GLASS SURFACES

PROCEEDINGS OF THE FOURTH ROLLA CERAMIC MATERIALS
CONFERENCE ON GLASS SURFACES,
ST. LOUIS, MISSOURI, USA
15-19 JUNE 1975

Editor: D. E. DAY

NORTH-HOLLAND PUBLISHING COMPANY

GLASS SURFACES

This page intentionally left blank

GLASS SURFACES

PROCEEDINGS OF THE FOURTH ROLLA CERAMIC MATERIALS
CONFERENCE ON GLASS SURFACES,
ST. LOUIS, MISSOURI, USA
15–19 JUNE, 1975

Guest Editor
D.E. DAY
University of Missouri-Rolla, Missouri

1975

NORTH-HOLLAND PUBLISHING COMPANY – AMSTERDAM · OXFORD
AMERICAN ELSEVIER PUBLISHING COMPANY, INC. – NEW YORK

ISBN North-Holland 0 7204 04193
ISBN American Elsevier 0444 11067 4

Publishers:

North-Holland Publishing Company – Amsterdam
North-Holland Publishing Company, Ltd. – Oxford

Sole distributors for the U.S.A. and Canada:

American Elsevier Publishing Company, Inc.
52 Vanderbilt Avenue
New York, N.Y. 10017

Reprinted from Journal of Non-Crystalline Solids
volume 19

The Conference was sponsored by:

Army Research Office, Durham
Corning Glass Works Foundation
National Science Foundation
Owens-Illinois Foundation
PPG Industries Foundation
in cooperation with
The International Commission on Glass

PRINTED IN THE NETHERLANDS

FOREWORD

This volume records the discussions on glass surfaces at the Fourth Rolla Ceramic Materials Conference held in Rolla, Missouri, 15–19 June 1975. The Rolla Conferences treat definite themes of ceramic research with the emphasis on free discussion yet full documentation by publication, now usually in a single regular issue of the Journal of Non-Crystalline Solids. The continuous sponsorship by many public and private institutions of the Rolla Conferences, held under the auspices of the International Commission on Glass, and the level of participation testify to the positive assessment of the conference format and topical selections. The topic of this conference was shared with the broader group of persons interested in surface chemistry and physics. A limited exhibit of new tools was made available to the participants. We are grateful to the sponsors of the Conference, to the Program Chairman Delbert E. Day, and to the Program Committee:

Dr. Charles, General Electric
Dr. Douglas, International Commission on Glass
Dr. Ernsberger, PPG
Dr. Hench, University of Florida
Dr. Oel, Germany
Dr. Wiederhorn, National Bureau of Standards

The Fifth Conference, on borate structures, will be held in 1977 at a Southwestern location.

Norbert J. KREIDL
Conference Director

This page intentionally left blank

CONTENTS

ADSORPTION

SURFACE COATINGS, FILMS AND TREATMENTS

Journal of Non-Crystalline Solids 19 (1975) 1–25

STRUCTURE OF SUBSURFACE LAYERS AND THEIR ROLE IN GLASS TECHNOLOGY

Woldemar A. WEYL
Evan Pugh Research Professor Emeritus, The Pennsylvania State University, University Park, Pennsylvania, USA

1. Introduction

Throughout science surfaces have played a unique role. Starting with Leonardo da Vinci one may follow the efforts of engineers to find the laws governing sliding friction of solid surfaces, or with Faraday and Tyndall and their work on the regelation of ice, including the arguments of Lord Kelvin. The problem of regelation would be simple if the surface of ice could be assumed to have a higher temperature and remain liquid below 0°C. This idea was rejected because water could not remain supercooled in contact with ice. Some of the problems are of immediate interest to glass technologists. Why do two freshly blown bottles weld together on the slightest contact at a temperature several hundred degrees below the softening range? We will see that the mechanism is the same as that which attracted Faraday and Tyndall to study the regelation of ice [1,2].

Can a chemist imagine a simpler system than SiO_2–H_2O, or a simpler process than water vapor condensing on the surface of capillaries made from pure silica? What could happen in such a system at ordinary temperature? A few years ago Russian scientists [3] reported that the pulsating condensation of water vapor in silica capillaries produced a dense liquid of high viscosity with a freezing point much lower than that of water, apparently a new, dense modification of water, a yet unknown polymer. After years of controversy, Deryaguin [4] solved the mystery. It was not a new modification of water, it was even more spectacular. At ordinary temperature the water vapor had reacted with the silica and with impurities to produce a gel. Long before this phenomenon was clarified it had been established that unexpected chemical reactions may occur at solid–liquid–gas boundaries [5–8].

Before turning to the subsurface of glass we want to examine some characteristic features which are common to all surfaces. The surface is a defect because all surface ions are in incomplete coordination. The asymmetry of a surface, like that of any other defect, causes abnormal interatomic distances. Also, the combination of a cation having a strong screening demand with an anion of high polarizability may lead to an ionic rearrangement that has a polarity, the Helmholtz electrical double layer. Using the mutual polarization of ions the distortions which exist in the sur-

face of a simple crystal can be calculated [9]. For sodium chloride the calculations show that the fifth atomic layer can be considered normal. Thus, a surface layer about 5 Å thick can be considered defective. Our present goal is to know more about the next 50, 1000 or 10 000 Å of the subsurface layer.

This subsurface layer is primarily responsible for the inability to attain the theoretical strength of a glass. The surface of a brittle solid develops a kind of defect known as 'Griffith flaw'. The structure of the subsurface layer is sufficiently different from the bulk to allow the glass surface to flow and be compacted during polishing. The surface is less brittle than the bulk so one can measure its indentation hardness. The mechanical and thermal properties of the subsurface layer are so different from the bulk glass that Murgatroyd [10], remarked that one should not call a fine fiber 'glass' because it scarcely resembles the material from which it is made. Thin glass fibers are, so to speak, only subsurface layers of the material.

Rigorous scientific treatment of subsurface layers faces two formidable obstacles: (1) the short range over which the cohesive forces in a solid are active, and (2) the fact that many phenomena offer no opening for introducing chemical binding forces. How does one approach the problem of the abrasion hardness of quartz that is higher in carbon tetrachloride than in butyl alcohol?

Our dynamic treatment of the constitution of glasses [5–8] overcomes these difficulties. The use of the phonon spectrum allows the subsurface layer to be treated as a modification of the glass. Analogous to a crystalline modification, a subsurface layer is characterized by having an energy and entropy different from those of the bulk. These differences are vested in the anharmonicity of thermal vibrations that taper off from a maximum value at the geometrical surface to the normal value in the interior. Our concept does not require the assumption of a depth action with respect to chemical forces. The extent of the subsurface layer, its thickness, is of colloidal dimensions.

The subsurface of a crystal, glass or liquid represents a modification that has a higher than average vibrational entropy. Since the concept of an absolute thermodynamic temperature was derived by Lord Kelvin using energy and entropy as fundamental, it is not surprising to find that in many respects a subsurface layer acts as if it had a higher temperature than the bulk. This description of a subsurface layer agreed with observations [11] where the surface of a liquid was found to have a superior solvent power when compared with its bulk. It also fits the observations of Deryaguin [4] who obtained a colloidal reaction product at ordinary temperature when water vapor condensed in thin vitreous silica capillaries. The assumption that ice, even at $-10^{\circ}C$, is coated with liquid water can explain the phenomena of regelation.

2. Derivation of a dynamic structure of a subsurface layer

Some important problems in glass technology require a dynamic interpretation of the atomic structures of glasses. This was illustrated by a pictorial description of

their liquid structures using three idealized liquids as the corners in a symbolic ternary diagram [6]. This dynamic model made it possible [12] to describe what occurs structurally, when a fining agent is added to a technical glass. This method, however, is limited because it is based on the assumption that a glass in its liquid or solid state is homogeneous. In recent years glass technologists became increasingly interested in surface phenomena. Jebsen-Marwedel [13–15] pointed out that the surface tension of glasses plays an important role in their homogenization. He has discussed a group of dynamic phenomena under the heading 'dynactivity'. These phenomena indicate that subsurface layers have dynamic structures which resemble those obtainable from soda-lime glasses by adding sodium sulfate or arsenic. Surfaces and interfaces accelerate several processes which involve material transport through diffusion and microcurrents. The energy crisis and the efforts of the glass industry to combat air pollution created a new interest in those phenomena which accelerate melting, homogenizing and fining. A critical analysis of dynactivity requires a detailed knowledge of the structure of surfaces and interfaces [8]. For simplicity we assume that the first few atomic layers of a crystal or glass are characterized by a high energy vested in the incomplete coordination of all atoms and the resulting abnormal interatomic distances. The first few atomic layers are treated as a defect. We may also assume that at a depth of about 5 Å the geometry of the bulk structure prevails.

Thermodynamically, the subsurface layer forms spontaneously hence it must lower the free energy of the system. A glass, being a metastable supercooled liquid, has two ways of lowering its free energy, namely devitrification and self-emulsification. The former increases its thermodynamic stability by lowering its internal energy, the second by increasing its vibrational entropy.

In arriving at a schematic picture for the structure of a subsurface layer one starts with a conventional idealized crystal structure and introduces the effects of atomic vibrations. For a metal or a sodium chloride crystal the usual description is an orderly array of atoms depicted by circles. This description can be modified by considering each circle as a volume element occupied by an atom or ion in its thermal motion. According to this interpretation the Na^+–Cl^- distance of 2.814 Å has no physical reality, but is simply the time average of internuclear distances between Na^+ and Cl^- ions in their thermal motions in a NaCl crystal.

The circular or spherical shape is justified as long as the ions are in a symmetrical environment. This, however, does not apply to surface atoms which vibrate in a highly asymmetrical environment. A correct structural model should use spheres only for depicting atoms in the interior of a solid, but ellipsoids for those which are close to a surface or an interface. The resulting schematic picture looks very different from conventional ones (fig. 1).

Our postulate that the structure is dynamic and that circles do not represent ions, but the larger volumes occupied by ions in their thermal motion solves a puzzling problem. How can a Na^+ ion in a rigid glass be replaced by a larger Rb^+ ion by merely being in contact with fused $RbNO_3$? This is possible because both the Na^+

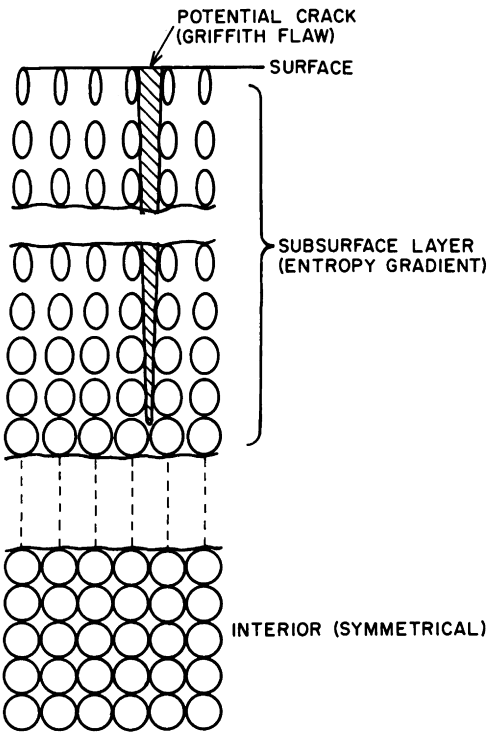

Fig. 1. Dynamic structure of a subsurface layer.

and Rb^+ ions are smaller than the space which they occupy in their thermal motion.

In refining our schematic picture to derive the physicochemical properties of the surfaces of condensed systems we have to be more specific. Starting with a liquid, the major difference between the surface structure and that of the bulk is the higher entropy vested in the greater anharmonicity of thermal vibrations. Since anharmonicity of thermal vibrations enhances material transport processes and reactivities, our picture suggests that a surface of a liquid is more reactive than its bulk in line with the superior solvent power of the surface of a liquid [11]. Spring's [16] thorough investigation of this phenomenon became the starting point of numerous investigations on corrosion. To the glass technologist it is of particular interest that molten glass does not react uniformly with the glass tank refractory, but is most corrosive at the glass–refractory–air line.

Applying our concept of the dynamic structure of the subsurface layer to a single crystal of a metal or anionic solid reveals some interesting features. Pauling [17] stated that metal atoms are smaller in the surface than in the bulk of a crystal. The elongated shapes of the volume elements occupied by metal atoms in their thermal motion gives the impression that the particles are smaller and do not touch each

other in the direction of the surface layers. It has been calculated [18] that a slice, one atom thick, cleaved from the face of a NaCl crystal would contract 5%. This can be understood from our schematic picture because there is some free space between the ions.

In spite of this difference between the surface and the bulk structure of a crystal one would not describe the surface as 'damaged'. Its delicate structure is in true thermodynamic equilibrium with the bulk structure. It represents a mechanically weak, fragile structure that can be damaged easily: a 'potential crack system'.

This schematic picture even suggests that the subsurface layer has some porosity in atomic dimensions because the directional vibrations do not fill all available space. This 'microporosity' has been examined for glasses by Poulter and Wilson [19] who diffused low molecular weight liquids into glasses under pressure. When the pressure is released slowly, these liquids, water, alcohol and ether, diffuse out of the glass without causing permanent damage. Rapid release of the pressure causes the glass to fracture.

This simple picture of the dynamics of subsurface layers could be refined, but it is sufficient that it conveys the following:

(1) The subsurface layer has a dynamic structure tapering off from the surface into the interior.

(2) The structure is the result of oriented vibrations caused by an asymmetry in the condensed system, solid or liquid. It is independent of the nature of the binding forces, metallic, ionic or molecular.

(3) In rigid glasses, or in the softening range, the structural difference is noticeable over a distance of about 100 μm, corresponding to thousands of atoms.

(4) The microporosity of the subsurface layer enables even a rigid glass to react with molecules, O_2, SO_2, H_2O and HCl, to a considerable depth. Mechanically this 'porous' structure is very weak, is easily damaged and can develop Griffith flaws.

(5) The depth of this microporous, reactive subsurface layer is a maximum for the glass--gas interface and decreases with increasing compatibility of the adjacent phase. This parameter is important for all ion-exchange reactions, including corrosion processes.

(6) Describing such a subsurface layer as a modification of the glass, means that this modification changes when the glass is in contact with different gases, liquids or solids. This is important for the flow of glass in contact with different polishing agents or for its indentation hardness.

(7) The drastic changes in the chemical reactivity caused by this phenomenon is exemplified by the surface hydrolysis of vitreous silica exposed to the pulsating condensation and vaporization of water at ordinary temperature.

(8) Essentially all properties are affected by the structural difference between the bulk and subsurface layer. For instance, anomalous values of refractive indices near the surface of PbO–BaO–B_2O_3 glasses were correctly attributed to a 'lattice disturbance' in the proximity of the surface [20].

As in many glasses, nucleation and crystallization in vapor-deposited Se films

starts at the glass–air subsurface layer. However, when the glass was deposited on metallic chromium, the selenium–chromium interface became the most reactive region [21]. The phenomenon that the mobility of a glass (nucleation rate and flow) can be affected by its contact with a metal may even contribute to the release of stresses on a macroscopic scale. In glass–metal seals the subsurface layer of the glass acted rheologically as if it had a higher temperature so that stress release occurred 125°C below the strain point [22].

3. Theoretical aspects

The basic problems involving glass surfaces, particularly contact angle and adhesion, were treated by Weyl and Marboe [7]. The limited usefulness of the total surface energy of a solid for understanding its wettability was explained. In dealing with physical realities it is necessary to divide the total surface energy into partial energies such as van der Waals' interaction, hydrogen bonding, metallicity, ionic interactions, etc. The fact that pure gold, in spite of its high surface energy, is not wetted by water illustrates that interactions between solids and liquids cannot be understood on the basis of total surface energies.

A similar situation applies to using entropy in thermodynamic treatments of surfaces. In our treatment, the vibrational entropy is the most important of the partial entropies. Within the field of glass technology, the mobility of particles and their anharmonic thermal vibrations are the major sources of the entropy.

3.1. Rate phenomena and absolute temperature

When dealing with a gas–glass interface or similar complex system we must consider that, no matter how uniform the temperature, the fundamental entity, the entropy, must not be uniform.

In discussing the superior solvent power of the surface, Spring reached the conclusion that this behavior could be understood if the surface layer was assumed to have a temperature higher than the interior of the liquid, but he did not dare to offer this as an explanation. He should have said that the subsurface layer of a liquid has the same temperature as the bulk when measured with a thermometer, but the fundamental entity on which absolute temperature is based, the entropy, is not uniform. It is actually higher in the subsurface layer than in the bulk of the liquid and tapers off from the geometrical surface to the interior.

Recently Weyl and Marboe [8] attempted to explain the significance of Jebsen-Marwedel's work on dynactivity for glass melting and energy conservation. They suggested that surfaces or interfaces should be thought of as having a higher temperature. For technologists who are not accustomed to thinking in terms of phonon spectra and vibrational entropy it is relatively simple to understand the behavior of glass on this basis. Why do freshly blown bottles weld together on contact at tem-

peratures far below the softening range? How could Murgatroyd deform thin glass fibers permanently at 100°C when the softening point of the glass was above 500°C? How can vitreous silica react with water at ordinary temperature and form a gel? Why is the surface of a glass melt more corrosive to the refractory lining of a glass tank? None of these questions is a problem if one realizes that surfaces and interfaces can act as if their temperatures were higher than that of the bulk.

Another interpretation of these phenomena avoids the concept that a temperature gradient exists in the glass [5–8]. Rate phenomena increase with increasing temperature for two reasons. First, because of the increase in energy that becomes available, i.e. kT. Second, because all thermal vibrations become less harmonic. Solid-state reactions and sintering require material transport. The anharmonicity at an interface between different oxides makes material transport possible at a temperature at which it is impossible for a pure oxide to diffuse.

No matter how we look upon the subsurface layer, its rheology and chemical reactivity behave as if it had a higher temperature. This concept can be very helpful in bracketing the rheology of subsurface layers of glass. They are not 'brittle' but they are also not 'plastic' in the strict rheological meaning of these words. They can be indented and they flow during polishing.

Thermodynamically the subsurface layer represents a glass in a critical region in which all thermodynamic parameters are subject to strong fluctuations. The subsurface layer acts like a crystal in the region of a phase transformation, e.g. like a metal in a state of superplasticity or a quartz crystal at the low–high transformation where it is extremely reactive and exhibits a high diffusivity.

3.2. Rebinder effects

Some properties of solids change drastically with environmental conditions. The color of finely subdivided gold depends upon the environment and particle size [23]. This reversible color change is distinctly different from the irreversible color change caused by the growth of the gold particles. The variations in the light absorption are caused by changes in the symmetry of the atomic vibrations. Gold films such as those used for the heat control of transparencies, lose metallicity when deposited on a soda-lime glass and become poor electronic conductors. Depositing the same amount of gold on oxides of increasing atomic weight, e.g. ZnO, PbO and Bi_2O_3, increases its electronic conductivity.

The effect of the environment upon the machinability of metals and the hardness of non-metallic crystals [24] called the 'Rebinder effect', is used to modify the mechanical properties of materials, e.g. to facilitate drilling operations, by using the proper 'cooling liquid'. The apparently straightforward explanation given by Rebinder [24] was that in drilling a hole a part of the energy is utilized for producing new surfaces. Wetting the surface with a surface-active agent lowers the surface energy and, thus the total energy needed for drilling. However, this explanation has two shortcomings. First, the surface has to be formed before it can be

wetted and second, the surface energy of a fractured crystal is only a relatively small part of the energy needed for fracture.

Other observations [25] speak strongly against any explanation based upon surface energy. The elastic moduli and internal friction of a glass fiber respond to wetting with an aqueous solution of amyl alcohol. Neither the elastic deformation nor the internal friction of a fiber involve the formation of new surfaces, both are strictly reversible processes. The Rebinder effect involves a change in the mechanical properties of the subsurface layers of materials. We regard this layer as a modification of the material, the nature of which depends upon the entropy induced by the asymmetry of the interface. Just like the light absorption and electronic conductivity of metallic gold, the fracture strength or brittleness of a material depends upon the environment.

Our explanation of the Rebinder effect is relatively simple. The asymmetry of the interface projects into a crystal or a glass as an entropy gradient. The subsurface layer becomes a different modification which, like a different polymorphic modification of a crystal, has different properties. The depth of this modification depends upon the system. We have evidence that the layer is at least 50 Å deep for a corundum crystal and can be on the order of several thousands of angstroms for a technical alkali-lime–silicate glass.

The major problem is the characterization of the parameter that induces the entropy gradient. For the Rebinder effect we need an equivalent of the parameters normally used for describing the stability of a polymorphous modification, namely temperature and pressure. The interaction of a surface with a liquid involves several mechanisms which we have discussed in some detail [7]. It might be midsleading to single out one parameter of a liquid and emphasize its effect upon a metal or glass. An ionic system such as fused NaCl or an alkali silicate glass interacts with platinum and adheres tenaciously to a platinum crucible on cooling. A proper alloy of platinum, either with gold or rhodium, interferes with the formation of image forces, i.e. the mechanism of adhesion, so the glass can be removed easily from the crucible. The interaction mechanism between a metal and glass is active in modifying the subsurface layer of a glass in contact with a noble metal. It changes the rate of nucleation, gas evolution, diffusion and phase separation. In fact, the influence of the nature of the solvent on fluorescence, color [26,27] and reaction rates [27,28] has been known for a long time. According to our experience, this interaction is dynamic and should be described by parameters which include not only the geometry of the molecules, their dielectric constants, dipole moments, etc. but also their masses.

3.3. von Schroeder's paradoxon

A thin film of gelatin exposed to a humid atmosphere absorbs water, increasing in both weight and volume. Swelling is a reversible process that leads to an equilibrium depending upon the temperature and the H_2O-vapor pressure. At room tem-

perature such a film of gelatin reaches its maximum degree of hydration after having been exposed for sufficient time to saturated water vapor. If this film is then immersed in liquid water it continues swelling and gaining weight. Immersed in liquid water the gelatin reaches another hydration equilibrium, higher than the one reached in the vapor phase at the same temperature. When removed from liquid water and kept in an atmosphere saturated with H_2O-vapor it begins to lose weight and shrinks. This unexpected behavior was discovered by von Schroeder [29]. It was found to be reproducible and means that the gelatin–water system at a given temperature has two well-defined equilibria, one for gelatin–liquid water and one for gelatin–water vapor. The phenomenon could not be explained and became known as von Schroeder's paradoxon [30] and was looked upon as an 'apparent violation of the second law of thermodynamics'. In order to understand it one has to realize that the difference between the gelatin–liquid water system and the gelatin–water vapor system is vested in the nature of the interface, namely the reversible transition of the solid–liquid interface into a solid–vapor interface. This change affects the symmetry of the system because the gelatin–liquid water interface has a higher order than the gelatin–vapor phase interface. Thermodynamically there is nothing paradoxical about the phenomenon, one only has to look upon the closed system and include the entropy of the interface-induced subsurface structure.

3.4. Interfaces as stabilizers of a system

The stability of colloidal systems with a large surface area or an extensive interface now need be considered strange no longer. In our view, the stability of a system can be increased not only by decreasing the surface area and with it the surface energy, but also by increasing the subsurface layers and with them the vibrational entropy that is induced by an increase of the interfacial area. Applied to glasses this means that the stability of such a metastable system can be increased not only by crystallization or devitrification but also by self-emulsification, i.e. the formation of extensive interfacial areas which increase the vibrational entropy.

The principle that an interface can stabilize a system, recently utilized in the manufacture of glassceramics, was discovered 150 years ago. Since its nature was not recognized, it was rediscovered many times and is still the basis of several new inventions. Like all thermodynamic treatments it lacks specificity but its history is fascinating and some examples should help glass technologists to better understand glassceramics.

In 1825 Magnus [31] discovered that thermal decomposition of organic iron compounds, the citrate or tartrate, produces metallic iron in a finely subdivided state. Exposure to air causes the metal to be oxidized, evolving heat. This pyrophoric iron was a laboratory curiosity. When similar experiments were performed with the organic salts of aluminum only the oxide, Al_2O_3, but no metal was obtained.

A mixture of an organic iron compound with a minor addition of a correspond-

ing aluminum compound produced a mixture of the finely subdivided metallic iron with Al_2O_3. This mixture, however, was no longer pyrophoric, the presence of Al_2O_3 seemed to have stabilized the iron. No chemical explanation could be given of the way an inert oxide could stabilize a metal, so Magnus' experiments remained an interesting laboratory curiosity.

In 1949 von Zeerleder and Irmann [32] discovered the 'dispersion hardening' of aluminum metal by a finely subdivided dispersion of Al_2O_3 in the metallic matrix. In metallic systems the strengthening of an alloy by the precipitation of finely subdivided crystals was well known, but the effect of an inert, insoluble oxide was startling.

There is no structural explanation for the increase of the melting point of a metal by an inert oxide, but the phenomenon can be easily understood by relating it to the freezing-point depression. Any substance that dissolves in water increases its entropy and lowers its freezing point, provided it does not enter the crystalline phase. Alumina would not remain colloidally dispersed in a fused metal, but dispersed in the solid it increases the vibrational entropy of the system. By stabilizing the solid through an increase of entropy, alumina increases the melting point of metals. This makes dispersion hardening strictly an entropy effect in which the strength or the melting point of Al_2O_3 or its E modulus do not enter as important parameters. Dispersion hardening does not require a solid, gas bubbles increase the sag resistance of tungsten wire [33].

Chemical and mechanical stabilization by the formation of large interfacial areas is a principle that has revolutionized whole industries. The automotive industry depends upon the strengthening of rubber by colloidal carbon. In dynamite inert diatomaceous earth has been replaced by combustible solids: the inertness of the colloidal silica is not the important property because the stabilization is an entropy effect that calls for vibrational entropy through interfaces. Some of the latest improvements concern the stabilization and strengthening of soft lead electrodes by inserting oxides.

In treating the subsurface layer as a polymorphic modification analogous to a high-temperature modification of a substance we deviate from classical thermodynamics where gradients of energy or entropy are not considered. Including gradients of any thermodynamic quantity leads to hysteresis phenomena and makes the stability of a phase a function of its particle size as is the case for whiskers and dendrites. A whisker can be flawless because its entropy is vested in its large surface to volume ratio, or the dimensions of its subsurface layer. Compounds which undergo polymorphic changes on cooling such as tridymite or zirconia can show characteristic hysteresis phenomena because their interfacial layers behave as an additional new phase. Classical thermodynamics has no way of dealing with these phenomena. This applies also to where the particle size enters as a parameter such as the formation of rhythmic precipitation (Liesegang rings). In only the smallest particles of fused ZrO_2 can the formation of the stable tetragonal modification be suppressed [34]. Undissolved crystals of feldspar were found responsible for producing 'brittle'

glass with a low resistance to shock and poor workability. The driving force of the solution process of a feldspar crystal changes with the melting time. As the size of the crystal decreases its surface to volume ratio increases, which may cause the driving force for dissolution to decrease. Sproull and Rindone [35] melted mixed-alkali glasses from mixtures of premelted $Li_2O \cdot 2SiO_2$ and $K_2O \cdot 2SiO_2$. Even at 1400°C and with repeated stirring it took many hours to homogenize the melt once the two phases, one rich in Li_2O and one rich in K_2O, had reached the dimensions of about 200–800 Å, where the interface becomes a stabilizer.

4. Fracture strength of glass and formation of Griffith flaws

Reliable estimates of the theoretical strength of glass give values $\approx 3 \times 10^6$ psi. Under special conditions values of this order of magnitude can be obtained experimentally [36].

For practical purposes the useful strength of a glass is only 0.1% of its theoretical value. The gross disparity between the theoretical and practical strength results from a weakness originating in the glass surface, but no generally accepted theory exists which explains the origin of this weakness. Griffith [37] assumed the existence of numerous flaws in all glasses and the most dangerous of these flaws, nearly always a surface flaw, limits the practical strength. No final decision has been made whether Griffith flaws are an intrinsic part of the glass structure or are the result of chemical or mechanical damage. Some scientists assume that the flaws form during testing due to stresses applied to the specimen. Practically, the differences are not important and, without expressing a preference, the author refers to even a pristine glass surface as a 'potential crack system'.

Since fracture starts at some point in the surface of glass, it is interesting to see how our concepts of the subsurface layer apply.

4.1. Thermodynamic aspects

Starting with an ideal glass, free of inhomogeneities, and having the structure of a supercooled liquid, the formation of the subsurface layer is unavoidable at all temperatures above absolute zero. As soon as thermal vibrations become significant they also become asymmetrical in the subsurface layer. The subsurface layer is in true thermodynamic equilibrium within a homogeneous glass. Its free energy is lower because of its high vibrational entropy.

For several glasses it has been observed that at temperatures slightly above absolute zero the fracture strength decreases sharply on heating. This decrease can be caused by the increase in amplitudes of all atomic vibrations that leads to the formation of a subsurface layer. It is not likely that this weakening effect is the result of a chemical reaction with the environment because it was found also by Ernsberger [38] when he used his technique which should eliminate such interactions.

Ernsberger [39] suggested, as a working hypothesis, that there is something real and very fundamental about the peculiar sigmoid curvature of the strength–temperature curve for glass. In fact, the formation of a subsurface layer and its effect upon fracture strength.

No such simple relationship will exist if the glass, during its thermal history, has undergone self-emulsification. This process also lowers the free energy by increasing the configurational and vibrational entropy, hence it lowers the driving force that produces the subsurface structure. This is most likely important for glassceramics because it might be the major cause of its superior mechanical properties.

4.2. Kinetic aspects

A subsurface layer can be described as a modification of the glass that is characterized by an entropy gradient that resembles a temperature gradient. The subsurface layer of a glass acts kinetically as if it had a higher temperature so that two pristine glass surfaces weld together on contact. For the same reason it is not possible to group glasses according to their Mohs scale hardness. Because of their 'stickiness' freshly drawn fibers and freshly blown bottles need the protection of lubricants. The surface vulnerability of glasses and the formation of Griffith flaws as described by Brearly and Holloway [40] involves this stickiness.

Marsh [41] assumes that plastic deformation of glasses at ordinary temperature plays a significant part in their fracture under stress. We prefer to go even further and state that the plasticity of the subsurface layer is responsible for the lack of a simple relationship between fracture strength of glasses and their cohesive forces or their E-moduli. Once a fracture has started in the subsurface layer it propagates in the 'plastic' subsurface layer. A crack is the center of an asymmetry and as such it produces a subsurface layer that will always precede the propagating crack.

The mobility of subsurface layers should interfere with the efficiency of strengthening fiber glass by ion exchange. Since glass fibers consist essentially of subsurface layers they have a certain relaxation behavior (plasticity) that prevents the establishment of major stress gradients. This seems to apply even to compact glasses at elevated temperatures. Garfinkel and King [42] discuss this problem in greater detail and their experiments reveal not only the higher diffusivity for cations in the subsurface layer, but also the higher rate of relaxation in this plastic part of the glass.

4.3. Structural aspects

Our schematic picture of the subsurface layer with its submicroscopic porosity justifies our description of pristine glass surfaces as 'potential crack systems'. Following the concepts of Brearly and Holloway [40] there is no practical difference between this expression and that of a Griffith flaw. However, with Ernsberger's new technique [38] significant differences may be found between strength measured in the absence of dust particles and values obtainable by older methods.