On the Manner of Molecular Grouping in Glass

By Usaburo Yoshida

Abstract

The idea of cybotaxis as affecting liquid and super-cooled liquid was extended to the case of glass, and various physical properties of glass such · as viscosity, specific heat, thermal expansion, electrolytic conduction and mechanical properties were examined from the standpoint of this idea. For plastic deformation of metals and the sintering of powder crystals of metals etc., an explanation based on this idea has been given. The fracture of glass at its elastic limit is. compared with the plastic deformation of metals.

Introduction

Recently the writer[1] proposed a hypothesis concerning the internal constitution of liquid, super-cooled liquid and amorphous solid, by assuming the presence of cybotactic groups or cybotactic crystals in these states of matter. A cybotactic group, the writer considered, is formed spontaneously in the liquid, by the aggregation of a few liquid molecules in a certain manner of configuration. The manner of molecular configuration will depend upon the number of constituent molecules ; and when this number is more than necessary to construct a unit cell of the crystal of the substance, the manner of molecular configuration will be the same as that of the crystal. This kind of cybotactic groups was called by the writer the " cybotactic crystal ". The presence of such cybotactic crystals and cybotactic groups in liquid, in super-cooled liquid and in amorphous solid was assumed by the writer, to conform with the results obtained with the diffraction experiments with x-rays and electron waves. The cybotactic groups in a liquid (including super-cooled state) at the temperatures higher than the solidifying temperature of the substance are of only momentary existence. They are formed spontaneously here and there in the liquid, and immediately decompose into free liquid molecules ; and statistical equilibrium between the cybotactic groups and the free liquid molecules is attained when the number of molecules forming

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1. U. Yoshida: These Memoirs, **23**, 207 (1941).

the cybotactic groups in unit time becomes equal to that decomposing into the free liquid molecules in the same time. As the molecular aggregation into the cybotactic groups is caused by the attractive force between molecules, their decomposition into free liquid molecules is brought about by overcoming the potential energy of the intermolecular attraction with the aid of the kinetic energies of the constituent molecules due to thermal agitation. Thus the decrease of temperature increases the chance of formation and decreases that of decomposition; and consequently the proportion of the total amount of the cybotactic groups to that of the free molecules in equilibrium will increase gradually with decreasing temperature. When the temperature is continuously so much reduced that it is far below the melting point of the substance, the total amount of the cybotactic groups will be increased correspondingly, and the substance will at last come to the state in which the major part of its molecules are in the state of cybotactic combination. This extreme case of the super-cooling of a substance was considered by the writer to be its glassy state or its state of amorphous solid. An enormous increase in the viscosity of the substance in transforming from the liquid to the amorphous solid state was hence considered by the writer as mostly due to the enormous increase of the cybotactic groups with decreasing temperature. In the following various physical properties of glass were investigated from the viewpoint of cybotaxis as simply stated above.

Viscosity

A high degree of viscosity of a glass in its annealing temperature range requires considerable time to reach the constant value characteristic of a given temperature when it is maintained at this temperature; when it is higher initially it decreases gradually and when it is lower initially it increases gradually to the same constant value. This time required to reach the constant value decreases with increasing temperature. If the constituent molecules were entirely free from each other and had not the property to form molecular aggregation or chemical change, the equilibrium value of the viscosity characteristic of a given temperature would be reached immediately as soon as that temperature was attained by the whole mass of the substance. Consequently the presence of considerable time-lag in reaching the equilibrium value of the viscosity seems necessarily to imply the occurrence of a change in the state of molecular aggregation or in chemical

combination in the process of heat treatment. As the latter, among the effects of these two causes, is not probable to take place always for various kinds of glasses at temperatures lower than the annealing temperature range, the presence of an immense number of cybotactic groups of considerable size seems to be necessary to explain the viscous property of glass at comparatively low temperature. Other than the viscosity, most of the physical properties of glass such as thermal expansion, specific heat, optical property and electrical conduction etc. are accompanied, in heat treatment, by the time-lag or the hysteresis of considerable amount at a comparatively low temperature, These facts seem to give powerful support to the cybotactic hypothesis. The process of annealing, when looked upon from the view-point of this hypothesis, is simply minimizing the nonuniformity in cybotactic states at different portions of the specimen by bringing these different states to the same one of equilibrium peculiar to the annealing temperature.

As was done in the former report, let x be the number of constituent molecules in a cybotactic crystal, n the number at a certain temperature of the cybotactic crystals in unit volume and N the total number of molecules in unit volume including both free and constituent ones of the cybotactic crystal; then the total number of free molecules in unit volume will be $N-xn$. Among these a certain fraction α per unit time will be aggregated to form the cybotactic crystals, and at the same time a certain fraction β of the cybotactic crystals per unit time will decompose into free molecules. Thus, in equilibrium, we have

$$\alpha\,(N-xn)=x\beta n,\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

$$\therefore\quad n=\frac{1}{1+\dfrac{\beta}{\alpha}}\,\frac{N}{x}.\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

For a certain kind of cybotactic crystal in a certain liquid, both α and β will depend only upon the temperature. With increase of temperature, except when it is very low, α will decrease and β will increase continuously in consequence of the increase of the kinetic energy of molecules; and thus n will decrease continuously with increasing temperature. However, with the glassy state of a substance, n should be considered to be very large, and the temperature dependence of α and β will be different in this case as is schematically represented by the curves drawn in full lines in Fig. 1. At the temperatute T_m, which may be looked for as the melting point of the cybotactic crystals, the
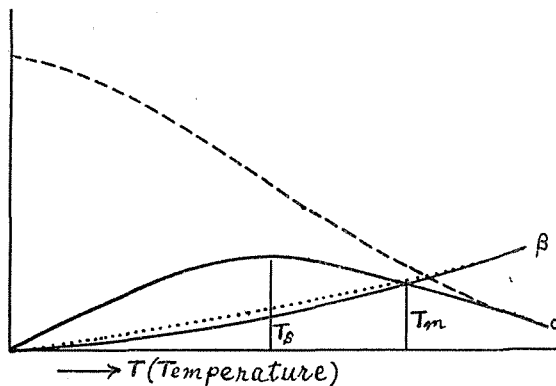
Fig. 1

values of α and β are equal; and half the total number of the molecules comes to be aggregated as cybotactic crystals. Below this temperature the number of molecules aggregated as cybotactic crystals increases with decreasing temperature, and the general aspect of the distribution of free molecules in narrow interstices between neighbouring cybotactic crystals will be such as shown by Fig. 2. In this state the stability or the average duration of persistence of the cybotactic crystals will be considerably increased due to the want of kinetic energies of molecules which are necessary to decompose the
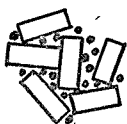

Fig. 2

crystals. Moreover this stability will be still more increased by the difficulty of expansion accompanying the decomposition of the cybotactic crystals against an enormous pressure which is supposed to be acting in the glassy state. Consequently the value of β will become smaller than in the ideal case where no remarkable pressure is acting against the expansion by decomposition of the cybotactic crystals. This ideal case is shown by the curve drawn in dotted line in Fig. 1. Next the rate of aggregation of free molecules into cybotactic crystals will be very much reduced, as compared with the case when the majority of molecules are free, by the lack of neighbouring and adjoining free molecules and also by the absence of free spaces to be occupied by the formation of individual cybotactic crystals. Because of these circumstances, α will not increase continuously with decreasing temperature as is shown by the broken line in Fig. 1, which corresponds to the ideal case containing no cybotactic groups in the substance; but after passing through a maximum, it will decrease again with decrease of the temperature. This tendency of lessening the value of α at low temperature will be much more remarkable in multi-component glass. In this case we must expect the presence of the cybotactic crystals of different composition, and every individual kind of cybotactic crystal is formed by the aggregation of a certain number of

molecules belonging to certain kinds of components. The chance for this to occur will be much smaller than in the case of one-component glass. The low values of both α and β at low temperatures mean that the stability or the duration of persistence of the molecules both in the free state and in the aggregated state as cybotactic crystals is great : i. e. that it requires a long time for the change to take place from the free state to the aggregated one or vice versa. Thus when temperature is changed, new equilibrium is only attained at low temperatures after a time-lag of considerable duration as is actually observed with viscosity and the other physical properties of glass.

In the case of annealing glass, the lower limit of the annealing temperature range was called " the strain point " by Littleton,[1] and was defined as that temperature from which a piece of glass can be quickly cooled without introducing permanent strain. If our consideration is correct that α has a maximum at a certain temperature as is shown in Fig. 1, then the temperature dependence of β/α will be such as shown in Fig. 3. The value of β/α will increase only slightly up to the temperature T_s, which is not much different from that corresponding to the maximum value of α, and then rapidly with increasing temperature. Corresponding to such slight change of β/α below T_s, the equilibrium number of the cybotactic crystals per unit volume at the temperature T_s will be almost the same as that at room temperature. Thus when the glass, after being kept for a long time at

Fig. 3

the temperature T_s, is cooled quickly to the room temperature, no remarkable change in its internal structure will be called forth throughout the whole portion of the specimen by this sudden change of temperature.
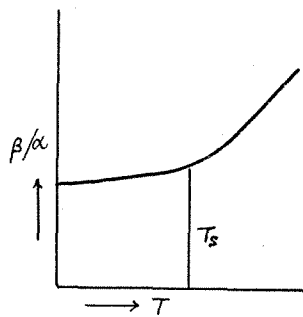
Though the change in the value of β/α is very slight below the temperature T_s, it will not be entirely free from temperature change ; and a slight decrease with decreasing temperature is expected even below T_s, Corresponding to this slight decrease in β/α a slight increase in the equilibrium number n of the cybotactic crystals accompanies decreasing temperature, indicating that the change in the equi-

1. Morey : Properties of Glass p. 174 (1938).

librium state in the internal structure is contraction with decreasing temperature. When glass in structural equilibrium at high temperature is cooled to room temperature, it requires a considerable time to attain the contracted state which is in structural equilibrium at room temperature, as is revealed by the " secular rise of the zero point" of a newly made thermometer. This secular rise of the ice point can be temporarily depressed by giving the thermometer glass a slight structural expansion by heating the thermometer to 100°C and cooling it quickly.

Specific Heat

Thomas and Parks[1] measured the specific heat of boric oxide glass with continuously changing temperature by means of a radiation calorimeter. The sample was prepared by heating it in a platinum crucible for 8 hours at 900°C., and pouring it into a silver calorimeter, kept at 500°C, then cooled quickly to 50°C in about 30 minutes. The specific heat of this quickly cooled specimen was then measured in a continuous series of observations, from 33°C to 345°C, in about 14 hours. The glass was then cooled slowly in 18 hours, and a second series of specific heat measurements was made during the cooling from 332°C to 112°C. The specific heat of this slowly cooled glass was again measured by heating it gradually from 35°C to 325°C. The results of these measurements are assembled in Fig. 4. There was a rapid increase in specific heat in the softening region of the sample.
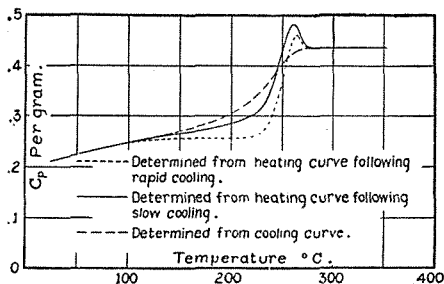
Fig. 4

From the view-point of the writer's hypothesis the explanation for this rapid increase is simple : it is due to the latent heat of fusion of the cybotactic crystals whose number decreases remarkably in the softening region by raising the temprature. The differences between the three curves in Fig. 4 arise from the lag or the hysteresis in the cybotactic change of the sample, just as in the case of viscosity. The specific heat determined from the heating curve following rapid cooling is smaller than that obtained from

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1. S. B. Thomas and G. S. Parks: J. Phys. Chem., **35**, 2091 (1931).

the heating curve following slow cooling. This is caused by a smaller content of the cybotactic crystals in the former case by virtue of the fact that the time elapsed during the cooling was very much shorter than in the latter, so that the departure from the cybotactic equilibrium at the cooled temperature was much more remarkable in the former case. The two curves obtained on heating show a hump just before flattening out. This is also due to the hysteresis in the cybotactic change and is caused by the release of the stored-up lag. The aspect of the hysteresis in the cybotactic change will be clearly understood if we compare the curve obtained from the cooling curve with that obtained from the heating curve following the preceding slow cooling. On heating curve the specific heat is smaller at lower temperatures by virtue of the lag in the cybotactic change; and then the stored-up lag is restored at a narrow range of higher temperatures by forming a hump in the specific heat curves. All the specific heat curves coincide entirely at temperatures higher than about 275°C. From the writer's view-point this is due to the fact that the lag in the cybotactic change is unnoticeable at these temperatures. Three specific heat curves coincide also at temperatures lower than about 100°C. At these temperatures, the content of the cybotactic crystals is supposed not to be the same. But the lag in the cybotactic change will be enormous in this case, and no noticeable change in the amount of the cybotactic crystals on heating or on cooling will take place at these low temperatures in any case.

Thermal Expansion

It is known that the glass expands almost linearly up to the lower critical point or the transition point, and then more rapidly with increasing temperature. It seems to the writer that the amount of the free molecules formed by decomposition of the cybotactic crystals becomes especially remarkable above this point; and that the more remarkable expansion above this point is due to the relaxation of the tight internal structure, caused by the increase in number of free molecules and by sufficient increase in kinetic energies of the molecules at this temperature. According to the experiment made by Turner and Winks,[1] glass chilled quickly from high temperature behaves abnormally about this point as is shown by the lowest curve in Fig. 5. At a temperature somewhat below this point its expansion lessens
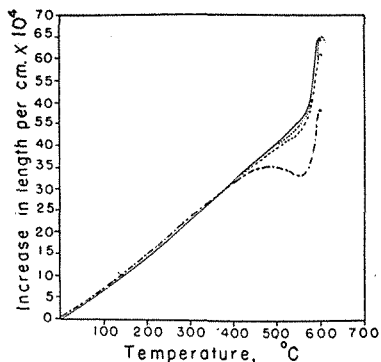
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1. Morey: The Properties of Glass, p. 266 (1938).

Fig. 5

remarkably when compared with that observed with annealed specimens, and again increases from the critical point. With this glass, the initial cybotactic state will be much nearer than the annealed one to that at high temperature from which it is chilled quickly, and the content of the cybotactic crystals will be much less at lower temperatures than that corresponding to the equilibrium value. When the temperature is raised to the value somewhat below the critical point, the equilibrium state will be approached by an increase in number of the cybotactic crystals rather than the decrease, by bringing forth the abnormal decrease in its thermal expansion. Such abnormal decrease in expansion coefficient can be made to occur at a certain temperature more abruptly by choosing the appropriate rate of temperature increase and the thermal history of the specimen, and this temperature is sometimes called the " transformation point ". Littleton[1] and Morey[2] consider that the effect observed is the result of failure of the glass to reach internal equilibrium at lower temperature with the result that, when the viscosity has been sufficiently diminished by heating, the frozen-in lag is suddenly released. Their view agrees entirely with the writer's in the sense that by the internal equilibrium the equilibrium in the cybotactic state is meant.

Electrolytic Conduction

It is well known that at higher temperatures ordinary glasses conduct electricity electrolytically. With proper experimental procedure we can even convey the Na ions from one side of soda glass to the other. The temperature dependence of the specific resistance of glasses has been measured by many authors; and it is known that the specific resistance runs, with temperature change, almost parallel, though not proportionally, with the coefficient of viscosity: i. e. that the specific conductivity of a glass changes, almost parallel, with its fluidity with temperature change. According to the cybotactic theory,

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1. Morey: The Properties of Glass, p. 267 (1938).
2. Morey: The Properties of Glass, p. 267 (1938).

the increase in fluidity of glass is due mostly to the increase in number of the free molecules in proportion to that of the cybotactic groups. Thus if we follow the same reasoning, the electrolytic conductivity of glass must be ascribed mostly to the transport of the ions along the interstices of cybotactic crystals, where the molecules and the ions are free to move at higher temperatures. As is evident from the cybotactic idea an individual cybotactic crystal has no permanent stability. It is formed spontaneously somewhere in the substance, and is of only a momentary existence at higher temperatures. Consequently the paths of the ions are not fixed, and they will change from moment to moment by chance. The transportation of the ions of considerable amount at temperatures not very high, where the glass is still in a solid state, seems to be explained by the presence of this circumstance; without which the transport of the ions would be very difficult if they were confined permanently along very narrow and irregular interstices between neighbouring cybotactic crystals.

Littleton and Wetmore[1] measured at various temperatures the change of resistivity with time of annealed and chilled glasses having the same composition, and found that the specific resistivity of the chilled glass increased with heating time; and that the specific resistivity of the annealed one, which was greater initially than that of the chilled glass, approaches the value of the chilled one as the time of heating is increased. This is a hysteresis effect in the cybotactic state, and is due to the fact that the initial amount of the cybotactic crystals in the chilled glass corresponding to the condition of the cybotactic equilibrium at a temperature higher than that of the experiment was smaller than that of the equilibrium state at the temperature of the experiment; whereas that of the annealed glass was initially greater than that of the chilled one corresponding to the equilibrium value at lower temperature.

Elastic Property and Fracture at Low Temperature, and Fluidity at High Temperature

The elasticity of glass at room temperature is almost perfect below its limit. Plastic bending or plastic flow at room temperature can be detected only when the glass is subjected continuously for a sufficiently long time to the deforming force. Moreover it is known that

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1. Morey, p. 462.

the internal stress existing in a glass can hardly be removed at room temperature however long it may be kept at that temperature. From the point of view of cybotaxis as was stated before, these facts indicate that the cybotactic exchange between the cybotactic crystals and the free molecules is almost, though not entirely, stopped at this temperature. In elongation testing, when the load is increased continuously the glass breaks just at its elastic limit, without showing the presence of the plastic deformation as is commonly observed with metals and other substances. Glass may be broken in many different ways, by tension, compression, twisting, or impact etc. It is probable, however, that in all the various methods of applying stress to glass, fracture always takes place in tension. The works of Griffith[1] and of Joffé[2] make probable the hypothesis that since the true ultimate strength in tension is that determined by the molecular cohesion the far lower values found in practice are caused by surface scratches or flaws. Griffith assumed that the molecules in the glass orient themselves in groups such that in certain directions the attractive forces are minimum, and that such groupings are incipient flaws. A similar supposition to Griffith may also be given from the stand point of the cybotactic hypothesis. As the distribution of the cybotactic crystals is entirely at random, the interstices between neighbouring cybotactic crystals will

Fig. 6

be of various widths and of various densities of free molecules, and consequently will be the fields of cohesive forces of various strengths. If so, the incipient flaws or fissures will be formed along the surfaces obtained by connecting the interstices of weakest cohesive force in the manner shown by the line A B in Fig. 6.

In the case of a metal, which is composed of micro-crystals, plastic deformation occurs beyond its elastic limit. This plastic deformation is considered to be due to the slip along certain atomic planes of the crystal. In doing this the portion of the micro-crystals where the slip has occurred will be broken down into very fine crystals even of the cybotactic size and will be distorted in their lattices by the expenditure of considerable amount of the applied work; and the local

1. Griffith: Trans. Roy. Soc., London, A, **221**, 162 (1920).
2. Joffé: The Physics of Crystals (1928).

heating along the slipped plane will be sufficient to melt the smashed crystals, owing to the fact that their melting point is much lower than that of the adult crystals. By subsequent rapid cooling, which takes place almost at the same time as the local heating, the melt will be brought to the super-cooled state immediately. Thus after the deformation, the defects which have been caused by deformation will be almost remedied, though not perfectly, by being cemented by the solidified super-cooled amorphous layer formed there, and the specimen becomes able to sustain again the applied stress in an elastic manner.

In the case of glass, since it is not, like metals, composed of microcrystals excepting those of cybotactic size, it cannot be deformed by means of slipping along some atomic plane. Thus when tension of sufficient strength is applied to a part of the glass in a certain direction, most of the deformation will take place by the separation of the two adjacent portions which are in contact at the surface of the incipient or embryonic flaws extending nearly perpendicularly to the direction of the applied tension; and no remarkable local heating, subsequent melting and solidification as in the case of metals, which is necessary to remedy the widely opened flaws, can be expected in the case of the glass. This seems to be the reason that the glass can not be deformed plastically beyond its elastic limit at room temperature and that it breaks abruptly at this limit. If the cybotactic exchange between the cybotactic crystals and the free molecules previously noted should be of remarkable degree, this would also take a part in remedying the separated flaws; but this seems to be of such minor degree at room temperature as to have escaped our detection as is stated before. With respect to this point Spencer's experiment[1] is worthy of mention. " He wrapped fibres of glass around a cylinder two centimeters in diameter, and held them for months. On cutting the fibres loose they immediately opend out to coils of about 60 cms in diameter, and seemed to have acquired a permanent set. They were left floating on mercury and they gradually diminished in curvature, but after five years they were still slightly curved ". Spencer's interesting experiment shows that the amount of cybotactic exchange was still very slight, if any, after storage for months at room temperature, and that the deformation impelled by coiling is almost recovered by the shrinkage of the flaws opened widely by coiling.

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1. Moyey: The Properties of Glass, p. 318 (1938).

In the case of abrasion and polishing of the surface of a glass the circumstances are different. In this cese local heating of such a degree as to cause a surface flow by softening its thin layer can be expected just as in the case of metals.

When the temperature of a glass is raised considerably from room temperature the values of both α and β will increase correspondingly, and consequently the cybotactic exchange becomes very active, so that the cybotactic equilibrium can be attained much more quickly than before ; and at the same time the number of the cybotactic crystals will diminish remarkably. In this state the glass is endowed with fluidity. Different parts of it can be displaced easily from each other, and separate pieces of it can coalesce by being pressed or merely brought in contact with each other. In relation to the fluidity of glass, the sintering of crystal powders at high temperatures is worth consideration. Jeffries and Archer[1] state : " It has been erroneously stated that metal powders will not sinter to form a coherent mass when heated unless the pressure is sufficient to cause fusion at the temperature used. As a matter of fact, tungsten powder can be sintered below the melting point with no pressure except that due to its own weight. In fact, it is very difficult to see how pressing a metal powder briquet could have any effect on the melting point except to raise it ". In ordinary sense the melting point of a crystalline substance signifies the equilibrium temperature at which the adult crystal coexists with its melt as is stated in a previous paper.[2] In this sense the melting point of a metal will not be much affected by pressure, and it will be rather raised by pressure with a metal such as tungsten as is stated by Jeffries and Archer. However if we accept the view that, when the crystals are smashed to extreme fineness comparable with the cybotactic crystals as is considered by the writer, their melting point or their stabibity is very much reduced, coalescense of crystal powders under pressure at high temperature will be easily understood just as in the case of the plastic deformation previously explained. The circumstance that the sintering of powder crystals is done usually at very high temperature greatly facilitates the melting of the finely divided crystals, and consequently in giving fluidity to the briquet of the powder crystals to form a coherent mass.

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1. Jeffries and Archer : The Science of Metals, p. 132 (1924).
2. Yoshida ; These Memoirs, A, **23**, 207 (1941).