass from a surface energy standpoint. Converted to c.g.s. units, the above value gives the energy of rupture of a single Si-O linkage as about 10^{-11} ergs.

The probable number of Si-O-Si linkages that are severed in fracturing a bar of fused silica 1 cm^2 in cross-sectional area may be estimated from the crystal structure of the mineral β-tridymite which has very nearly the same density as silica glass and is composed of silica tetrahedra with the same Si-O-Si angle. β-tridymite exhibits two sets of planes in which separation would occur at the junctions of adjacent tetrahedra. The number of linkages severed per square centimeter, averaged over these two sets of planes, is about 3.3×10^{14} linkages/cm^2.

On this basis, the estimated energy of fracture of the fused silica bar is equal to $(3 \cdot 5 \times 10^{14}) \times 10^{-11} = 3500$ ergs and the estimated surface energy would be 1750 ergs/cm^2. Substituting this value into equation (7) and assigning "a" equal to the equilibrium oxygen-silicon separation (1·6Å) a value of the theoretical strength of $2 \cdot 8 \times 10^{11}$ dynes/cm^2 or about 4 million lb/in^2 is again obtained. In this case, however, all parameters necessary for the calculation have been derived from measurable quantities.

It is of interest that a number of investigators have shown fine glass fibers to possess a strength in excess of 1 million lb/in^2 and of these the presently reported record value is 3·5 million lb/in^2 which was obtained on an extremely fine fused silica fiber. Recently experiments have shown that carefully prepared fused silica rods (approximately 1 mm in diameter) can be pulled in direct tension to a stress of 2×10^6 psi. A further result from this work has bearing on the calculations performed at the beginning of this section. For most materials one expects a theoretical strength varying between E/20 and E/5 where E is the Young's modulus. The generally quoted E for fused silica is about 10^7 psi and thus the previously calculated theoretical strength would be between E/3 and E/2.5. Direct measurements give a theoretical strength of between E/5 and E/2.5. The remarkable demonstration in the above experiments is that E for fused silica increases as the load level exceeds 10^6 psi. In a simple mechanistic fashion this result is interpreted to mean that at low load the extension of silica is achieved mainly by flexing oxygen tetrahedra at corners whereas at high loads the extension is associated with atom separation. Thus the appropriate E to be used in estimating theoretical strengths is not presently available and thus these strengths may indeed lie between 10% and 20% of the effective high load modulus.

In this connection there are other recent high strength measurements which are similar to those given above except that the glass involved was of a window glass composition containing relatively large amounts of sodium and calcium rather than the simple silica glass. If not taken too literally, Figure IV-2 may be considered to represent a two-dimensional analogue of such a glass. In this glass it was noted that at high loads (approximately 10^6 psi) the Young's modulus continuously decreased from the value exhibited at low load. It is concluded that the alkali cations present in the glass must severely limit local modes of deformation of the silica network structure such that the forces applied result mostly in atom separation. With reference to Figure IV-3 it is noted that this is the most generally expected behavior.

The foregoing discussion has been based on what may be a highly idealized concept of glass structure (i.e., Figures IV-1 and IV-2). Increasing evidence is presently forthcoming that multicomponent silicate glasses exhibit a fine structure related to the prevalent tendencies of these glasses to unmix. Such unmixing may play a significant role in the response of these systems to stress and it is felt by many that an important factor in preventing experimental strength measurements in excess of one or two million psi may have to do with these structural and compositional fluctuations.

Further, there has been reawakened interest recently in the possibility that inorganic glasses should be considered as elastic-plastic materials even at low temperatures. Thus, it is claimed, perfectly formed glass fibers may never exhibit their ultimate strengths but will rupture at some lower stress at which macroscopic flow occurs. Evidence in favor of this concept is meager but two types of observations would not be inconsistent with this idea. One of them concerns the fact that diamond point indentations on glass cause a permanent set which, whether it be due to irreversible compaction or time dependent flow, results in a change in the spatial arrangements of atoms. The second is concerned with the fact that numerous investigators have reported a remarkably small scatter in high strength data for fine fibers. The conclusion is made that either these fibers fail at their true ultimate strengths or that a well defined flow stress is operative. It is also shown that the actual strength levels observed seem much lower than those expected for ultimate values and thus there is a possibility that flow intervenes to assist failure. Further, much of the limiting crack velocity data cannot be correlated simply to the Young's moduli of the investigated glasses as is expected. A better correlation is obtained using a function related to diamond indentation hardness. Over-all, it appears that if one permits a small amount of plastic work to occur during glass fracture, the existing data on fracture velocities can be better interpreted.

In summary this outline is concerned with some present concepts of glass structure and the relation of theoretically expected and experimentally obtained strengths to this structure. Theory and experiment show reasonable agreement but one may conclude that further correlation will require significantly greater precision in defining fine scale glass structures. For the present, compilations and empirical relationships that predict elastic properties of inorganic glasses as a function of composition are of most use in assessing theoretical strengths of these materials. Methods and data such as given by Phillips [Glass Technology, 5, No. 6, pp. 216-223 (1964)] are particularly useful.

SECTION V - THE STRENGTH OF ORGANIC POLYMERS

A. INTRODUCTION

The basic structural feature of organic polymers is the chain of covalently bonded atoms. However, the chain may contain branch-points, and consequently a large number of topologically different molecular structures are possible—e.g., "ladder" molecules, planar nets, and three-dimensional networks. Some of these are indicated in Figure V-1.

In general, the polymer molecule contains "pendant" atoms or groups which are attached to the chain or net by covalent bonds. Adjacent polymer molecules are held together by intermolecular forces which are much weaker than the covalent bonds which constitute the molecular skeleton. However, diamond may be looked at as a limiting case of a highly cross-linked three-dimensional network polymer; and graphite may be considered as a limiting case of a highly cross-linked two-dimensional (planar) network polymer. In such limiting structures, every atom is part of the primary skeleton.

The term "organic" implies that carbon is involved in the structure, but even in organic polymers atoms other than carbon can be present in the molecular skeleton as well as in pendant groups.

Linear polymers may be crystalline or amorphous. Current technology cannot produce large single crystals of crystallizable organic polymers. Useful objects composed of crystalline polymers are polycrystalline masses with complicated morphology, including many crystal imperfections. However, theoretical strength calculations (for crystalline polymers) should be based upon the idealized large perfect crystal if upper limits are to be placed upon possible strengths.

Because intermolecular forces are much weaker than the skeletal covalent bonds, the tensile strength of a perfect crystal (or of a highly oriented amorphous linear polymer) will be highly anisotropic. This

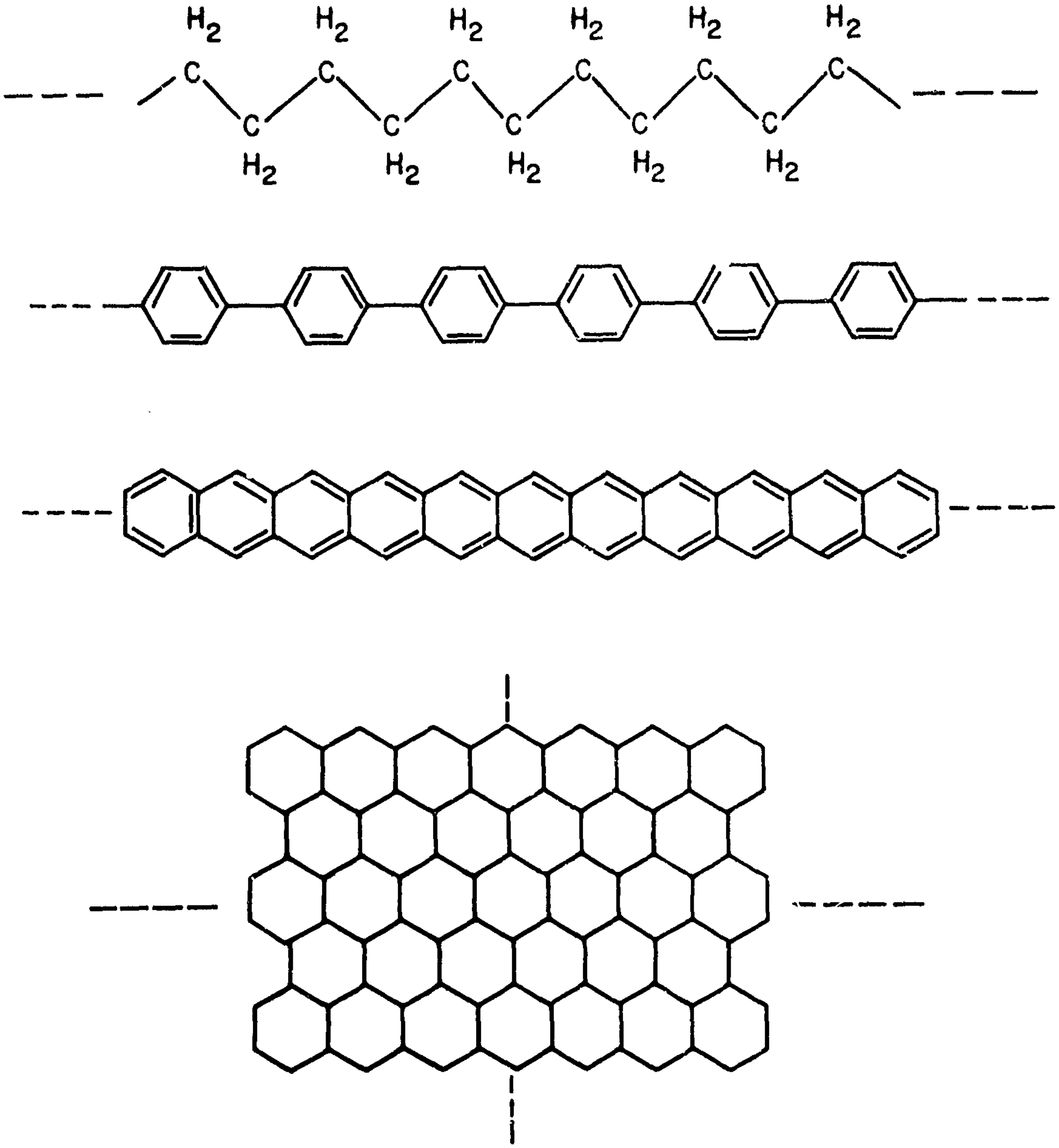
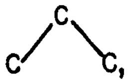


Figure V-1.

fact must be kept in mind when such theoretical strengths are used. Complete uni-directional molecular orientation leads to the highest possible theoretical tensile strength in the direction of orientation, but this is necessarily at the expense of other physical properties (such as transverse tensile strength; and as a corollary, resistance to multiaxial stresses). In practice, when molecular orientation is controlled in polymeric materials, the highest attainable uni-directional orientation usually is deliberately avoided in order to obtain some desired compromise set of physical properties.

Bond angles must also be considered in the attempt to estimate theoretical strengths of polymers. Acetylene (H-C≡C-H) is a truly linear molecule, in the sense that all four atoms lie on a straight line; presumably the polyene (-C≡C-C≡C-C≡C-C≡C-C≡C- --) would also be truly linear. Most so-called "linear" polymers, however, are zig-zag structures even in their most oriented (extended) conformations. Typical approximate bonded angles are: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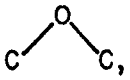
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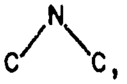
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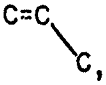

120°.

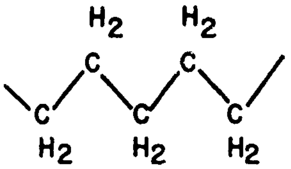
When such a zig-zag chain molecule is subjected to tension, bond angles as well as bond lengths are altered. This is also true in the case of double-stranded chains, planar networks, and three-dimensional networks.

The analysis of the stress-strain behavior of the single zig-zag chain molecule can provide a basis for rough theoretical strength estimates for many multi-stranded chains and network polymers, provided that the symmetry of such structures is appropriate. To be more specific on this point: Whenever a multi-connected structure (e.g., two-stranded chain, or two-dimensional network) possesses a symmetry which insures that the response to a uni-directional tension can be reduced to the symmetrically repeated displacement of individual atoms relative to adjacent covalently bonded neighbors, this displacement being opposed by a bond-angle stiffness and a bond-length stiffness, the problem of calculating the stress-strain curve to failure becomes basically identical with the corresponding problem with linear (zig-zag) polymethylene.

B. THE LINEAR (ZIG-ZAG) POLYMETHYLENE CHAIN

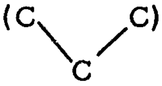
As stated previously, both covalent bonds and intermolecular forces are encountered in organic polymers. The primary structural elements are chains, or sheets, or three-dimensional networks, of covalently bonded atoms. The chains or sheets are attached to their neighbors by (weaker) intermolecular forces.

In this discussion, consideration will be given to the theoretical strength of a linear polymer containing only C-C single bonds in the chain—i.e.,



— — — —. The highest theoretical strength in one direction would require that the chains be extended in the direction of the applied tensile stress, thus exhibiting the hypothetical behavior of a large perfect single crystal of very high molecular weight, perfectly linear, polyethylene. Since the intermolecular forces between hydrocarbon molecules are much weaker than the covalent C-C bonds, such a crystal would be relatively weak in the transverse directions.

The polymer chains in such a crystal will respond to a uni-directional tensile stress in two ways: stretching of the C-C bonds, and opening of the



bond angles. By symmetry, the response of the entire chain can be reduced to the displacement of a single carbon atom relative to its covalently bonded neighbor.

In the unstressed equilibrium arrangement, the C-C bond length is 1.54 Å, and the bond angle is approximately 109°. The location of a chain atom relative to its neighbor can be expressed either in Cartesian coordinates (x, y) or in polar coordinates (r, θ).

The potential energy of this system, when deformed in an arbitrary manner away from the equilibrium arrangement, is not known satisfactorily for the present purposes; therefore, various estimations of the potential function $V(r, \theta)$ or $V(X, Y)$ must be made.

For very small displacements from equilibrium, V can be satisfactorily represented by the expression: $2V = 2V_o + K_1 (r-r_o)^2 + K_2(\theta - \theta_o)^2$.

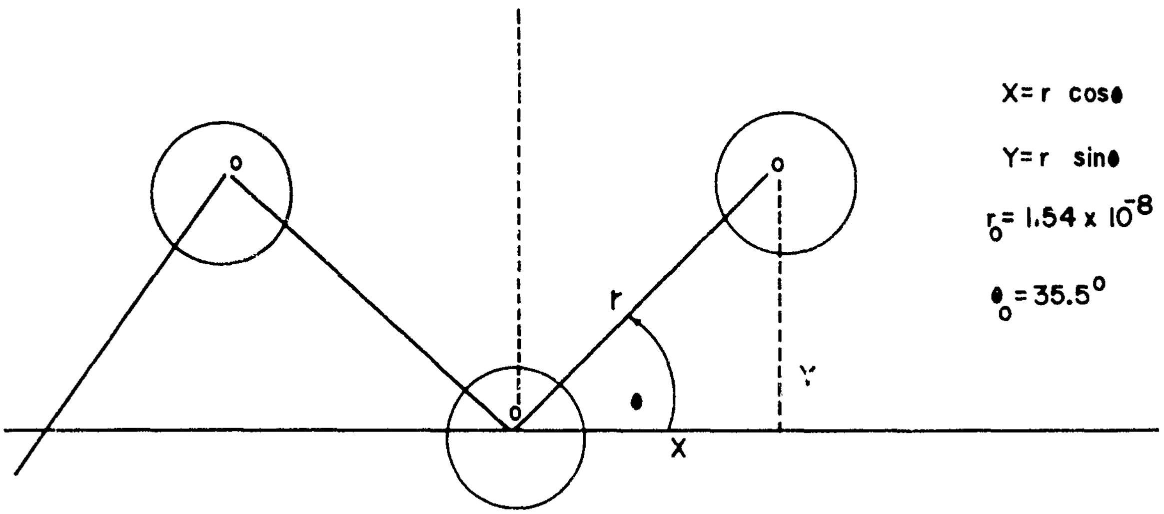


Figure V-2.

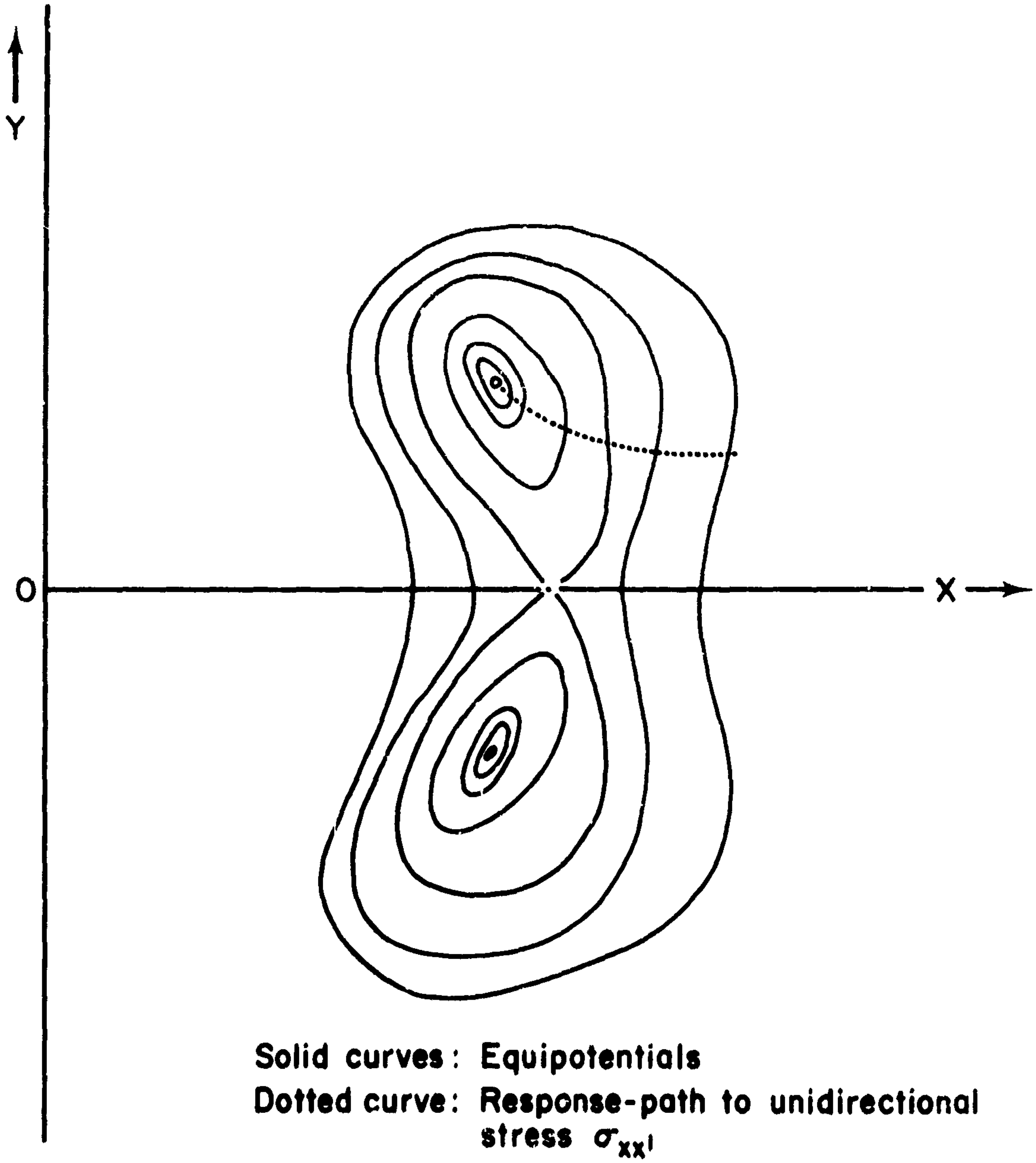
Furthermore, spectroscopic data can provide numerical values for K_1 and K_2, which are sufficiently accurate for the present purposes. Also, V_o can be satisfactorily estimated from thermodynamic data. Potential energy contours, for small displacements, are ellipses with principal axes aligned parallel and perpendicular to the bond direction (i.e., at 35.5° and 125.5° relative to the X-axis).

The serious uncertainties arise when large displacements from the unstressed equilibrium arrangement are examined.

The general character of $V(X, Y)$ is indicated in Figure V-3.

For large displacements, V cannot be adequately represented by a sum of two separate functions, one depending upon bond length $(r-r_o)$ and one depending upon bond angle $(\theta - \theta_o)$. However, a start can be made by examining the manner in which V varies with r (holding $\theta = \theta_o$) and with θ (holding $r = r_o$), designating these two functional relationships by the respective symbols $V^*(r)$ and $V^*(\theta)$.

The function $V^*(r)$ can be approximated by the Morse function, using the three known quantities (V_o, r_o, and K_1) to fix the Morse parameters, designating the Morse approximation to $V^*(r)$ by the symbol $V_m^*(r)$. Although it can be expected that $V_m^*(r)$ will be a good approximation to



Solid curves: Equipotentials

Dotted curve: Response-path to unidirectional stress $\sigma_{xx'}$

Figure V-3.

$V^*(r)$ in the vicinity of r_o, its accuracy near the inflection point is subject to the same uncertainties which have been discussed in earlier sections of the report. With this qualification, the following estimate for $V_m^*(r)$ can be made:

$$V_m^*(r) = (5.5 \times 10^{-12})\left[e^{-4.04 \times 10^8 (r-1.54 \times 10^{-8})} - 2e^{-2.02 \times 10^8 (r-1.54 \times 10^{-8})}\right]$$

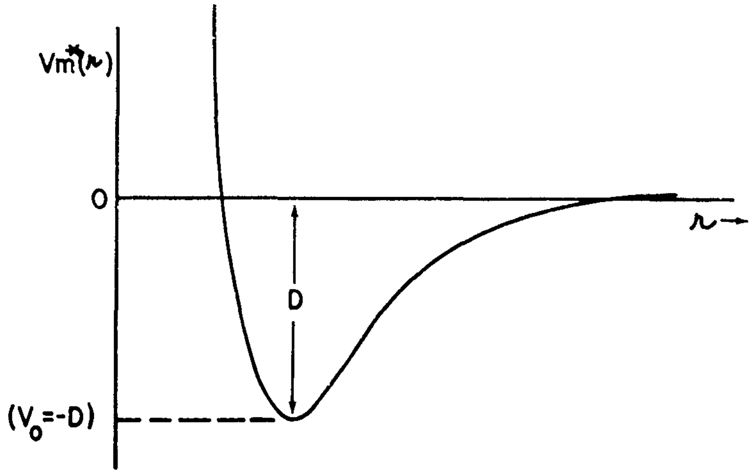


Figure V-4.

The angular potential function, $V^*(\theta)$, corresponding to $r = r_o$, is of the general form indicated in Figure V-5.

In attempting to develop a satisfactory approximation to this (unknown) $V^*(\theta)$, the estimations are handicapped by the fact that only two reasonably accurate known quantities are available to start with: θ_o and the value of $\left(\frac{d^2 V^*(\theta)}{d\theta^2}\right)$ at $\theta = \theta_o$. The height of the potential maximum $(V_L^* - V_o)$ cannot be derived from thermodynamic data.

A simple expression which exhibits the required qualitative form shown in Figure V-5 is given below, and designated at $V_I^*(\theta)$—i.e., as a first approximation to the unknown $V^*(\theta)$: (Note: θ is measured in degrees.)

$$V_I^*(\theta) = V_L^* - C_1(\theta)^2 + C_2(\theta)^4$$

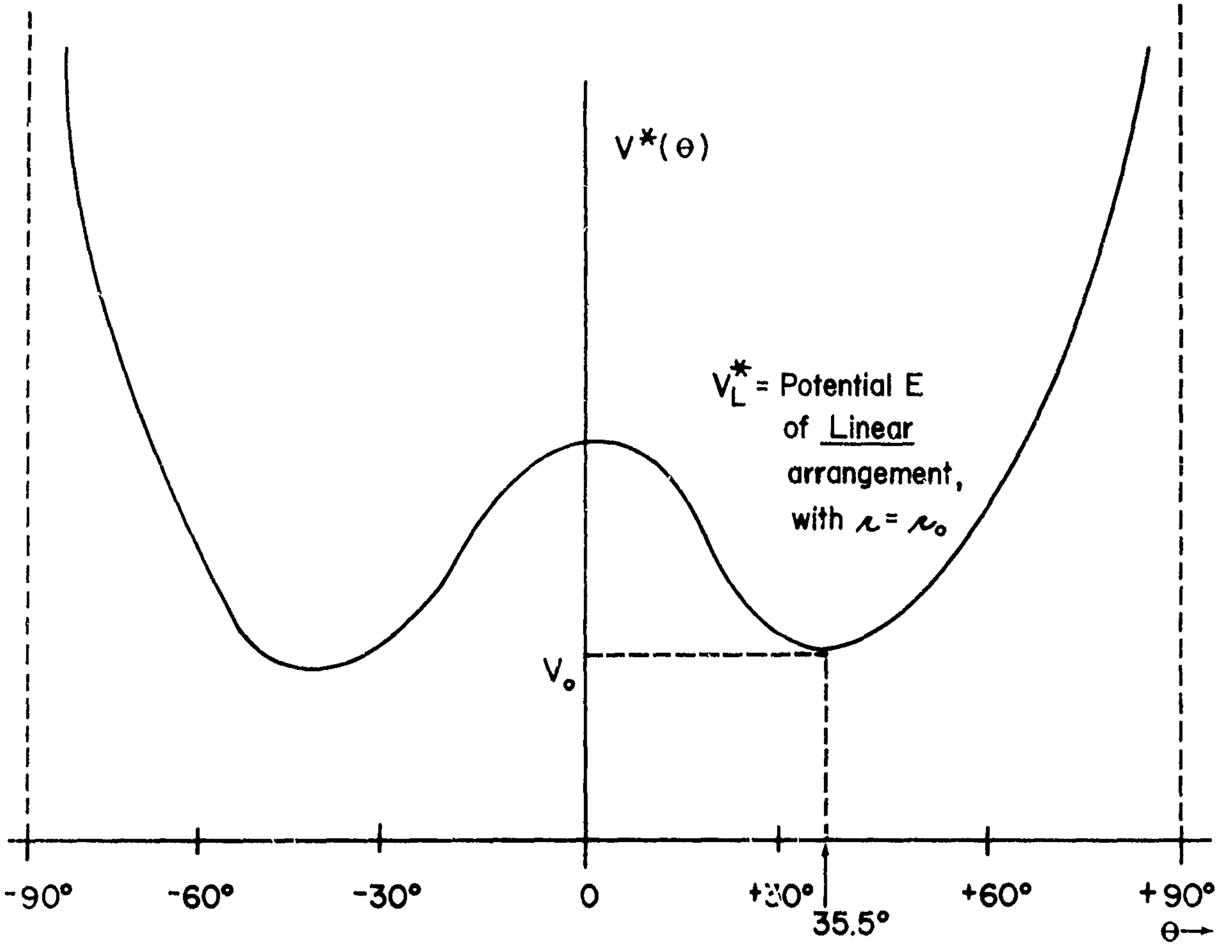


Figure V-5.

This approximate function can be fitted at $\theta = \theta_0$, where the second derivative is obtainable from spectroscopic data, thereby resulting in the specific equation:

$$V_I^*(\theta) = (V_o + 2.08 \times 10^{-12}) - 3.3 \times 10^{-15}(\theta^2) + 1.31 \times 10^{-18}(\theta^4)$$

θ in degrees
V in ergs

This approximation, $V_I^*(\theta)$, cannot be considered to be reliable for large angular displacements. It forces the "inversion energy" of the chain to be 2.08×10^{-12} erg/atom (approx. 29 kcal/mole). In a later

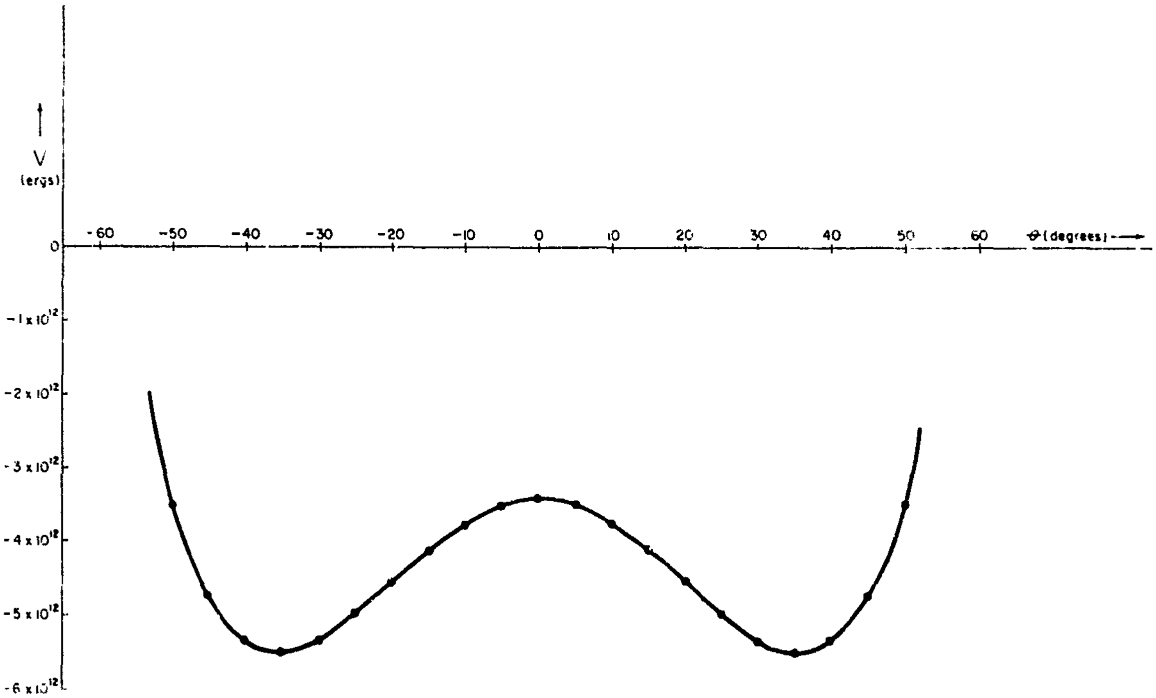


Figure V-6.

discussion, an improved approximation will be advanced, $V_{II}^{*}(\theta)$, which can accommodate different values for this inversion energy. However, before doing this, the crude function $V_I^{*}(\theta)$ can be used, together with the function $V_m^{*}(r)$, to illustrate the problems encountered when large displacements of bond length and bond angle are simultaneously present.

If the system is first deformed to a large $(\Delta\theta)$ and then the bond lengths are increased from r_o to infinity, the total energy required should be the same as if the bonds were stretched at $\theta = \theta_o$. An approximate expression for $V(r, \theta)$ which exhibits this feature can be constructed from $V_I^{*}(\theta)$ and a Morse function in which the dissociation energy depends upon θ: specifically, $D = -V_I^{*}(\theta)$. The resulting approximation to $V(r, \theta)$ will be designated as $V_I(r, \theta)$.

$$V_I(r, \theta) = (-3.42 \times 10^{-12} - 3.3 \times 10^{-15}\,\theta^2 + 1.31 \times 10^{-18}\,\theta^4)\cdot \left(-e^{-4.04 \times 10^{8}(r - 1.54 \times 10^{-8})} + 2e^{-2.02 \times 10^{8}(r - 1.54 \times 10^{-8})}\right)$$

This function is plotted in Figure V-7.

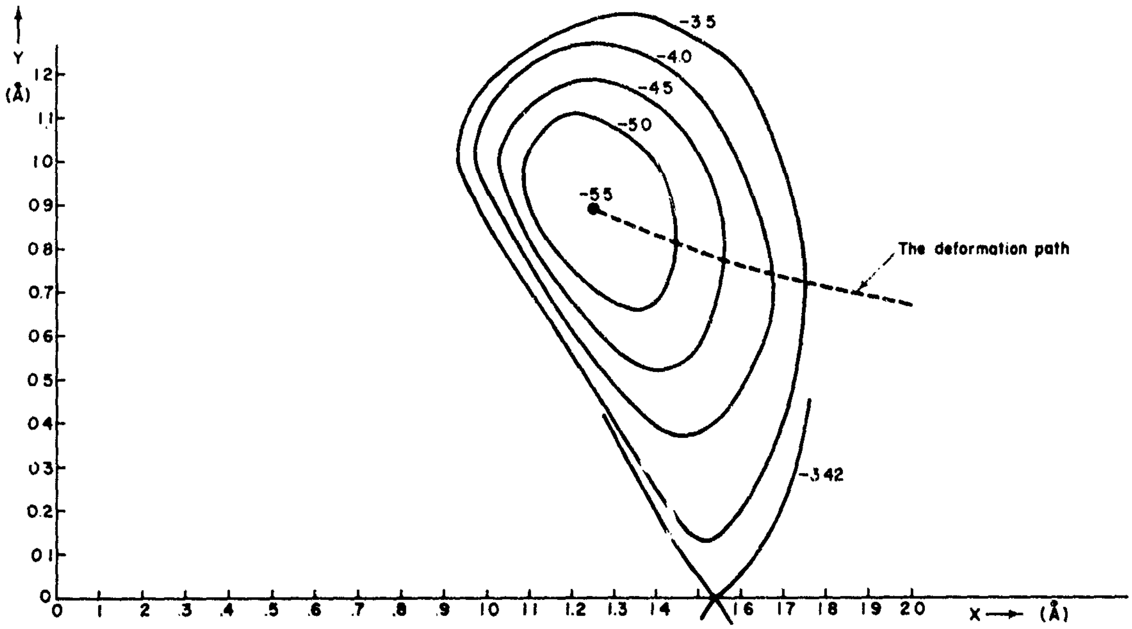


Figure V-7. Contour Plot of $V_I(r, \theta)$.

The response of the system to a uniaxial tensile stress, σ_{xx}, can now be examined, which results in a force F_x exerted upon the atom by its neighbor. The force F_y is zero. Since $F_y = -\left(\frac{\partial V}{\partial y}\right)$, the path of the atom (assuming elastic equilibrium as F_x is slowly increased) is defined by the locus of points where $\left(\frac{\partial V}{\partial y}\right) = 0$. The force F_x is given by $-\left(\frac{\partial V}{\partial X}\right)$, and the maximum value of this force corresponds to the theoretical strength of the polymer.

The density of the model polymer is very close to 1 g/cm^3. In the X direction, there are 7.41×10^7 carbon atoms per centimeter. There are 5.84×10^{14} chains per cm^2 of area (y - z planes). Hence the theoretical strength (dynes/cm^2) is given by:

Theoretical Strength = $5.84 \times 10^{14} \times \left(\frac{\partial V}{\partial X}\right)_{max}$. (Note: $\left(\frac{\partial V}{\partial X}\right)_{max}$ is the maximum value of $\left(\frac{\partial V}{\partial X}\right)$ encountered along the path defined by $\left(\frac{\partial V}{\partial y}\right) = 0$.

The complete theoretical stress-strain curve of the polymer, corresponding to the approximate potential function $V_I(r, \theta)$, can be similarly developed. At any point the nominal stress = $5.84 \times 10^{14} \times \left(\frac{\partial V}{\partial X}\right)$, and the strain = $\frac{\Delta X}{1.35 \times 10^{-8}}$. This is given in Figure V-8.

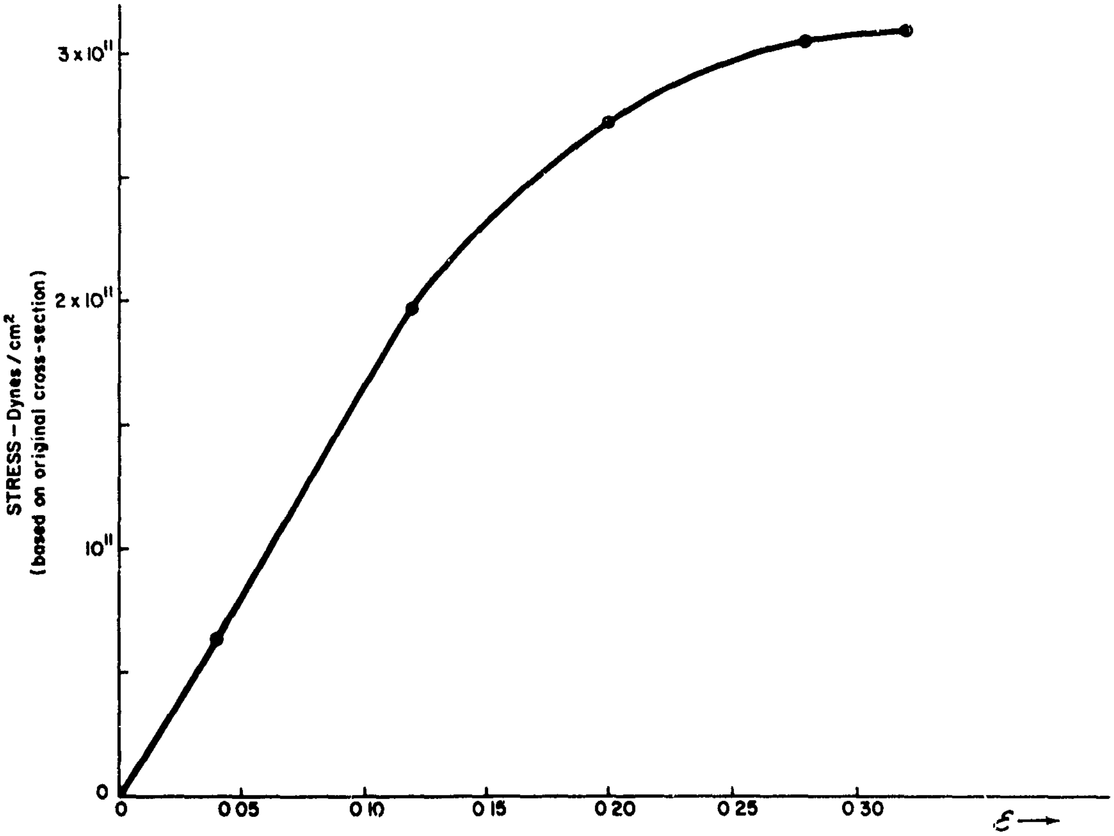


Figure V-8. Theoretical Stress-Strain Curve Corresponding to $V_I(r, \theta)$.

Having now used the crude approximation $V_I^*(\theta)$ to illustrate the approach to developing an approximation to $V(r, \theta)$, and the method of estimating the theoretical strength therefrom, the angular dependence can now be re-examined and an improved approximation $V_{II}^*(\theta)$ developed. An alternative function, which is of the desired qualitative form in the region $(-35.5 < \theta < +35.5)$, would be $V_o + C(1 + \cos 5.07\ \theta)$. If this is forced to fit the known second derivative at $\theta = \theta_o$, we obtain: $V_o + (1.69 \times 10^{-12})(1 + \cos 5.07\,\theta)$. While this function, by itself, does not provide a good approximation to $V^*(\theta)$, it can be combined with $V_I^*(\theta)$, introducing an adjustable parameter α and arriving at the following approximation for $V_{II}^*(\theta)$:

$$V_{II}^*(\theta) = V_o + \alpha(2.08 \times 10^{-12} - 3.3 \times 10^{-15}\,\theta^2 + 1.31 \times 10^{-18}\,\theta^4) + (1-\alpha)(1.69 \times 10^{-12})(1 + \cos 5.07\,\theta)$$

This function can be adjusted (via α) to fit any desired value of V_L, as well as the region near θ_o.

$V_{II}^*(\theta)$ can now be combined with the Morse potential for r, to obtain a second approximation to $V(r, \theta)$:

$$V_{II}(r,\theta) = V_{II}^*(\theta)\ 1\left(-e^{-4.04 \times 10^{8}(r - 1.54 \times 10^{-8})} + 2e^{-2.02 \times 10^{8}(r - 1.54 \times 10^{-8})}\right)$$

This potential function has been evaluated numerically for several values of the parameter α, corresponding to several assumed values of the inversion-energy $(V_L - V_o)$. Table I gives the results of these calculations.

TABLE I

α	$(V_L - V_o)$ (ergs)	Young's Modulus (dynes/cm^2)	Theor. Strength (dynes/cm^2)	Theor. Strength (psi)	Theor. Breaking Strain
0	3.38×10^{-12}	1.6×10^{12}	3.3×10^{11}	4.7×10^{6}	31.5%
0.5	2.73×10^{-12}	same	3.25×10^{11}	4.6×10^{6}	32.0%
1.0	2.08×10^{-12}	same	3.1×10^{11}	4.3×10^{6}	32.0%
1.5	1.43×10^{-12}	same	2.85×10^{11}	4.05×10^{6}	32.5%

It is seen that the theoretical strength and the theoretical breaking strain are not very sensitive to the value chosen for the "inversion energy," $(V_L - V_o)$.

As the parameter α is varied from 0 to 1.5 (corresponding to more than a 2:1 variation in $(V_L - V_o)$, the theoretical strength changes only from 2.85×10^{11} to 3.3×10^{11}. The breaking strain is even more insensitive.

The approximate potential function $V_{II}(r, \theta)$ must be used with the same reservations which have been pointed out for the Morse potential itself. However, $V_{II}(r, \theta)$ does generate a smooth surface of the correct general form in the region of interest $(-35.5^\circ < \theta < +35.5^\circ)$; and it can be made to fit all of the following quantities:

$$V_o,\ r_o,\ \theta_o,\ \left(\frac{\partial^2 V}{\partial r^2}\right)_o,\ \left(\frac{\partial^2 V}{\partial \theta^2}\right)_o,\ \text{and } (V_L - V_o).$$

Five of these quantities are experimentally accessible, and by choosing a set of reasonable values for $(V_L - V_o)$, useful insight into the large deformation behavior should be obtainable from this function.

The line of reasoning represented by the potential function $V_{II}(r, \theta)$ thus leads to the following estimates:

Theoretical Strength: approximately 3×10^{11} dynes/cm^2

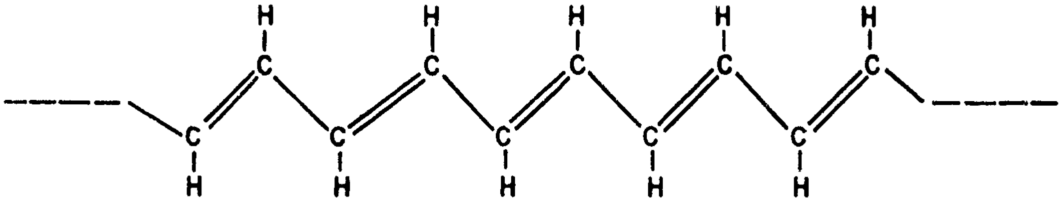
Theoretical Strain: approximately 30%.

These estimates are subject to all of the uncertainties of the Morse potential. However, present lack of knowledge of the "inversion energy" does not seem to contribute a large additional uncertainty in theoretical strength.

C. EXTENSION TO OTHER MOLECULAR STRUCTURES

The theoretical stress-strain behavior of the oriented linear polymethylene chain provides a basis for estimating theoretical strengths of a variety of other polymeric structures. The following sections will consist of qualitative and semi-quantitative comments regarding various structures, without going through actual numerical analyses.

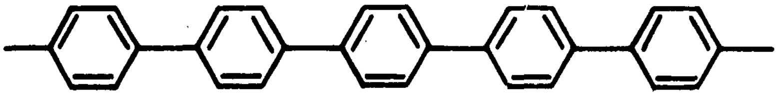
a) The Conjugated Linear (Trans) Polyene Chain



The close similarity of this problem to the polymethylene problem is obvious. The above structural formula is drawn with the double bonds localized, but resonance with the alternate electronic structures makes all C-C bonds equivalent (roughly "1-1/2 bonds" between each pair of carbon atoms). The bond angles are close to 120°. The CC bond lengths are intermediate between the normal C-C and C=C distances. The number of chains per square centimeter would be somewhat greater than in polymethylene. The significant difference between the two cases is the increase in bond-order from 1.0 to 1.5; consequently, a crude estimate of theoretical strength would be:

$$5 \times 10^{11} \text{ dynes/cm}^2.$$

b) The Polyphenylene Chain



This material would have a density of approximately 1.3 —and hence approximately 4.5×10^{14} chains per cm^2 (compared with $5.8_4 \times 10^{14}$ in polymethylene). This chain is an alternating series of strong, rigid units and weaker, more compliant units (respectively the phenylene rings and the single C-C bonds which connect the rings). The Young's modulus of such a structure will be significantly higher than that of polymethylene, but the expected theoretical strength will be lower. An estimate for this strength is 2.5×10^{11} dynes per cm^2.

This example brings out the fact that no universal ratio between theoretical strength and Young's modulus can be expected to hold for all polymeric structures.

c) The Truly Linear Molecular Solid

Consider a hypothetical solid consisting of linear molecules of nearly infinite length in a hexagonal array with strong covalent forces between atoms in the chain and weak van der Waals forces between chains. A single potential function will be used for the covalent bonds. Van der Waals will be neglected. A unit cube will be assumed for convenience. Then the potential energy is

$$U = nU_{ij}$$

where "n" is the number of bonds per unit volume and U_{ij} is the potential energy of the bond.

Taking the same direction for the bonds and the external force, the external displacement is the sum of equal bond displacements in one molecule.

$$\begin{aligned} \Delta Z &= \Sigma \Delta r \\ &= \Delta r / re = \phi \end{aligned}$$

where the reciprocal of the equilibrium bond distance, re is the number of bonds on a one centimeter length molecule.

The potential energy of the solid may be differentiated with respect to the displacement to obtain the strength:

$$\frac{du}{d\phi} = \frac{ndU_{ij}}{d\phi} = 1/2\ aDn$$

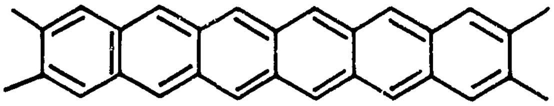
if the Morse function is assumed. "a" and "D" are parameters in the Morse potential function:

$$a = re \sqrt{\frac{K}{2D}}$$

re being the normal bond distance, K the bond force constant, and D the bond dissociation in energy, nD is the cohesive energy per unit volume of solid.

If the linear molecules in the solid are assumed to be carbon atoms with double bonds, the bond parameters may be estimated from similar molecules: re, 1.33 Å, K, 7.4×10^5 dynes/cm; D, 1×10^{-11} erg/atom; nD, 8×10^{11} ergs/cm^3; a, 2.5. These estimates give a strength of approximately 10^{12} dynes/cm^2. The elongation is about 28 per cent at the maximum strain.

d) The Double-Stranded Linear Chain Composed of Condensed Aromatic Rings

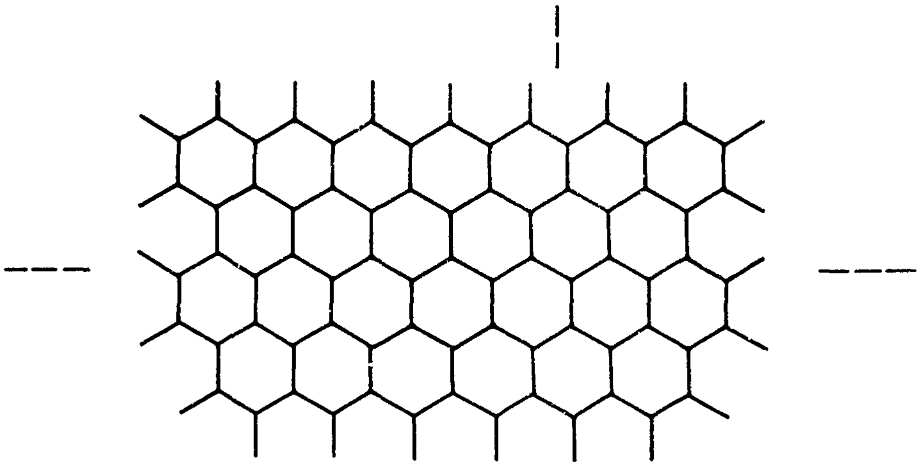


This double-stranded chain could be expected to have a density of approximately 1.5, corresponding to 4.36×10^{14} double chains per square centimeter. By symmetry, this double-stranded chain can be postulated to respond to uni-directional tension in the same general manner as the single-stranded polymethylene chain. (This postulate should be made with reservation, since there might be some asymmetric mode of large deformation of these aromatic rings which would accommodate a large macroscopic tensile strain at a lower stress level than the symmetric mode.)

Taking into account the large number of chains per unit area, and assuming a bond-order of 1.5 for the zig-zag sequence of bonds, a rough estimate of theoretical strength would be: 6.7×10^{11} dynes/cm^2.

e) The Two-Dimensional (Graphite) Network

Taking graphite as the limiting case of a two-dimensional carbon network polymer, the following is obtained:



The density of graphite is 2.2, and the bond length is 1.42 Å - corresponding to about 13 x 10^{14} zig-zag chains per cm^2. An assumed bond order of 4/3 leads to the following rough value for the theoretical strength of this structure:

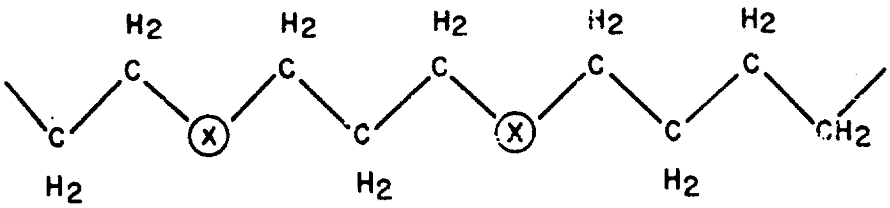
$$17 \times 10^{11} \text{ dynes per cm}^2$$

A large graphite single crystal should exhibit a high (theoretical) tensile strength in all directions in the plane of the layers, but not necessarily equal values in all directions. Unlike all polymer structures considered earlier, this two-dimensional net should have a high (theoretical) strength in biaxial loading in the plane of the layers. It would be much weaker in in the third direction.

f) Use of Foregoing Ideal Carbon Chains and Networks to Provide Upper Limits for Theoretical Strengths of Various Other Polymer Structures

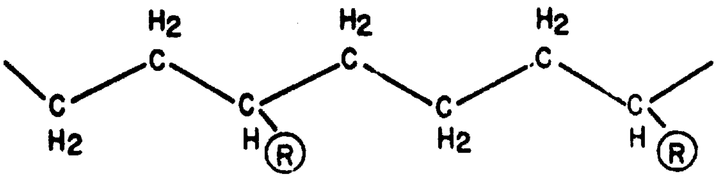
The previous theoretical strength estimates for linear polymethylene, linear poly-ene, polyphenylene, double-stranded condensed aromatic rings, and graphite, can be used as upper limits to the theoretical strengths of various other polymers, as follows:

1. Polymethylene chain with sparse substitution of some other atom for C in the skeletal chain, e.g.:



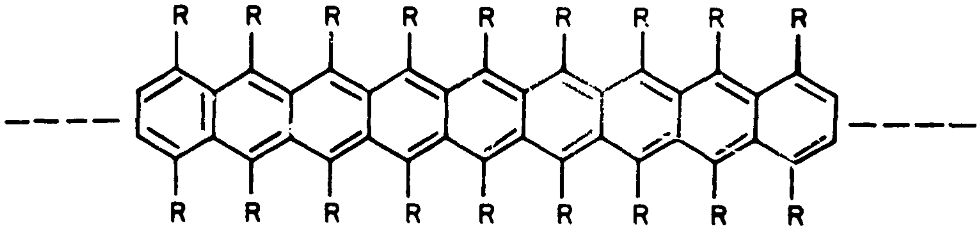
The optimum assumptions for such a system are that the geometry is not seriously altered from that of the parent polymethylene, and that the $\mathrm{C}\overset{\textcircled{X}}{\diagup\diagdown}\mathrm{C}$ unit is at least as strong as the $\mathrm{C}\overset{\mathrm{C}}{\diagup\diagdown}\mathrm{C}$ unit. The theoretical strength of the modified structure will, under these optimum conditions, be essentially equal to that of polymethylene. If the $\mathrm{C}\overset{\textcircled{X}}{\diagup\diagdown}\mathrm{C}$ unit (or the $\textcircled{X}\overset{\mathrm{C}}{\diagup\diagdown}\mathrm{C}$ unit) is significantly weaker than the $\mathrm{C}\overset{\mathrm{C}}{\diagup\diagdown}\mathrm{C}$ unit, the theoretical strength will be lower; but if the modified units are stronger than $\mathrm{C}\overset{\mathrm{C}}{\diagup\diagdown}\mathrm{C}$, this fact will not lead to an appreciably higher theoretical strength. Thus the theoretical strength of polymethylene can be taken as an upper limit to the theoretical strengths of this general class of polymers; but without further investigation of individual structures it should not be taken as a lower limit. Cases where every second carbon atom is replaced require further analysis.

2. Polymethylene Chain with Pendant Substituents



Bulky pendant groups require space. They must reduce the number of skeletal chains per cm^2. Their own load-bearing contributions (via relatively weak intermolecular forces) will almost certainly be less than required to compensate for this reduction in the density of covalent chains. In vinyl polymers, which have a substituent group on every second chain atom, the skeletal chain will usually be forced out of the planar zig-zag conformation (by rotation about the C-C bonds). Such a helical structure might turn out to have an unusually high ratio of theoretical strength to modulus, but this would be because of a relatively low modulus, rather than a high theoretical strength. It is difficult to imagine the theoretical strength of such a structure exceeding that of linear zig-zag polymethylene; again, this can be taken as an upper limit.

3. Substituted Double-Stranded Carbon Chains

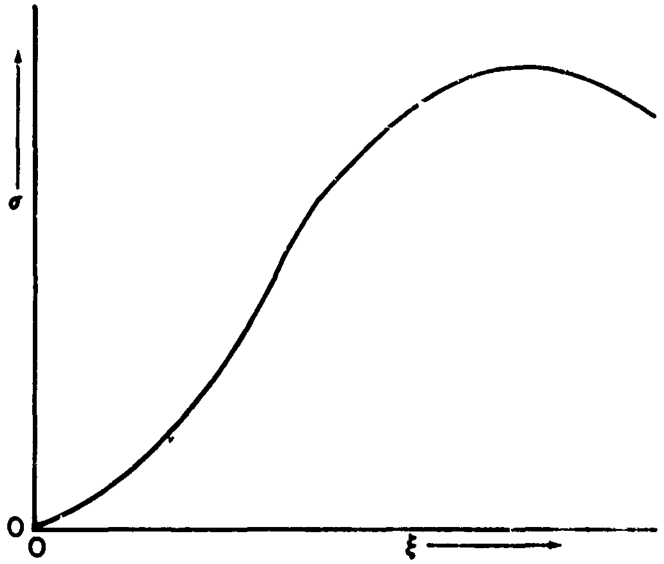


By the same reasoning as employed above, the value of 6.7×10^{11} dynes/cm^2 can be taken as an upper limit for theoretical strengths of this class of structures.

4. Comments Regarding the Estimation of Theoretical Strengths of Polymers from Young's Moduli by Means of Some Universal Ratio

A nearly universal structural feature of organic polymers is the presence of bent covalent chains as the strongest structural elements. The valence forces are strongly directional. The potential energy of a given atomic configuration depends upon bond angles as well as bond lengths. A tensile stress parallel to the general chain direction tends to open bond angles as well as to stretch bonds.

In the small-strain region, a substantial part of the elastic compliance results from bond-angle alteration. As the bonds become oriented more nearly parallel to the direction of stress, the ratio of bending moment (acting on the bond angle) to tensile force acting along the bond decreases. Consequently, the stress-strain curve exhibits a different form from that characteristic of (for example) a close-packed metal crystal pulled along a line of atoms. In extreme hypothetical cases, the predicted elastic stress-strain curve of a zig-zag polymer chain can be S-shaped, as below:



This effect probably leads to a ratio of theoretical strength to Young's modulus which is somewhat higher than that of many atomic crystals.

In the case of chains which are twisted out of the planar zig-zag conformation, this characteristic feature is probably accentuated. Thus, in a crystal composed of parallel helical molecules (e.g., isotactic polypropylene) the Young's modulus taken at very small strains might be considerably lower than that of a linear polymethylene single crystal. In addition to bond angle and bond length response, the system could deform elastically by forced rotation about the out-of-plane single bonds. The chief resistance to this bond rotation would reside in the relatively weak intermolecular (actually inter-group) forces between non-bonded bulky pendant groups which would be forced more closely together. The stress-strain curve for such a polymer might be strongly S-shaped, and the ratio of theoretical strength to Young's modulus might be quite high. No attempt has been made to analyze such twisted chains quantitatively, but it seems extremely probable that the use of a standard ratio of theoretical strength to Young's modulus would significantly underestimate the potential theoretical strengths of these materials.

SECTION VI - EXAMPLES OF THEORETICAL STRENGTH CALCULATIONS

A. SUMMARY—DISCUSSION OF METHODS OF CALCULATION

From the material presented in previous sections of this report, it is clear that there are several approaches to the problem of estimating the theoretical strengths of materials. Each has its basis in the fundamental nature of interatomic forces and their interactions in an assembly of atoms. Each approach is beset by characteristic difficulties which seem to preclude an exact calculation. The situation really resolves itself into the problems associated with making calculations which are clearly approximate, and then attempting to assess the magnitudes of the uncertainties in the results.

These difficulties arise because of the present lack of understanding of the detailed behavior of an array of atoms. It is obvious that a better understanding is needed, but because of the complexity of the general problem it is questionable whether any simple extension of present understanding would represent a significant advance. A whole new dimension of the problem is needed. However, in spite of the apparent difficulties, the concept of theoretical strength is important for the characterization of useful materials.

It may be helpful to summarize the methods of strength calculation which have been discussed earlier. Basically there are two methods which have as their common root a potential energy function. In the first, one sets out to establish, as accurately as possible, the actual potential energy function appropriate to the material at hand. This involves knowledge of the interatomic forces, the structure, and the mode of deformation under applied stress. As pointed out previously, a quantitative evaluation of the potential energy as a function of strain leads directly to the theoretical strength. Unfortunately, the region of critical strain is incapable of experimental verification because it involves strains considerably greater than can be observed with real materials. For any except the simplest cases, this approach is one of very considerable complexity, the available data are something less than adequate, and the approximations involved may sometimes be unrealistic.

The second method is much more practical, although not necessarily more reliable. It is based on the consideration that if the potential energy function is assumed to have a particular mathematical form, it is possible to develop quantitative relationships between the theoretical strength and other properties of the material. These are properties which are susceptible to measurement, and which minimize the differences between real and ideal substances; such as the heat of sublimation, Young's modulus of elasticity, the coefficient of thermal expansion, and the surface energy. The second method is more practical in the sense that it leads directly to a result, but the uncertainties involved in the result must be estimated.

One must recognize that magnitudes of the properties which a substance exhibits can be more or less dependent upon direction. A property such as heat of sublimation is a scalar (isotropic) quantity, whereas the Young's modulus, or the thermal expansion coefficient can have quite different values associated with specific directions of measurement. The suggested methods of calculation take this anisotropy into account to a limited extent. The user of these methods should recognize the degree to which the assumption of isotropy is involved and be especially careful when considering substances with pronounced directional behavior.

Still another source of uncertainty is encountered when one considers a substance that is composed of several phases in intimate combination, e.g., a high strength steel. In such a case one is forced to assume, on the basis of present knowledge, that the same general relationships between properties and theoretical strength will hold as for a simple single phase. However, the interphase boundaries in certain cases may be quite weak.

The temperature dependence of theoretical strength is important, and here again a detailed treatment of the problem presents great difficulties. The dependence of measured properties upon temperature provides some basis for calculation, but it is obvious that some properties provide more reliable indications than others. Some substances undergo phase transformations which may change the critical mode of deformation. Other properties, as for instance the thermal expansion of the iron nickel alloys, have a quite anomalous behavior in certain temperature ranges. Nevertheless, a general knowledge of material behavior can go far in ruling out obviously unreliable solutions.

In spite of all of these uncertainties, it is possible to estimate the reliability of the results obtained. Such an estimate must be based upon the best judgment of people closly concerned with the problem, and should provide a suitable guide to those interested in the application of the results.

For substances of relatively simple structure and substantially isotropic behavior, the calculated theoretical strength should be reliable to within a factor of two. In the case of substances having complex structures or exhibiting considerable anisotropy, the factor would be between three and four depending to the extent to which pertinent data were available. A calculation reliable to within an order of magnitude should be possible even with quite limited information concerning a substance and its properties.

The following illustrative examples will indicate the way in which the calculations are made and the nature of the results.

B 1. SAMPLE CALCULATIONS FOR THEORETICAL STRENGTH OF IRON CRYSTALS

General References for Data:

K. A. Gschneidner - "Physical Properties and Interrelationships of Metallic and Semi-metallic Elements," Solid State Physics 16, 275 (1964).

H. B. Huntington - "The Elastic Constants of Crystals," Solid State Physics 7, 214 (1958).

W. B. Pearson - Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, London (1958).

C. J. Smithells - Metals Reference Book, Third Edition, Butterworths (1962).

R. A. Swalin - Thermodynamics of Solids, J. Wiley & Sons, New York (1962).

Method I - (heat of sublimation)

Equation: $\sigma_{coh} \simeq 0.024\left(\frac{nm}{n - m}\right) H_s$

Required Data:

Suggested values of (n, m) for iron, taken from text = (4, 9); this yields:

$$\left(\frac{nm}{n - m}\right) = \frac{36}{5} = 7.2$$

Thermodynamic data from J. F. Elliott, M. Gleiser - "Thermochemistry for Steelmaking," p. 58, Addison-Westey, Reading, Massachusetts (1960).

Reaction	Heat
$Fe(\ell, 3150^\circ K) \rightarrow Fe(v, 3150^\circ K)$	$\Delta H_v = +84,180$ cal/mole
$Fe(s, 298^\circ K) \rightarrow Fe(s, 3150^\circ K)$	$\Delta H_{cs} = +25,650$ " "
$Fe(v, 3150^\circ K) \rightarrow Fe(v, 298^\circ K)$	$\Delta H_{cv} = -16,240$ " "
$Fe(s, 3150^\circ K) \rightarrow Fe(\ell, 3150^\circ K)$	$\Delta H_m = +3,700$ " "

Sum = Heat of Sublimation at 298°K = $\Delta H_s = 97,300$ " "

Substitution and Results:

$$\sigma_{coh} \simeq 0.024\,(7.2)\,\Delta H_s = 0.173\,\Delta H_s$$

$$\simeq 0.173(97,300\ \frac{cal}{mole})\ (4.18 \times 10^7\ \frac{ergs}{mole})\ (\frac{1}{7.1}\ \frac{mole}{cm^3})$$

$$\simeq 9.9 \times 10^{10}\ d/cm^2$$

$$\simeq (9.9 \times 10^{10}\ d/cm^2)\ (1/6.89 \times 10^4\ \frac{psi - cm^2}{d})$$

$$\simeq \boxed{1,400,000\ psi}$$

Method II - (elastic stiffness)

Equation:
$$\sigma_{coh} \doteq \frac{\langle C'_{11} \rangle}{\beta}$$

where $\langle C'_{11} \rangle$ is the average elastic stiffness in order to make this method comparable with the other examples.

$$\langle C'_{11} \rangle = \frac{(C_{44} - d/5)\,(2C_{12} + C_{11})}{(C_{44} + C_{12} - 2d/5)}$$

$$d = 2C_{44} + C_{12} - C_{11}$$

Required Data:

Taken from K. S. Aleksandrov, T. V. Ryshova, Sov. Phys. Crystallography 6, 228 (1961).

$C_{11} = 24.2 \times 10^{11}\ d/cm^2$

$C_{12} = 14.6 \times 10^{11}\ d/cm^2$

$C_{44} = 11.2 \times 10^{11}\ d/cm^2$

$d \doteq 2.60 \times 10^{11}\ d/cm^2$

$\langle C'_{11} \rangle = 22.3 \times 10^{11}\ d/cm^2 = 3.25 \times 10^7$ psi

Value for β suggested in the text = 20.

Substitution and Results:

$$\begin{aligned} \sigma_{coh} &\simeq 22.3/20 \times 10^{11}\ d/cm^2 \\ &\simeq 1.12 \times 10^{11}\ d/cm^2 \\ &\simeq \boxed{1{,}600{,}000 \text{ psi}} \end{aligned}$$

Method III - (thermal expansion coefficient)

Equation:
$$\sigma_{coh} \simeq \frac{k}{2\alpha eV}$$

Required Data:

Expansion coefficient is high temperature (nearly constant) value taken from Pearson (1958; see list of general references).

$\alpha_1 = 15.4 \times 10^{-6}/^\circ C$

$V = (7.1\ cm^3/mole)\ (1/6.023 \times 10^{23}\ mole/atom)$

$= 1.18 \times 10^{-23}\ cm^3/atom$

$k = 1.38 \times 10^{16}\ ergs/^\circ C$

$e = 2.718$

Substitution and Results:

$$\sigma_{coh} \simeq (1.38 \times 10^{16} ergs/^\circ C) \div [2(15.4 \times 10^{-6}/^\circ C)\ (2.718)\ (1.18 \times 10^{-23}\ cm^3)]$$

$$\simeq 1.37 \times 10^{11}\ d/cm^2$$

$$\simeq \boxed{2,000,000\ psi}$$

Method IV -

Equation:

$$\sigma_{coh} \simeq \left[\frac{2\gamma_1 C'_{11}}{x_o e^2} \right]^{1/2}$$

Required Data:

From the book by Swalin (1962, see list of general references):

γ (liquid iron) $\simeq$ 1450 ergs/cm^2

γ (2 x grain boundary value) $\simeq$ 1500 ergs/cm^2

γ (cleavage on {100} planes) $\simeq$ 1360 ergs/cm^2

so we take $\langle \gamma \rangle = 1450\ ergs/cm^2$

$\langle C'_{11} \rangle = 22.3 \times 10^{11}\ d/cm^2$

$X_o = d_{110} = a_o/\sqrt{2} = \frac{2.86}{1.41} \times 10^{-8}\ cm$

$= 2.02 \times 10^{-8}\ cm$

$e = 2.718$

Substitution and Results:

$$\sigma_{coh} \simeq \left[\frac{2(1450\ \text{ergs/cm}^2)(22.3 \times 10^{11}\ \text{d/cm}^2)}{(2.02 \times 10^{-8})\ (2.718)^2} \right]^{1/2}$$

$$\simeq (4.35 \times 10^{22})^{1/2}$$

$$\simeq 2.08 \times 10^{11}\ \text{d/cm}^2$$

$$\simeq \boxed{2,900,000\ \text{psi}}$$

2. THEORETICAL STRENGTH CALCULATIONS FOR A TYPICAL GLASS COMPOSITION

The following glass is representative of a large group of glasses in commercial use and exhibits the following measured properties;* Composition—69.2% SiO_2, 12.0% K_2O, 0.9% Na_2O, 11.8% Al_2O_3, 4.5% CaO, 0.9% MnO. Young's modulus—6.4×10^{11} dynes/cm^2 (9.01×10^6 psi). Poisson's ratio—0.251. Density—2.4 gms/cc. Surface tension at 298°K (extrapolated)—560 ergs/cm^2.

a.) Theoretical Strength Estimate Based on Young's Modulus

The silicon-oxygen bond, which predominates in this glass, is partially ionic and partially electron sharing whereas the alkali-oxygen bonds are ionic. Therefore, on the basis of Table II, Section III, a ratio of $\sigma_{coh}/E \approx 1/10$ appears reasonable. Thus

$$\sigma_{coh} \approx (6\text{-}7) \times 10^{10}\ \text{dynes/cm}^2\ (9 \times 10^5\ \text{psi})$$

b.) Estimate Based on Surface Energy

Since the glass under consideration is one based on a network of silica tetrahedra joined at the corners, the equilibrium spacing of atoms pertinent to strength calculations is the Si-O or Al-O separation. This spacing has a value of approximately 1.6 Å. Equation 8, Section 3, based on a force-separation law with exponential characteristics, gives therefore,

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*Griffith, A. A., Phil. Trans. A221, 163, 1921.

$$\sigma_{coh} = \left(\frac{2}{e^2}\,\frac{\gamma E}{X_o}\right)^{1/2} = 0.52\left(\frac{560(6.4)10^{11}}{1.6 \times 10^{-8}}\right)^{1/2}$$

$$= 7.8 \times 10^{10} \text{ dynes/cm}^2 \ (1.1 \times 10^6 \text{ psi}).$$

Equation 7, Section IV, based on the simpler sinusoidal approximation, gives a somewhat higher value,

$$\sigma_{coh} \approx \left(\frac{\gamma E}{X_o}\right)^{1/2} = 1.5 \times 10^{11} \text{ dynes/cm}^2$$

$$(2.2 \times 10^6 \text{ psi})$$

c.) Estimate Based on Sublimation Energy

On the basis that the energy required to separate atoms and form new surface may, by Zwicky's hypothesis, be approximated by the heat of sublimation per unit volume (i.e., approximately $\frac{2S}{X_o}$), Equation 8 (Section III) and 7 (Section IV) take the forms

$$\sigma_{coh} \approx 0.52\left(\frac{E\Delta H_s}{2V_m}\right)^{1/2} \quad \text{or} \quad \sigma_{coh} \approx \left(\frac{E\Delta H_s}{2V_m}\right)^{1/2}$$

where ΔH_s is the sublimation energy in ergs/mole and V_m is the molar volume of the material.

For the glass under discussion the molar volume calculates to be 27.3 cc. In such a glass, consideration of bond types leads to the conclusion that the alkali metal oxide bonds contribute little to strength, Young's modulus or sublimation energy. It has been shown (Phillips) that additivity theories for Young's moduli of glasses are reasonably accurate, and thus we might also expect additivity theories for sublimation energies to be reasonably accurate. The following table may therefore be constructed.

TABLE I

Sample Calculations

Component	wt %	mole% M	Modulus Factor, f(a)	Calculated Contribution to Modulus (f x M)	$\Delta H_s'$, ergs/mole of Component	Calculated Contribution to ΔH_s/mole of Glass
SiO_2	69.2	76.8	7.3×10^9	5.60×10^{11}	6.3×10^{12} (b)	4.82×10^{12}
K_2O	12.0	8.5	0	0	--	--
Na_2O	0.9	1.0	1	0.01	--	--
Al_2O_3	11.8	7.6	12.1	0.92	18.8 (c)	1.42
CaO	4.5	5.3	12.6	0.67	2.8 (d)	0.15
MnO	0.9	0.8	--	--	--	--
			Calc. Total =	7.2×10^{11} dynes/cm^2	Total	$\approx 6.4 \times 10^{12}$ ergs/mole
			(measured E =	6.4×10^{11} dynes/cm^2		≈ 150 kcal/mole

(a) Phillips, C. J., Glass Tech., 5. No 6, pp. 216-223 (1964).

(b) Bethe, H. A. and Adams, M. C., J. Aero-Space Sci., 26 (6), 321 (1959) and also Porter, R. F., Chupka, W. A., and Inghram, M. G., J. Chem. Phys. 23, 216 (1955).

(c) Goldsmith et al., Handbook of Thermophysical Properties of Solid Materials, Vol. III, Ceramics, Pergammon Press, N.Y. (1961).

(d) From (c), estimated from value for SrO.

Thus,

$$\left(\frac{E\Delta H_s}{2V_m}\right)^{1/2} \approx \left(\frac{6.4 \times 10^{11}(6.4)10^{12}}{2(27.3)}\right)^{1/2}$$

$$\approx (7.5 \times 10^{22})^{1/2} \approx 2.7 \times 10^{11}$$

and therefore the two values for σ_{coh}, depending on the forms illustrated previously would be

$$\sigma_{coh} = 1.4 \times 10^{11} \text{ dynes/cm}^2 \ (2 \times 10^6 \text{ psi}) \quad \text{or}$$
$$2.7 \times 10^{11} \text{ dynes/cm}^2 \ (4 \times 10^6 \text{ psi})$$

d.) Estimate Based on Thermal Expansion

Because of the structural complexity of glasses and their often irregular behavior in thermal expansion, no attempt is made to utilize this approach to the theoretical strength.

These several methods all lead to theoretical strength estimates lying between 1 and 4 million psi. It may be noted from the previous listing of properties of this glass that the example considered here is the glass chosen by Griffith for the experimental demonstration of the celebrated theory which bears his name. It is of interest that Griffith substituted a minimum conceivable crack length of 2 Å into his equation and arrived at a theoretical strength (1×10^6 psi) comparable to the above values.

3. SPECIFIC EXAMPLE OF CALCULATION FOR ORGANIC POLYMER

The dissociation energy of the C-C single bond is taken as equal to 5.5×10^{-12} ergs. The pertinent valence force constants are taken from Schachtschneider and Snyder, Spectrochimica Acta 19, 117 (1963).

$K_1 = 4.47_2$ mdynes/Å (Stretching)

$K_2 = 1.08_4$ mdynes/Å/(rad)^2 (Bending)

When converted to metric units, these force constants take the values:

$$K_1 = 4.47_2 \times 10^5 \text{ dynes/cm}$$
$$K_2 = 3.3 \times 10^{-15} \text{ ergs/(degree)}^2$$

Since the angle θ used in our potential function is half the bond angle, we must multiply the second force constant by 4:

$$\left(\frac{\partial^2 V}{\partial r^2}\right)_{\substack{\text{at } r = 1.54 \times 10^{-8} \\ \theta = 35.5^\circ}} = 4.47 \times 10^5$$

$$\left(\frac{\partial^2 V}{\partial \theta^2}\right)_{\substack{\text{at } r = 1.54 \times 10^{-8} \\ \theta = 35.5^\circ}} = 1.32 \times 10^{-14}$$

Further,

$$\left.\begin{array}{l} \left(\frac{\partial V}{\partial \theta}\right) = \left(\frac{\partial V}{\partial r}\right) = 0 \\ \text{and } V = -5.5 \times 10^{-12} \end{array}\right\} \text{ at } \left\{\begin{array}{l} r = 1.54 \times 10^{-8} \\ \theta = 35.5^\circ \end{array}\right.$$

For our potential function in this example, we will use:

$$V(r_1 \theta) = \left[V_o + A(1 + \cos 5.07\theta)\right]\left[-e^{-B(r-r_o)} + 2e^{-\frac{B}{2}(r-r_o)}\right]$$

and evaluate the numerical parameters to fit the above values at $r = 1.54 \times 10^{-8}$, $\theta = 35.5°$.

$$-\left(\frac{5.07}{57.3}\right)^2 \cdot A \cdot \cos 5.07\,\theta = \left(\frac{\partial^2 V}{\partial \theta^2}\right)_{r = 1.54 \times 10^{-8}}$$

$$A = \left(\frac{57.3}{5.07}\right)^2 \times 1.32 \times 10^{-14}$$

$$\underline{A = 1.69 \times 10^{-12}}$$

$$\left(\frac{\partial^2 V}{\partial r^2}\right)_{\theta = 35.5^\circ} = (-5.5 \times 10^{-12})\left[-B^2 e^{-B(r-r_o)} + \frac{B^2}{2} e^{-\frac{B}{2}(r-r_o)}\right]$$

$$4.47 \times 10^5 = 5.5 \times 10^{-12} \times \frac{B^2}{2}$$

$$\underline{B = 4.04 \times 10^8}$$

Thus, our potential function is:

$$V(r_1 \theta) = \left[-5.5 \times 10^{-12} + 1.69 \times 10^{-12} (1 + \cos 5.07\, \theta)\right] \cdot$$

$$\left[- e^{-4.04 \times 10^{8}(r-r_o)} + 2\, e^{-2.02 \times 10^{8}(r-r_o)}\right]$$

$$(\text{where } r_o = 1.54 \times 10^{-8})$$

$$\left(\frac{\partial V}{\partial x}\right)_y = 10^{-4} \left[-5.5 + 1.69(1 + \cos 5.07\, \theta)\right]\left(\frac{x}{\sqrt{x^2 + y^2}}\right)$$

$$\left[4.04\, e^{-4.04 \times 10^{8}(r-r_o)} - 4.04\, e^{-2.02 \times 10^{8}(r-r_o)}\right]$$

$$-10^{-12}(8.56)(\sin 5.07\, \theta)\left(\frac{y}{x^2 + y^2}\right)$$

$$\left[e^{-4.04 \times 10^{8}(r-r_o)} - 2\, e^{-2.02 \times 10^{8}(r-r_o)}\right]$$

$$\left(\frac{\partial V}{\partial y}\right)_x = 10^{-4} \left[-5.5 + 1.69\, (1 + \cos 5.07\, \theta)\right]\left(\frac{y}{\sqrt{x^2 + y^2}}\right)$$

$$\left[4.04\, e^{-4.04 \times 10^{8}(r-r_o)} - 4.04\, e^{-2.02 \times 10^{8}(r-r_o)}\right]$$

$$-10^{-12}(8.56)\, (\sin 5.07\, \theta)\left(\frac{x}{x^2 + y^2}\right)$$

$$\left[-e^{-4.04 \times 10^{8}(r-r_o)} + 2\, e^{-2.02 \times 10^{8}(r-r_o)}\right]$$

$\left(\frac{\partial V}{\partial x}\right)_y$ and $\left(\frac{\partial V}{\partial y}\right)_x$ are evaluated numerically at a large number of locations (x, y). The locus of the relation $\left(\frac{\partial V}{\partial y} = 0\right)$ is determined, and the values of $\left(\frac{\partial V}{\partial x}\right)$ along this path are noted. The maximum value of $\left(\frac{\partial V}{\partial x}\right)_y$ found on this path is used to estimate the theoretical strength of the polymer.

$$\text{Theoretical strength} = 5.84 \times 10^{14} \times \left(\frac{\partial V}{\partial x}\right)_{max} .$$

for a material with 5.84×10^{14} chains per square centimeter of cross-section.

C. PERTINENT LITERATURE REFERENCES ON PROPERTIES OF MATERIALS

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APPENDIX

OFFICE OF THE DIRECTOR OF DEFENSE RESEARCH AND ENGINEERING
Washington 25, D. C.

11 July 1963

Dr. Frederick Seitz
President
National Academy of Sciences
2101 Constitution Avenue, N.W.
Washington 25, D. C.

Subject: MAB Assignment on Theoretical Properties of Materials

Dear Dr. Seitz:

Materials personnel within the Department of Defense believe it would be advantageous to know the theroetical limits of high strength - high temperature materials in order to guide research and development programs. It is recognized that current theory cannot predict the expected strength increases and temperature resistance with a high degree of accuracy. Nevertheless, a summary of the procedures for making such estimates, together with a discussion of the assumptions made and their limitations should provide a useful framework to guide materials research people in selecting objectives and approaches for the development of advanced materials.

The experience gained by recent activities of Committee 2, Metals, MAB supports the desirability of such a study. In this exercise the maximum theoretical fracture and flow stresses were calculated as a function of temperature and used as a reference frame for presentation of current capabilities and estimated future progress and requirements. The reaction of all personnel acquainted with this experience has been quite favorable.

Since the methods of predicting theoretical strength vary with the type of bonding, e.g., metallic, ionic and covalent bonds and van der Waals forces, it is suggested that only examples of calculations of maximum strength be described for each case. Given the procedure for calculating theoretical strength and temperature limitations for any class the user could proceed with calculations for his specific material.

It is requested that an ad hoc group be formed to accomplish the above objectives.

It is understood that this project will not require additional MAB funding.

Sincerely yours,

(signed) Earl T. Hayes

Earl T. Hayes
Assistant Director (Materials)

cc: Secretary of the Army
Secretary of the Navy
Secretary of the Air Force
Dr. C. Sherwin
Mr. R. B. Crozier, MAB
Lt. Col. L. G. Klinker, Army Research Office
Mr. N. Promisel, BuWeps
Lt. Col. J. B. Shipp, Jr., AFRST-AS

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13. ABSTRACT

This report is in six sections, i.e., Introduction, Theoretical Considerations for Ideal Solids, Cohesive Strength of Crystals, Strength of Inorganic Glassy Solids, Strength of Organic Polymers, and Examples of Theoretical Strength Calculations. Equations suitable for engineering purposes are developed for each class, along with a discussion of the assumptions involved, their limitations and uncertainties applicable to the expression of strength in terms of other and more basic properties. The report sets forth the considerations upon which the concept of theoretical strength is based, the methods by which calculations can be made, the information required to make the calculations quantitative, the sources of such information, and the level of confidence to be placed upon the results applicable to various types of materials.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Theoretical strength						
Crystals						
Glassy solids						
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