

# Specific Heat of Amorphous State\*

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## Synopsis

A general model for supercooled liquid is proposed which involves the "Ideal Supercooled Liquid," crystal nucleus, microcrystallite and crystal. In this model, in homogeneity which appears in supercooled liquid is attributed to these nuclei and microcrystallites. The authors consider that in amorphous state, heat energy is absorbed in two ways, one by the kinetic portion and the other by the configurational portion. While the former absorbs heat energy instantaneously, the latter absorbs through the molecular relaxating process. From this simple model, the authors derive a formula for the specific heat of amorphous substance, which shows that (1) supercooled liquid to glassy transition is superficial one depending on the heating rate in the measurement, and (2) if perfect equilibrium is maintained at all temperatures in measuring process, we get perfect continuous  $C_p \sim T$  curve.

In addition, the method to determine the true equilibrium value by the use of Nernst's method is proposed. Some characteristics of specific heat curve are discussed with success.

## 1. Introduction

There have been many investigations<sup>(1)</sup> upon a transformation of supercooled liquid into glassy state. Especially the abrupt variation of the specific heat near the softening point of glass has been believed as a characteristic property of glass, which may be supposed to attribute to a kind of a transition among the equilibrium systems, for instance, an order-disorder transition concerning the orientation of the molecules or radicals in the molecules. Further, from the fact that the light scattering of supercooled liquid increases as the temperature is lowered, one may be able to assume a considerable inhomogeneity in supercooled liquid. And the existence of such a second phase in supercooled liquid would lead inevitably to a more or less sharp transition. But, careful experiments of viscosity and dilatometric measurement tell us that the sharp and distinct "supercooled liquid to glassy" transition is superficial one and it becomes question that this kind of transition occurs abruptly. And if the perfect equilibrium were attained in the process, the transition would occur quite continuously.

In our present paper, we will indicate that the idea of "Ideal Supercooled Liquid" by Simon<sup>(2)</sup> is also consistent with the specific heat data. That is, such a sharp change observed in the specific heat at distinct temperature is also superficial and must be

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(1) W. Kauzmann, *Chem. Rev.*, **43** (1948), 219.

(2) F. Simon, *Zeits. allg. u. anorg. Chem.*, **203** (1931), 229.

explained without any use of second phase. About the inhomogeneity which appears in the light scattering, we propose a general model of supercooled state involving the so-called glassy state.

## 2. Absorption of Heat in Amorphous State

*General aspect of supercooled liquid.* In supercooled state there exists as metastable state a quite homogeneous phase which was named by Simon an "Ideal Supercooled Liquid" (henceforth we note as I.S.L.). We might supercool any liquid to an "I.S.L."—we propose a free energy diagram in Fig. 1.—

If the barrier for transformation to crystal nucleus or microcrystallite which is represented by the portion of the curve between "I.S.L." and crystal, is low, we will find that real supercooled liquid we obtain, is inhomogeneous because of containing the nuclei or microcrystallites. Namely, in our model inhomogeneity comes only from the nucleus or microcrystallites and there is not any kind of second phase in supercooled state\*.

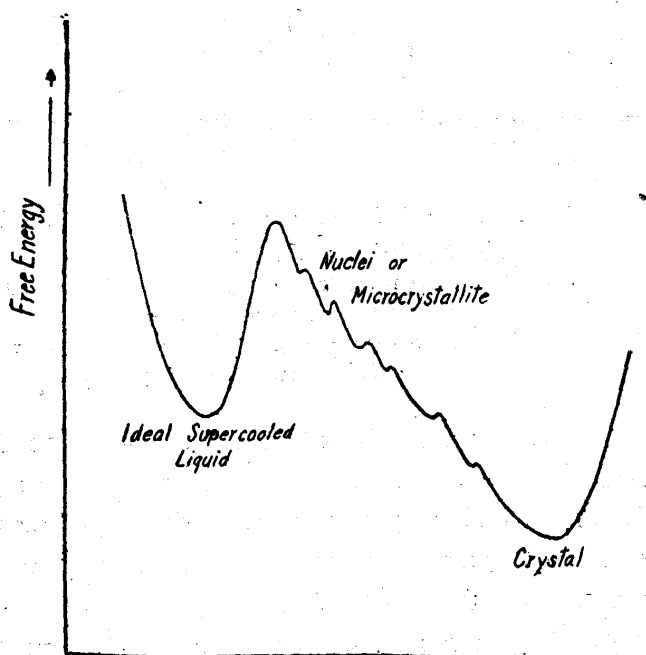


Fig. 1. Schematic Representation of Supercooled Liquid.

*Absorption of heat in amorphous state.*

We assume that in amorphous state, heat is absorbed in two ways, one by the kinetic portion and the other by configurational portion. Here we mean by the configurational portion the relative orientations and aggregation of molecules\*\* The kinetic portion absorbs heat instantaneously, but the configurational portion through the relaxing process. The temperature of the substance should be determined by the heat energy absorbed in the kinetic portion. These considerations are shown schematically in Fig. 2. In these pictures, location of rods represents configuration of molecules involving their orientation and aggregation, and their length indicate the amount of energy of their kinetic portion.

\* Large distance fluctuation of reflection index obtained by P. Debye<sup>(3)</sup> in Lucite and optical glasses is very interesting, but we think it does not mean the existence of any second phase. Of course, it is necessary to make clear such fluctuation for full understanding of supercooled liquid.

(3) P. Debye and A. M. Buche, *J. Appl. Phys.*, 20 (1949), 518.

\*\* cf. our preceding paper.

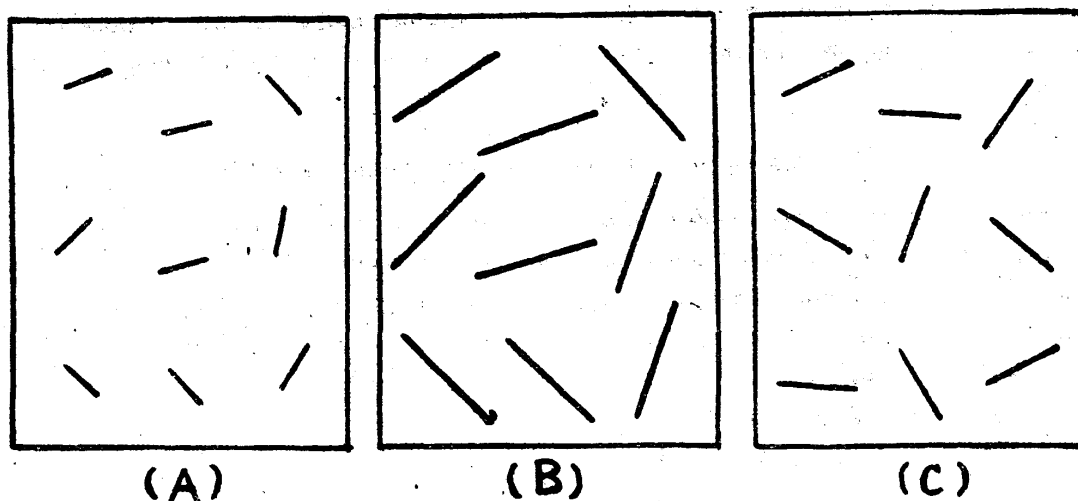


Fig. 2. Schematic Representation of Absorption of Heat by Amorphous Substance.

- (A): Equilibrium at  $T_1$ .  
 (B): Heat is absorbed in kinetic portion only, being represented by longer rods with same orientation as (A).  
 (C): Equilibrium at  $T_2$ . Orientations change more randomly and kinetic energy shifts to configurational portion.

When a substance is heated from  $T_1$ , it is obvious that the kinetic motions of the molecules increase and at the same time orientations of molecules with one another begin to change. But till the relaxation process of the configurational change is completed, the given heat energy mostly remains in kinetic portion, hence the temperature of the material should be higher than that at the true equilibrium.

The idea like this is used with success in the investigation of absorption of sound wave in liquids and gases. Richards<sup>(4)</sup> made an analogical comparison of specific heat of glassy state with absorption of sound wave, explaining that the sharp transition was due to the relaxation process. But it is clear the mechanism of absorption of cyclic sound waves is not applied to absorption of heat energy in specific heat measurement.

In the following, we will derive a simple formula which expresses that specific heat shows an apparent sharp transition in the temperature interval dependent on the measuring method, practically on the rate of heating.

Now, if heat energy  $\Delta Q$  is supplied at  $t=0$ , according to the above mentioned consideration, the energy is absorbed entirely in the kinetic portion at  $t=0$ , dissipating into configurational change, and the distribution of heat among these portions attains its equilibrium value at  $t=\infty$ . The energy absorbed in the kinetic portion at time  $t$ , is given by the following formula:

$$q_t = \Delta Q \cdot \left\{ \frac{c_1}{c_1 + c_2} + \frac{c_2}{c_1 + c_2} e^{-\frac{t}{\tau}} \right\} \quad (1)$$

(4) W. T. Richards. Rev. Mod. Phys., 11 (1939), 36.

where  $c_1$ : specific heat of kinetic portion.  
 $c_2$ : " " " " , configurational portion.  
 $\tau$ : relaxation time for configurational change.

In specific heat measurement we supply heat energy successively in the time interval of  $t$ . The temperature rise measured at time  $t$  is given by

$$\Delta T = \frac{1}{c_1} \int q_0 \cdot dt. \quad (2)$$

The specific heat thus obtained is given by

$$c = \frac{\Delta Q \cdot t}{\Delta T} = c_1 / \left\{ \frac{c_1}{c_1 + c_2} - \frac{c_2}{c_1 + c_2} \frac{\tau}{t} \left( e^{-\frac{t}{\tau}} - 1 \right) \right\} \quad (3)$$

In Fig. 3 we plot Eq. (3) as function of temperature with a parameter  $t$ . Here we use relaxation time  $\tau$  given by Maxwell's relation  $\eta = G \cdot \tau$ . We take a value of  $10^{12} \sim 10^{13}$  for instantaneous rigidity  $G$ . In practice  $c_1$  is almost the same as the specific heat of the crystal, and  $c_2$  is given by the difference between  $c_1$  and the specific heat of super-cooled liquid.\*

The curve shown in Fig. 3 represent (1) if we can keep  $t/\tau \gg 1$  at all temperatures, we get quite smooth curve corresponding to a true equilibrium specific heat, (curve *a*), (2) conversely, if we can keep  $t/\tau \ll 1$ , we only get a value corresponding to a kinetic portion, namely almost the same value as crystal, (curve *d*), and (3) a marked sharp transition appears at temperatures where  $t$  and  $\tau$  become comparable order. In Fig. 3 curve *b* corresponds to the usual Nernst's method where  $t$  becomes comparable to  $\tau$  at so-called  $T_g$ . Curve *c* corresponds to a measurement with larger heating rate. At higher temperature,  $t$  becomes comparable to  $\tau$  showing an apparent transition.

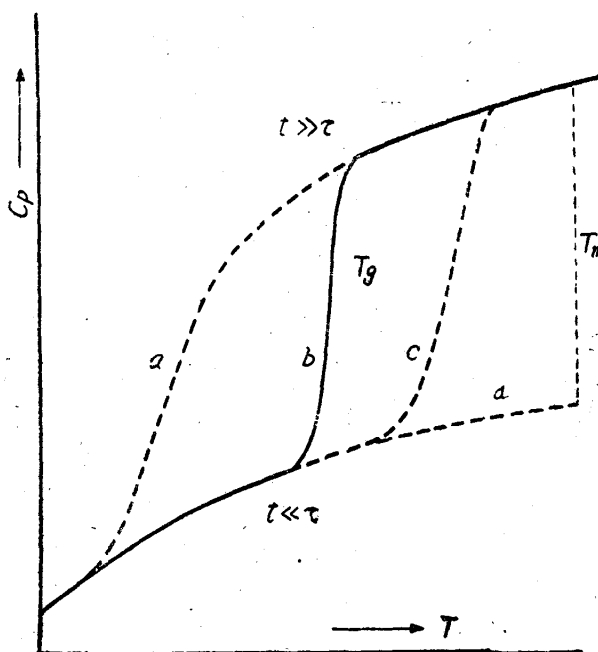


Fig. 3. Calculated specific heat curve.

\* As the experimental value of supercooled state below  $T_g$  is not given, we use the extrapolated value from higher temperatures.

### 3. Comparison with Experiments

We will mention in this section about some characteristic features of specific heat curve of amorphous substances already obtained by various authors.

(1) Apparent agreement of transition temperature between various investigations. In the usual Nernst's method of specific heat measurement,  $t$  is always of the order of  $10^3$  sec., and can not be of  $10^2$  or  $10^4$  sec. from the experimental restriction. From Maxwell's relation  $\tau$  reaches  $10^3$  sec., when  $\eta$  becomes  $10^{15}\sim 10^{16}$  poise, and in such a high viscosity range  $\eta$  changes sharply with temperature—ten times in a few degree. Excellent agreement of  $T_g$  is attributed to the nearly same value of  $t$  in all investigations and the sharp change of specific heat at  $T_g$  to the sharp change of  $\eta$  at low temperatures. In our estimate, in the Nernst's method the apparent transition appears at temperature where  $\eta=10^{15}\sim 10^{16}$  poise. It corresponds with the fact that in the Nernst's method  $T_g$  always appears  $10^\circ\sim 20^\circ$  lower than the so-called softening temperature from the viscosity. ( $\eta=10^{18}$ ).

(2) Experimental determination of true specific heat. We take the following procedure to get the equilibrium value by the Nernst's method. The specific heat curve

of a sample which has been supercooled slowly enough to attain equilibrium at  $T_1$ , is represented by  $abc$  in Fig. 4. Now, if we supercool again the sample down to  $T_2$  very slowly, we will have the curve like  $ab'c$  having a higher hump at  $T_g$ . Because, if our above consideration is correct, internal energy which is contained between  $T_1$  and  $T_2$  and would contribute to specific heat value at these temperatures, would not be able to contribute to specific heat on account of the lack of time to complete the configurational change, and thus internal

energy should contribute only above  $T_g$  through relaxation. Thus, difference of internal energy in configurational portion between  $T_1$  and  $T_2$ , is given by the area between  $b$  and  $b'$ . So, we get the true equilibrium specific heat by adding the value of the area divided by  $(T_1-T_2)$ . With this procedure, we have got the equilibrium value\* of

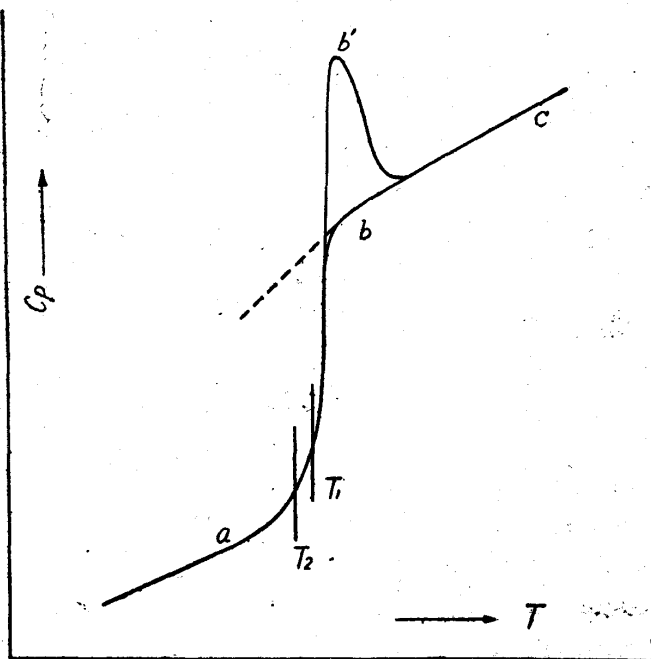


Fig. 4. Determination of true specific heat.

\* will be soon published.

specific heat.

The area between  $b$  and  $b'$  increases as the sample has been kept longer at  $T_2$ , and approaches to a definite value as the equilibrium at  $T_2$  becomes perfect. This fact makes it impossible to explain the anomaly at  $T_g$  as any kind of equilibrium transition, say, order-disorder transition.

(3) Parks and other<sup>(5)</sup> noticed that it needed abnormally long period for obtaining reproducible values of specific heat near  $T_g$ . This is explained easily by our present theory. Detail of this investigation is now under research.\*

### Conclusion

From the above considerations we can conclude as follows.

The true specific heat of glassy state measured under the condition of perfect equilibrium comes to the elongation of the supercooled liquid and the sharp decrease disappears. The sharp transition which has been attributed to the existence of some second phase is superficial one, and it is not proper to calculate the entropy of the glassy state from the specific heat curve obtained by means of the usual Nernst's method.<sup>(6)</sup>

In addition, we will notice that the comparison of the relaxation time obtained experimentally in the specific heat measurement with other relaxation times, such as those from viscosity, dielectric constant and sound wave which have different physical meanings, is interesting in the research for the configurational motion of molecules in the glassy state.

This research has been aided by a fund from the Scientific Research Expenditure of the Department of Education.

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\* will be soon published.

(5) G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, **31** (1927), 1842.

(6) F. Simon and F. Lange, *Zeits. f. Phys.*, **38** (1926), 227. G. E. Giggson and W. F. Giauque, *J. Am. Chem. Soc.*, **45** (1923), 93.