Theory of Glass Transition of Sodium Disilicate Glass

—Calculation of Thermal Expansion—

By

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1. Introduction

The theoretical investigations of glass transition have been performed by many researchers, whose investigations are, however, seldom based upon the microstructure of the glass. Among a few exceptional cases we find two papers, one of which is the analysis on the basis of the free volume theory by Turnbull¹⁾, and another is the well-known theory of glass transition of the polymer solution by Gibbs et al.²⁾. The free volume does not seem to be defined so clearly in Turnbull's work, and it is difficult to calculate it on the basis of his theory. Although Gibbs et al. has intended to explain the glass transition in the high polymer solution, it is doubtful if their theory can describe the state of glass at room temperature. It seems to be impossible to represent a glass state by a single formula which applies at both high and room temperature regions, because the state at room temperature does not change due to the change of the structure which occurs in the high temperature region but mainly changes due to the dilatation.

In the case of the high polymer, the interaction between macromolecules is regarded as the one of Van der Waals' type, the direction of bonds in macromolecules is perfectly random and linear³⁾, but in the glass structure a sort of short range order exist and the bonding continues stereometrically.

In this paper the discrete ion structure is taken as a model of glass structure which was first proposed by Mackenzie⁴⁾ and a discrete molecule is regarded as the smallest unit. The change in the structure of a discrete ion which is mainly due to the change in the length of Si-O bonds in that ion is neglected, because its contribution to thermal expansion of the system can be regarded as very small. Therefore the system is considered as an assembly of a great many discrete molecules which interact with one another.

It is regarded that a main cause of the glass transition comes from the bonding such as seen in the hydrogen bond. The bonding of a modifier atom such as sodium with the oxygen atom

in a discrete ion has a character intermediate between an ionic and covalent bond. Any modifier atom does not belong to any discrete ion so distinctly. This character is the main cause of glass transition. A sodium atom bonds with an oxygen atom in a certain discrete ion at a temperature above the transition point and it bonds, however, two oxygens of which one belong to another discrete ion at a temperature below the transition point, where the sodium atom plays a role like the hydrogen atom in a hydrogen bonding. This bonding of a character like the hydrogen bonding lowers the binding energy between discrete molecules appreciably.

The theory is developed in the following steps. First, an effective interaction potential between two oxygens each belonging to two different discrete molecules which comes from the hydrogen-bond like role of modifier atoms, is assumed. The derivation of this effective interaction potential will be discussed in following paper. A molecule interacts only with its nearest neighbouring surroundings by the above mentioned effective interaction potential. The discrete molecules beyond the nearest neighbouring ones are regarded to effect the Van der Waals' type interaction between their centers. Secondly, it is investigated how the number of empty cells around each discrete molecule changes as temperature varies. That number of cells increase as temperature rises. The entropy of the system also increases accordingly. The probability function that a certain number of cells around each molecule are occupied is investigated by making use of the hole theory. Thirdly, it is assumed that the molecules beyond the nearest neighbouring ones distribute at random and the radial distribution function is used. Fourthly, the partition function of the system of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass is got, in which unknown number of noninteracting oxygens and the mean distance between the nearest lattice points are determined by the condition of the minimum free energy.

In this calculation, the radial distribution function involved in the partition function remains

unknown, which is determined by making use of Born-Green-Yvon integral equation. This integral equation should be solved in parallel with the equations which are obtained from the condition of the minimum free energy.

2. Nomenclatures

$\mathbf{R}_i$: coordinate of the i -th lattice.

$\mathbf{r}$: vector from a lattice point to the center of a discrete molecule.

$\boldsymbol{\zeta}_{ij}$: vector from the i -th lattice point to the center of the j -th discrete molecule beyond the nearest neighbouring molecules.

$\mathbf{S}_p$: vector from the center to one of nonbridging oxygens in a discrete molecule.

R : a mean distance between the nearest neighbouring lattice points.

Z_i : number of the nearest neighbouring molecules around the i -th discrete molecule.

c : number of the nearest neighbouring cells.

M : total number of cells in the whole space.

N : total number of discrete molecules.

$V_0(\mathbf{R}_i + \mathbf{S}_p + \mathbf{r}, \mathbf{R}_j + \mathbf{S}_q + \mathbf{r}')$: interaction energy between two nonbridging oxygens inter mediated by sodium atoms.

$u_2(\mathbf{R}_i + \mathbf{r}, \mathbf{R}_j + \mathbf{r}')$, $u_2(\boldsymbol{\zeta}_{ij})$: interaction energy of Van der Waals' type between two molecules.

3. Cohesive state

The investigation is developed thermostatically on the following assumptions.

- The interaction between two oxygens inter mediated by two sodium atoms is determined as a function of the distance.
- These sodium atoms intermediate only two oxygens.
- A rotational motion of a discrete molecule can not occur.
- Nearest neighbouring lattice point of a certain lattice point built as follows. Let us put the center of a discrete molecule on that lattice point and then connect the center with one of its nonbridging oxygens by a straight line. We put a nearest neighbouring lattice point on the elongation of that line.
- The translation motion of the discrete molecule is neglected because we investigate the glass system in the vicinity of the transition point, and concern only with the structural partition function.

3.1 Partition function

In order to get the structural partition function, we take into account only the potential energy

$$2U = \sum_{i=1}^N \sum_{j=1}^{Z_i} \{V_0(\mathbf{R}_i + \mathbf{S}_p + \mathbf{r}, \mathbf{R}_j + \mathbf{S}_q + \mathbf{r}')\}$$

$$+ u_2(\mathbf{R}_i + \mathbf{r}, \mathbf{R}_j + \mathbf{r}')\} + \sum_{i=1}^N \sum_{j=1}^{N-Z_i} u_2(\boldsymbol{\zeta}_{ij}) \\ \equiv \sum_{i=1}^N \sum_{j=1}^{Z_i} u_1(\mathbf{R}_i + \mathbf{r}, \mathbf{R}_j + \mathbf{r}') + \sum_{i=1}^N \sum_{j=1}^{N-Z_i} u_2(\boldsymbol{\zeta}_{ij}) \quad \dots\dots\dots (1)$$

from which we can obtain the partition function

$$Q_N = \frac{1}{N!} \int \exp\left(-\frac{U}{\kappa T}\right) d\mathbf{r}^{(N)} \\ \equiv \frac{1}{N!} Z_N \quad \dots\dots\dots (2)$$

We apply the hole theory to calculate Q_N ⁹⁾. The whole space is divided into a number of small volumes (M in all) which are greater than the total number N of molecules. The total number of ways of distributing N molecules in M cells is given, if only one molecule can occupies a cell, by

$$\Omega = \frac{M!}{N!(M-N)!} \quad \dots\dots\dots (3)$$

The partition function (2) can be written as

$$\frac{Z_N}{N!} = \sum_q \frac{Z^{(q)}}{q} \quad \dots\dots\dots (4)$$

with the use of

$$Z^{(q)} = \int_{\Delta q_1} \int_{\Delta q_2} \dots \int_{\Delta q_N} \exp\left(-\frac{U}{\kappa T}\right) d\mathbf{r}^{(N)} \quad \dots\dots\dots (5)$$

which is the contribution of a certain distribution of N molecules into M cells, say the q -th one. We represent the canonical probability function of the whole system approximately by a product of the probability functions for individual molecules which move in certain cells. After a simple calculation, $Z^{(q)}$ can be rewritten in this approximation in the form

$$Z^{(q)} = \exp\left\{-\frac{N(N-1)}{2\kappa T} \bar{E}\right\} \prod_{i=1}^N v_i(q) \quad \dots\dots (6)$$

where $v_i(q)$ denotes the free volume of the i -th molecule in the q -th distribution. It is very difficult to determine $v_i(q)$, but we assume the one-molecule distribution function approximately proportional to a delta-function, we can express it as

$$v_i(q) = \int_{\Delta} \exp\left[-\frac{1}{\kappa T} \left\{ \sum_{j=1}^{Z_i} u_1(\mathbf{R}_i + \mathbf{r}, \mathbf{R}_j) + \sum_{j=Z_i+1}^{N-Z_i} u_2(\mathbf{R}_i + \mathbf{r}, \boldsymbol{\zeta}_j) - (N-1)\bar{E} \right\}\right] d\mathbf{r} \\ \equiv \int_{\Delta} \exp\left\{-\frac{\psi_i(\mathbf{r}, q)}{\kappa T}\right\} d\mathbf{r} \quad \dots\dots\dots (7)$$

The quantity $\bar{E}$ in (6) can be written as

$$\bar{E} = \frac{2}{N(N-1)} \left[\sum_{i < j} u_1(\mathbf{R}_i, \mathbf{R}_j) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^{N-Z_i} u_2(\mathbf{R}_i, \boldsymbol{\zeta}_j) \right] \quad \dots\dots\dots (8)$$

where the representation in the bracket means the internal energy of the whole system in which all molecules are fixed at the lattice points in the q -th distribution. In order to rewrite (7) and (8) in simple forms we introduce the following

parameters.

N_{AA} : total number of a pair of molecules interacting by the potential u_1 .

N_{AB} : total number of nonbridging oxygens whose nearest neighbouring sites are empty.

h_k : number of the discrete molecules with k holes in its nearest neighbouring cells.

$G_{kl}(\zeta_{ij})$: radial distribution function of a pair of discrete molecules, say the i -th and j -th molecules. The i -th molecule has k holes in its nearest neighbouring cells, and the j -th has l holes. ζ_{ij} denotes the vector connecting the centres of these two molecules.

S : radius of the sphere with the same volume as the mean volume of a discrete molecule.

Among these parameters there are the following relations.

$$2N_{AA} = cN - N_{AB} \quad \dots\dots\dots (9)$$

$$\sum_{k=0}^c h_k = N \quad \dots\dots\dots (10)$$

$$\sum_{k=0}^c kh_k = N_{AB} \quad \dots\dots\dots (11)$$

We can rewrite the summations in the right-hand side of (8) as

$$\sum_{i < j} u_1(\mathbf{R}_i, \mathbf{R}_j) = N_{AA} u_1(\mathbf{R}) \quad \dots\dots\dots (12)$$

$$\begin{aligned} & \frac{1}{2} \sum_{i=1}^N \sum_{j=Z_i+1}^{N-Z_i} u_2(\mathbf{R}_i, \zeta_j) \\ &= \frac{N}{2V} \sum_{k=0}^c h_k \int_{1.5R}^{\infty} u_2(\zeta) G_{kl}(\zeta) 4\pi \zeta^2 d\zeta \quad \dots\dots\dots (13) \end{aligned}$$

We have assumed that the nearest neighbouring molecules of a certain molecule localize on the sphere of radius R where centre coincides with that of the cell occupied by that molecule.

Now, we extend this assumption to the molecules which are farther than the nearest neighbouring cells. That is; we assume that they localize on the sphere with radius of integral times of R from the central lattice point. Then we can write down $G_{kl}(\zeta)$ as

$$G_{kl}(\zeta) = R \sum_{i=2}^{\infty} \bar{G}_{kl}(\zeta) \delta(\zeta - iR) \quad \dots\dots\dots (14)$$

which $\bar{G}_{kl}(\zeta)$ tends to the unity similarly to the radial distribution function defined ordinarily as is shown in Appendix I. By substituting (14) into (13), one gets

$$\begin{aligned} & \frac{1}{2} \frac{N}{V} \sum_{k=0}^c h_k \int_{1.5R}^{\infty} u_2(\zeta) G_{kl}(\zeta) 4\pi \zeta^2 d\zeta \\ &= \frac{1}{2} \sum_{k=0}^c h_k \sum_{i=2}^{\infty} u_2(iR) C_k^i \quad \dots\dots\dots (15) \end{aligned}$$

where C_k^i means the mean number of molecules on the sphere of radius iR when k holes exist in the nearest neighbouring cells and it is given by

$$C_k^i = \frac{N}{V} \int_{iR-0.5R}^{iR+0.5R} 4\pi R \zeta^2 \bar{G}_{kl}(\zeta) \delta(\zeta - iR) d\zeta \quad \dots\dots\dots (16)$$

We can now rewrite down (7) and (8) as

$$\begin{aligned} (N-1)\bar{E} &= \frac{2}{N} N_{AA} u_1(R) \\ &+ \frac{1}{N} \sum_{k=0}^c h_k \sum_{i=2}^{\infty} u_2(iR) C_k^i \quad \dots\dots\dots (17) \end{aligned}$$

$$\begin{aligned} \psi_i(\mathbf{r}, q) &= \sum_{\substack{j=1 \\ j \neq i}}^{Z_i} u_1(\mathbf{R}_i + \mathbf{r}, \mathbf{R}_j) - \frac{2}{N} N_{AA} u_1(R) \\ &+ \frac{N}{V} \int_{1.5R}^{\infty} u_2(|\zeta - \mathbf{r}|) G_{kl}(|\zeta - \mathbf{r}|) \\ &\times 4\pi (|\zeta - \mathbf{r}|)^2 d(|\zeta - \mathbf{r}|) \\ &- \frac{1}{N} \sum_{k=0}^c h_k \sum_{i=2}^{\infty} u_2(iR) C_k^i \quad \dots\dots\dots (18) \end{aligned}$$

We symmetrize the potential u_1 and u_2 spherically. The latter is that of Lennard-Jones type. The fourth term in (18) is sum of the function of iR , the third term is a mean of the Lennard-Jones potential in respect of the radial distribution function and it can be calculated in the same way as he did⁶⁾, because we have assumed that the localized radial distribution function vanishes except on the sphere. It becomes equal to the fourth term when $\mathbf{r}$ is put equal to zero. If the i -th molecule has k holes around its all nearest neighbouring lattice points, we have

$$Z_i = c - k \quad \dots\dots\dots (19)$$

$$\sum_{\substack{j=1 \\ j \neq i}}^{Z_i} u_1(\mathbf{R}_i + \mathbf{r}, \mathbf{R}_j) = \frac{c-k}{c} U(r) \quad \dots\dots\dots (20)$$

where $U(r)$ is the spherically symmetric potential which is contributed from the nearest neighbouring cells all filled with molecules (Appendix II). In the same way the contribution of the molecules farther than the nearest neighbours can be expressed as

$$\begin{aligned} & \frac{N}{V} \int_{1.5R}^{\infty} u_2(|\zeta - \mathbf{r}|) G_{kl}(|\zeta - \mathbf{r}|) 4\pi \\ & \times (|\zeta - \mathbf{r}|)^2 d(|\zeta - \mathbf{r}|) \\ &= \sum_{i=2}^{\infty} \frac{c}{C_k^i} U_i''(r) \quad \dots\dots\dots (21) \end{aligned}$$

$$\frac{1}{N} \sum_{k=0}^c h_k \sum_{i=2}^{\infty} u_2(iR) C_k^i = \sum_{k=0}^c \frac{h_k}{N} \sum_{i=2}^{\infty} \frac{c}{C_k^i} U_i''(0) \quad \dots\dots\dots (22)$$

In this approximation, we can obtain the function $\psi_i(\mathbf{r}, q)$, in which we have changed the vector $\mathbf{r}$ to r corresponding to the spherical symmetric potential.

Now, it is useful to change the suffix i in such quantities as $\psi_i(r, q)$ and $v_i(q)$ into k which has the meaning of the number of holes in the all nearest neighbouring cells around a certain cell. With this change we have

$$\begin{aligned} \psi_i(\mathbf{r}, q) &\rightarrow \psi_k(r, q) \\ &= \frac{c-k}{c} \{U(r) - U(0)\} + \lambda_k(r) \quad \dots\dots\dots (23) \end{aligned}$$

where

$$\lambda_k = \sum_{i=2}^{\infty} \frac{C_k^i}{c} \{U_i''(r) - U_i''(0)\}$$

and

$$\begin{aligned} v_i(q) &\rightarrow v_k(q) \dots\dots\dots (24) \\ &= 4\pi \int_0^{0.5R-S} r^2 \exp\left[-\frac{1}{\kappa T} \psi_k(r, q)\right] dr \\ &\equiv 4\pi T(k) \end{aligned}$$

The integration range in (24) is limited so that any part of a discrete ion never go out of the cell. Therefore we can obtain the partition function which corresponds to the q -th configuration and is given by

$$\begin{aligned} Z^{(q)} &= \exp\left[-\frac{1}{2\kappa T} \left\{ (cN - N_{AB}) u_1(R) \right. \right. \\ &\quad \left. \left. + \sum_{k=0}^c h_k \sum_{i=2}^{\infty} \frac{C_k^i}{c} U_i''(0) \right\}\right] \prod_{k=0}^c \{4\pi T(k)\}^{h_k} \end{aligned} \dots\dots\dots (25)$$

where the parameters h_k , C_k^i and R remain unknown. We determine these parameters by the condition of the minimum free energy on the assumption that h_k does not depend on the method of distribution.

The method of approximation of which use is made in the theory of the cooperative phenomena such as in the order-disorder problem in alloys and in ferromagnetism may be useful to discuss the present problem. We make use of the Bethe approximation here.

Then we have

$$\begin{aligned} p(k) &= \frac{4\pi}{Z_B} T(k) \exp\left[-\frac{1}{\kappa T} \left\{ (c-k) u_1(R) \right. \right. \\ &\quad \left. \left. + \sum_{i=2}^{\infty} \frac{C_k^i}{c} U_i''(0) \right\}\right] \dots\dots\dots (26) \end{aligned}$$

$$\begin{aligned} Z_B &= 4\pi \sum_{k=0}^c T(k) \exp\left[-\frac{1}{\kappa T} \left\{ (c-k) u_1(R) \right. \right. \\ &\quad \left. \left. + \sum_{i=2}^{\infty} \frac{C_k^i}{c} U_i''(0) \right\}\right] \dots\dots\dots (27) \end{aligned}$$

where $p(k)$ means the probability function that an arbitrary molecule has k holes around it, and the distribution h_k is approximated as

$$h_k = N p(k) \dots\dots\dots (28)$$

In this approximation $Z^{(q)}$ can be written as

$$\begin{aligned} Z^{(q)} &= \left[\exp\left\{-\frac{1}{2\kappa T} (c u_1(R) \right. \right. \\ &\quad \left. \left. + \sum_{k=0}^c p(k) \sum_{i=2}^{\infty} \frac{C_k^i}{c} U_i''(0) \right\}\right] \\ &\quad \times \prod_{k=0}^c [4\pi T(k)]^{p(k)} \exp\left\{\frac{N_{AB} u_1(R)}{2\kappa T}\right\} \end{aligned} \dots\dots\dots (29)$$

It can be expressed as

$$Z^{(q)} = x^{N_{AB} y^N} \dots\dots\dots (30)$$

with the use of the quantities x and y given by

$$x = \exp\left\{\frac{u_1(R)}{2\kappa T}\right\} \dots\dots\dots (31)$$

$$\begin{aligned} y &= \left[\exp\left\{-\frac{1}{2\kappa T} (c u_1(R) \right. \right. \\ &\quad \left. \left. + \sum_{k=0}^c p(k) \sum_{i=2}^{\infty} \frac{C_k^i}{c} U_i''(0) \right\}\right] \end{aligned}$$

$$\times \prod_{k=0}^c [4\pi T(k)]^{p(k)} \dots\dots\dots (32)$$

By substituting (30) into (4) and taking account (2), we obtain

$$Q_N = y^N \sum_{N_{AB}} g(N, N_{AB}, M) x^{N_{AB}} \dots\dots\dots (33)$$

where $g(N, N_{AB}, M)$ denotes

$$\begin{aligned} g(N, N_{AB}, M) &= \left[\frac{M!}{N! (M-N)!} \right]^{1-c} \\ &\quad \times \left[\frac{M!}{\left(N - \frac{N_{AB}}{c}\right)! \left(M - N - \frac{N_{AB}}{c}\right)! \left(\frac{N_{AB}}{c}\right)!^2} \right]^{c/2} \end{aligned} \dots\dots\dots (34)$$

We approximate Q_N by its maximum term in the summand of (33), where the maximum condition for the parameters

$$a = \frac{N_{AB}}{cM}, \quad b = \frac{N}{M} \dots\dots\dots (35)$$

is represented by

$$\left(\frac{b}{1-b}\right)^{c-1} \left(\frac{1-b-a}{b-a}\right)^{c/2} = \frac{1}{y} \dots\dots\dots (36)$$

$$\frac{(b-a)(1-b-a)}{a^2} = \frac{1}{x^2} \dots\dots\dots (37)$$

By substituting these equations for (2), we get for the partition function Q_N

$$\ln Q_N = M \left\{ (c-1) \ln(1-b) - \frac{c}{2} \ln(1-b-a) \right\} \dots\dots\dots (38)$$

3.2 The mean distance R between a pair of nearest neighbouring lattice points

We can determine the mean distance R on the basis of the principle of the minimum free energy. Then we have (Appendix III)

$$\frac{\partial}{\partial R} \left(\frac{\ln Q_N}{M} \right) = ca \frac{\partial}{\partial R} \ln x + b \frac{\partial}{\partial R} \ln y = 0 \dots\dots\dots (39)$$

We can express the derivatives of $\ln x$ and $\ln y$ as

$$\frac{\partial}{\partial R} \ln x = \frac{1}{2\kappa T} \frac{d}{dR} u_1(R) \dots\dots\dots (40)$$

$$\begin{aligned} \frac{\partial}{\partial R} \ln y &= -\frac{1}{2\kappa T} \left[c \frac{d}{dR} u_1(R) \right. \\ &\quad \left. + \frac{3}{R} \sum_{k=0}^c p(k) \sum_{i=2}^{\infty} C_k^i \varepsilon_i \left\{ 2 \left(\frac{r^*}{iR} \right)^6 - 3 \left(\frac{r^*}{iR} \right)^{12} \right\} \right] \\ &\quad + \sum_{k=0}^c \frac{p(k)}{T(k)} \left[\frac{m^2}{2} \exp\left[-\frac{1}{\kappa T} \right. \right. \\ &\quad \times \left. \left. \left\{ \frac{c-k}{c} (U(m) - U(0)) + \lambda_k(m) \right\} \right] \right. \\ &\quad \left. + \frac{1}{\kappa T} \frac{c-k}{c} \int_0^m r^2 \frac{d}{dR} (U(0) - U(r)) \right. \\ &\quad \left. \times \exp\left[-\frac{1}{\kappa T} \left\{ \frac{c-k}{c} (U(r) - U(0)) + \lambda_k(r) \right\} \right] dr \right] \end{aligned} \dots\dots\dots (41)$$

where $m = (R/2) - S$ and the derivatives of $G_{kl}(iR)$ with respect to R has been neglected. By replacing (39) by (40) and (41), we can obtain the equation which determines R .

$$S(R) = D(R, T) \dots\dots\dots (42)$$

where

$$S(R) = c \left(1 - \frac{a}{b} \right) \frac{d}{dR} u_1(R) + \frac{3}{R} \sum_{k=0}^c p(k) \sum_{i=2}^{\infty} C_k i^{\varepsilon_2} \times \left\{ 2 \left(\frac{r^*}{iR} \right)^6 - 3 \left(\frac{r^*}{iR} \right)^{12} \right\} \dots (43)$$

$$D(R, T) = \sum_{k=0}^c \frac{p(k)}{T(k)} \left[\kappa T m^2 \times \exp \left[-\frac{1}{\kappa T} \left\{ \frac{c-k}{c} (U(m) - U(0)) + \lambda_k(m) \right\} \right] + 2 \frac{c-k}{c} \int_0^m r^2 \frac{d}{dR} (U(0) - U(r)) \times \exp \left[-\frac{1}{\kappa T} \left\{ \frac{c-k}{c} (U(r) - U(0)) + \lambda_k(r) \right\} \right] dr \right] \dots (44)$$

3.3 Radial distribution function

We shall determine the unknown function $G_{kl}(iR)$ in this section. We consider a certain molecule, say the i -th one, with $c-k$ nearest neighbouring molecules and further another molecule, say the j -th one, distant from the i -th molecule by ζ_{ij} and surrounded by $c-l$ nearest neighbouring molecules. We enumerate the $c-k$ molecules surrounding the i -th molecule as the i_1 -th... i_{c-k} -th respectively and $c-l$ molecules surrounding the j -th molecule as the j_1 -th... j_{c-l} -th respectively. We represent this configuration by the distribution function

$$\rho^{(2c-k-l+3)}(i, j; i_1, \dots, i_{c-k}, j_1, j_2, \dots, j_{c-l}) \dots (45)$$

Corresponding to the configuration in which the position ζ_n of one more molecule, say the n -th one, is also designated, we define an unsymmetrical distribution function

$$\rho^{(2c-k-l+3)}(i, j, n; i_1, i_2, \dots, i_{c-k}, j_1, \dots, j_{c-l}) \dots (46)$$

We can write down the so-called Born-Green-Yvon equation for the $(2c-k-l+3)$ -body distribution function. By confining the coordinates of the molecules in this equation to such a special configuration as we have explained above and shall explain in detail in the following, we get

$$-\kappa T \rho \ln \rho^{(2c-k-l+2)}(i, j; i_1, \dots, j_{c-l})$$

$$\begin{aligned} & \rho^{(2c-k-l+3)}(i, j, n; i_1, \dots, j_{c-l}; p, q) \\ & \rho_j^{(c-k+1)}(i; i_1, \dots, i_{c-k}; p) \rho_i^{(c-l+1)}(j; j_1, \dots, j_{c-l}; q) \rho(n) \\ & = \frac{\times G_{kl}(i, j; i_1, \dots, j_{c-l}; p, q) G_{kn}(i, n; i_1, \dots, i_{c-k}; p) G_{ln}(j, n; j_1, \dots, j_{c-l}; q)}{\rho^{(2c-k-l+2)}(i, j; i_1, \dots, j_{c-l}; p, q)} \\ & = \rho(n) G_{kn}(i, n; i_1, \dots, i_{c-k}; p) G_{ln}(j, n; j_1, \dots, j_{c-l}; q) \dots (50) \end{aligned}$$

By substituting (48) and (50) into (47), we get

$$\begin{aligned} & -\kappa T \rho \{ \ln \rho_j^{(c-k+1)}(i; i_1, \dots, i_{c-k}; p) + \ln G_{kl}(i, j; i_1, \dots, j_{c-l}; p, q) \} \\ & = \sum_s^{c-k} \rho_i u_1(r_{is}) + \sum_s^{c-l+1} \rho_j u_2(\zeta_{js}) + \frac{N}{V} \int \rho_i u_2(\zeta_{in}) G_{kn}(i, n; i_1, \dots, i_{c-k}; p) G_{ln}(j, n; j_1, \dots, j_{c-l}; q) d\zeta_n \end{aligned} \dots (51)$$

where

$$\rho(n) = \frac{N}{V}$$

By making a mean over $\langle \rho_i \rangle$ and $\langle \rho_j \rangle$ partitions of molecules among c nearest neighbouring lattice points, we have

$$\begin{aligned} & = \sum_s^{c-k} \rho_i u_1(r_{is}) + \sum_s^{c-l+1} \rho_j u_2(\zeta_{js}) \\ & + \int \rho_i u_2(\zeta_{in}) \rho \\ & \times \rho^{(2c-k-l+3)}(i, j, n; i_1, \dots, j_{c-l}) d\zeta_n \dots (47) \end{aligned}$$

The i -th molecule can move in the i -th cell, but its nearest neighbouring molecules are fixed as mentioned before. The t -th neighbouring molecules ($t \geq 2$) can move on the sphere of radius iR with the centre at the i -th lattice point. The partition of the nearest neighbouring molecules on the nearest neighbouring lattice points should be enumerated. The total number of ways of distributing $c-k$ molecules among c cells are equal to $\binom{c}{k} = z_p$ in which the respective configurations designated by the suffices 1, 2, ..., z . We distinguish these partition by p and q and rewrite the distribution function

$$\begin{aligned} & \rho^{(2c-k-l+2)}(i, j; i_1, \dots, j_{c-l}) \text{ as} \\ & \rho^{(2c-k-l+2)}(i, j; i_1, \dots, j_{c-l}; p, q) \end{aligned}$$

We define the radial distribution function $G_{kl}(i, j; j_1, \dots, j_{c-l}; p, q)$ by

$$\begin{aligned} & \rho^{(2c-k-l+2)}(i, j; i_1, \dots, j_{c-l}; p, q) \\ & = \rho_j^{(c-k+1)}(i; i_1, \dots, i_{c-k}; p) \\ & \times \rho_i^{(c-l+1)}(j; j_1, \dots, j_{c-l}; q) \\ & \times G_{kl}(i, j; i_1, \dots, j_{c-l}; p, q) \dots (48) \end{aligned}$$

where the lower suffices in $\rho_j^{(c-k+1)}(i; i_1, i_2, \dots, i_{c-k}; p)$ and $\rho_i^{(c-l+1)}(j; j_1, j_2, \dots, j_{c-l}; q)$ represent that they are concerned with the j -th molecular group and the i -th one. We integrate (48) on the positions of the j -th molecular group except the j -th molecule itself, then we have

$$\begin{aligned} & \rho^{(c-k+2)}(i, j; i_1, \dots, i_{c-k}; p) \\ & = \rho_j^{(c-k+1)}(i; i_1, \dots, i_{c-k}; p) \\ & \times \rho(j) G_{kl}(i, j; i_1, \dots, i_{c-k}; p) \dots (49) \end{aligned}$$

We find that the radial distribution function depends on how many molecules occupy the nearest neighbouring cells around the i -th molecule and around the j -th molecule respectively. In the same approximation, the unsymmetrical distribution function can be written with the use of the radial distribution function as

$$\begin{aligned}
& -\kappa T \nabla_i \ln G_{kl}(i, j) \\
& = -\frac{1}{z_k} \sum_p \left[-\kappa T \nabla_i \ln \rho_j^{(c-k+1)}(i; i_1, \dots, i_{c-k}; p) \right. \\
& \quad \left. - \sum_s^{c-k} \nabla_i u_1(\mathbf{r}_{ii_s}) \right] \\
& \quad + \frac{1}{z_l} \sum_q \sum_s^{c-l+1} \nabla_i u_2(\zeta_{ij_s}) \\
& \quad + \frac{N}{V} \int \nabla_i u_2(\zeta_{in}) G_{kn}(i, n) G_{ln}(j, n) d\zeta_n \\
& \dots\dots\dots (52)
\end{aligned}$$

The difference between

$$-\kappa T \frac{1}{z_k} \sum_p \nabla_i \ln \rho_j^{(c-k+1)}(i; i_1, \dots, i_{c-k}; p)$$

and

$$-\frac{1}{z_k} \sum_p \sum_{s=1}^{c-k} \nabla_i u_1(\mathbf{r}_{ii_s})$$

can be regarded as the effect of the j -th molecule and its $c-l$ nearest neighbouring molecules that

$$W(\mathbf{R}_{if}) = \frac{c-k}{c} U(\mathbf{r}) \left[\frac{\exp\left\{-\frac{U(\mathbf{r})}{\kappa T}\right\}}{\int_d \exp\left\{-\frac{U(\mathbf{r})}{\kappa T}\right\} d\mathbf{r}} - \frac{\exp\left[-\frac{1}{\kappa T} \{U(\mathbf{r}) + u_2(\zeta_{ij}) - \bar{u}_2(\zeta_{ij})\}\right]}{\int_d \exp\left[-\frac{1}{\kappa T} \{U(\mathbf{r}) + u_2(\zeta_{ij}) - \bar{u}_2(\zeta_{ij})\}\right] d\mathbf{r}} \right] \dots\dots (54)$$

where $u_2(\zeta_{ij})$ and $\bar{u}_2(\zeta_{ij})$ denote the fluctuating potential and its mean due to the j -th molecule. One can assume the fluctuation $u_2(\zeta_{ij}) - \bar{u}_2(\zeta_{ij})$ as much small compared to the thermal energy κT and make an expansion in respect of the small ratio between these two quantities. Thus one can obtain

$$\begin{aligned}
\sum_{f=1}^{c-k} \nabla_i W(\mathbf{R}_{if})_{i,j \text{ component}} &= - \sum_{f=1}^{c-k} \cos \theta \cdot \frac{d}{d\eta} W(R) \\
&= - \frac{\partial}{\partial \eta} \left[\frac{2}{3} \cdot \frac{c-k}{c} \cdot \frac{u_2(\eta) - \bar{u}_2(\eta)}{\kappa T} \cdot \frac{\int_0^m r^2 U(r) \exp\left\{-\frac{U(r)}{\kappa T}\right\} dr}{\int_0^m r^2 \exp\left\{-\frac{U(r)}{\kappa T}\right\} dr} \right]_{\eta=tR} \\
&\equiv - \frac{\partial}{\partial \eta} \left[\frac{2}{3} \cdot \frac{c-k}{c} \cdot \frac{u_2(\eta) - \bar{u}_2(\eta)}{\kappa T} \cdot \frac{M_1(R)}{M_0(R)} \right]_{\eta=tR} \dots\dots\dots (55)
\end{aligned}$$

where the mean $\bar{u}_2(\zeta_{ij})$ is given by

$$\bar{u}_2(tR) = \frac{1}{tR M_0(R)} \int_0^m dr \int_{|tR-r|}^{tR+r} d\xi \cdot \xi u_2(\xi) r \exp\left\{-\frac{U(r)}{\kappa T}\right\} \dots\dots\dots (56)$$

We approximate all the coordinates of the j -th and its nearest neighbouring molecules as that of the j -th lattice point in the third term in the right-hand side of (53), which then can be rewritten as

$$\frac{1}{z_l} \sum_q \sum_s^{c-l+1} \nabla_i u_2(\zeta_{ij_s}) = -(c-l+1) \left[\frac{\partial}{\partial \eta} u_2(\eta) \right]_{\eta=tR} \dots\dots\dots (57)$$

By substituting (55) and (57) into (52), we obtain

$$\begin{aligned}
& -\frac{\partial}{\partial \eta} \left[\kappa T \ln G_{kl}(\eta) + (c-l+1) u_2(\eta) + \frac{2}{3} \cdot \frac{c-k}{c} \cdot \frac{u_2(\eta) - \bar{u}_2(\eta)}{\kappa T} \cdot \frac{M_1(R)}{M_0(R)} \right]_{\eta=tR} \\
& = \frac{\pi N}{V} \int_{2R}^{\infty} \frac{\partial}{\partial s} u_2(s) G_{kl}(s) ds \int_{|\eta-s| \geq 2R}^{\eta+s} \frac{s^2 + \eta^2 - r^2}{\eta^2} r G_{ln}(r) dr \dots\dots\dots (58)
\end{aligned}$$

where the radial distribution function $G_{kl}(r)$ will tend to $R \sum_{i=2}^{\infty} \delta(r-iR)$ as r increases infinitely. With use of the same process as calculation of the two-body distribution function, the substitution of (14) into (58) gives

$$\begin{aligned}
\kappa T \ln \bar{G}_{kk}(tR) &= -(c-l+1) u_2(tR) - \frac{2}{3} \cdot \frac{c-k}{c} \cdot \frac{u_2(tR) - \bar{u}_2(tR)}{\kappa T} \cdot \frac{M_1(R)}{M_0(R)} \\
& \quad + \frac{3bR}{4t} \left[\sum_{j=2}^t \frac{d}{dR} u_2(jR) \bar{G}_{kk}(jR) \sum_{i=t-j \geq 2}^{t+j} \frac{i}{j} \{j^2 - (t-i)^2\} \{\bar{G}_{kk}(iR) - 1\} \right. \\
& \quad \left. + \sum_{j=t+1}^{\infty} \frac{d}{dR} u_2(jR) \bar{G}_{kk}(jR) \sum_{i=t-j \geq 2}^{t+j} \frac{i}{j} \{j^2 - (t-i)^2\} \{\bar{G}_{kk}(iR) - 1\} \right] \dots\dots\dots (59)
\end{aligned}$$

where the parameters l and n have been replaced by $\bar{k}$ which makes the probability function $p(\bar{k})$ maximum.

modifies the forces acting on the i -th molecule due to its nearest neighbouring molecules. This modification

$$\begin{aligned}
& \frac{1}{z_k} \sum_p \left[-\kappa T \nabla_i \ln \rho_j^{(c-k+1)}(i; i_1, \dots, i_{c-k}; p) \right. \\
& \quad \left. - \sum_{s=1}^{c-k} \nabla_i u_1(\mathbf{r}_{ii_s}) \right] \\
& \text{of the forces is assumed in the form} \\
& - \sum_{f=1}^{c-k} \nabla_i W(\mathbf{R}_{if}) \dots\dots\dots (53)
\end{aligned}$$

where $\mathbf{R}_{if}$ denote the vector from the i -th to one of its nearest neighbouring lattice sites and $W(\mathbf{R}_{if})$ represents an effective potential function.

By making use of the potential fluctuation due to the fluctuation in the position of the j -th molecule, one can write the effective potential $W(\mathbf{R}_{if})$ as

4. Calculations and discussions

In this section numerical calculation is carried out on the basis of the formal theory which has been developed in the preceeding sections, where an effective potential function which is shown in Appendix IV is assumed.

By eliminating the parameter a in (36) and (37), one can get for $Z=(1-b)/b$

$$Z^{-2/3} = y^{-1/3} - xy^{-1/6}(Z^{1/6} - Z^{-5/6}) \dots\dots\dots (60)$$

By making use of (36), (37) and the probability function (26) in the Bethe approximation, we can see that the parameter b tend to value 1 and 1/2 respectively in the limits of vanishing and infinitely rising temperature. Correspondingly the parameter Z has the limits 0 and 1 respectively. The limiting values of both sides of (60) corresponding to 0 and 1 of Z and the ratio between both sides of (60) in the limit of small values of Z are as follows.

$$\begin{aligned} \text{right-hand side} &= \begin{cases} y^{-1/3}, & Z=1 \quad b=1/2. \\ \infty, & Z=0 \quad b=1. \end{cases} \\ \text{left-hand side} &= \begin{cases} 1, & Z=1 \quad b=1/2. \\ \infty, & Z=0 \quad b=1. \end{cases} \end{aligned} \dots\dots\dots (61)$$

$$\lim_{Z \rightarrow 0} \frac{\text{right-hand side}}{\text{left-hand side}} \rightarrow \infty$$

These limiting values give us the information that (60) has a solution of b between 1 and 1/2, because $y^{-1/3}$ is smaller than unity. By expanding (36) and (37) in respect of the parameter Z we obtain

$$b(T) = 1 - \frac{1}{Y_0(T)} \left\{ 1 - \frac{1 + 4Y_\infty(T)}{Y_0(T)} \right\} \dots\dots\dots (62)$$

$$a(T) = \{1 - b(T)\} \left[1 - x^{-1} y^{-1/c} \left\{ \frac{1 - b(T)}{b(T)} \right\}^{(c-1)/c} \right] \dots\dots\dots (63)$$

where we have made use of the notations

$$Y_0(T) = yx^{-c},$$

$$4Y_\infty(T) = -cx^{-4} \left\{ 1 + \frac{cx^{-4}}{Y_0(T)} \right\} \dots\dots\dots (64)$$

The temperature dependence of b which is obtained by means of the numerical calculation of (62) and (63) is shown in Fig. 1. We can see there that b decreases quite sharply with the rising of temperature and the system is considered to change gradually into random structure. We can see in Table 1 that the probability function $p(k)$ in the Bethe approximation which is regarded as a parameter of the short range order varies with temperature in the same manner. Corresponding to these changes of quantities b and $p(k)$ the glass changes from the solid to liquid state with the rising of temperature.

We next investigate the temperature dependence of the mean distance between the pair of nearest neighbouring molecule. For that purpose we

Table 1. Probability $p(k)$ of the Bethe approximation.

Temp. (°K)	k						
	0	1	2	3	4	5	6
300	0.99998	0.00002					
400	0.99913	0.00087					
550	0.99661	0.00338	0.00001				
650	0.99128	0.00864	0.00008				
750	0.98245	0.01723	0.00032	0.00001			
850	0.96916	0.02985	0.00096	0.00003			
950	0.95031	0.04712	0.00243	0.00013	0.00001		
1050	0.92354	0.07038	0.00556	0.00046	0.00004		
1150	0.88252	0.10318	0.01244	0.00157	0.00021	0.00004	0.00003
1250	0.83621	0.13606	0.02272	0.00395	0.00074	0.00016	0.00016
1350	0.80537	0.15542	0.03075	0.00632	0.00139	0.00036	0.00039
1450	0.77353	0.17329	0.03977	0.00947	0.00241	0.00071	0.00082
1555	0.74066	0.18948	0.04961	0.01374	0.00389	0.00130	0.00158

Fig. 1. Temperature dependence of the fraction b of lattice points occupied by the discrete ions.

discuss a function $F(R, T) = S(R) - D(R, T)$ of the mean distance R and temperature T , where $S(R)$ and $D(R, T)$ have been defined in (43) and (44). As we have seen in (42) we can determine the mean distance R as a function of temperature by solving $F(R, T) = 0$. The function $F(R, T)$ is an increasing function of R and $D(R, T)$ is the same one of T . The solution R increases with rising of temperature. But $D(R, T)$ continuously decreases as $R < a_2$ and increases continuously as $R > a_2$, where a_2 is given by (A-13). Thus the derivative of $F(R, T)$ with respect to R in the region $R > a_2$ is smaller than that in the region

Fig. 2. Temperature dependence of the free volume, in which an inflection point corresponding to the transition point is seen.

Fig. 3. Thermal expansion of the mean distance between the lattice points near the transition point.

Fig. 4. Thermal expansion of the mean distance between the lattice points from liquid to solid.

$R < a_2$. The value a_2 corresponds to the deflection point of the free volume change as shown in Fig. 2. Each sodium atom interacts equally with the

Fig. 5. Feature of the effective potential between the nonbridging oxygen atoms and its derivative, in which numbers represent temperatures corresponding to the mean distances.

nearest neighbouring two oxygen atoms so far as $R < a_2$, and begins to interact preferably with only some one of them as R exceeds a_2 .

This point a_2 may be considered to correspond to the transition point. We show the R - T relation in the vicinity $R = a_2$ in Fig. 3. The distance R increases sharply as shown in Fig. 4 until it reaches the inflection point of the effective potential $V_0(R)$ seen in Fig. 5, above which the system is considered to change into the liquid state because the hole formation begins to effect on the thermal expansion of the glass system.

We next calculate the thermal expansion coefficient by making use of the result obtained in the preceeding sections. The volume of the system can be regarded to be proportional to $R^3 M$ and it can be written as

$$\alpha(T) = \frac{1}{\Delta T} \left[\frac{R(T + \Delta T)}{R(T)} \left\{ \frac{b(T)}{b(T + \Delta T)} \right\}^{1/3} - 1 \right] \quad \text{..... (65)}$$

where $R(T)$ and $b(T)$ denote the mean distance R between a pair of the nearest neighbouring lattice points and the fraction b of the lattice points occupied by the molecules respectively at temperature T . The result is shown in Fig. 6, where we can see a feature which is quite similar to the case of order-disorder system. In the present case, however, the system does not exhibit such a sharp transition as seen in the order-disorder system. A part in the vicinity of the transition point is pictured in a large scale in Fig. 7. Another part of the thermal expansion coefficient which is contributed from the formation of holes

Fig. 6. Temperature dependence of the thermal expansion coefficient.

Fig. 7. Temperature dependence of the thermal expansion coefficient near the transition point.

Table 2. Thermal expansion by hole formation.

Temp. (°K)	Thermal expansion
1050	0.844×10^{-9}
1150	0.358×10^{-8}
1250	0.675×10^{-8}
1350	0.134×10^{-7}
1450	0.241×10^{-6}
1550	

is shown as a function of temperature in Table 2. This contribution is negligibly small compared to the part which comes from the temperature

variation of the mean distance R between the pair of nearest neighbouring molecules, but is expected to increase so much more sharply with the rising of temperature in the liquid state that it can not be neglected.

Next we calculate the entropy, which is regarded to have a configurational origin, and can be calculated from the derivative of the partition function Q_N in respect of temperature. In that derivative we have the part which is proportional to $\partial \ln T(k)/\partial T$ and that is given as

$$\begin{aligned}
 & T \frac{\partial}{\partial T} \ln T(k) \\
 &= \frac{1}{\kappa T} \cdot \frac{1}{T(k)} \int_0^m \left\{ \frac{c-k}{c} (U(r) - U(0)) + \lambda_k(r) \right\} \\
 & \quad \times r^2 \exp \left[-\frac{1}{\kappa T} \left\{ \frac{c-k}{c} (U(r) - U(0)) \right. \right. \\
 & \quad \left. \left. + \lambda_k(r) \right\} \right] dr \\
 & \equiv \frac{1}{\kappa T} \left\{ \frac{c-k}{c} (U(r) - U(0)) + \lambda_k(r) \right\} \dots\dots (66)
 \end{aligned}$$

By making use of (66) we get for the entropy

$$\begin{aligned}
 \left(\frac{E_n}{\kappa M} \right) &= (c-1) \ln b - \frac{c}{2} \ln(b-a) - \frac{ca}{2\kappa T} u_1(R) \\
 & \quad - \frac{(1-b)}{2\kappa T} \left\{ cu_1(R) \right. \\
 & \quad \left. + \sum_{k=0}^c p(k) \sum_{i=2}^{\infty} \frac{C_i^k}{c} U_i''(0) \right\} \\
 & \quad + \sum_{k=0}^c p(k) \left[\ln T(k) \right. \\
 & \quad \left. + \frac{b}{\kappa T} \left\{ \frac{c-k}{c} (U(r) - U(0)) + \lambda_k(r) \right\} \right] \dots\dots\dots (67)
 \end{aligned}$$

Fig. 8. Entropy variation with temperature by configurational origin.

Table 3. Localized radial distribution function at integral times i of the mean distance R .

Temp. (°K)	i						
	1	2	3	4	5	6	7
300	1.999993	1.247002	1.065975	1.019333	1.006911	1.002460	1.000886
450	1.999710	1.113974	1.019886	1.004357	1.001232	1.000362	
550	1.998867	1.084470	1.013029	1.002675	1.000728	1.000216	
650	1.997067	1.066802	1.009484	1.001860	1.000477		
750	1.994053	1.054954	1.007353	1.001411	1.000361		
850	1.989380	1.046045	1.005875	1.001111	1.000284		
950	1.982523	1.039028	1.004788	1.000895	1.000229		
1050	1.972280	1.033158	1.003931	1.000729	1.000187		
1150	1.955317	1.027805	1.003191	1.000588	1.000151		
1250	1.934470	1.023816	1.002660	1.000481			
1350	1.918140	1.021614	1.002382	1.000431			
1450	1.900217	1.019727	1.002148	1.000388			
1550	1.879763	1.018081	1.001948	1.000352			

which is shown as a function of temperature in Fig. 8. The increase of the entropy with rising of temperature is mainly due to the change in the free volume.

In the usual hole theory of the liquid state the effect on a molecule of its distant molecule is neglected, where the calculated values of the specific volume and entropy in the liquid state are smaller than the experimental values. We have tried to relieve this fault by taking into account the effect of the distant molecules.

The second term of the left-hand side in (43) gives an effect of estimating R larger. The larger R results in lowering magnitude of energy $u_1(R)$, and decreasing of parameter b . Thus the volume has been estimated larger than by the usual hole theory. For example, the second term of the left-hand side in (43) at 1550°K estimated as 0.2×10^{-4} . Without the effect of this term we would have estimated R smaller by about 0.0015. We show the temperature dependence of the localized radial distribution function used in this calculation in Table 3, in which the values at the nearest neighbouring lattice sites are calculated by making use of the probability function given in Table 1.

We have hitherto investigated the glass system on the basis of the thermostatical theory in equilibrium state. The state of actual glass, however, can not be regarded in an equilibrium state but in a metastable or supercooled state. The equilibrium values of the parameters a and b which are defined by (35) are determined by the condition of the minimum free energy but they are kept at certain values at a higher temperature in the liquid state. It is seen in (43) that the function $S(R)$ is estimated smaller by keeping a and b constant. On the other hand, the quantity $D(R, T)$ is hardly influenced by keeping a and b constant because it does not contain these parameters explicitly. In result the mean distance

which is determined the condition $S(R) = D(R, T)$ is influenced and it is found that that distance becomes larger in the case of the supercooled state. In other words, the specific volume becomes larger than in the equilibrium state.

Let us cool the glass system at the temperature T_L down to a temperature T_s through the melting point T_m and above the glass transition point T_g ($T_g < T_s < T_m$), as shown in Fig. 9. Then we have the system at a supercooled state at temperature T_s ($s=1, 2, \dots$). The mean distance R in the supercooled state at temperature T_s is larger than that is the (fictive) equilibrium state at this temperature, and the difference increases as the temperature T_s is lowered to the glass transition point T_g . If the system is further supercooled through T_g down to $T_s (< T_g)$, the above difference does not increase but remains nearly constant. This is due to the fact that b is kept nearly constant under the glass transition temperature T_g in the (fictive) equilibrium state. (A value of b below T_g is negligible small as

Fig. 9. Temperature dependence of the mean distance R in the (fictive) equilibrium glass and in the real glass.

shown in Fig. 1. If change of b is the same amount, it may be regarded to remain nearly constant in room temperature). In result one obtains the curves with two branches as shown in Fig. 9, in which the two branches show the relations of the mean distance R between the pair of nearest neighbouring molecules with temperature in the supercooled state and in the (fictive) equilibrium state. It is seen there that the curve deflect down more unsharply in the supercooled state than in the (fictive) equilibrium state and therefore it is not easy to define T_g as a deflexion point of the curve in the real supercooled state. One usually defines the glass transition point as a meeting point between the elongation line of the R - T curve in the glass state and the tangent of the R - T curve in the supercooled state but this is not so meaningful from the present point of view. That meeting point represent only a certain relaxation property in the supercooled state, I think, the glass transition point should be considered to be the point $R=a_2$.

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Appendix I Localized radial distribution function

A radial distribution function is defined as follows.

$$\rho^{(2)}(\zeta_1, \zeta_2) = \rho^{(1)}(\zeta_1) \rho^{(1)}(\zeta_2) g(\zeta_1, \zeta_2) \dots \dots \dots (A-1)$$

If the structure in an ensemble is perfectly random, total number of molecules are obtained as

$$N-1 = \frac{N}{V} \int_0^\infty 4\pi\zeta^2 g(\zeta) d\zeta \dots \dots \dots (A-2)$$

The number of molecules in a spherical shell of a sufficiently larger radius r and thickness dr are given by

$$\lim_{\zeta \rightarrow \infty} \frac{N}{V} 4\pi\zeta^2 g(\zeta) d\zeta = \frac{N}{V} 4\pi\zeta^2 d\zeta \dots \dots \dots (A-3)$$

When we assume the distribution function $G_{kl}(\zeta)$ is

proportional to a delta-function, we can get for the same quantity.

$$\lim_{i \rightarrow \infty} \frac{N}{V} \int_{iR-0.5R}^{iR+0.5R} 4\pi\zeta^2 \{\text{const } \bar{G}_{kl}(\zeta)\} \delta(\zeta - iR) d\zeta \dots \dots \dots (A-4)$$

By equating (A-4) with (A-3) we can determine the precise form and obtain (14).

Appendix II Interaction between a pair of nearest neighbouring molecules intermediated by the bonding between their nonbridging oxygens

As we have assumed that the molecule make no rotational motion. every oxygen in its molecule make the same translational displacement r as the centre of the molecule does. As shown in Fig. (A-1), nonbridging oxygen, say O , in Fig. (A-1), can move in a sphere of radius $(R/2)-S$, shown as Σ in Fig. (A-1). The oxygen is situated at the centre of the sphere Σ when the centre of the molecule is just at the lattice point L in Fig. (A-1). The centre of the molecule can only move in the sphere with radius $(R/2)-S$ and with the centre at the lattice point L . The vector ζ connecting a non-

Fig. (A-1). Structural model of the discrete ion and locations of its nearest neighbouring ions.

Fig. (A-2). Effective model for the potential between the nonbridging oxygen atoms.

bridging oxygen $O_i (i=1\cdots 6)$ with its counterpart oxygen $O_{i'}$ in the nearest neighbouring molecule can be transferred to the central part of the molecule as shown in Fig. (A-2). If a potential energy $V_0(\mathbf{r}_i)$ act between the oxygens O_i and $O_{i'}$, we have the interaction potential $\sum_{i=1}^6 V_0(\mathbf{r}_i)$ between a pair of nearest neighbouring molecules which distribute uniformly on the sphere with the centre at L , we can obtain the average potential energy of the central molecule due to the nearest neighbours as

$$U'(r) = \frac{c}{2} \int_0^\pi V_0(\xi) \sin \theta d\theta \quad (\text{A-5})$$

where

$$\xi^2 = r^2 + (R-2S)^2 - 2r(R-2S) \cos \theta \quad (\text{A-6})$$

Appendix III Derivative of $(\ln Q_N/M)$

The variables a and b in (36) and (37) are replaced by A and B as

$$a = A - B \text{ and } b = 1 - A \quad (\text{A-7})$$

Then the derivatives (prim sign) of (36) and (37) are calculated as

$$\begin{aligned} & -2B(1-A)A' + (A-2A^2+B)B' \\ & = B(A-B)(1-2A+B)x^2(x^{-2})' \quad (\text{A-8}) \end{aligned}$$

and

$$\begin{aligned} & \{(1-c)B(1-2A+B) + cBA(1-A)\}A' \\ & + \frac{c}{2}A(1-A)(1-2A)B' \\ & = AB(1-A)(1-2A+B)y(y^{-1})' \quad (\text{A-9}) \end{aligned}$$

respectively. By eliminating the derivatives A' and B' of A and B from the above equations, $(\ln A)'$ and $(\ln B)'$, that is, $(\ln(1-b))'$ and $(\ln(1-b-a))'$, are obtained as

$$\begin{aligned} (\ln(1-b))' &= \frac{b}{(c-2)b(b-1) + (c-1)a} \\ & \times [ca(2b-1)(\ln x)' + \{2b(b-1) \\ & + a\}(\ln y)'] \quad (\text{A-10}) \end{aligned}$$

and

$$\begin{aligned} (\ln(1-b-a))' &= -\frac{2}{(c-2)b(b-1) + (c-1)a} \\ & \times [a\{(1-b)(b-a) + cb(1-b)\}(\ln x)' \\ & + b^2(1-b)(\ln y)'] \quad (\text{A-11}) \end{aligned}$$

By substituting these equations into the derivative of

$\ln Q_N/M$, we get

$$\left(\frac{\ln Q_N}{M}\right)' = ca(\ln x)' + b(\ln y)' \quad (\text{A-12})$$

Appendix IV Effective potential function

$$V_0(\mathbf{R}_i + \mathbf{S}_p + \mathbf{r}, \mathbf{R}_j + \mathbf{S}_q)$$

By the assumption described in the appendix II, the vectors $\mathbf{S}_p$ and $\mathbf{S}_q$ are on the line from $\mathbf{R}_i$ to $\mathbf{R}_j$. We denote distance from p to q as RD ($RD=2m=R-2S$), and represent the effective potential approximately by following function,

$$V_0(R) = \begin{cases} \varepsilon_1 \left\{ \left(\frac{a_1}{RD} \right)^{12} - 2 \left(\frac{a_1}{RD} \right)^6 \right\}, & a_2 \geq RD > 0 \\ \dots\dots\dots & (\text{A-13}) \end{cases}$$

$$\begin{cases} \varepsilon_1 [\gamma + \beta(RD - a_2) + \alpha_1(RD - a_2)^2 \\ \times \exp\{-a_2(RD - a_2)\}], & RD > a_2 \\ \dots\dots\dots & (\text{A-14}) \end{cases}$$

In this equation, the parameters, γ and β , must be determined so as to constitute (A-14) with (A-13) as a continuous functional of R , because (43) and (44) include the derivative of $V_0(R)$ with respect to R . The parameter α_1 must give (A-14) larger increase of R in $RD > a_2$ than (A-13) if it is used in that region, corresponding to the hydrogen-like interaction of the sodium atoms. The maximum increase point which corresponds to the melting point is determined by a_2 . Of course, each parameters should be set to follow a calculated potential curve.

In this paper, values of the parameters to carry out numerical calculation are assumed as follows; (atomic unit)

$$\begin{aligned} S &= 7.255, & c &= 6, & \varepsilon_1 &= 1.00 \times 10^{-2}, \\ a_1 &= 10.00, & a_2 &= 10.35, & \alpha_1 &= 0.22917, \\ a_2 &= 0.87165, & \beta &= 0.17590, & \gamma &= -0.96522. \end{aligned}$$

The values of the parameters in the potential function of Lennard-Jones' type are assumed as

$$\varepsilon_2' = 0.50 \times 10^{-3} \text{ and } \gamma^{*'} = 24.51$$

in the case of the interaction between a molecule and its nearest neighbouring molecule, and

$$\varepsilon_2'' = 0.60 \times 10^{-3} \text{ and } \gamma^{*''} = 24.51$$

in the case of the interaction between a molecule and the molecule beyond the nearest neighbours.

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Na₂O·2 SiO₂ ガラスのガラス変態理論 (熱膨脹計算)

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Na₂O·2 SiO₂ ガラスは多くの discrete ion により構成されているというモデルの基に、異なった discrete ion 中の非架橋酸素間の有効ポテンシャル関数を仮定して(続報で検討する), このガラスの体積温度関係を統計熱力学的に検討する。

その結果, ガラス変態は, 近似関数として使用されて

いる Lennard-Jones 型ポテンシャル関数の最小値より少し大きな距離で, この関数に比較して急に立上がるようなポテンシャル関数の形によって決定される。終りに, この理論の観点より実際のガラスの体積温度関係を検討する。

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