

Factors determining glass transition temperature and relaxation time of poly(vinyl chloride)

Motosuke Naoki and Akira Owada

Department of Textiles and Polymers, Faculty of Technology, Gunma University, Kiryu-shi, Gunma 376, Japan

(Received 5 October 1982; revised 27 December 1982)

Glass transition properties were obtained by measurements of the dilatometric glass transition temperature T_g at elevated pressure by isobaric cooling at a constant rate. The properties include the pressure–volume–temperature (P – V – T) relations of the liquid, the specific heat capacity and the dielectric properties for a single sample of poly(vinyl chloride). From the experimental results, various thermodynamic excess quantities such as the free volumes and the configurational entropy and energies were evaluated as factors determining T_g and the relaxation time τ . Some empirical rules concerning T_g , which have been proposed by Simha and Boyer, and Wunderlich, are also examined. The main conclusions are as follows: (1) the free volume is not an essential factor determining T_g and τ ; (2) the Adam–Gibbs parameter is slightly superior to the other excess entropy and energies defined as the difference of the entropy and energies between the liquid and the hypothetical crystal whose thermal expansivity and compressibility are the same as those of the corresponding glasses; and (3) the glass transition may not be treated as a quasi-equilibrium thermodynamic transition to which one of the Ehrenfest relations applies.

Keywords Glass transition; free volume; configurational entropy; configurational energy; P – V – T relation; Ehrenfest relation

INTRODUCTION

Many theoretical^{1–3} and experimental^{4–12} investigations of glass transition phenomena have been focused on the applicability of the Ehrenfest relations:

$$dT_g/dP = \Delta\beta/\Delta\alpha \quad (1)$$

$$dT_g/dP = TV\Delta\alpha/\Delta C_p \quad (2)$$

where Δ denotes the difference between the properties of the liquid and the glass, and α , β and C_p refer to the thermal expansivity, the isothermal compressibility and the specific heat capacity, respectively. Most examinations of the Ehrenfest relations^{4–13} show that equation (1) is inadequate. This leads to the conclusion that the glass transition is determined by the configurational entropy or energies rather than by the free volume⁵, since it is viewed as a freezing-in process of some configurational quantity in the liquid state. In this case, the configurational quantities are defined as quantities determined by the difference in temperature dependence between the thermodynamic properties measured at equilibrium and those obtained by an extremely fast experiment. The fast experiment, in which the timescale is much faster than that required for regression of long-range fluctuations in the liquids^{1,10}, is conceptually regarded as representing thermodynamic equilibrium conditions.

There have been proposed some viscosity equations expressing the mobility of molecular motions in the liquid^{14–17}. In these equations, the relaxation time τ has been obtained as a single-valued function of the configurational quantity Z_c such as the free volume V_f ^{14–16},

the Adam–Gibbs parameter $TS_c^{1/2}$ or the configurational entropy S_c ¹⁸. The term ‘configurational’ has been used in many different ways by many investigators.

Doolittle¹⁴ and Cohen and Turnbull¹⁶ defined V_f as the increment of the liquid volume from the liquid volume extrapolated to 0K or the van der Waals volume as quoted by Bondi¹⁹. V_f used in the WLF viscosity equation¹⁵ is similar to that employed in the thermodynamic representation of T_g ²⁰. Adam and Gibbs¹⁷ discussed the configurational entropy derived from the configurational partition function corresponding to the potential energy. In the experimental analyses, moreover, the excesses from the thermodynamic quantities of the crystal at the same temperature and pressure have frequently been used as the configurational ones^{21–24}. In precise examinations of the factor determining T_g and τ , therefore, we should make definitions of the configurational quantities clear.

When T_g is obtained from isobaric experiments¹¹, the pressure dependence of T_g , dT_g/dP , has been known to agree approximately with the tangent of the isochronal T – P relation, $(\partial T/\partial P)_c$, obtained from dielectric⁴ and dynamic mechanical²⁵ time–temperature–pressure superposition. T_g has been argued to be an isoviscous or an iso-relaxation-time state^{10,11,26}. If this argument is valid, the factor determining T_g should be identical with the factor determining τ :

$$dT_g/dP = (\partial T/\partial P)_c = (\partial T/\partial P)_{Z_c} \quad (3)$$

where Z_c is the configurational factor which determines T_g and τ .

On the other hand, several quantities that are constant

at T_g have been proposed for many different polymers. The rules proposed by Simha and Boyer are²⁷

$$\Delta\alpha T_g \approx 0.113 \quad (4a)$$

$$\alpha^l T_g \approx 0.164 \quad (4b)$$

$$\Delta C_p T_g \approx 25 \text{ cal g}^{-1} \quad (4c)$$

where α^l is the thermal expansivity of the liquid. In the bead model proposed by Wunderlich²⁸, ΔC_p is

$$\Delta C_p/\text{bead} \approx 2.6 \text{ cal K}^{-1} \text{ mol}^{-1} \quad (5)$$

If the rules mentioned above are essentially universal, each quantity such as $\Delta\alpha T$, $\alpha^l T$, $\Delta C_p T$ and ΔC_p should be constant at T_g under any pressure.

This paper reports the pressure–volume–temperature (P – V – T) data of the liquid, the heat capacity and variations of the dielectric relaxation time with temperature and pressure for poly(vinyl chloride) (PVC). P – V – T data of the glasses formed by isobaric cooling at a constant rate under several pressures have been reported previously²⁹. The purpose of the present study is first to verify experimentally the argument that the glass transition is an iso-relaxation-time state^{10,11,26}, and secondly to examine various configurational quantities and the empirical rules for the essential factor governing the glass transition and the dielectric relaxation.

EXPERIMENTAL

Sample

All measurements were made on a PVC sample supplied by Toyo Soda Co. The number average molecular weight was 44000. After being purified by swelling with tetrahydrofuran and deswelling with methanol, the PVC sample in fine fibrous form was dried for a week at 60°C in a vacuum oven. All of the test specimens were cut from 0.4 mm thick sheets moulded in a vacuum press under 350 kg cm⁻² at 150°C. Then gold films were evaporated onto the specimens for dielectric experiments.

Glass transition temperature and P – V – T relations

The glass transition temperature and the P – V – T relations were measured by use of a pressure dilatometer with a variable differential transformer. Details of the pressure dilatometer and the treatment of data are given elsewhere²⁹. The values of T_g were obtained in the following way. The dilatometer containing the sample and mercury was heated under atmospheric pressure to a temperature T_x which was higher by about 25K than $T_g(P_g)$, where P_g is the pressure at which the glass would be formed. Then the pressure was increased to P_g . After the pressure and temperature were held at P_g and T_x for ~30 min, the dilatometer was isobarically cooled down at a rate of 0.24K min⁻¹ while the V – T relations were measured at 1K intervals. To find T_g , the usual extrapolation of the linear parts of the V – T isobars was made. Isothermal dilatometric experiments were also used to obtain the P – V – T data at 4K intervals over a temperature range of 355–385K.

Heat capacity

The heat capacity was measured by a differential scanning calorimeter (Model DSC-1B, Perkin–Elmer). Sample temperature in the DSC-1B was calibrated at the melting temperatures of standard materials, i.e. mercury,

water, gallium and indium, which were fitted to the second-order polynomial in the programmed temperature range by the least-squares method. Determination of C_p with the DSC-1B was made by O'Neill's method³⁰, i.e. by a superposition of recorder traces obtained with an empty pan, with the samples and with α -alumina as a standard, of which heat capacity data were taken from ref. 31. The d.s.c. measurements were carried out on eight different masses of the sample scanned at 8K min⁻¹ through three temperature regions, i.e. the glassy region of 210–310K, the glass transition region of 310–410K, and the liquid region of 370–435K. The glass sample, which was the same as the 0 glass in ref. 29, used for the d.s.c. measurements in the glassy and transition regions was prepared as follows. The sample in the pan was evacuated and heated to 370K. After being kept there for 30 min, the temperature was lowered to room temperature at a cooling rate of 0.24K min⁻¹, which was the same rate as that used in the measurements of T_g and the P – V – T data.

Dielectric measurements

Dielectric measurements were made in a three-terminal electrode system in conjunction with a General Radio 1620-A Capacitance Measuring Assembly with a 1310-B Oscillator (General Radio) used to make small changes in frequency near the dielectric loss peaks. The sample and electrodes were set in a cylindrical cavity of the pressure vessel, which was immersed in a bath controlled to an accuracy of ± 0.01 K. Liquid paraffin was used to transmit the hydrostatic pressure. The pressure was measured by a Heise bourdon tube gauge with an automatic compensator (Dresser Ind.) and the temperature was measured by an alumel–chromel thermocouple inserted in the guard electrode.

The dielectric measurements were carried out in a frequency range of 0.1–100 kHz at 2K intervals over a temperature range of 365–390K. The pressure was changed in increments of 50 kg cm⁻² in the 1–300 kg cm⁻² region and in increments of 100 kg cm⁻² in the 300–500 kg cm⁻² region. Simultaneously, d.c. conductivities were also measured to obtain the leakage current. The dielectric loss factor was corrected by subtraction of the loss due to the leakage current.

RESULTS

P – V – T relations

The liquid state P – V – T data are contained in the values of the specific volume V expressed by the polynomials in T at each pressure P :

$$V = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \quad (6)$$

Since the experimental temperature range for the liquid was rather narrow at higher pressures, the values of a_2 and a_3 calculated by the least-squares method were scattered at pressures above 300 kg cm⁻². We approximated the preliminary values of a_3 below 300 kg cm⁻² by a quadratic equation in P , from which the final values of a_3 were determined. By use of the values of a_3 , the values of a_0 , a_1 and a_2 were obtained by least-squares calculation. The results and the standard deviation σ in the specific volume are tabulated in Table 1. The V – P isotherms and the thermal expansivity α calculated from equation (6) are shown in Figures 1 and 2, respectively.

The thermal pressure coefficient γ was obtained from

Table 1 Specific volume (equation (6)) and glass transition temperature

P (kg cm^{-2})	a_0 ($\text{cm}^3 \text{g}^{-1}$)	$a_1 \times 10^4$ ($\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$)	$a_2 \times 10^6$ ($\text{cm}^3 \text{g}^{-1} \text{K}^{-2}$)	$a_3 \times 10^9$ ($\text{cm}^3 \text{g}^{-1} \text{K}^{-3}$)	$\sigma \times 10^5$ ($\text{cm}^3 \text{g}^{-1}$)	T_g (K)	Region (K)
1	0.59656	5.449	-1.1372	1.724	8.5	352.49	357-385
75	0.57032	6.885	-1.320	1.639	15.1	354.4	360-385
150	0.62897	3.732	-0.882	1.556	11.5	354.8	363-385
220	0.62942	3.640	-0.847	1.481	15.1	356.2	363-385
300	0.64236	2.945	-0.738	1.397	13.1	357.4	366-385
400	0.65217	2.312	-0.620	1.295	14.3	358.6	366-385
500	0.65975	1.617	-0.470	1.198	14.0	359.9	369-385
600	0.65958	1.634	-0.454	1.104	14.2	360.8	369-385

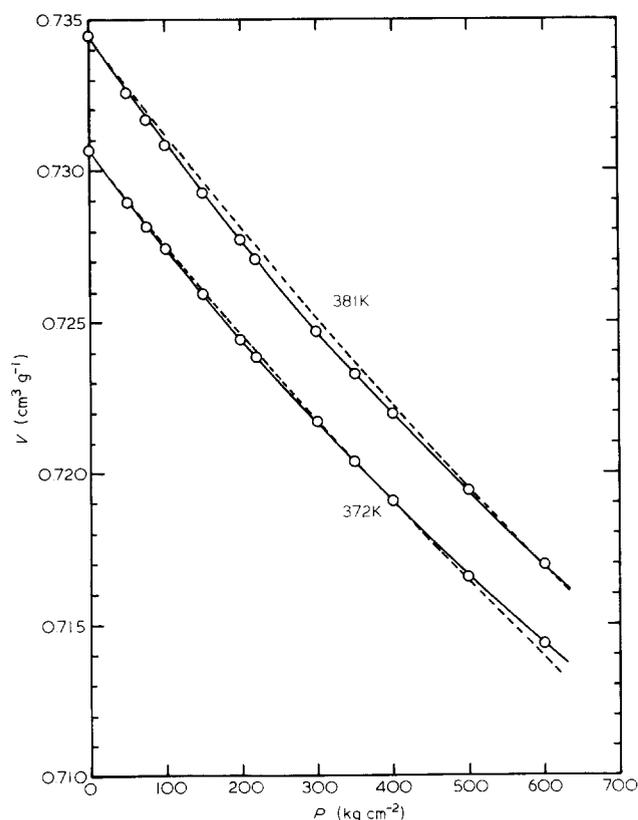


Figure 1 V - P isotherms: full lines, Tait equation with equations (11) and (12); broken lines, Tait equation with equation (10) determined by Simha *et al.*³⁴

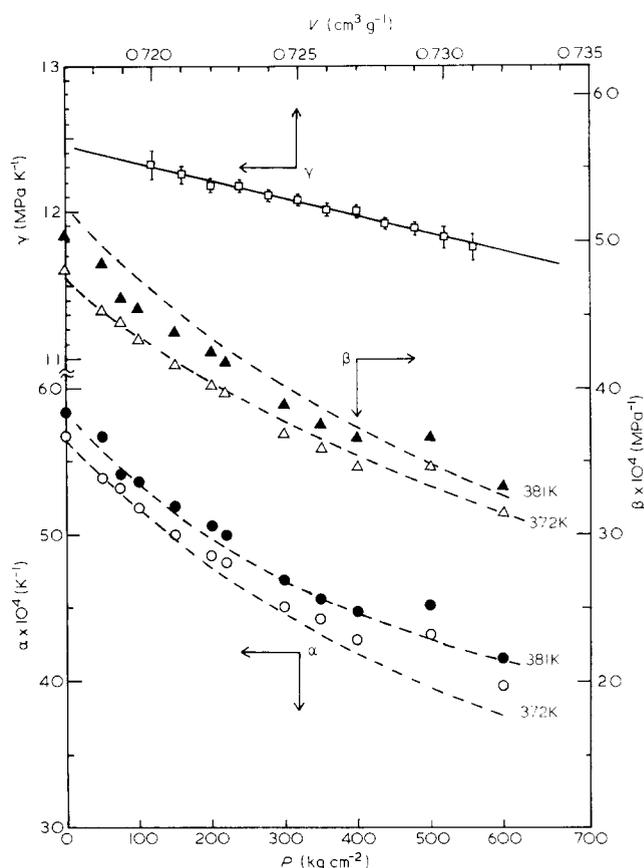


Figure 2 Thermal expansivity α , isothermal compressibility β and thermal pressure coefficient γ : full line, equation (7); broken lines, Tait equation with equations (11) and (12)

the slopes of the P - T isochores, which were linear over the present temperature and pressure ranges. It has a linear relation to V :

$$\gamma = -4.797V + 4.685 \text{ MPa K}^{-1} \quad (7)$$

which is indicated by the full line in Figure 2. The isothermal compressibility β calculated from the thermodynamic relation

$$\beta = \alpha/\gamma \quad (8)$$

is also shown in Figure 2.

The Tait equation, which is suitable for smoothing the data and convenient for comparison with data by others³², is commonly written as:

$$V/V_0 = 1 - C \ln [1 + (P - P_0)/B] \quad (9)$$

where P_0 and V_0 are the reference pressure (1 atm) and the specific volume at P_0 , respectively, and B and C constants which depend on temperature only. Simha *et al.*^{33,34} have

shown that C can be assumed to have the universal value of 0.0894 and B can be expressed by

$$B = b_1 \exp(-b_2 T) \quad (10)$$

Comparisons between the Tait equation and experiment are shown in Figures 1 and 2. The V - P isotherms in Figure 1 are not well represented by the Tait equation with the universal value of C and equation (10), in which values of b_1 and b_2 were determined by Simha *et al.*³⁴ from the P - V - T data reported by Hellwege *et al.*³⁵ The deviation, however, is considered to be within the limit of experimental errors in the data of Hellwege *et al.*

The Tait equation calculated for the present P - V - T data using the universal value of C and equation (10) resulted in a standard deviation in relative volume of 5×10^{-4} , which exceeded the experimental error. Hence we have allowed the constants B and C to vary with

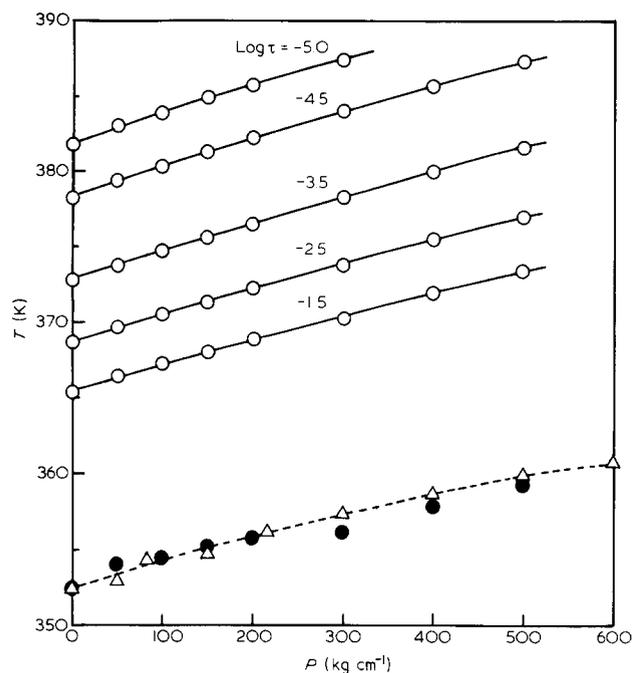


Figure 3 Dilatometric glass transition temperatures and dielectric isochronal T - P relations: triangles, glass transition temperatures; open circles, intercepts at constant relaxation time; full circles, extrapolations of the VFTH equation (16)

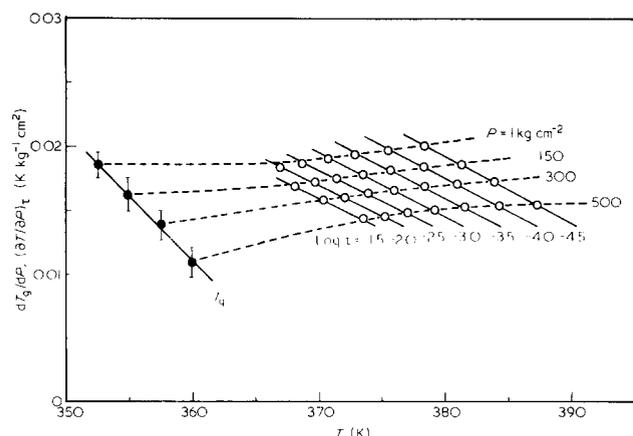


Figure 4 Pressure derivative of the glass transition temperature and tangents of the isochronal T - P relation

temperature according to the polynomials in T :

$$C = 0.2114 - 4.303 \times 10^{-4} T \quad (11)$$

$$B = 3847 - 17.93T + 0.02117T^2 \text{ MPa} \quad (12)$$

The parameters in these equations were obtained by the least-squares method. The Tait equation with equations (11) and (12) gave an overall deviation in relative volume of 1.8×10^{-4} .

Figure 2 shows the thermal expansivity and the compressibility, which are not precisely represented by the Tait equation with equations (11) and (12). Therefore, we have not employed the Tait equation in the present analyses of T_g and τ . The derivatives of V and α with respect to P , i.e. $(\partial V/\partial P)_T$ and $(\partial \alpha/\partial P)_T$, required in the analyses can be calculated from equation (8) and the thermodynamic relation:

$$-(\partial \alpha/\partial P)_T = (\partial \alpha/\partial T)_P/\gamma - V\alpha^2(d\gamma/dV)/\gamma^2 \quad (13)$$

Glass transition temperature

The values of T_g determined from the intersection points of the volume isobars between the liquid and the glass are shown in Figure 3 and Table 1. The variation of T_g with the pressure P at which the glass was formed is expressed in the form of a quadratic equation by the least-squares method:

$$T_g = 352.4 + 1.856 \times 10^{-2} P - 7.70 \times 10^{-6} P^2 \text{ K} \quad (14)$$

where P is in kg cm^{-2} . The broken curve in Figure 3 was calculated from equation (14). The standard deviation is 0.3K. Figure 4 shows the coefficient of T_g against P , dT_g/dP , calculated from equation (14). The values of dT_g/dP are approximately equal to the value $1.35 \times 10^{-2} \text{ K atm}^{-1}$ reported by Hellwege *et al.* from dilatometric measurements³⁵ and smaller than the value $2.15 \times 10^{-2} \text{ K atm}^{-1}$ reported by Sasabe and Saito from d.c. conduction measurements³⁶.

Heat capacity

The actual C_p data for eight samples were averaged at each temperature. The mean scatter in C_p is $\pm 0.021 \text{ J K}^{-1} \text{ g}^{-1}$ in the glassy region, $\pm 0.028 \text{ J K}^{-1} \text{ g}^{-1}$ in the glass transition region and $\pm 0.012 \text{ J K}^{-1} \text{ g}^{-1}$ in the liquid region. Figure 5 shows the variation of the averaged C_p with temperature. C_p obtained in the transition region is in a continuous line with that in the glassy region, but not with that in the liquid region. This discontinuity may be due to changes in contact conditions between the sample and the pan as the sample relaxes near T_g . C_p of the glass and the liquid was approximated by the following quadratic equation:

$$C_p = C_0 + C_1 T + C_2 T^2 \quad (15)$$

The values of C_0 , C_1 , C_2 and the standard deviation σ are listed in Table 2. The present result agrees with those reported by others^{37,38}.

A small deviation at about 240K may be due to the so-called β relaxation process pertaining to the localized mode of motions in the localized potential energy field.

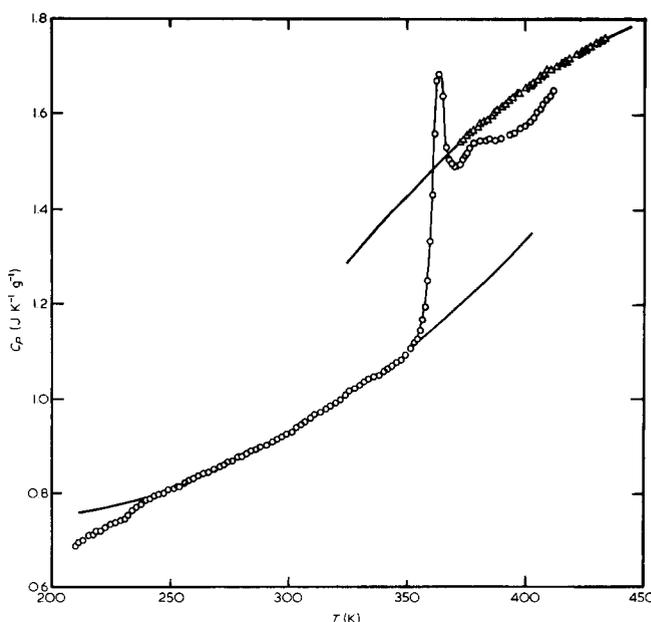


Figure 5 Specific heat capacity: circles, glassy and transition regions; triangles, liquid region; lines, equation (15)

Table 2 Specific heat capacity at 1 atm (equation (15))

	C_0 (J K ⁻¹ g ⁻¹)	$C_1 \times 10^2$ (J K ⁻² g ⁻¹)	$C_2 \times 10^5$ (J K ⁻³ g ⁻¹)	σ (J K ⁻¹ g ⁻¹)	Region (K)
Liquid	-2.496	1.706	-1.670	0.020	372.3–453.9
Glass	1.708	-0.392	1.142	0.014	250–335

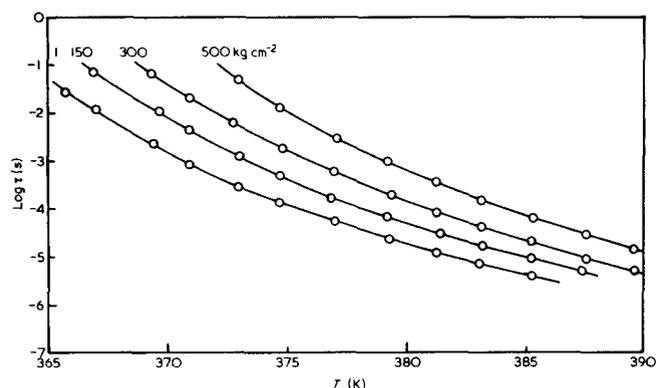


Figure 6 Relaxation-time isobars: lines, the VFTH equation (16)

Relaxation time

The relaxation process pertaining to the microbrownian motion in the liquid range is called the α relaxation process. The dielectric behaviour of the α process is in qualitative agreement with that reported by Koppelman and Gielessen³⁹ and Saito *et al.*⁴⁰, i.e. the relaxation magnitude and the shape and breadth of the loss curves are almost the same as those reported by them. Therefore, dielectric data are omitted from this paper. The relaxation spectrum of the α process of PVC is somewhat broader than a typical spectrum found by Williams *et al.* for many polymers⁴¹ and for *o*-terphenyl solutions⁴². Since the relaxation spectrum of PVC depends on temperature and pressure^{39,40}, the time–temperature–pressure superpositions with respect to the dielectric loss curves are not available. We express the location of the α process in terms of the so-called characteristic relaxation time τ defined by $\tau = 1/2\pi f_m$. Here f_m is the frequency of the maximum loss in the isothermal plots of the dielectric loss against logarithmic frequency.

Variations of τ with temperature are shown in *Figure 6*. The τ isobars are well represented by the Vogel–Fulcher–Tammann–Hesse (VFTH) equation^{43–45}:

$$\log \tau = -A + B/(T - T_0) \quad (16)$$

The values of A , B , T_0 and the standard deviation σ determined by the least-squares regression are listed in *Table 3*. Since the experimental frequency range is limited, the temperature range where the dielectric loss reaches a maximum is rather narrow. Consequently long extrapolations of equation (16) may lead to a large uncertainty.

The T - P relations at constant τ calculated from equation (16) are shown in *Figure 3*. Their slopes are very similar to that of the T_g - P relation shown in the same figure. The isochronal T - P relation extrapolated to $\log \tau = 6.466$ by using equation (16) lies approximately on the T_g - P curve. In *Figure 4*, the isochronal pressure coefficient of temperature, $(\partial T/\partial P)_\tau$, is compared with dT_g/dP . The agreement is excellent. This supports the argument that the glass transition is in the iso-relaxation-time state^{10,11,26}, and it enables us to carry out a simultaneous

Table 3 The VFTH constants in equation (16)

P (kg cm ⁻²)	T_0 (K)	A	B (K)	σ
1	336.87	11.07	272.38	0.014
100	339.63	10.56	257.01	0.016
200	340.07	11.00	273.83	0.020
300	338.22	11.58	323.59	0.010
400	339.71	11.67	328.62	0.005
500	341.49	11.48	319.33	0.016

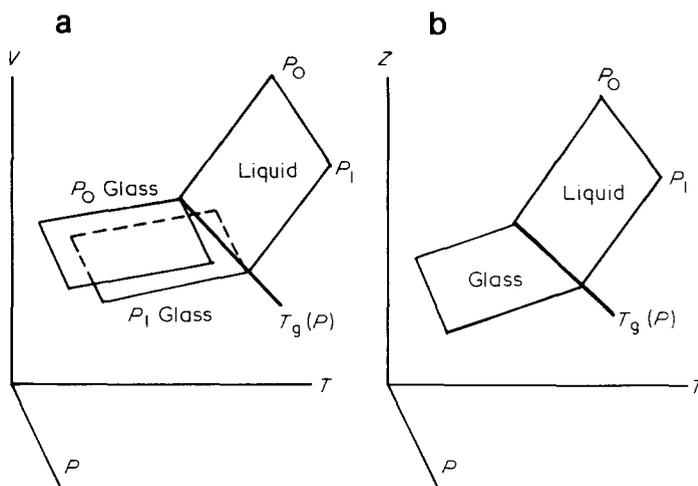


Figure 7 Schematic diagram illustrating liquid and glass surfaces. (a) V - P - T space: P_0 and P_1 glasses are the glasses formed by isobaric cooling under the pressures P_0 and P_1 , respectively. (b) Z - P - T space: the glass surface is contiguous with the liquid surface

examination of the essential factors governing both the glass transition and the molecular mobility.

DISCUSSION

dT_g/dP and (∂T/∂P)_τ in terms of various configurational quantities

As a consequence of the experiment on $(\partial T/\partial P)_\tau$, the dilatometric T_g may be regarded as the temperature at which a characteristic relaxation time is attained, i.e. a high frequency in the dielectric measurements may correspond to a fast cooling rate in the dilatometric measurements. In other words, the isobars of $(\partial T/\partial P)_\tau$ in *Figure 4* may be identical with the dT_g/dP isobars. On this basis, we will obtain expressions for $(\partial T/\partial P)_\tau$ and dT_g/dP in terms of various configurational quantities.

Figure 7a shows a three-dimensional representation of the P - V - T relations of the liquid and glasses prepared by isobaric cooling experiments under the pressures P_0 and P_1 . Surfaces of the liquid and various glasses are continuous only through the $T_g(P)$ line, which is formed by intersection points of the liquid and glass surfaces, as shown in *Figure 7a*¹¹. If the glass transition can be

Table 4 dT_g/dP and $(\partial T/\partial P)_T$ in terms of various configurational quantities

Determining variable ^a	$dT_g/dP, (\partial T/\partial P)_T$	Indices in Figures 8 and 9
$V_f[1], V_f[2]$	$\Delta\beta/\Delta\alpha$	(1)
$S_c[1], S_c[2], H_c[1], TS_c[1]$	$TV\Delta\alpha/\Delta C_p$	(2)
$E_c[1], E_c[2]$	$(TV\Delta\alpha + PV\Delta\beta)/(\Delta C_p - PV\Delta\alpha)$	(3)
$TS_c[2]$	$TV\Delta\alpha/(\Delta C_p + S_c)$	(4)
$H_c[2]$	$(TV\Delta\alpha - V_f)/\Delta C_p$	—
$V_f[3]$	$1/\gamma^l$	(5)
S^l	$TV\alpha^l/C_p^l$	(6)
E^l	$(TV\alpha^l + PV\beta^l)/(C_p^l - PV\alpha^l)$	(7)
$\Delta\alpha T$	$-T(\partial\Delta\alpha/\partial P)_T/[\Delta\alpha + T(\partial\Delta\alpha/\partial T)_P]$	(8)
$\alpha^l T$	$-T(\partial\alpha^l/\partial P)_T/[\alpha^l + T(\partial\alpha^l/\partial T)_P]$	(9)
$\Delta C_p T$	$T^2\Delta(\partial^2 V/\partial T^2)_P/[\Delta(T\partial C_p/\partial T)_P + C_p]$	(10)
ΔC_p	$T\Delta(\partial^2 V/\partial T^2)_P/\Delta(\partial C_p/\partial T)_P$	(11)

^a Definitions of the configurational quantities are indicated in square brackets

regarded as a quasi-equilibrium thermodynamic transition (for example, ref. 2), an appropriate choice of a thermodynamic quantity Z may give a glass surface that is contiguous with the liquid surface in the Z - T - P space, as shown in Figure 7b. The surfaces of the glasses formed under different pressures should coincide with each other. In this case, the Ehrenfest relation in terms of Z can be applicable to the glass transition:

$$dZ^l = dZ^g \quad (17)$$

$$dT_g/dP = -\Delta(\partial Z/\partial P)_T/\Delta(\partial Z/\partial T)_P = (\partial Z_c/\partial P)_T/(\partial Z_c/\partial T)_P \quad (18)$$

where superscripts l and g index the liquid and the glass, respectively, and Z_c is the configurational quantity and its differential is defined by:

$$dZ_c = dZ^l - dZ^g \quad (19)$$

The definition by equation (19) is hereinafter referred to as Definition 1. Replacing Z in equation (18) by the thermodynamic variables such as the volume, the entropy, the enthalpy H , the internal energy E and the product TS , we obtain dT_g/dP in terms of each variable, which are summarized in Table 4. From Definition 1, the expressions in terms of H and TS are identical with that in terms of S , because of continuity of the isobars of the volume and the entropy at T_g . For an example, when Z in equation (18) is replaced by H , we obtain

$$dT_g/dP = -[\Delta V + T\Delta(\partial S/\partial P)_T]/T\Delta(\partial S/\partial T)_P \quad (20)$$

Since the volume isobar is continuous at T_g between the liquid and the glass under the pressure at which the glass was formed, the term ΔV in equation (20) vanishes. Then equation (20) reduces to

$$dT_g/dP = -\Delta(\partial S/\partial P)_T/\Delta(\partial S/\partial T)_P \quad (21)$$

which is identical with dT_g/dP in terms of S , as pointed out by Goldstein⁵.

Apart from the treatment of the glass transition as a thermodynamically quasi-equilibrium one, we can also deal with it based on its kinetic nature. It should be noted that the following treatment is not concerned with the phase diagram of the liquid and the glass and that the contiguity between the liquid and glass surfaces is not the

point. If a configurational quantity Z_c determines τ , we have

$$(\partial T/\partial P)_T = (\partial T/\partial P)_{Z_c} = -(\partial Z_c/\partial P)_T/(\partial Z_c/\partial T)_P \quad (22)$$

We define Z_c as the increment of Z^l measured at equilibrium from Z^c of a hypothetical crystal:

$$Z_c = Z^l - Z^c \quad (23)$$

and adopt the assumption that the dependences of entropy and volume of the hypothetical crystal on temperature and pressure are the same as those of the corresponding glass, i.e. $dS^c = dS^g$ and $dV^c = dV^g$. This above definition of Z_c is referred to as Definition 2. Replacing Z_c in equation (22) by the configurational variables such as the free volume V_f , the configurational entropy S_c , the configurational enthalpy H_c , the configurational internal energy E_c and the Adam-Gibbs parameter TS_c , we obtain $(\partial T/\partial P)_T$ in terms of each variable, which are summarized in Table 4. In this case, V_f and S_c do not vanish at T_g , and $(\partial T/\partial P)_T$ in terms of H_c and TS_c from Definition 2 are not identical with dT_g/dP in terms of H and TS from Definition 1.

The hypothetical crystal is essentially different from the real crystal. The thermal pressure coefficient of the glass, γ^g , is usually much smaller than that of the liquid^{11,29}, γ^l , whereas the coefficient of the real crystal is similar to or larger than γ^l (for instance, refs 24 and 46). This may be due to the β relaxation process pertaining to the localized mode of motions which occurs in the liquid state as well as in the glassy state⁴³, but not in the crystalline state. In Definition 2, therefore, we have made an assumption that the localized mode of motions has no participation in the liquid mobility and, subsequently, in the glass transition.

In the equilibrium statistical treatments, the configurational quantities are usually defined as the residues obtained by subtraction of the kinetic contribution from the liquid quantities⁴⁸. These configurational quantities can be calculated from the configurational partition function corresponding to the potential energy. The calculations, however, depend on the statistical models adopted and any examination by use of these configurational quantities may be significantly influenced by the appropriateness of the models. In the present paper, we will examine none of them, except for V_f which is practically regarded to be independent of the models*. Doolittle¹⁴ and Cohen and Turnbull¹⁶ regarded V_f as the difference between the liquid volume at equilibrium and the liquid volume at 0K, i.e. $V_f(T) = V^l(T) - V^l(0)$. By assuming that $V^l(0)$ is independent of P , we find that $\partial V_f/\partial T = \partial V^l/\partial T$ and $\partial V_f/\partial P = \partial V^l/\partial P$. The definition of V_f is referred to as Definition 3. The result obtained by replacing Z_c in equation (22) by V^l is listed in Table 4.

If the empirical rules concerning T_g , i.e. equations (4) and (5), are universally valid, the quantities $\Delta\alpha T$, $\alpha^l T$, $\Delta C_p T$ and ΔC_p should be constant on the $T_g(P)$ line in Figure 7, and should behave similarly to Z_c in equation (18). The results obtained by replacing Z_c in equation (18) by such quantities are summarized in Table 4.

* Strictly the free volume depends on the functional form of the potential energy field which confines a molecule within its cage constructed by surrounding molecules. For instance, ref. 49

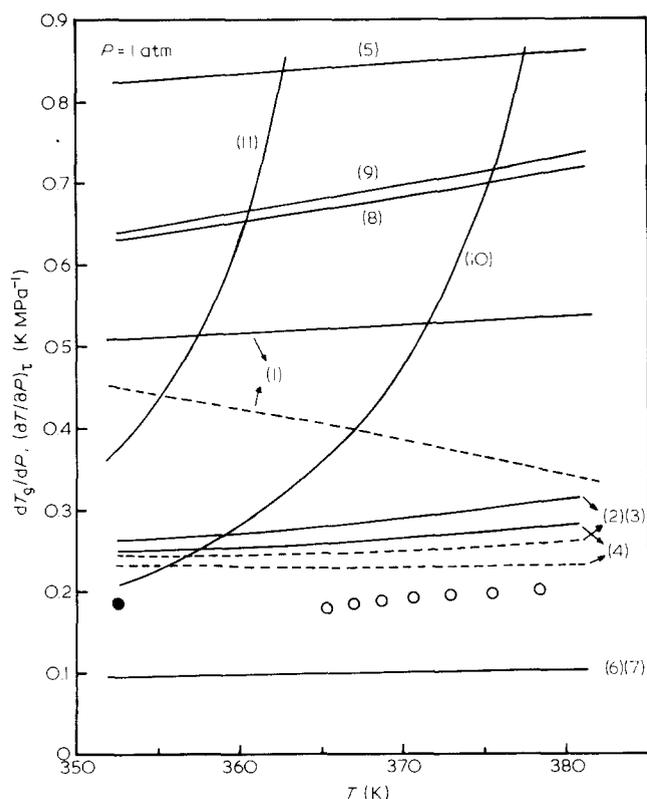


Figure 8 Examination of factors determining the glass transition temperature and the relaxation time at 1 atm: full circle, dilatometric; open circles, dielectric; full lines, simple extrapolations of the P - V - T relations of the 0 glass; broken lines, extrapolations by use of the principle of corresponding states for the glasses. Indices of each line are indicated in Table 4

Comparison with experiment

In comparing dT_g/dP and $(\partial T/\partial P)_t$ in Table 4 with the experiments in Figure 4, one requires the values of the thermodynamic properties of the liquid and the glasses such as α , β , γ , C_p and their derivatives over the temperature and pressure range in Figure 4. The thermal expansivities for the glasses formed by isobaric cooling at a rate of 0.24K min^{-1} are given in a linear relation²⁹:

$$\alpha^g = \alpha_0 + \alpha_1 T \quad (24)$$

The values of α_0 and α_1 are $1.370 \times 10^{-4} \text{K}^{-1}$ and $1.779 \times 10^{-7} \text{K}^{-2}$, respectively, at 1 atm. for the 0 glass formed in vacuum, and $1.165 \times 10^{-4} \text{K}^{-1}$ and $1.369 \times 10^{-7} \text{K}^{-2}$, respectively, at 500kg cm^{-2} for the 500 glass formed under 500kg cm^{-2} . The γ of the glasses is independent of the pressure history and is approximated as a function of volume only²⁹:

$$\gamma^g = 4.274 - 4.887V \text{ MPa K}^{-1} \quad (25)$$

We can readily obtain the values of α^g , β^g , γ^g , $(\partial\alpha/\partial P)_t^g$ and $(\partial^2 V/\partial T^2)_p^g$ at any temperature and pressure by extrapolations of equations (24) and (25) with the aid of equation (8). Results yielded by substitution of such glass properties into dT_g/dP and $(\partial T/\partial P)_t$ in Table 4 are indicated by the full lines in Figures 8 and 9.

Since the glasses formed at temperatures higher than T_g , i.e. the glasses formed at faster cooling rate than 0.24K min^{-1} , may differ from the 0 glass, the thermodynamic properties of the former might not be approximated as the simple extrapolations of equation (24). In the preceding paper²⁹, we have shown that the P - V - T relations of the

glasses with different pressure histories are described by the principle of corresponding states, and that the universal function of the product αT at fixed reduced pressure is approximated by²⁹

$$\alpha T = M + N \log V \quad (26)$$

where M and N are constants common to all of the pressure densified glasses. Values of M and N are 0.6065 and 3.751, respectively, at 1 atm. and 0.4799 and 2.858, respectively, at 500kg cm^{-2} . If the principle is also applicable to the glasses formed at various timescales, equations (25) and (26) enable us to calculate the P - V - T relations of the glasses. Results for dT_g/dP and $(\partial T/\partial P)_t$ yielded from the glass properties extrapolated by use of the principle of corresponding states are indicated by the broken lines in Figures 8 and 9.

The C_p^g data are given only for the 0 glass, since the uncertainty inherent in the d.s.c. measurements masks slight effects of the pressure history. Chang and others have shown that C_p^g depends on the timescale of glass formation⁵⁰. However, the dependence is only slight⁵⁰, and we have ignored the differences in C_p^g among various glasses in the present examination. Values of C_p^g were calculated from equation (15) with the effect of pressure only being corrected by use of the second derivative of volume by temperature.

Values of S_c and V_f are needed in calculation of $(\partial T/\partial P)_t$ in terms of TS_c and H_c of Definition 2. S_c might be approximated by

$$S_c = \int_{T_2}^T \Delta C_p/T dT \quad (27)$$

where T_2 is the temperature when the configurational entropy vanishes. The results in Figures 8 and 9 were

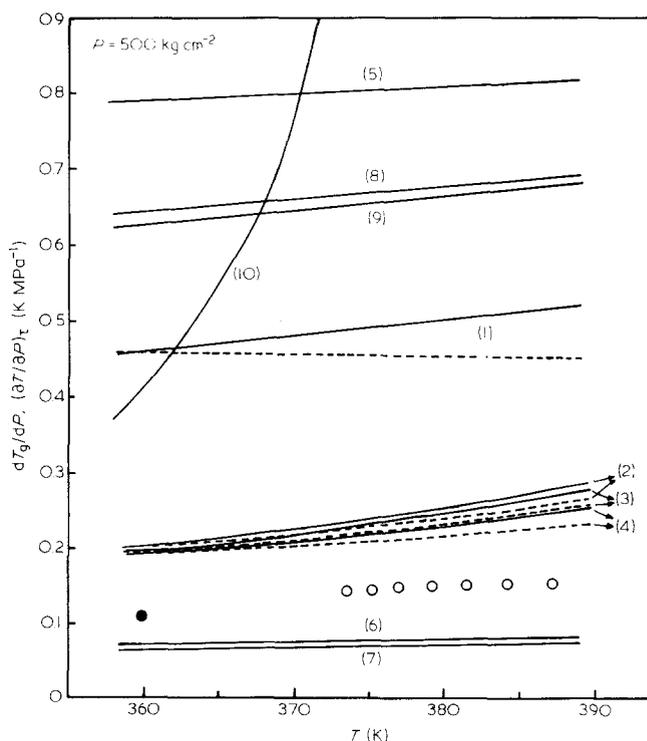


Figure 9 Examination of factors determining the glass transition temperature and the relaxation time at 500kg cm^{-2} : full lines, simple extrapolations of the P - V - T relations of the 500 glass. The other symbols are the same as those in Figure 8 and Table 4

obtained by use of S_c calculated from equation (27) with the assumption that $T_2 = T_0$, where T_0 is the parameter appearing in the VFTH equation (16). However, the present experimental range of the dielectric measurements was so limited that the values of T_0 may include large uncertainty. T_0 's in Table 3 are higher than that argued usually, i.e. $T_0 \sim T_g - 50$ K. Therefore, the calculation from equation (27) with T_0 in Table 3 might underevaluate S_c , i.e. the value of $(\partial T/\partial P)_\tau$ in terms of TS_c might be somewhat larger.

By analogy with the Doolittle¹⁴ and Adam-Gibbs¹⁷ viscosity equations, H_c might be reduced to zero at T_0 as τ approaches infinity. However, there exists no basis for simultaneous extinction of H_c and V_f at T_0 .^{*} Since there seems no useful method for determination of the absolute value of V_f , we abandon the attempt to examine H_c of Definition 2 in the present study.

Comparisons between the calculations and experiment with respect to dT_g/dP and $(\partial T/\partial P)_\tau$ are summarized in Figure 8 for 1 atm and in Figure 9 for 500 kg cm⁻². The rough situations are not effectively different between 1 atm and 500 kg cm⁻².

With respect to the free volumes, i.e. V_f 's of Definitions 1-3 indexed by (1) and (5), and the rules closely related to the free volume theories, i.e. $\Delta\alpha T$ and $\alpha^l T$ indexed by (8) and (9), respectively, no agreement is found between the calculations and experiment. It is considered to be very natural that V_f of Definition 1 is invalid, since the pressure densification phenomenon was really observed as shown in Figure 7a^{11,29}. The result on $\Delta\alpha T$ is in quantitative agreement with that for poly(vinyl acetate) obtained by Goldstein^{10,11}. The calculation indexed by (5) is much larger than the experiment, i.e. γ^l is much smaller than $(\partial P/\partial T)_\tau$. Since γ of the real crystal is usually estimated to be larger than γ^g ,⁴⁶ the free volume defined as the increment of V^l from the volume of the real crystal may also fail. In conclusion, the free volumes, even if any definition is adopted, may not be an essential factor which governs the glass transition and the molecular mobility.

The broken line indexed by (1) obtained from V_f by use of the principle of corresponding states of the glasses seems to approach the experiment at higher temperature under 1 atm, as shown in Figure 8. The free volume may be expected to be useful in the region $T \gg T_g$ at lower pressure.

The calculations in terms of S_c , E_c and TS_c indexed by (2), (3) and (4), respectively, are considered to be approximately in agreement with the experiment. The Adam-Gibbs parameter appears to be slightly superior to the others. If S_c is calculated by use of the value of T_0 calculated from $T_0 = T_g - 50$ K instead of that in the VFTH equation, a somewhat better agreement may be expected at 1 atm. However, the refinement may still be insufficient at 500 kg cm⁻².

Included in Table 4 and in Figures 8 and 9 for comparison are the cases when the liquid entropy and internal energy or the configurational entropy and internal energy defined as the excesses from the kinetic ones which are assumed to be independent of temperature and pressure are the factors determining T_g and τ . These quantities give the values of $(\partial T/\partial P)_\tau$ to be approximately

half those from experiment. This implies that the examinations of the appropriateness of the configurational entropy and energies would be significantly affected by the definitions of the 'configurational' quantities. In order to find the predominance among them, therefore, the validity of the definitions should first be examined.

With respect to the rules concerning the increment of C_p at T_g , i.e. $\Delta C_p T$ and ΔC_p indexed by (10) and (11), respectively, the present study has failed to make a significant examination because of the large uncertainty in extrapolations of $(\partial^2 V/\partial T^2)_P$ and $(\partial C_p/\partial T)_P$. It should be noted that $\Delta C_p T$ at 1 atm seems to be in agreement with the experiment near T_g , where the extrapolation is short.

CONCLUSION

The present study affords a way to examine what factor governs the glass transition and the molecular mobility in the liquid. The examination is based on the experimental evidence that the dilatometric T_g determined by isobaric cooling corresponds to the iso-relaxation-time state. The results indicate an invalidity of various free volumes, an approximate validity of the configurational entropy and energies, and a slight superiority of the Adam-Gibbs parameter. From the fact that the calculations of dT_g/dP in terms of various quantities in Definition 1 are not in precise agreement with the experiment, it may be concluded that the glass transition should not be treated as a quasi-equilibrium thermodynamic transition to which one of the Ehrenfest relations applies. The glass transition, therefore, may essentially differ from the second-order transition at T_2 argued by Gibbs and Dimarzio⁵². This may be due to the fact that the glass differs from the real crystal in the configurational properties owing to a participation of the localized mode of motions²⁹. Moreover, the glass transition might be accompanied by changes in the kinetic modes as argued by Goldstein⁵³ and Roe and Tonelli⁵⁴.

It should be noted that the concept of the simple additivity of the thermodynamic variables adopted in the present study has not yet been verified experimentally, although the concept has been employed by many investigators. The assignment of the excess quantities from the hypothetical crystal of which thermal expansivity and compressibility are the same as those of the corresponding glass to the configurational ones includes the assumptions that the kinetic modes are independent of the thermodynamic states and that the localized mode of motions does not affect the molecular mobility in the liquid.

The separation of the liquid quantities into the configurational and kinetic contributions is based on the experimental evidence that the thermal pressure coefficient of most liquids is well approximated as a function of volume only⁴⁸. From some thermodynamic considerations, this leads to a simple additivity concept that the internal energy and entropy can be separated into a volume-dependent term and kinetic ones. The former, known as the configurational term, is related to the configurational partition function corresponding to the potential energy.

It has been found that the simple additivity concept applies to the pressure-densified glasses of PVC also²⁹. The energy parameters, which characterize the configurational properties of the glasses, change with the

* Miller has suggested, however, that the excess enthalpy and volume of *o*-terphenyl and some polymers extrapolate to zero at about the same temperature⁵¹.

pressure history²⁹. This leads to the conclusion that the glass transition is accompanied by freezing-in or rearrangements of the intermolecular neighbour coordination. The conclusion agrees with the argument obtained by Roe and Tonelli⁵⁶ from the analysis of the increment of *C_p* at *T_g*. Therefore, the configurational quantities obtained from the excesses from the hypothetical crystal may be only conceptual.

As has been discussed in the preceding section, the superiority among the configurational entropy and energies depends significantly on their definition. Configurational quantities based on the experimental evidence are desirable in the present examination. Unfortunately, it seems very difficult to evaluate the numerical values of the quantities without the help of some statistical model of which appropriateness to the system rather than the appropriateness of the configurational variables may affect the result of the examination.

ACKNOWLEDGEMENT

We thank Professor Shigeyuki Ueda of this laboratory for his interest in this work and the encouragement he provided.

REFERENCES

- 1 Davies, R. O. and Jones, G. O. *Proc. R. Soc. London, A* 1953, **217**, 26; *Adv. Phys.* 1953, **2**, 370
- 2 DiMarzio, E. A. *J. Appl. Phys.* 1974, **45**, 4143; Goldstein, M. J. *Appl. Phys.* 1975, **46**, 4153; Gupta, P. K. and Moynihan, C. T. *J. Chem. Phys.* 1976, **65**, 4136
- 3 Nose, T. *Polym. J.* 1971, **2**, 445
- 4 O'Reilly, J. M. *J. Polym. Sci.* 1962, **57**, 429
- 5 Goldstein, M. J. *J. Chem. Phys.* 1963, **39**, 3369; *ibid.* 1965, **43**, 1852
- 6 Karasz, F. E., Bair, H. E. and O'Reilly, J. M. *J. Phys. Chem.* 1965, **69**, 2657
- 7 Gee, G. *Polymer* 1966, **7**, 177
- 8 Ichihara, S., Komatsu, A., Tsujita, Y., Nose, T. and Hata, T. *Polym. J.* 1971, **2**, 530; Ichihara, S., Komatsu, A. and Hata, T. *ibid.* 1971, **2**, 644, 650
- 9 Rao, K. J., Helphrey, D. B. and Angell, C. A. *J. Phys. Chem. Glasses* 1973, **14**, 26
- 10 Goldstein, M. J. *J. Phys. Chem.* 1973, **77**, 667
- 11 McKinney, J. E. and Goldstein, M. J. *Res. Natl. Bur. Stand. A* 1974, **78**, 331
- 12 Naoki, M. and Nose, T. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1747
- 13 Oels, H. J. and Rehage, G. *Macromolecules* 1977, **10**, 1036
- 14 Doolittle, A. K. *J. Appl. Phys.* 1951, **22**, 1471
- 15 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
- 16 Cohen, M. H. and Turnbull, D. *J. Chem. Phys.* 1959, **31**, 1164; Turnbull, D. and Cohen, M. H. *ibid.* 1961, **34**, 120
- 17 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139
- 18 Bestul, A. B. and Chang, S. S. *J. Chem. Phys.* 1964, **40**, 3731

- 19 Bondi, A. *J. Phys. Chem.* 1954, **58**, 929
- 20 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn., Wiley, New York, 1970
- 21 Greet, R. J. and Turnbull, D. *J. Chem. Phys.* 1967, **46**, 1243; *ibid.* 1967, **47**, 2185
- 22 McCall, D. W., Douglass, D. C. and Falcone, D. R. *J. Chem. Phys.* 1969, **50**, 3839
- 23 Chang, S. S. and Bestul, A. B. *J. Chem. Phys.* 1972, **56**, 503
- 24 Naoki, M. and Tomomatsu, T. *Macromolecules* 1980, **13**, 322
- 25 McKinney, J. E. and Belcher, H. V. *J. Res. Natl. Bur. Stand. A* 1963, **67**, 43
- 26 Miller, A. A. *Macromolecules* 1971, **4**, 757
- 27 Simha, R. and Boyer, R. F. *J. Phys. Chem.* 1962, **37**, 1003
- 28 Wunderlich, B. *J. Phys. Chem.* 1960, **64**, 1052; Wunderlich, B. and Jones, L. D. *J. Macromol. Sci. B* 1969, **3**, 67
- 29 Naoki, M., Mori, H. and Owada, A. *Macromolecules* 1981, **14**, 1567
- 30 O'Neill, M. J. *Anal. Chem.* 1966, **38**, 1331
- 31 Onodera, N., Kimoto, A., Sakiyama, M. and Seki, S. *Bull. Chem. Soc. Jpn.* 1971, **44**, 1463
- 32 Cutler, W. G., McMickel, R. H., Webb, W. and Scieszner, R. W. *J. Chem. Phys.* 1958, **29**, 727
- 33 Nanda, V. S. and Simha, R. *J. Chem. Phys.* 1964, **41**, 3870; Quach, A. and Simha, R. *J. Appl. Phys.* 1971, **42**, 4592
- 34 Simha, R., Wilson, P. S. and Olabisi, O. *Koll. Z. Z. Polym.* 1973, **251**, 402
- 35 Hellwege, K. H., Knappe, W. and Lehmann, P. *Koll. Z. Z. Polym.* 1963, **183**, 110
- 36 Sasabe, H. and Saito, S. *Polym. J.* 1972, **3**, 631
- 37 Hoffmann, R. and Knappe, W. *Koll. Z. Z. Polym.* 1970, **240**, 784
- 38 Dunlap, L. H., Foltz, C. R. and Mitchell, A. G. *J. Polym. Sci. A-2* 1968, **6**, 1297
- 39 Koppelman, J. and Gielessen, J. Z. *Elektrochem.* 1961, **65**, 689
- 40 Saito, S., Sasabe, H., Nakajima, T. and Yada, K. *J. Polym. Sci. A-2* 1968, **6**, 1297
- 41 Williams, G. and Watts, D. C. *Trans. Faraday Soc.* 1970, **66**, 80; Williams, G., Watts, D. C., Dev, S. B. and North, A. M. *ibid.* 1971, **67**, 1323; Williams, G., Cook, M. and Hains, P. J. *J. Chem. Soc. Faraday Trans. II* 1972, **68**, 1045
- 42 Williams, G. and Hains, P. J. *J. Chem. Phys. Lett.* 1971, **10**, 585; Shears, M. F. and Williams, G. *J. Chem. Soc. Faraday Trans. II* 1973, **69**, 608, 1050
- 43 Vogel, H. *Physik. Z.* 1921, **22**, 645
- 44 Fulcher, G. S. *J. Am. Chem. Soc.* 1925, **8**, 339
- 45 Tammann, G. and Hesse, W. *Z. Anorg. Allgem. Chem.* 1926, **156**, 245
- 46 Karasz, F. E., Couchman, P. R. and Klempner, D. *Macromolecules* 1977, **10**, 88
- 47 Johari, J. P. and Goldstein, M. J. *J. Chem. Phys.* 1970, **53**, 2372; *ibid.* 1971, **55**, 4245; Johari, J. P. *ibid.* 1973, **58**, 1766
- 48 Nanda, V. S. and Simha, R. *J. Phys. Chem.* 1964, **68**, 3158
- 49 Lennard-Jones, J. E. and Devonshire, A. F. *Proc. R. Soc. London A* 1937, **163**, 53; *ibid.* 1938, **165**, 1
- 50 Chang, S. S., Horman, J. A. and Bestul, A. B. *J. Res. Natl. Bur. Stand. A* 1967, **71**, 293; Chang, S. S. and Bestul, A. B. *ibid.* 1971, **75**, 113; *J. Chem. Phys.* 1972, **56**, 503
- 51 Miller, A. A. *Macromolecules* 1970, **3**, 675
- 52 Gibbs, J. H. and Dimarzio, E. A. *J. Chem. Phys.* 1958, **28**, 373, 807
- 53 Goldstein, M. J. *J. Chem. Phys.* 1976, **67**, 4767
- 54 Roe, R. J. and Tonelli, A. E. *Macromolecules* 1978, **11**, 114
- 55 Rowlinson, J. S. 'Liquids and Liquid Mixtures', 2nd Edn. Butterworths, London, 1971
- 56 Roe, R. J. and Tonelli, A. E. *Macromolecules* 1979, **12**, 878