polymer reviews

Thermodynamic functions of glass-forming systems and their dependence on cooling rate

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(Received 8 October 1990; accepted 17 December 1990)

Using the concepts of the thermodynamics of irreversible processes, the temperature dependence of the thermodynamic functions of glass-forming systems is investigated. A simple model is used to extrapolate the temperature dependence of the specific heat, of the thermodynamic potential and of the other thermodynamic functions of fictive undercooled melts below the glass transition temperature T_g. Expressions are derived for the dependence of T_g on cooling rate and thus for the change of thermodynamic functions of glasses vitrified at different cooling rates. Particular attention is given to the problem of maximum deviation from equilibrium in vitrified systems.

(Keywords: thermodynamics; glasses; frozen-in systems; cooling rate)

INTRODUCTION

Glasses and polymer glasses in particular are non-equilibrium systems. Their thermodynamic treatment requires a special approach—the introduction of frozen-in parameters of state. This is usually done in the framework of the thermodynamics of irreversible processes and by employing de Donder's concepts[1] of time- and temperature-dependent reaction coordinates ξ_i. The details concerning this approach are described elsewhere[2,3]. Its particular application to different aspects of the vitrification processes has been given in references 4–8.

In order to describe the structure or more generally the degree of order in a simple or polymer melt, a different number of reaction coordinates or parameters ξ_i can be used depending on the desired accuracy of description and on the complexity of the particular model used.

Besides one or more parameters portraying the topological order in the system, we have in general to introduce reaction coordinates connected with the possibility of chemical or molecular changes in the melt (e.g. temperature-dependent degree of polymerization, change of molecular composition, etc.) or corresponding to different states of mobility of its building units (e.g. rigidity or flexibility of chain-folding polymers). Experience obtained in recent years with more or less realistic lattice-hole models of vitrifying polymer melts[9–13] shows that in general three structural parameters are necessary to describe with sufficient accuracy the thermodynamic state of a simple or polymer glass-forming melt: one for the topological order (i.e. for the free volume of the system), one for the complexity of its building units (e.g. the degree of polymerization) and one for the probability of the system to exist in different conformations, which is determined by its flexibility. The use of more than one structural parameter is also a necessity in order to obtain a proper value for the so-called Prigogine–Defay ratio (see ref. 2 and analysis on this subject given in ref. 14).

In the present contribution we restrict our discussion to only one structural reaction parameter ξ, assuming, however, that it describes in some generalized way all the essential structural features and the whole configurational part of the partition function of a vitrifying melt. Let us also assume that ξ is defined in such a way that it varies from zero (complete configurational order) to unity (complete configurational disorder).

In this way a simple description of the metastable undercooled melt as well as of the frozen-in system (the glass) is possible and analytical expressions for the dependence of its thermodynamic properties on the cooling rate are easily achieved. A comparison with existing experimental evidence gives the possibility to determine the necessary constants appearing in the derived formulae.

STRUCTURAL PARAMETERS AND THERMODYNAMIC FUNCTIONS

In the framework of de Donder's method it is assumed that at equilibrium the structural parameter ξ is a single-valued function of state and that for every system with constant composition it is determined only by the temperature T (at constant pressure p), i.e.:

$$\xi = \xi(T)_p \tag{1}$$

In a similar way, at equilibrium every thermodynamic function χ (the enthalpy H, the entropy S, the thermodynamic potential G) of the melt (denoted by the subscript f) can be written in the form:

$$\chi_f = \chi(T, \xi)_p = \chi(T)_p \tag{2}$$

i.e. it turns out that at equilibrium χ depends only on T. The equilibrium value of ξ is determined from the condition for the minimum of the thermodynamic potential of the melt:

$$\left(\frac{\partial G_f(T,\xi)}{\partial \xi}\right)_{p,T} = 0 \qquad \left(\frac{\partial^2 G_f(T,\xi)}{\partial \xi^2}\right)_{p,T} > 0 \tag{3}$$

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0032-3861/92/030451-10

However, when the state of the melt is abruptly changed (e.g. by very fast cooling) its structure (i.e. ξ) cannot follow the alteration of the temperature. In such cases at lower temperatures the melt remains 'frozen-in' in a state of order or disorder:

$$\tilde{\xi} = \xi(\tilde{T}) \qquad (1a)$$

corresponding to the initial temperature $\tilde{T}$. For the non-equilibrium state thus obtained:

$$\left(\frac{\partial G_f(T,\xi)}{\partial \xi}\right)_{p,T} \neq 0 \qquad (4a)$$

and as long as for the frozen-in system ξ does not change with time t we have:

$$\left(\frac{\mathrm{d}\xi}{\mathrm{d}t}\right)_{T,p}\Bigg|_{T<\tilde{T}} \equiv \left(\frac{\mathrm{d}\tilde{\xi}}{\mathrm{d}t}\right)_{T,p} = 0 \qquad (4b)$$

The thermodynamic functions of the vitrified melt (i.e. the glass, denoted by the index g) become:

$$\chi_g = \chi(T, \tilde{\xi})_p \qquad (5)$$

i.e. they depend on the additional parameter $\tilde{\xi}$ and through it on the temperature $\tilde{T}$ (the so-called Tool's temperature^{15}), corresponding to the frozen-in structure of the melt.

In reality the freezing-in process of the melt takes place in a broad temperature interval. However, following Simon^{16} we can assume that at temperatures $T > T_g$ the undercooled melt behaves as a metastable system in internal equilibrium while for $T < T_g$ the melt is frozen-in to a glass. In the framework of such a simplified treatment it holds that $\tilde{T} = T_g$, where T_g is the conventional glass transition temperature.

In considering the thermodynamic properties of crystals (denoted in the following by the index c) we assume $\xi = \text{const} = 0$.

Using the notations given with equation (2) the total differential of any thermodynamic function χ of the melt becomes (at $p = \text{const}$):

$$\mathrm{d}\chi_f = \left(\frac{\partial \chi_f}{\partial T}\right)_{p,\xi} \mathrm{d}T + \left(\frac{\partial \chi_f}{\partial \xi}\right)_{T,p} \mathrm{d}\xi$$

Taking into account that for the crystal $\xi = 0$, the second term in the analogous expression for $\mathrm{d}\chi_c$ is zero.

Recalling that the definition of the specific heat of a system reads:

$$C_p = (\mathrm{d}H/\mathrm{d}T)_p$$

and accounting for the above considerations we have:

$$C_{p,f} = \left(\frac{\partial H_f}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H_f}{\partial \xi}\right)_{T,p} \frac{\mathrm{d}\xi}{\mathrm{d}T} \qquad (6a)$$

for the melt and:

$$C_{p,c} = \left(\frac{\partial H_c}{\partial T}\right)_{p,\xi} \qquad (6b)$$

for the crystal. The last equation defines in fact the crystal-like (phonon) part of the specific heat of our system ($C_{p,c} \simeq C_{p,\mathrm{ph}}$) (undercooled melt, glass or crystal) while the configurational part is given by the second term of equation (6a):

$$C_{p,\mathrm{config}}(T) = \left(\frac{\partial H_f}{\partial \xi}\right)_{T,p} \frac{\mathrm{d}\xi}{\mathrm{d}T} \qquad (7)$$

Thus we have:

$$C_{p,f}(T) = C_{p,\mathrm{ph}}(T) + C_{p,\mathrm{config}}(T) \simeq C_{p,c}(T) + \Delta C_p(T) \qquad (8)$$

where $\Delta C_p(T) \equiv C_{p,\mathrm{config}}(T)$.

Using well known formulae all thermodynamic functions of the melt can be obtained from the ΔC_p dependence by integration. With equation (8) the thermodynamic functions of the melt split into two parts:

$$\chi_f(T) = \chi_{f,\mathrm{ph}}(T) + \chi_{f,\mathrm{config}}(T) \simeq \chi_c(T) + \Delta\chi(T) \qquad (9a)$$

which correspond to the phonon and to the configurational part of the partition function of the system. In the following the notation:

$$\Delta\chi(T) \equiv \chi_{f,\mathrm{config}}(T) = \chi(\xi) \qquad (9b)$$

will be used.

The difference between the thermal expansion coefficients of the melt and of the crystal $\Delta\beta$ can be defined as:

$$\Delta\beta = \frac{1}{V}\left(\frac{\mathrm{d}\Delta V(T)}{\mathrm{d}T}\right)_p \cong \left(\frac{\mathrm{d}\theta(T)}{\mathrm{d}T}\right)_p \qquad (10)$$

Here $\Delta V(T) = V_f(T) - V_c(T)$ and accounting for the fact that this difference gives approximately the relative free volume θ of our system (i.e. assuming that $\Delta V/V \simeq \theta$) it is evident that equation (10) determines the temperature coefficient of the relative free volume of the melt. Applying a similar approach to that used for ΔC_p the configurational part of $\Delta\beta$ can be written in the form:

$$\Delta\beta_{\mathrm{config}} = \left(\frac{\partial \theta(T)}{\partial \xi}\right)_{T,p} \frac{\mathrm{d}\xi}{\mathrm{d}T} \qquad (11)$$

Upon vitrification it holds that:

$$\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_p\Bigg|_{T<\tilde{T}} \equiv \left(\frac{\mathrm{d}\tilde{\xi}}{\mathrm{d}T}\right)_p = 0 \qquad (12)$$

For temperatures $T < T_g$ from equations (7) and (11) it follows that:

$$C_{p,\mathrm{config}}(T) = \Delta C_p(T) = 0 \qquad (12a)$$

and

$$\Delta\beta_{\mathrm{config}}(T) \simeq 0$$

Considering equations (5) and (9) it is evident that upon vitrification the configurational part of any thermodynamic function is frozen in:

$$\Delta\chi(\xi)|_{T<\tilde{T}} = \Delta\chi(\tilde{\xi}) = \Delta\chi_g \qquad (13)$$

With equation (1a) the above relation shows that the dependence of $\Delta\chi_g$ on the cooling rate q (where $q = \mathrm{d}T/\mathrm{d}t$) can be constructed in every case where the $\Delta\chi(T)$ function of the undercooled melt in internal equilibrium is known for a known relation between the freezing-in temperature $\tilde{T}$ (or T_g) and q.

The construction of this $\Delta\chi_g(q)$ dependence is the main aim of the present contribution. It follows from equation (9) that the phonon part of the thermodynamic functions does not depend on q. Thus at temperature T the thermodynamic functions of any glass obtained under different cooling rates can be written in the form:

$$\chi_g(T) = \chi_{g,\mathrm{ph}}(T) + \Delta\chi_g(q) \qquad (14)$$

where the approximation $\chi_{g,\mathrm{ph}}(T) \simeq \chi_c(T)$ can be used. Particular attention in this respect is given to the course of the $\Delta S(T)$ function, as it is directly connected with the configurational structure of the vitrifying system.

Moreover, as shown in one of the following paragraphs, $\Delta S(T)$ also determines the rheological properties of the melt and thus the T_g vs. q dependence.

The temperature course of the configurational part of the thermodynamic potential $\Delta G(T)$ is also considered in detail, as it gives the most general measure for the non-stability of the vitrified frozen-in melt.

In constructing the thermodynamic functions of undercooled melts below T_g (i.e. for the fictive undercooled melt) we either have to use results obtained with more or less complicated statistical models or we have to extrapolate $\Delta\chi$ to $T\to 0$, relying on some suitable thermodynamic approximation. Such an approximation is introduced in the following.

A SIMPLE THERMODYNAMIC MODEL

The simplest temperature dependence of $\Delta C_p(T)$ of an undercooled melt leading to $\Delta\chi(T)$ functions, corresponding to the general requirements[17–19] of the thermodynamics of two coexisting phases in internal equilibrium, is:

$$\frac{\Delta C_p(T)}{\Delta S_m}=\begin{cases}\text{const}=a_0 & 1>x\geqslant x_0\\ 0 & x_0>x>0\end{cases} \qquad (15)$$

Here ΔS_m is the entropy of melting. The possibilities and limitation of this $\Delta C_p(T)$ function are discussed in detail in refs. 11 and 20. Accounting for this approximation and using well known thermodynamic relations, the following set of equations can be easily derived:

$$\frac{\Delta S(T)}{\Delta S_m}=\begin{cases}1+a_0\ln x\\ 0\end{cases} \qquad (16a)$$

$$\frac{\Delta H(T)}{\Delta S_m T_m}=\begin{cases}1-a_0(1-x)\\ 1-a_0(1-x_0)\end{cases} \qquad (16b)$$

$$\frac{\Delta G(T)}{\Delta S_m T_m}=\begin{cases}(1-a_0)(1-x)-a_0 x\ln x\\ (1-a_0)(1-x_0)-a_0 x_0\ln x_0\end{cases} \qquad (16c)$$

where $\Delta S_m T_m=\Delta H_m$ is the enthalpy of melting and x is the reduced temperature, i.e. the actual temperature divided by the temperature of melting T_m (i.e. $x=T/T_m$, $x_g=T_g/T_m$, etc.). The limits of validity of the top and bottom lines in equations (16) are the same as in equation (15). In the above approximations the ratio $\Delta C_p(T_m)/\Delta S_m=\Delta C_p(T_g)/\Delta S_m=a_0$ is a material constant depending on the structure and on the individual characteristics of the system. The value of x_0 can be determined from the condition $\Delta S(T_0)=0$ as being:

$$x_0=T_0/T_m=\exp(-1/a_0) \qquad (17)$$

In one of the following paragraphs it is shown that experimentally determined a_0 values are within limits from 1 to 2. For $a_0=1.0$, 1.5 and 2.0, equation (17) gives $x_0=0.37$, 0.51 and 0.6, respectively. A schematic representation of the temperature dependences following from equations (15) and (16) is shown in *Figure 1*.

Approximating the logarithmic function in equations (16) as $\ln x\simeq x-1$, equation (16c) can also be written in the form:

$$\frac{\Delta G(T)}{\Delta S_m T_m}\simeq\begin{cases}\dfrac{\Delta H(T)}{\Delta S_m T_m}(1-x) & 1>x\geqslant x_0\\[2ex] \dfrac{\Delta H(T)}{\Delta S_m T_m}(1-x_0) & x_0>x>0\end{cases} \qquad (18a)$$

where $\Delta H(T)/\Delta S_m T_m$ is given by equation (16b). It is also evident from equations (16a) and (16b) that in the framework of this approximation:

$$\frac{\Delta S(T)}{\Delta S_m}\simeq\frac{\Delta H(T)}{\Delta S_m T_m} \qquad 1>x\geqslant x_0 \qquad (18b)$$

In a similar way (see equation (15)) the temperature dependence of the thermal expansion coefficient can be approximated with a broken function, e.g. as:

$$\Delta\beta=\begin{cases}\text{const}=f_0 & 1>x\geqslant x_0\\ 0 & x_0>x>0\end{cases} \qquad (19)$$

Thus the temperature dependence of the relative free volume of the melt can be written in the form:

$$\theta(T)=\begin{cases}f_0T_m(x-x_0)\\ 0\end{cases} \qquad (20a)$$

The above dependence is also illustrated in *Figure 1d*. In drawing this diagram it has been assumed that x_0 is determined by the condition $\theta(T_0)=0$ and $\theta(T_m)=0.37$. The second assumption follows from the hole theory of liquids[11,20]. In the framework of the first assumption the constant in equation (19) turns out to be:

$$f_0=\frac{\theta(T_m)}{(1-x_0)}\frac{1}{T_m} \qquad (20b)$$

The second assumption specifies the value of f_0 to $f_0T_m\simeq 0.75$.

The simple approximation indicated with equations (15) is quite common for the temperature dependence of ΔC_p for a great number of simple and polymer glass-forming substances, as demonstrated by experimental ΔC_p data. An example in this respect is the case of glycerol (*Figure 2*) according to the classical measurements of Giauque[21] and Simon[16]. The temperature dependences ΔH, ΔS and ΔG for glycerol can be constructed from the $\Delta C_p(T)$ curve given in *Figure 2* as done by Simon[16,22] many years ago. The calculated temperature functions correspond exactly to the drawings given in *Figure 1*.

In other cases where an increasing or decreasing $\Delta C_p(T)$ course is observed in the T_m–T_g region (see the examples discussed in ref. 12) the approximation $\Delta C_p(T)\simeq$const can be introduced as a mean value for the temperature range T_m–T_0 assuming that:

$$\Delta S(T)=\int_0^{T_m}\frac{\Delta C_p(T)}{T}\mathrm{d}T$$

$$\simeq\int_{T_0}^{T_m}\frac{\Delta C_p(T)}{T}\mathrm{d}T\simeq\Delta C_p(T_g)\int_{T_0}^{T_m}\frac{\mathrm{d}T}{T}$$

The right-hand side of the above equation, which is only valid for $\Delta C_p=$const, gives directly equation (17). The structural significance of different $\Delta C_p(T)$ dependences has already been discussed in the framework of existing lattice-hole models of simple and polymer melts[11,17,23].

KINETICS OF VITRIFICATION

The kinetics of the vitrification process is determined by the Frenkel–Kobeco[24–26] relation, which connects q and $\tilde{T}$ (or q and T_g):

$$q\tau(T)|_{T\to\tilde{T}}=\text{const}=c_0 \qquad (21)$$

Here $\tau(T)$ is the molecular relaxation time of the melt

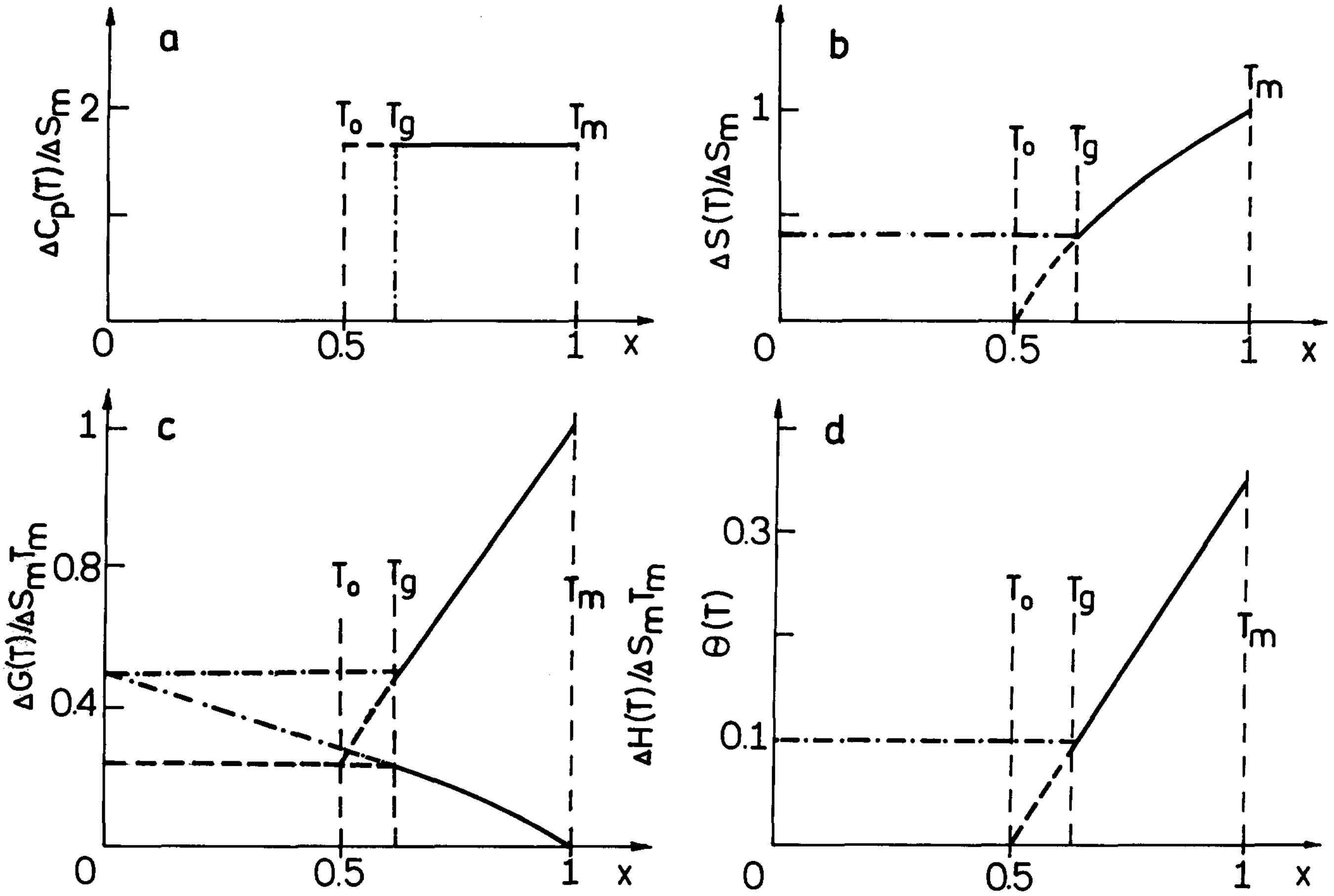

Figure 1 Temperature dependence of the configurational part of the thermodynamic functions at $a_0 = 1.5$ according to equations (15) and (16): (a) specific heats; (b) entropy; (c) free energy and enthalpy; (d) relative free volume. Full bold lines, undercooled melt; broken bold lines, fictive undercooled melt below T_g; chain bold lines, vitrified melt

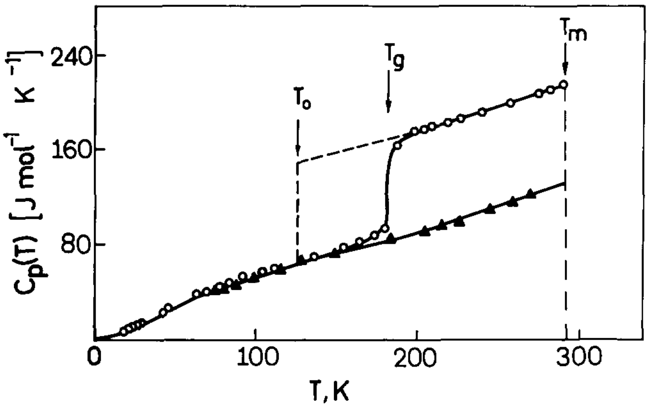

Figure 2 The temperature dependence of the specific heats of glycerol. Open circles: from T_m to T_g, undercooled melt; below T_g, vitrified melt. Full triangles: crystal; experimental data after Giauque[21] and Simon[16]. T_0 is calculated according to equation (17)

and the constant c_0 is assumed to be nearly equal to unity[26]. Equation (21) follows from very general considerations. Its derivation has been given by Volkenstein and Ptizyn[27] in the framework of a kinetic model of vitrification with two energetic levels.

Different temperature functions can be used in order to describe the temperature dependence of the relaxation time of a vitrifying melt. Usually the temperature course of $\tau(T)$ is presented in terms of an Arrhenius dependence:

$$\tau = \tau_0 \exp\left(\frac{U(T)}{RT}\right) \tag{22}$$

where τ_0 is the time of eigenvibrations of the building units of the melt. For τ_0 a nearly constant value equal to 10^{-12}–10^{-13} s can be expected for simple and polymer melts. Assuming $U(T) = U_0 = \text{const}$ and introducing equation (22) into equation (21), the well known Bartenev–Ritland equation[20,24] follows:

$$1/T_g = c_1 - c_2 \log q \tag{23}$$

where $c_1 = c_2 \log(c_0/\tau_0)$ and $c_2 = 2.3R/U_0$. Experimental data reported by Bartenev[26] give $c_0 \simeq 5$ K for practically all glass-forming systems. Thus $\log(c_0/\tau_0) \simeq 12$–$13$ can be accepted as a possible estimate.

The applicability of equation (22) with $U_0 = \text{const}$ is restricted only to small temperature intervals. We prefer here another expression for the temperature dependence of the molecular relaxation time which can be applied to the whole temperature interval from T_m to T_g (ref. 28). According to ref. 28 the relation connecting $\tau(T)$ and the configurational entropy $\Delta S(T)$ of the melt reads:

$$\tau = \tau_0 \exp\left(\frac{B_0 \Delta S_m}{\Delta S(T)}\right) \tag{24}$$

This equation follows readily from Doolitle's formula:

$$\tau = \tau_0 \exp\left(\frac{b_0}{\theta(T)}\right) \tag{24a}$$

connecting τ (or the viscosity η) with the relative free volume $\theta(T)$ of the melt. In terms of the mean-field approximation (m.f.a.) of lattice-hole models of liquids the dependence of $\Delta S(T)$ on θ can be written to give:

$$\Delta S(T) = -R\left(\frac{\theta}{1-\theta}\ln\theta + \ln(1-\theta)\right) \qquad (25)$$

For θ values that are of interest here (that is to say from $\theta(T_0)=0$ to $\theta(T_m)=0.37$ where according to equation (25) $\Delta S(T) \simeq R$ which in m.f.a. models corresponds to the melting point) equation (22) can be approximated[20] by $\Delta S(T) \simeq 3R\theta$.

Following such a derivation, which has been made by Gutzow in 1975[29] (more recently a similar result has also been obtained by Ramachandrarao *et al.*[30]), equation (24) is readily obtained from equation (24a). The similarity (but also the difference) of equation (24) and an expression due to Adams and Gibbs[31] is also obvious.

In terms of Doolitle's equation the factor in equation (24) is a constant $B_0 = 3b_0$. It depends on the nature and the complexity of the building units of the melt. For simple (non-associated melts) $b_0 \simeq 1$ is to be expected. The activation energy $U(T)$ in equations (22)–(24) is given by the relation:

$$U(T) = 2.3R\frac{\mathrm{d}(\log\tau)}{\mathrm{d}(1/T)} = B_0\Delta C_p(T)RT\frac{1}{\Delta S^2(T)} \qquad (26)$$

Combining equations (21) and (24) and expressing $\Delta S(T)$ by equation (16a) (for T_g values higher than T_0) we have:

$$\ln x_g = -(1/a_0)z \qquad (27a)$$

where

$$z = \left[1 - \frac{3b_0}{2.3}\left(\frac{1}{\log(c_0/\tau_0) - \log q}\right)\right] \qquad (27b)$$

As long as it can be taken that $\ln x_g \simeq x_g - 1$ and if $(1-a_0) \ll a_0 x_g$ equation (27) can be written to give in analogy to the Bartenev–Ritland equation:

$$T_m/T_g \simeq c_1' - c_2' \log q \qquad (23a)$$

where, however, $c_2' = 2.3a_0/3b_0$ and $c_1' = c_2' \log(c_0/\tau_0)$. The x_g vs. q dependence according to equation (27) is illustrated in *Figure 3* for different a_0 and b_0 values and for the already mentioned value of $\log(c_0/\tau_0)$.

Equation (27) indicates that to every q value there corresponds a different $\tau(T_g)$ value. However, if vitrification is performed under standardized conditions (e.g. at cooling rates $q = 10^0$ to $10^2\ \mathrm{K\,s^{-1}}$, as used in the case of typical glass-formers) the molecular relaxation time should have a nearly constant value (for the mentioned standard cooling rates $\tau(T_g) \simeq 10^2\ \mathrm{s}$). Accounting for equation (17) we can write equation (27) in the form:

$$x_g = [\exp(-1/a_0)]^z = x_0^z \qquad (28a)$$

From equations (27) and (28) it is obvious that z can be determined from the slope of the $\log(T_g/T_m)$ vs. $\Delta S_m/\Delta c_p$ dependence and that the factor b_0 can be evaluated according to:

$$b_0 = \frac{2.3}{3}(1-z)\left[\log\left(\frac{c_0}{\tau_0}\right) - \log q\right] \qquad (28b)$$

It is also evident that two structural parameters appear in equation (28): a thermodynamic one (a_0) determining the temperature dependence of the configurational part of the thermodynamic function (cf. equations (15) and (16)) and a kinetic one (b_0) determined by the rheological behaviour of the system and by the complexity of the rheological unit taking part in the flow process. It is obvious that for substances with similar structures (i.e. as long as a_0 and b_0 can be considered as having nearly constant values) and for standard cooling rates ($\log q \simeq$ const, cf. equations (27a) and (28)) it is to be expected in accordance with the Beaman–Kauzmann rule that:

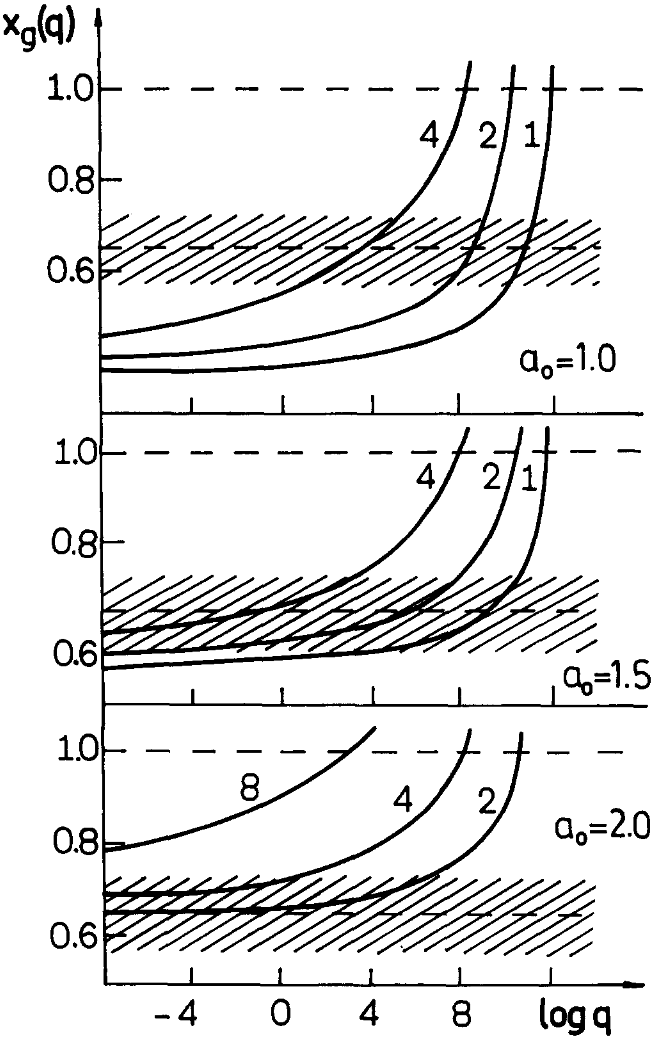

Figure 3 Dependence of the reduced temperature of vitrification $x_g(q)$ on cooling rate q according to equations (27). Different values of the thermodynamic parameter a_0 are indicated on the right-hand side of each triad of curves and b_0 is given as a parameter on each curve. Shaded area: the most probable T_g/T_m value and standard deviation from it for typical glass-formers (cf. *Figure 8*)

$$T_g/T_m = x_g \simeq \mathrm{const}_1 \qquad (29a)$$

Using equation (29a) to express T_m in equations (19) and (20), another empirical rule proposed years ago by Boyer and Simha[32] (see also ref. 33) can be derived:

$$\Delta\alpha T_g = \frac{\theta(T_m)}{(1-x_0)}\frac{\mathrm{const}_1}{3} = \mathrm{const}_2 \qquad (29b)$$

where $\Delta\alpha \simeq \Delta\beta/3$ is the coefficient of linear thermal expansion. However, we have to keep in mind that the above rules (equations (29)) connecting the thermodynamic constants of the system (T_m, $\Delta\beta$) with the kinetic characteristics of the vitrification process are only applicable for glasses obtained at standardized or nearly equal cooling rates.

THERMODYNAMIC FUNCTIONS OF THE VITRIFIED MELT

According to the formalism developed in the earlier sections, we have to expect that below the respective vitrification temperature the values of ΔC_p and $\Delta\beta_0$ drop to zero (cf. equations (7), (11) and (12)). According to equation (13) for the thermodynamic functions of glass we have:

$$\Delta S(T)|_{T<\tilde{T}} = \Delta S(\tilde{\xi}) = \Delta S_g = \text{const} \tag{30a}$$

$$\Delta H(T)|_{T<\tilde{T}} = \Delta H(\tilde{\xi}) = \Delta H_g = \text{const} \tag{30b}$$

$$\Delta\theta(T)|_{T<\tilde{T}} = \Delta\theta_g = \text{const} \tag{30c}$$

By introducing equations (30a) and (30b) into the well known formula:

$$\Delta G(T) = \Delta H(T) - T\Delta S(T) \tag{31}$$

the thermodynamic potential difference of the frozen-in melt becomes:

$$\Delta G(T)|_{T<\tilde{T}} = \Delta H_g - T\Delta S_g \tag{32}$$

The last dependence shows that for every glass irrespective of the particular value of $\tilde{\xi}$ (i.e. irrespective of the particular frozen-in temperature and the corresponding cooling rate) we always have to expect a linear increase of ΔG_g with falling temperature ($\mathrm{d}\Delta G_g/\mathrm{d}T = -\Delta S_g$). In defiance of the third law of thermodynamics this temperature dependence of $\Delta G_g(T)$ of the frozen-in system is expected to be valid even when zero temperatures are approached; at $T \to 0$ we have:

$$\Delta G_g(T)|_{T\to 0} = \Delta H_g$$

In order to determine the desired dependences of ΔS_g, ΔH_g and ΔG_g on the cooling rate q we have to introduce x_g through equations (27) and (28) into our thermodynamic model, defined with equations (15), (16) and (20a). In this way we obtain the following $\Delta\chi_g(q)$ dependences:

$$\frac{\Delta S_g(q)}{\Delta S_m} = \begin{cases} 1 - z \\ 0 \end{cases} \tag{33a}$$

$$\frac{\Delta H_g(q)}{\Delta S_m T_m} = \begin{cases} 1 - a_0(1 - x_0^z) \\ 1 - a_0(1 - x_0) \end{cases} \tag{33b}$$

$$\Delta\theta_g(q) = \begin{cases} f_0 T_m(x_0^z - x_0) \\ (1 - a_0)(1 - x_0) \end{cases} \tag{33c}$$

Proceeding in the same manner and using for $\Delta G_g(T)$ the approximate expression (18a) it follows that:

$$\frac{\Delta G_g(T)}{\Delta S_m T_m} = \begin{cases} (1 - a_0)(1 - x_0^z)(1 - x) \\ (1 - a_0)(1 - x_0) \end{cases} \tag{34}$$

The value of z and its dependence on q is defined by equation (27); the upper line in the above relations is valid in the limits $1 > x_g > x_0$. At infinitely slow cooling rates ($q \to 0$) according to equation (27) $z \to 1$ and equation (28) gives $x_g \to x_0$ and the bottom line of the corresponding equations has to be used. At $\log q = \log(c_0/\tau_0) - 3b_0/2.3$ it is expected that $x_g \to 1$ (cf. equation (23a)).

The maximal cooling rate that is physically permissible according to the discussed model is $\log q = \log(c_0/\tau_0)$. This maximal cooling rate corresponds to the velocity of eigenvibrations of the building units of the melt and it exceeds by several orders of magnitude the possibilities even of present-day splat cooling techniques ($q \simeq 10^5$ to $10^8\,\mathrm{K\,s^{-1}}$).

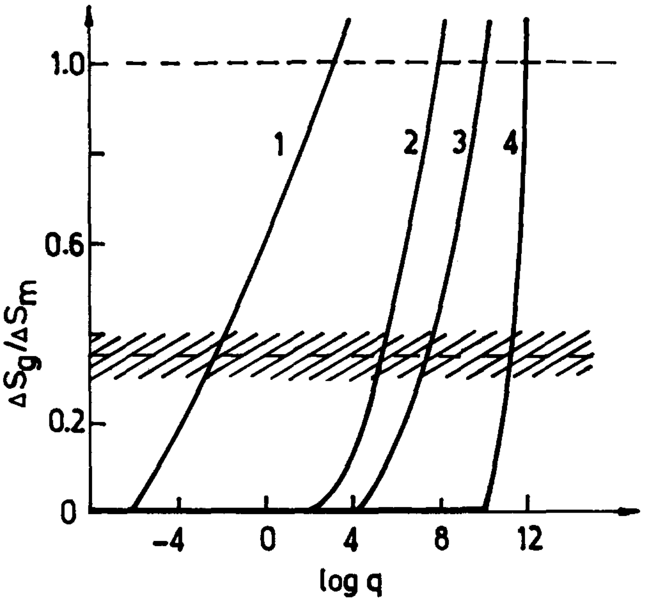

Figure 4 Configurational entropy of frozen-in glasses, obtained at different cooling rates q according to equations (27a) and (33a). Each curve corresponds to a distinct b_0 value indicated as a parameter; curve 1, $b_0 = 8$; curve 2, $b_0 = 4$; curve 3, $b_0 = 2$; curve 4, $b_0 = 1$. For all curves $\log(c_0/\tau_0) = 13$. Shaded area around dashed line is the most probable experimental $\Delta S_g/\Delta S_m$ value and the deviation from this value(cf. *Figure 10*)

The $\Delta S_g(q)$ dependence following from equations (27b) and (33a) is illustrated in *Figure 4* for different b_0 values. In a similar way *Figure 5* gives the $\Delta H_g(q)$ and $\Delta G_g(q)$ diagrams for two a_0 values according to equations (33b) and (34). A coincidence of the $\Delta H_g(q)$ and $\Delta G_g(q)$ curves can be expected only at $q \to 0$. The $\Delta G_g(T)$ curves in this figure are drawn defining the x value in the round brackets in equation (34) as $x = x_g(q)$.

Finally *Figure 6* drawn according to equation (34) illustrates the temperature dependence of $\Delta G_g(T)$ for several glasses vitrified at different cooling rates, indicated as the respective $\log q$ value on each curve (again for two a_0 values). In this way the influence of cooling rate on the possible deviation of the frozen-in system from equilibrium is easily demonstrated.

It is also to be noted here that in the framework of the above simplified model description the influence of the cooling rate on ΔC_p is manifested as a shift of the vertical line indicating T_g on the $\Delta C_p(T)$ dependence (the chain line in *Figure 1a*). The dependence of this shift on q is again determined by equation (27).

Equations (33) and (34) and *Figures 4*, *5* and *6* show that similar $\Delta\chi(q)$ dependences are to be expected at every pair of a_0 and b_0 values. The nature of the rheological processes in glass-forming melts and especially their exponential temperature dependence (equations (22) and (24)) restricts the influence of cooling rate q on the value of the thermodynamic properties of glasses to the logarithmic function, which according to equation (27) determines z and in this way the value of $\Delta\chi$. It is evident that only significant changes in q can measurably affect the structure and the thermodynamic properties of the frozen-in glass. This also explains the relative reproducibility of the thermodynamic characteristics and of the structure of glasses obtained even under seemingly different conditions.

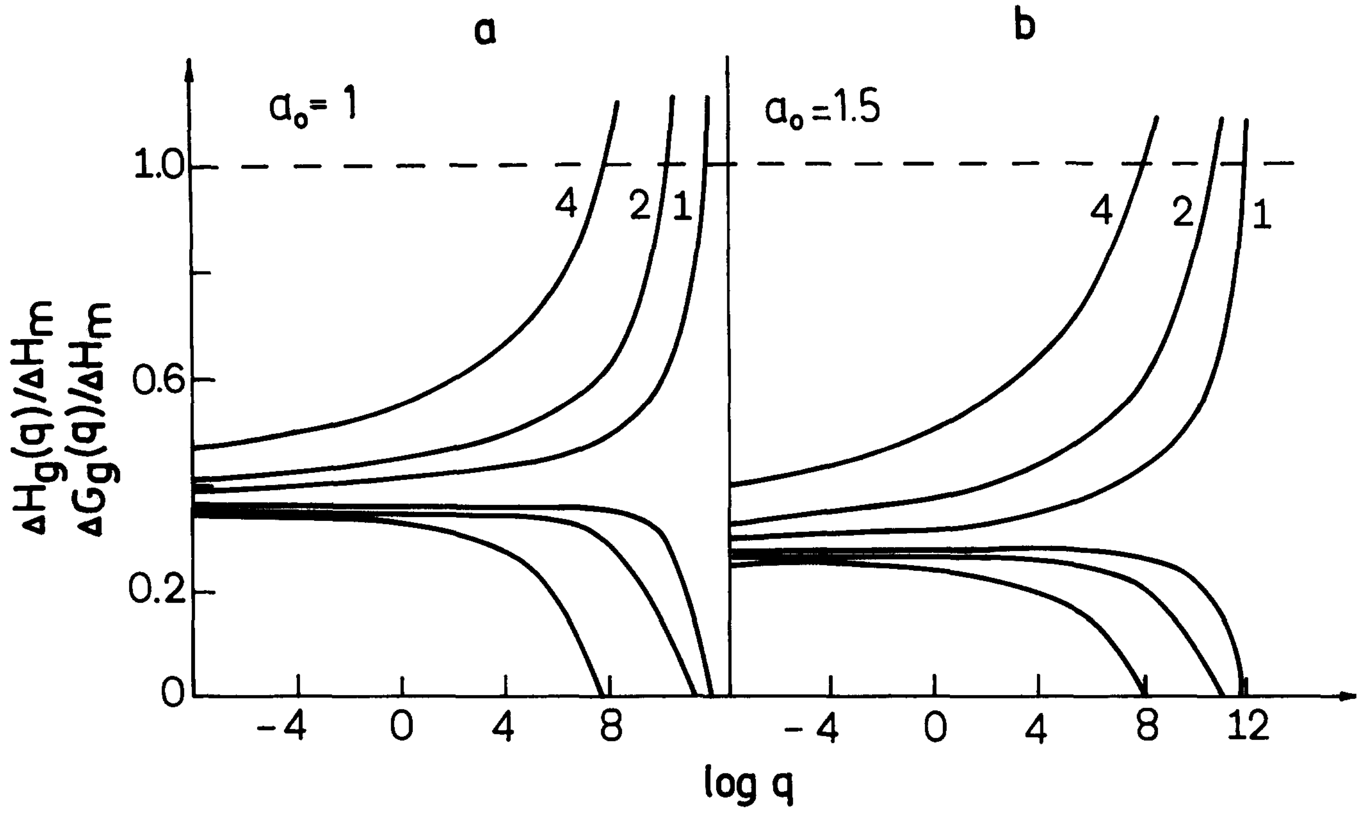

Figure 5 Enthalpy (upper curves) and free energy (lower curves) diagrams for two vitrifying systems according to equations (33b) and (34) with thermodynamic structural factor $a_0 = 1$ and $a_0 = 1.5$, respectively. The value of b_0 corresponding to each curve is indicated as a parameter

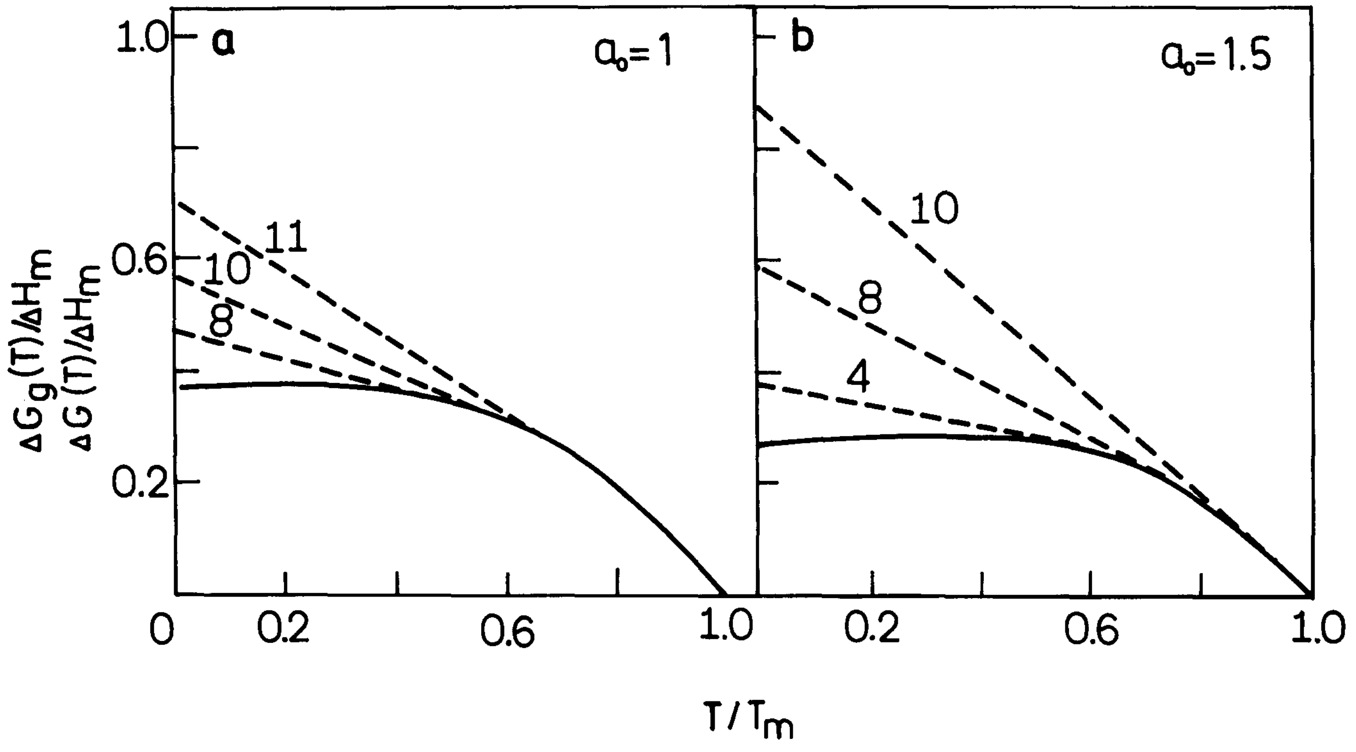

Figure 6 Possible deviations from equilibrium in two glass-forming systems (with $a_0 = 1$ and $a_0 = 1.5$) vitrified at different x_g values at different cooling rates q according to equation (28a). Full curves: $\Delta G(T)$ at equilibrium. Broken lines: $\Delta G_g(T)$ dependences according to equation (34) for different $\log q$ values (indicated as a parameter)

However, the above dependences and *Figures 3*, *4* and *5* also show that for every structural class of glass-forming melts (i.e. for every pair of a_0 and b_0 values) there is a range of critical cooling rates q where an almost linear dependence of the $\Delta\chi(q)$ function on $\log q$ is observed. For higher b_0 values this is the range of 'normal' cooling rates ($q = 10^0$ to $10^2\,\mathrm{K\,s^{-1}}$); for $b_0 \simeq 1$ to this range corresponds the interval of q values realized at the extreme conditions of splat cooling experiments ($q = 10^6$–$10^8\,\mathrm{K\,s^{-1}}$).

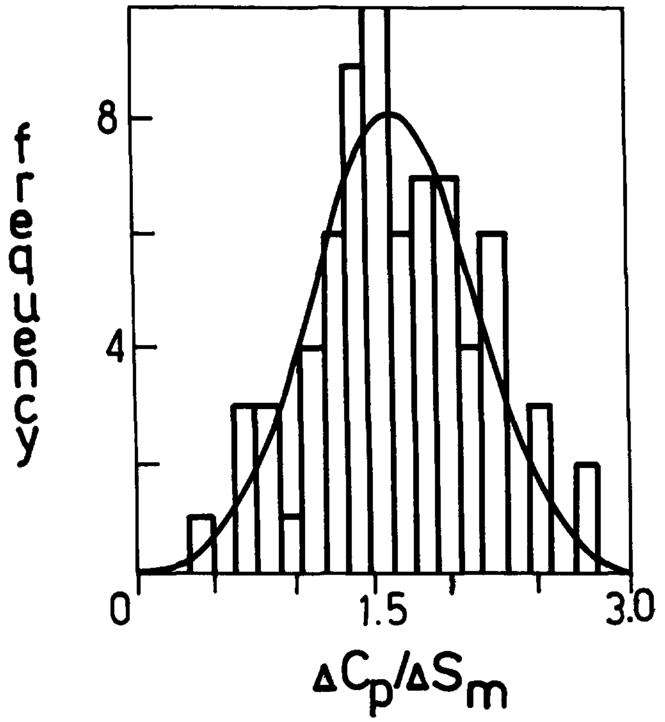

Figure 7 Frequency distribution histogram of experimental $\Delta C_p/\Delta S_m$ values for 22 typical glass-formers (see text) vitrified at approximately standard cooling rates (median value 1.56); experimental data after refs. 12, 20 and 34–36

The above figures show also that, at cooling rates below the respective critical limits, no vitrification takes place and even equilibrium $\Delta\chi$ values corresponding to the metastable melt can be reached.

COMPARISON WITH EXPERIMENTAL DATA

Now we have to determine the values of the constants appearing in the above theoretical derivations from existing experimental data. The comparison with experimental evidence also gives a possibility of verifying some of the assumptions made.

The values of the ratio $\Delta C_p/\Delta S_m = a_0$ for typical glass-forming substances are summarized in *Figure 7* as they are given in existing critical surveys[12,20,34–36]. The resulting frequency distribution histogram shows that the most probable value of this ratio is $a_0 = 1.56$. Practically all simple and polymer glass-forming melts for which the respective calorimetric measurements have been performed are included. The substances summarized in *Figure 7* are representatives of different types of glass-forming melts: oxides (SiO_2, B_2O_3), halides (BeF_2, $ZnCl_2$), simple borate, silicate and phosphate glasses (e.g. $Na_2B_4O_7$, Na_2SiO_3, $NaPO_3$, etc.), elementary glasses (Se), glass-forming organic compounds (e.g. CH_3OH, C_2H_5OH, glycerol, etc.), organic acids and oxyacids as well as a number of more complicated aromatic organic substances (phenolphthalein, α-naphthylbenzene, etc.) The a_0 values for all organic polymer glasses, as they are given in ref. 36, are also accounted for.

The universal value of $\Delta C_p(T_g)/\Delta S_m \simeq 1.5$ for typical glass-formers has been mentioned also by previous authors[34]. However, it is to be noted that a closer examination of the existing experimental data shows that for another class of materials, metal glass-forming alloys[37] as well as halide substances[38], $a_0 \simeq 1$ should be taken as the most representative value while for organic high polymers $a_0 = 2$ is very common[36]. These representative values of the thermodynamic structural factor have been used in the already discussed *Figures 4, 5* and *6*.

The T_g/T_m values for 108 substances are summarized in *Figure 8*. All substances given in *Figure 7* are included in this figure too. The median value of the T_g/T_m frequency distribution histogram specifies in accordance with the Beaman–Kauzman rule[20] the constant in equation (29) to $\text{const}_1 = 0.65$.

All substances given in *Figures 7* and *8* have one common feature: they are to be considered as typical glass-formers in the sense that they vitrify at 'normal' cooling rates. The z factor for the same substances, calculated according to equation (27a) with the mentioned values for a_0 and T_g/T_m, is equal to $z = 0.7$ (*Figure 9*). Using equation (28b) and the mentioned 'normal' values of c_0, τ_0 and q it turns out that for typical glass-formers $b_0 = 2$ to 3 has to be expected for the kinetic factor.

With the mentioned median values of a_0 and T_g/T_m, equation (16a) gives $\Delta S_g/\Delta S_m = 0.35$ for the entropy, frozen-in at 'normal' conditions. The experimental $\Delta S_g/\Delta S_m$ values summarized in *Figure 10* according to the data given elsewhere[12,19,20,35,36] indicate that the most probable value $\Delta S_g/\Delta S_m = 0.37$ has to be expected. A similar coincidence between $\Delta\chi_g$ values calculated according to our model and experimental evidence is also found for the value of the frozen-in enthalpy. According to equation (16b) with $a_0 = 1.56$ and $T_g/T_m = 0.65$ the value of $\Delta H_g/\Delta H_m$ is equal to 0.52. From 20 experimental determinations[19,20] we find $\Delta H_g/\Delta H_m = 0.48$ as a mean value.

Finally let us note that the most probable value of $\Delta\alpha T_g$ (equation (29b)) is calculated to be 0.15 using the above-mentioned values of a_0 (resp. x_0), $\theta(T_m)$ and const_1.

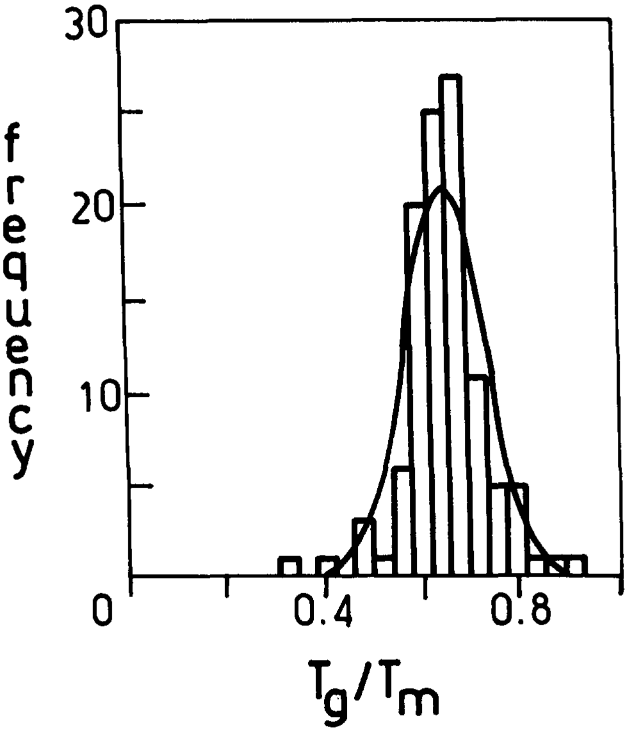

Figure 8 Frequency distribution histogram of experimental T_g/T_m values for typical glass-forming substances vitrified at normal cooling rates (108 entities, median value 0.65 with standard deviation $\Delta\sigma = 0.08$); experimental data after refs. 12, 19, and 36

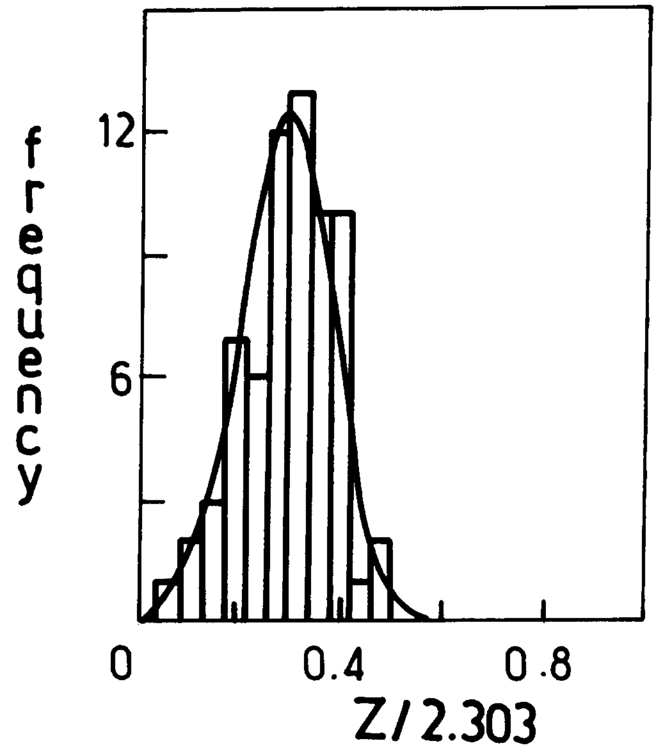

Figure 9 Frequency distribution histograms of z values calculated from $\Delta C_p(T_g)/\Delta S_m$ and T_g/T_m (cf. *Figures 7* and *8*) according to equation (27a) (67 entities, median value $z/2.303=0.3$, $\Delta\sigma=0.08$)

Thus the calculated value is very close to the experimental evidence ($\Delta\alpha T_g=0.11$, after Boyer and Simha[32]).

In this way the foregoing analysis and comparison with experimental data allows us to formulate the following simple rules for the most probable values of the thermodynamic functions of typical glass-forming systems vitrified at 'normal' conditions:

$$T_g/T_m \simeq 2/3 \qquad T_0/T_m = x_0 \simeq 1/2 \tag{35a}$$

$$\Delta C_p/\Delta S_m = a_0 \simeq 3/2 \qquad \Delta\alpha T_g \simeq 1/8 \tag{35b}$$

$$\Delta S_g/\Delta S_m \simeq 1/3 \tag{35c}$$

$$\Delta H_g/\Delta H_m \simeq 1/2 \tag{35d}$$

Accounting for equations (35), equation (32) can be written in the form:

$$\frac{\Delta G_g(T)}{\Delta S_m T_m} = \frac{1}{2} - \frac{1}{3}x \tag{36}$$

For such substances equation (27b) transforms into (with $b_0 \simeq 2$–3):

$$z = 1 - [13 - \log q]^{-1} \tag{37}$$

and in this way using equations (28), (33) and (34) the dependences of T_g, ΔS_g, ΔH_g, $\Delta\theta_g$ and ΔG_g on cooling rate q can be simply evaluated.

The values given above apply only to typical glass-formers including organic polymers. For substances that vitrify only at extreme cooling rates (e.g. metallic alloys halides[38]) the following set of rules can be recommended:

$$T_g/T_m \simeq 1/2 \qquad T_0/T_m = x_0 \simeq 1/3 \tag{38a}$$

$$\Delta C_p/\Delta S_m = a_0 \simeq 1 \qquad \Delta\alpha T_g \simeq 1/10 \tag{38b}$$

$$\Delta S_g/\Delta S_m \simeq 1/3 \tag{38c}$$

$$\Delta H_g/\Delta H_m \simeq 1/2 \tag{38d}$$

for the most probable values of the thermodynamic functions of such substances vitrified at conditions 'normal' for them (e.g. at $q=10^6$–$10^8\,\mathrm{K\,s^{-1}}$; cf. *Figures 4* and *5*). The above dependences follow from experimental evidence collected by Davies[4], Battezatti[37] and Gutzow *et al.*[19]. Considering equations (38c,d) it is obvious that equation (36) can be used also for metallic alloy systems. In this way for metallic alloy systems we calculate $z \simeq 0.6$ and $b_0 \simeq 1$ using equations (27a) and (28b), respectively. For the dependence of z on q it holds:

$$z = [1 - 1.5(13 - \log q)^{-1}] \tag{39}$$

The values of a_0 and b_0 obtained here for both groups of glass-forming substances are very reasonable. For more complex structures, higher a_0 values should be expected; and for metallic and halide melts, it is to be anticipated that only one structural unit determines the flow process (i.e. $b_0 \simeq 1$).

Finally let us note that the curves drawn through the frequency distribution histograms (*Figures 7–10*) are the respective Gaussian curves. They give an indication of the extent to which the scatter in experimental values can be treated as a sequence of chance deviations (caused by different cooling rates) from a single most probable value.

DISCUSSION

Equation (36) gives the possible deviation from equilibrium that should be expected in a glass frozen-in under conditions 'normal' for its preparation. From equation (36) it is evident that the maximal value of $\Delta G_g(T)/\Delta S_m T_m$ that can be obtained by vitrification (at $T \to 0$) is approximately equal to $0.5\Delta S_m T_m$.

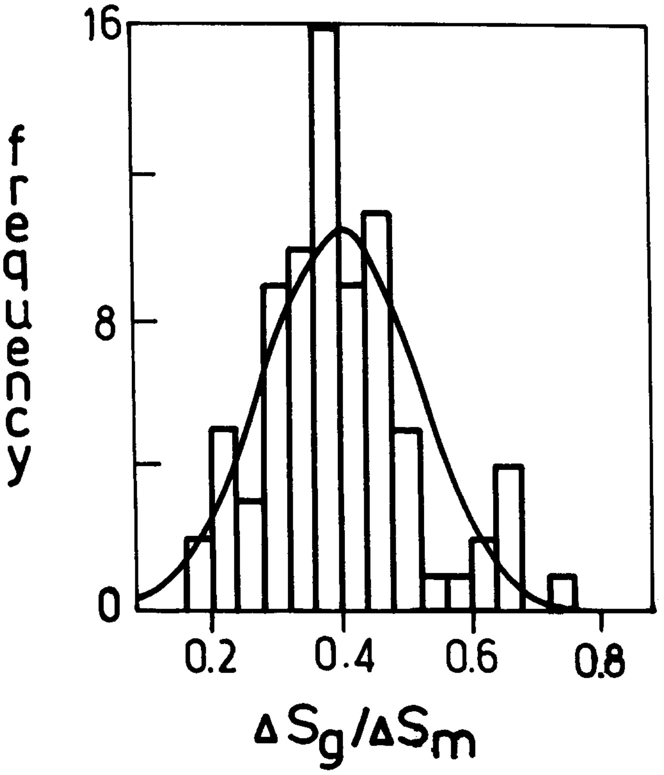

Figure 10 Frequency distribution histogram of configurational entropy, frozen-in in typical glass-formers (see text) (79 entities with median value of 0.37 and a standard deviation $\Delta\sigma=0.15$; experimental data are taken after refs. 12, 19, 20, 35 and 36

The dependence of the thermodynamic functions of a vitrified melt on cooling rate is given by equations (33) and (34). In these equations the factor z can be evaluated as a function of the cooling rate using either equation (37) for typical glass-formers or equation (39) for systems having $b_0 \simeq 1$.

It turns out that at cooling rates normal for a given system similar $\Delta S_g/\Delta S_m$, $\Delta H_g/\Delta S_m T_m$ and $\Delta G_g/\Delta S_m T_m$ values are obtained. The limits of possible deviations from these values are given by the standard deviation $\Delta\sigma$ of the existing experimental values (cf. the $\Delta\sigma$ values in *Figures 7* to *10*). These possible deviations are indicated by the shaded area in *Figures 3*, *4* and *5*.

The possibilities for obtaining glasses with thermodynamic properties substantially different from those obtained by the usually applied methods are evident from equations (33) and (34) and from *Figures 4*, *5* and *6*.

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