Use of the Adam-Gibbs Equation in the Analysis of Structural Relaxation

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Narayanaswamy's model of structural relaxation has been shown to provide an excellent description of the behavior of a variety of glasses. In the standard formulation, the relaxation time, τ, is represented by the Arrhenius equation, with the activation energy partitioned between the temperature and fictive temperature. That form for τ is successful, but lacks theoretical justification. In this paper, the Adam-Gibbs equation is shown to describe accurately both τ and the viscosity of NBS 710 (alkali lime silicate) glass. This equation is expected to be accurate over a wider range of temperature and fictive temperature than the Arrhenius equation.

I. Introduction

WHEN a liquid is cooled into the glass-transition region, its properties become time-dependent because the time required for rearrangement of the molecular structure is similar to the duration of a typical experiment. The gradual approach of the properties to their equilibrium values is known as structural relaxation.* This subject has received considerable theoretical and experimental attention in recent years. In a classic paper, Narayanaswamy[1] presented a phenomenological theory that has been notably successful in describing the structural relaxation

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*The term "physical aging" is sometimes used, but this may also be applied to cases of chemical attack, devitrification, and other types of degradation. We prefer the unambiguous and appropriate expression "structural relaxation."
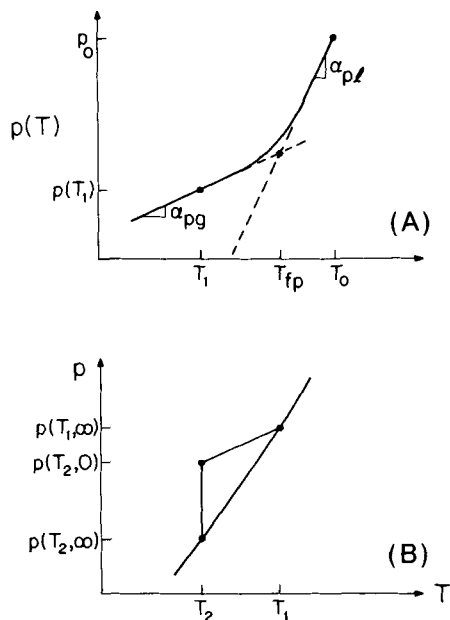

Fig. 1. (A) Temperature dependence of property p of glass-forming liquid; $\alpha_{pl} = dp/dT$ for equilibrium liquid; $\alpha_{pg} = dp/dT$ for glass; T_{fp} is fictive temperature for property p. (B) Variation of property p following equilibration at temperature T_1 and sudden change to T_2: $p(T_2,0) - p(T_1,\infty) =$ instantaneous response; $p(T_2,\infty) - p(T_2,0) =$ delayed, structure-dependent response.

behavior of a variety of materials.[2,3] The present paper concerns the mathematical form for the relaxation time to be used in Narayanaswamy's model. To date, most authors have used the Arrhenius equation, but the way in which it has been used lacks theoretical justification. We will show that, on theoretical and practical grounds, the Adam-Gibbs[4] equation is the most satisfactory expression available.

In the next section, the Narayanaswamy model is presented, along with the expressions for the relaxation time that have been considered previously. The Adam-Gibbs (AG) expression is compared with the others and, in Section III, it is applied to data for NBS 710 glass. Section IV provides a discussion of structural relaxation at large departures from equilibrium.

II. Form of $\tau(T, T_f)$

Figure 1 shows the evolution of some property, p, of a liquid as it is cooled through the glass transition. At low temperatures, the temperature dependence is governed by the vibrations of the atoms which are frozen into a fixed arrangement; the slope of the curve in that glassy region is $dp/dT = \alpha_{pg}$. Above the transition region, there is an additional contribution to $p(T)$ as the mobility of the atoms permits rearrangements of the structure; in the liquid, $dp/dT = \alpha_{pl}$ and the difference, $\alpha_{ps} = \alpha_{pl} - \alpha_{pg}$, is the structural contribution to the temperature dependence of the property. The fictive temperature, T_{fp}, is defined as the intersection of the extrapolations of the liquid and glass curves, as shown in Fig. 1(A). We can write the property of a glass in terms of its fictive temperature as follows:

$$p(T_1) = p_0 + \alpha_{pl}(T_{fp} - T_0) + \alpha_{pg}(T_1 - T_{fp}) \tag{1}$$

This means that the value of p is the same as that for a liquid equilibrated at $T = T_{fp}$, then quenched instantly to $T = T_1$. It should *not* be interpreted to mean that the structure of the glass is the same as that of a liquid in equilibrium at $T = T_{fp}$. Since the latter condition is not met, the fictive temperatures for different properties (e.g., enthalpy and refractive index) may be different[5]; that is why the subscript p is appended to the fictive temperature.

Figure 1(B) illustrates the variation in $p(T, t)$ during a sudden change from temperature T_1 to T_2, after equilibration at T_1. Immediately after the temperature change, $T_{fp} = T_1$ and

$$p(T_2, 0) = p(T_1, \infty) + \alpha_{pg}(T_2 - T_1) \tag{2}$$

and after relaxation is complete, $T_{fp} = T_2$ and

$$p(T_2, \infty) = p(T_1, \infty) + \alpha_{pl}(T_2 - T_1) \tag{3}$$

During relaxation,

$$\frac{p(T_2, t) - p(T_2, \infty)}{p(T_2, 0) - p(T_2, \infty)} = \frac{T_{fp}(t) - T_2}{T_1 - T_2} \equiv M_p \tag{4}$$

where M_p is the relaxation function for property p. M_p, which varies from 1 to 0 as relaxation proceeds, can be measured in temperature jump experiments of the type just described (e.g., Ref. 6) or by fitting data obtained during continuous cooling and reheating.[5] Narayanaswamy[1] showed that the evolution of a property during an arbitrary thermal history, $T(t)$, can be described by

$$p(T, t) = p(T_0, \infty) + \alpha_{pl}(T - T_0) - \alpha_{ps} \int_0^\xi M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi' \tag{5}$$

where ξ is the reduced time defined by

$$\xi = \tau_{pr} \int_0^t \frac{dt'}{\tau_p(T, T_{fp})} \tag{6}$$

and τ_p is the relaxation time for property p. Narayanaswamy proposed the expression

$$\tau_p = \tau_0 \exp\left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_{fp}}\right] \tag{7}$$

where ΔH is the activation energy, R is the gas constant, and τ_0 and x are constants, where $0 \leq x \leq 1$. It is generally found that ΔH for τ_p is identical to the activation energy of the viscosity, η. In effect, x partitions the activation energy between a purely temperature-dependent term and a purely structure-dependent term. At equilibrium, $T_{fp} = T$, and Eq. (7) reduces to the Arrhenius equation,

$$\tau_p = \tau_0 \exp(\Delta H/RT) \tag{8}$$

In Eq. (6), $\tau_{pr} = \tau_p(T_r, T_r)$ where T_r is an arbitrary reference temperature; τ_{pr} is included to give ξ, the units of time. At equilibrium, when $T = T_r$, then $\xi = t$.

Although this model has been very successful in describing relaxation data, the form of Eq. (7) is unsatisfying, because the partition of the activation energy lacks a theoretical foundation. There are other expressions which seem more appropriate.[7,8]

Macedo and Litovitz (ML)[9] suggested an equation having the form

$$\tau = \tau_0 \exp[(\gamma V_c/V_f) + (Q/RT)] \tag{9}$$

where τ_0 and γ are constants ($\frac{1}{2} < \gamma < 1$), V_c is the core or occupied volume of the atoms, V_f is the free volume, $V_f = V - V_c$, V is the total volume, and Q is an activation energy. The rationale for Eq. (9) is that $\exp(Q/RT)$ is proportional to the probability of an atom attempting a jump, and $\exp(\gamma V_c/V_f)$ is proportional to the probability of there being a hole into which the atom may move. An equivalent expression was used by Spaepen and coworkers[10,11] in studies of structural relaxation in metallic glasses. As shown in the appendix, Eq. (9) may be written in terms of the volume fictive temperature, T_{fV}:

$$\tau = \tau_0 \exp\left[\frac{\gamma}{\int_{T_1}^{T_f} V\alpha_s \, dT} + \frac{Q}{RT}\right] \tag{10}$$

where T_1 is the temperature at which $V_f = 0$, $\alpha_s = \alpha_l - \alpha_g$, and α_l and α_g are the volume thermal expansion coefficients of the liquid and glass, respectively. (In terms of the previous notation, $\alpha_l = \alpha_{Vl}/V$, $\alpha_g = \alpha_{Vg}/V$, and $\alpha_s = (\alpha_{Vl} - \alpha_{Vg})/V$.) It has been shown[7] that the use of Eq. (10) in place of Eq. (7) in Narayanaswamy's model leads to significantly different predictions for the change in properties at high cooling rates. Unfortunately, there are some inherent difficulties with Eq. (10). The relaxation time should be

$$\tau_p = \eta/K_p \tag{11}$$

where K_p is the relaxation modulus for property p; that is, τ and η have the same temperature dependence. When T_{fp} is constant, the apparent activation energy for τ_p or η is, according to Eq. (10),

$$R \frac{d \ln \tau_p}{d(1/T)}\bigg|_{T_{fp}=\text{constant}} = Q \tag{12}$$

which is to be compared with the quantity $x\Delta H$ in Eq. (7). Numerous studies of structural relaxation[1-3] and of isostructural viscous flow[12,13] in oxide glasses have shown that $x \approx \frac{1}{2}$, so $Q \approx 250$ to 330 kJ/mol. However, at high temperatures the total activation energy for viscous flow for the same glasses is less than 250 kJ/mol. Therefore, the ML equation cannot represent the temperature dependence of η over a broad range of temperature. Of course, it fits better than the Arrhenius equation, but its failure to describe the whole viscosity curve raises doubts about its validity. In addition to this basic problem, there is a practical problem with the use of the ML equation. It is generally observed[14] that α_s

decreases linearly with temperature near T_g, where both α_l and α_g can be measured:

$$\alpha_s = \alpha_0 + \alpha_1 T \tag{13}$$

where α_1/α_0 approximates $-10^{-4}/°C$. However, leaving α_0 and α_1 as free parameters and fitting the ML equation to the viscosity of NBS 710 glass, one obtains[7] α_1/α_0 of approximately $-10^{-3}/°C$. Not only is this value unexpectedly large, but it also leads to nonphysical negative values of α_s at $T > 1000$ K. This limits the utility of the ML equation to the same narrow temperature range that the Arrhenius equation describes. The source of the problem is not simply the failure of the linear approximation in Eq. (13); the strong temperature dependence of α_s is demanded because of the large value of Q that is needed to describe isostructural flow at low temperatures.

Another form for τ was suggested by Mazurin *et al.*[15]:

$$\tau = \tau_0 \exp\left[\frac{A}{T_{fp} - T_0} + \frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_{fp}}\right)\right] \tag{14}$$

where τ_0, A, T_0, and Q are constants. At equilibrium, when $T_{fp} = T$, Eq. (14) reduces to the Vogel-Fulcher equation,

$$\tau = \tau_0 \exp[A/(T - T_0)] \tag{15}$$

and when T_{fp} is constant, it has the form of the Arrhenius equation with an activation energy of Q. Equation (14) is strictly empirical, but is able to describe the equilibrium curve over a large temperature range, as well as providing for the observed Arrhenian behavior under isostructural conditions. It seems unlikely that Q could be independent of T_{fp}, because it would exceed the total activation energy for flow at high temperatures. Unfortunately, there are as yet no experimental data (on isostructural flow at high fictive temperatures) to resolve this question.

Another model for the structural relaxation time is based on the suggestion of Gibbs and DiMarzio[16] that flow involves the cooperative rearrangement of increasingly large numbers of molecules as temperature decreases. According to this view, the experimentally observed glass transition is the kinetic manifestation of a second-order thermodynamic transition that would occur at a slightly lower temperature. Using assumptions that apply specifically to polymeric liquids, Adam and Gibbs (AG)[4] obtained an expression for τ involving the configurational entropy, S_c:

$$\tau = \tau_0 \exp[A/TS_c] \tag{16}$$

where A is a constant given by

$$A = \Delta\mu S_c^*/k \tag{17}$$

where $\Delta\mu$ is the potential barrier hindering rearrangement, k is Boltzmann's constant, and S_c^* is the configurational entropy of the smallest group of molecules that can undergo a rearrangement. If we write

$$S_c^*/k = \ln W^* \tag{18}$$

then W^* is the number of configurations available to that group of molecules; W^* is expected to be ≈ 2. The configurational entropy is given by

$$S_c(T) = \int_{T_2}^T (\Delta C_p/T) \, dT \tag{19}$$

where $\Delta C_p = C_{pl} - C_{pg}$, and C_{pl} and C_{pg} are the isobaric heat capacities of liquid and glass, respectively. T_2 is the temperature at which $S_c = 0$, i.e., the temperature of the second-order transition. Equation (19) is based on the idea that C_{pg} is a measure of the vibrational contribution to specific heat, and that the difference between C_{pg} and C_{pl} results from molecular rearrangements in the liquid. Goldstein[17] raised the possibility that a significant fraction of ΔC_p actually arises from anharmonic vibrations and secondary relaxations. Those processes are not relevant to the cooperative rearrangement involved in flow, so their contribution to ΔC_p should be subtracted before calculating S_c from Eq. (19). The shape of the curve generated from Eq. (16) is quite similar to that

Table I.   Composition of NBS 710 Glass

Oxide	Amount (wt%)
SiO_2	70.5
Na_2O	8.7
K_2O	7.7
CaO	11.6
Sb_2O_3	1.1
SO_3	0.2
R_2O_3	0.2

Table II.   Best-Fit Parameters for Adam-Gibbs Equation

Parameter	Value
τ_{0n}	2.93×10^{-15} s
τ_{0H}	5.50×10^{-15} s
η_0	1.13×10^{-5} Pa·s
Q/R	8052 K
T_2	493.5 K
C	-8.0×10^{-4} K^{-1}
K_n	3.86×10^9 Pa
K_H	2.05×10^9 Pa

obtained from Eq. (15), which has been found to represent the viscosity of oxide glasses over a wide temperature interval. The AG equation represents the viscosity well for some organic liquids,[18] but fails for others.[19] Those problems, particularly the appearance of improbably large $\Delta\mu$ values, may result from the inappropriate use of the total ΔC_p, without correction for anharmonic contributions. The entropy model of Gibbs and DiMarzio has been much more successful than the free volume theory in accounting for the pressure dependence of the glass-transition temperature.[20]

The configurational entropy is a function of the fictive temperature of the enthalpy as it depends on the existing structure rather than the equilibrium one. Therefore,

$$S_c = \int_{T_2}^{T_{fH}} (\Delta C_p/T)\, dT \tag{20}$$

Experimentally one finds that, near the transition range,

$$\Delta C_p = C_0 + C_1 T \tag{21}$$

Substituting Eqs. (20) and (21) into Eq. (16) we find

$$\tau_p = \tau_0 \exp\left[\frac{(Q/RT)}{\ln\,(T_{fH}/T_2) + C(T_{fH} - T_2)}\right] \tag{22}$$

where $Q = AR/C_0$ and $C = C_1/C_0$. Note that Eq. (22) indicates that the relaxation time for any property depends on the fictive temperature of the enthalpy. This contradicts the suggestion of Narayanaswamy[1] that $\tau_p = \tau_p(T, T_{fp})$. Gonchukova[21] showed that enthalpy relaxation data are better represented using $\tau_H = \tau_H(T, T_{fH})$ than using $\tau_H = \tau_H(T, T_{fn})$. Since H and η exhibit different relaxation kinetics, it must also be true that $\tau_n \neq (T, T_{fH})$. It seems likely that the relaxation time should be

$$\tau_p = \tau_0 \exp\left[\frac{(Q/RT)}{\ln\,(T_{fp}/T_2) + C(T_{fp} - T_2)}\right] \tag{23}$$

for the following reason. Saying that different properties have different fictive temperatures is simply an abstract way of acknowledging that structural changes affect different properties to different extents. For example, the viscosity of an oxide glass may be more sensitive to the arrangement of bridging oxygens, while the heat capacity might depend more on the arrangement of nonbridging oxygens. Those structural units, having different mobilities, could equilibrate at different rates, causing different relaxation kinetics for η and H. Equation (23) could be interpreted to mean that the relaxation of a property is controlled by those
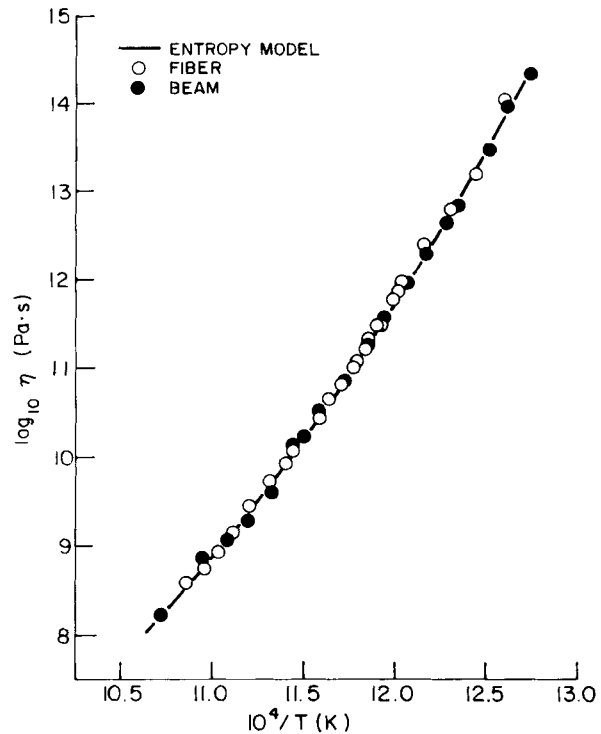

Fig. 2. Viscosity of NBS 710 glass; experimental points from Ref. 22, curve calculated from Adam-Gibbs equation using parameters from Table II.

cooperative rearrangements involving the structural units to which it is most sensitive. We shall adopt this view in the following. When the fictive temperature is constant, the activation energy is

$$R\frac{d\ln \tau_p}{d(1/T)}\bigg|_{T_{fp}=\text{constant}} = \frac{Q}{\ln\,(T_{fp}/T_2) + C(T_{fp} - T_2)} \tag{24}$$

Thus, the AG equation predicts Arrhenian behavior for isostructural flow, but indicates that the activation energy decreases as T_{fp} increases. In the next section we test the performance of the AG equation, using data from the literature for NBS 710 glass.

III.   Application of the AG Equation

NBS 710 is a soda lime silicate glass provided by the U.S. National Bureau of Standards for use as a viscosity calibration standard. Consequently, very accurate data are available for the equilibrium viscosity of the liquid from 10 to 10^{14} Pa·s. In addition, the isostructural viscosity and structural relaxation behavior of this glass have been studied. The nominal composition of the glass is given in Table I. In this section, the AG equation is shown to provide a good description of the flow and relaxation data.

(1)   Viscous Flow

The equilibrium viscosity of NBS 710 in the range $8 \leq \log_{10} \eta(\text{Pa·s}) \leq 14$ was reported by Napolitano et al.[22] We have fit those data to the AG equation in the form

$$\eta = \eta_0 \exp\left[\frac{(Q/RT)}{\ln\,(T/T_2) + C(T - T_2)}\right] \tag{25}$$

with η_0, Q, T_2, and C all treated as free parameters. Not surprisingly, it was found that several sets of values for these four quantities gave equally good fits. These sets were then tested against the relaxation data (described below) to find the values giving the best description of all the data. The values thus obtained are given in Table II. Figure 2 shows the curve calculated from Eq. (25) with these parameters, together with the data of Napolitano et al. The fit is very good, but this is to be expected for

a four-parameter fit. A more interesting test is provided in Fig. 3, which compares the prediction of the AG equation,

$$\eta = \eta_0 \exp\left[\frac{(Q/RT)}{\ln (T_{fn}/T_2) + C(T_{fn} - T_2)}\right] \qquad (26)$$

with the data of Mazurin et al.[12] They measured the rate of iso-structural flow with T_{fn} fixed at 522°C. The measured isostructural activation energy of 297 kJ/mol compares well with the predicted value of 283 kJ/mol.

It is important to test the physical significance of all of the fitting parameters. The preexponential factor agrees with the value $\approx 10^{-5}$ Pa·s obtained by extrapolation of high-temperature data for many glasses.[13] The specific heat for this glass has been measured[23] with the result:

$$\Delta C_p(\text{J/g·K}) = 0.984 - 8.83 \times 10^{-4}\, T(\text{K}) \qquad (27)$$

so that $C = C_1/C_0 = -(9.0 \pm 0.5) \times 10^{-4}/\text{K}$. This error bound, based on the reported experimental uncertainty, may be an underestimate.[24] Nevertheless, the value is in reasonable agreement with the value (-8.0×10^{-4}) obtained from the fit. To be self-consistent, let us use the latter value of C and the experimental results $C_{pl} = 1.46$ and $C_{pg}(750\text{ K}) = 1.13$ J/g, and revise Eq. (26) to

$$\Delta C_p(\text{J/g·K}) = 0.805 - 6.44 \times 10^{-4}\, T(\text{K}) \qquad (28)$$

Noting that $Q/R = A/C_0$ and using $C_0 = 0.805$ J/g·K and a formula weight of 61.9 g/mol, we find $A = 400$ kJ/mol. Assuming that $\Delta\mu \approx 420$ kJ/mol, roughly the strength of an Si–O bond, we find $W^* = 2.6$, which is a reasonable value. The value of the transition temperature, T_2, is difficult to assess, since no absolute entropy data are available.

Equation (25) with the given parameters is in error by $\log_{10} \eta \approx 0.2$ when $\eta = 10^5$ Pa·s, so the linear approximation (Eq. (21)) to ΔC_p is satisfactory over ≈ 9 orders of magnitude in η. We can extract ΔC_p from the viscosity data by noting that the AG equation predicts

$$\Delta C_p = T\frac{d}{dT}\left[\frac{A}{T \ln (\eta/\eta_0)}\right] \qquad (29)$$

To find the derivative of the viscosity data, it is best to use the empirical equation suggested by the NBS, which applies for $1.0 \leq \log_{10} \eta \leq 12.0$:

$$\log_{10} \eta(\text{Pa·s}) = -2.626 + \frac{4236}{T(°C)-266}(\pm.020) \qquad (30)$$

With this result, Eq. (29) predicts that ΔC_p passes through zero near 1300°C, where $\log_{10} \eta \approx 1.5$. This is near the range of viscosity where Goldstein[25] showed that the concept of a potential barrier to flow becomes meaningless. That is, the nonphysical negative ΔC_p values are only required in the temperature range beyond the *theoretical* applicability of the AG equation. Note that we have used the total ΔC_p. Our success implies that anharmonicity and secondary relaxations are not important in this glass.

(2) Structural Relaxation

The structural relaxation of NBS 710 glass has been studied by careful measurements of the refractive index, n, following sudden changes in temperature.[26] In one case, in a so-called cross-over experiment, the glass was equilibrated at 830 K, then held at 704 K to allow partial relaxation, then raised to 798 K. During the last hold, n is observed to move away from equilibrium initially, then to return toward equilibrium. This behavior reveals the presence of more than one relaxation mechanism.[27,28] Those index data have been compared with measurements of the relaxation of the
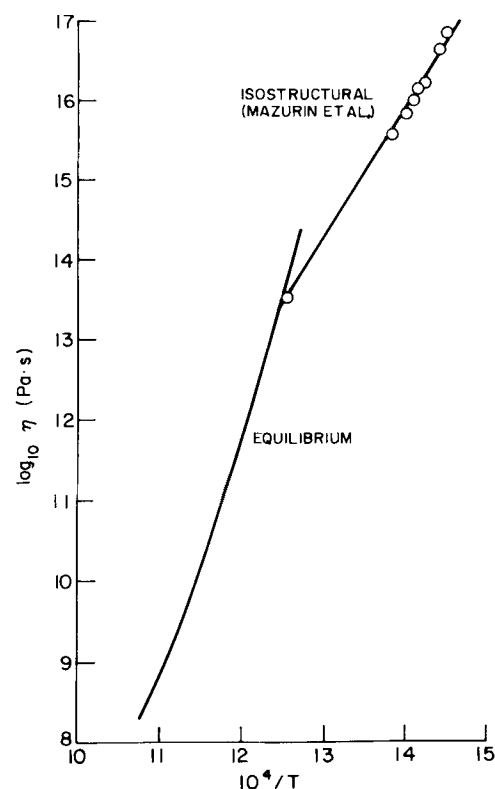
Fig. 3. Viscosity of NBS 710 glass; equilibrium and isostructural curves calculated from Adam-Gibbs equation using parameters from Table II, data from Ref. 12.

Table III.   Parameters of Relaxation Function

k	W_k	λ_k
1	0.0850	36.6
2	0.305	3.90
3	0.470	0.637
4	0.140	0.210

enthalpy,[23] H, leading to the conclusion that H and n have identical relaxation kinetics.

To test the utility of the AG equation, we used the more precise refractive index data. Values of M_n were calculated using Eq. (4) and ξ/τ_{nr} was calculated from Eq. (6) using Eq. (23). First, the set of parameters corresponding to (the experimentally determined value) $C = -9 \times 10^{-4}/\text{K}$ was used to generate ξ/τ_{nr}; then those values and the experimentally determined M_n data were fit to

$$M_n(\xi) = \sum_{k=1}^{4} W_k \exp[-\lambda_k \xi/\tau_{nr}] \qquad (31)$$

where W_k and λ_k are constants. This function was then used to predict the course of relaxation during the cross-over experiment. After a poor fit resulted, the value of C was reduced; the best fit was given by $C = -8.0 \times 10^{-4}/\text{K}$ with the other parameters in Table II, and with M_n defined by the constants given in Table III. This function is almost identical to the function found by Sasabe et al.[23] and DeBolt[26]:

$$M_n(\xi) = \exp[-(\xi/\tau_{nr})^{0.63}] \qquad (32)$$

The curve calculated from Eq. (31) is compared in Fig. 4 with one of the sets of DeBolt's data that fits least well. Figures 5 and 6 show calculated curves based on the AG equation and measured data; the fit is very good. Note that n has been converted to T_{fn} using the experimentally determined relation[23]
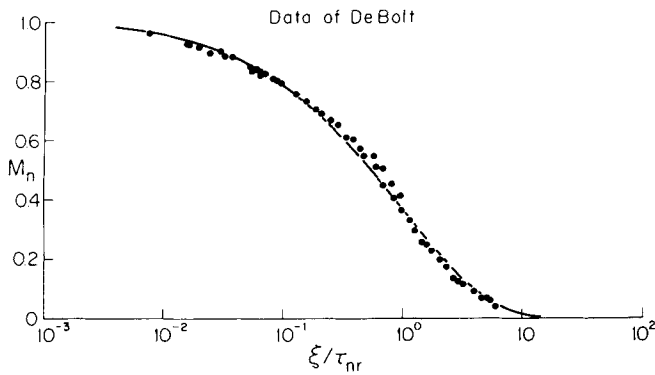
Fig. 4. Relaxation function for refractive index; data from Ref. 26, curve calculated from Eq. (31) with parameters given in Table III.
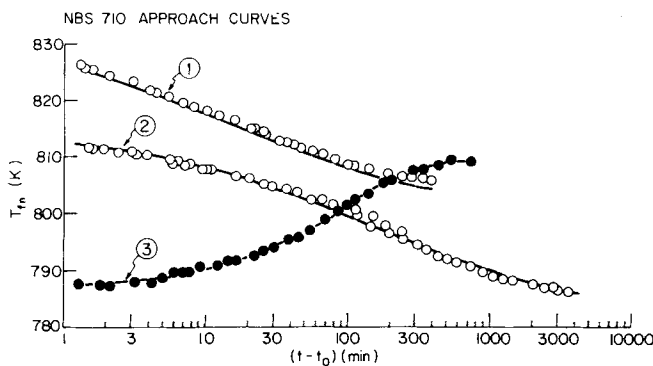

Fig. 5. Change in T_{fn} during hold at T_1, following temperature step at time t_0 from equilibrium at T_0: curve 1, $T_0 = 832.5$ K, $T_1 = 804.4$ K; curve 2, $T_0 = 813.6$ K, $T_1 = 785.7$ K; curve 3, $T_0 = 786.5$ K, $T_1 = 808.5$ K; data from Ref. 26; curves calculated using Adam-Gibbs equation for τ_n.
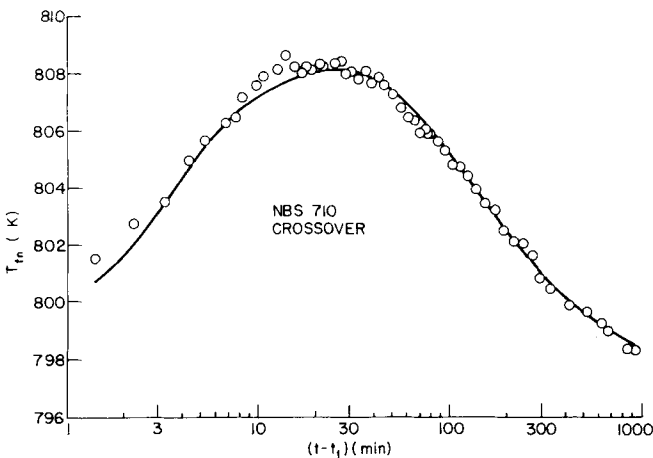

Fig. 6. Change in T_{fn} for NBS 710 glass equilibrated at $T_0 = 830.3$ K, suddenly cooled to $T_1 = 704.0$ K at time $t_0 = 0$, and then suddenly heated to $T_2 = 797.9$ K at time $t_1 = 2687$ min; data from Ref. 26; curves calculated using Adam-Gibbs equation for τ_n.

$$T_{fn}(K) = 809.1 - (n - 1.52075)/2.31 \times 10^{-5} \tag{33}$$

The heat-capacity data were then fit using the same relaxation function, i.e., $M_H = M_n$. It was necessary to increase the pre-exponential factor, τ_{0H}, by a factor of ≈ 2 compared to τ_{0n}. The fit is shown in Fig. 7, and is seen to be very good. The calculated curves are not smooth, because of the small number of terms in
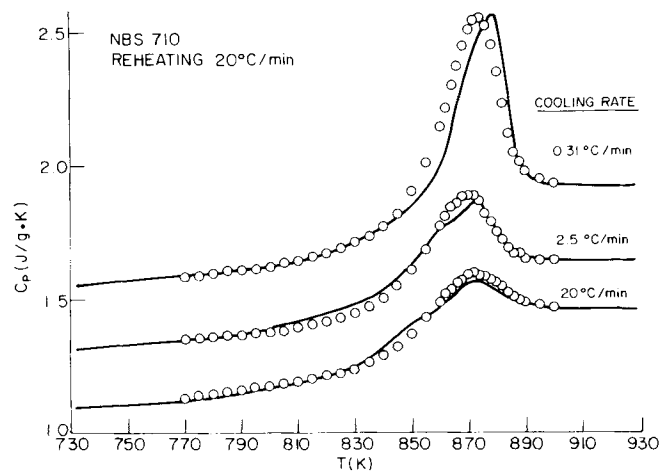

Fig. 7. Heat capacity of NBS 710 glass during heating at 20°C/min following cooling at 0.31°, 2.5°, and 20°C/min; data from Ref. 23; curves calculated using Adam-Gibbs equation for τ_H.

Eq. (31). Each exponential term has its own "glass transition," which appears as a bump. If Eq. (32) were used for these calculations, those bumps would not be observed. The difference in τ_{0n} and τ_{0H} (Table II) indicates that the relaxation rates for n and H are slightly different, in contrast to the conclusions of Sasabe *et al.*[23]

Thus, the AG equation fits both the equilibrium and nonequilibrium viscosity data for NBS 710. Used with Narayanaswamy's model, it accurately represents the structural relaxation data for refractive index and enthalpy. All of the parameters, including the preexponential constants, have physically reasonable values. Given this success, and the plausible theoretical foundation of the AG equation, it appears to be the most suitable form for $\tau(T, T_f)$ for the analysis of structural relaxation. It will be interesting to see whether these results are unique to NBS 710, or whether the AG equation applies as well to other oxide glasses. It will be particularly interesting to test the prediction that the activation energy for isostructural flow decreases as T_{fp} increases.

In the next section, we consider the implications of the AG equation for relaxation far from equilibrium. This is of interest for very rapidly quenched (e.g., splat-cooled or fiberized) glass and for glass annealed far below T_g.

IV. Relaxation Far from Equilibrium

(1) Effect of Cooling Rate on T_g

As a material is cooled, the fictive temperature approaches a lower limit, T_g, known as the glass-transition temperature, which is a function of the cooling rate. Using Eqs. (1) and (5), Narayanaswamy[1] found

$$T_{fp} = T - \int_0^\xi M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi' \tag{34}$$

This result can be used to calculate T_g for various values of $q[\equiv(dT/dt)]$; results obtained with Eq. (34) are shown in Fig. 8. The circles show the calculated T_g for various q: The solid curve is a plot of the equilibrium viscosity from Eq. (25) with the parameters in Table II; the dashed line is the Arrhenius approximation used by Sasabe *et al.*[23]:

$$\ln \eta(Pa \cdot s) = -61.29 + 73658/T(K) \tag{35}$$

The curve of $\log(1/|q|)$ vs $1/T_g$ parallels the plot of $\log \eta$ vs $1/T$, so we can write

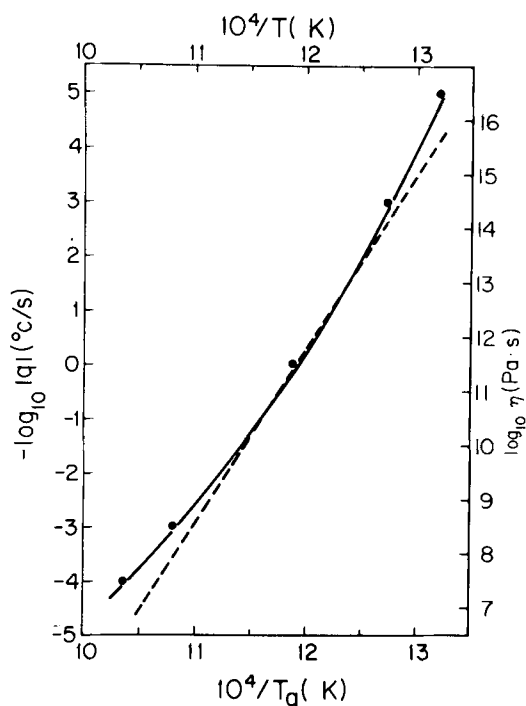$$\log_{10} \eta(Pa \cdot s) = 11.3 - \log_{10}|q| \ (°C/s) \tag{36}$$

Fig. 8. Circles represent values of T_g vs $-\log_{10}|q|$, where $q = dT/dt$, calculated using Adam-Gibbs equation for τ_H; curves represent equilibrium viscosity (right ordinate, upper abscissa) according to Adam-Gibbs equation (solid line) and Arrhenius equation (dashed line).

or, using K_H from Table II,

$$\log \tau_H(s) = 2.0 - \log_{10}|q| \ (°C/s) \tag{37}$$

so that

$$\left.\frac{d \ln \tau_H}{d \ln |q|}\right|_{T=T_g} = -1 \tag{38}$$

If τ_H were given by Eq. (8), then Eq. (37) would become

$$\frac{d(1/T_g)}{d \ln |q|} = -\frac{R}{\Delta H} \tag{39}$$

which is the result given by Moynihan et al.[29] Equation (38) generalizes the earlier result of Ritland,[30] Moynihan's modification, and the present numerical results. For modest cooling rates, $-1.5 \leq -\log_{10}|q| \leq 2.0$, Eq. (39) would be closely obeyed, but for more extreme rates, the predictions of the AG equation and the Arrhenius equation diverge.

(2) Relaxation After Quenching

From Fig. 8 it is evident that the differences between the predictions of the AG and Arrhenius equations become important at extreme cooling rates. If a sample were splat-cooled at 10^6 °C/s and reheated, the evolution of its properties would not be correctly predicted using the Arrhenius equation. To test the magnitude of the errors in such cases, we have simulated the heat capacity during reheating after cooling at high rates. To avoid the "lumpiness" of the curves in Fig. 7, the 4-term approximation to M_H is replaced with a fit to

$$M_H = \exp[-(\xi/\tau_{Hr})^{0.65}] \tag{40}$$

using 9 exponential terms, with the constants determined by Moynihan et al.[31] T_{fH} was calculated from Eq. (34) and the plotted function is given by[29]

$$\left.\frac{dT_{fH}}{dT}\right|_{T=T'} = \frac{[C_P - C_{pg}]_{T=T'}}{[C_{pl} - C_{pg}]_{T=T_{fH}}} \tag{41}$$
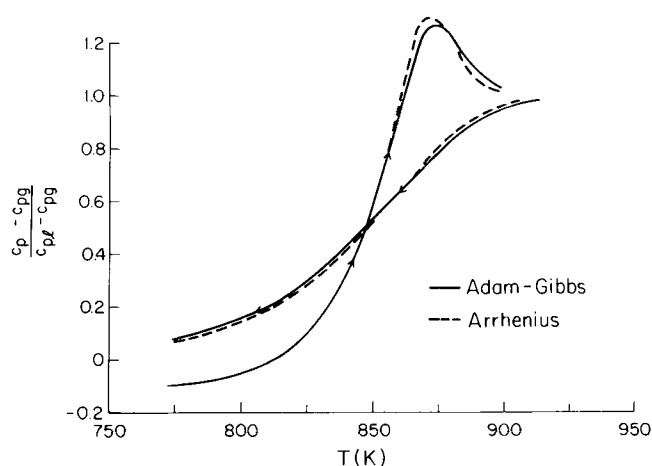

Fig. 9. Heat capacity curves calculated using Eqs.(34) and (40), with τ_H given by Adam-Gibbs and Arrhenius equations, for cooling at $q_c = -1$°C/s and heating at $q_H = 20$°C/min.
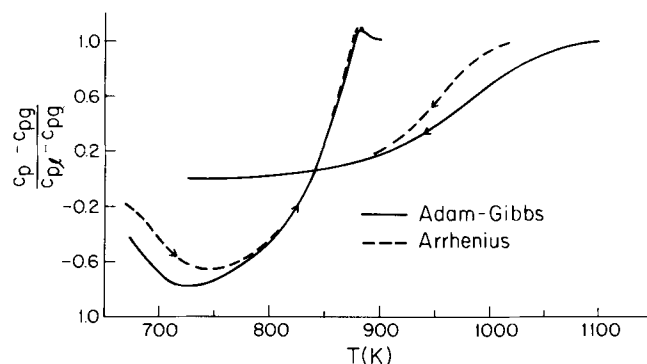

Fig. 10. Same as Fig. 9, except $q_c = -10^4$°C/s.

For the calculations based on the Arrhenius equation, we used Eq. (7) with $\Delta H = 612$ kJ/mol and $x=0.44$, as found by Sasabe et al.[23] The preexponential constant was chosen to be $\tau_{oH} = 7.5 \times 10^{-37}$ s to make the calculation coincide with the result based on the AG equation when $q = -1$°C/s; that value of τ_{oH} is close to that $(1.09 \pm 0.29 \times 10^{-36}$ s$)$ found by Sasabe et al. For the AG equation, the constants were those in Table II. Figure 9 compares the calculated curves for cooling at 1°C/s and reheating at 20°C/min; the predictions based on the AG and Arrhenius equations are in good agreement. However, Figs. 10 and 11 show that the differences become substantial as the cooling rate is increased.

Figure 12 shows the change in n calculated from Eqs. (33) and (34) for an isothermal hold at 500°C, following cooling at 1°C/s. The relaxation function is again based on a 9-term fit to

$$M_n = \exp[-(\xi/\tau_{nr})^{0.65}] \tag{42}$$

The calculation based on the AG equation used the constants in Table II; for the Arrhenius equation, we used Eq. (7) with the same x and ΔH given above and $\tau_{0n} = 4.0 \times 10^{-37}$ s, which makes the calculations agree when $q = -1$°C/s. The results are also in good agreement for a hold at 450°C, following cooling at 100°C/s. However, as illustrated in Fig. 13, at high quenching rates the Arrhenius and AG equations lead to different fictive temperatures. The higher T_f predicted using the AG equation leads to faster relaxation during isothermal annealing. This prediction remains to be tested experimentally.

V. Conclusions

Narayanaswamy's[1] model of structural relaxation is very successful at describing the nonequilibrium properties of viscous liq-
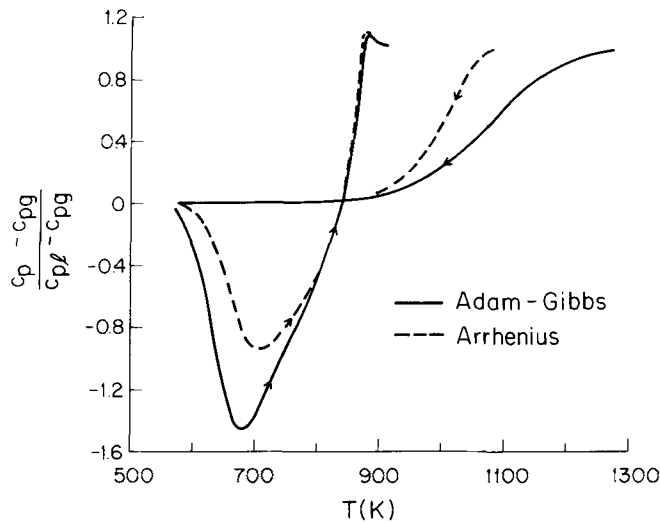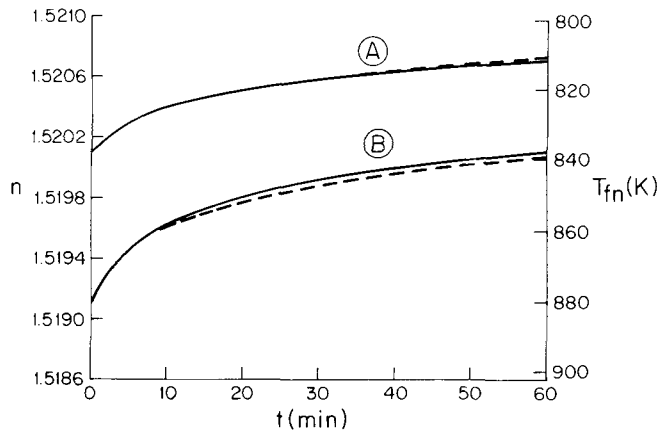
Fig. 11. Same as Fig. 9, except $q_c = -10^6\,°C/s$.

Fig. 12. Predicted refractive index during isothermal hold at (*A*) $T_H = 500°C$ and (*B*) $T_H = 450°C$ following cooling at $q_c = -1°C/s$ and $-100°C/s$, respectively, calculated using Adam-Gibbs (solid line) and Arrhenius equation (dashed line) for τ_n.

uids. The ad hoc partitioning of the activation energy of τ (Eq. (7)) gives a satisfactory representation of the influence of structure on τ over a substantial range of temperatures. The Adam-Gibbs equation has been shown to give an equally good representation of the dependence of τ on T and T_f, while providing a superior theoretical foundation. The AG equation leads to different predictions of relaxation behavior following very rapid cooling, which may be important for such materials as glassy metals and optical fibers.

APPENDIX

Dependence of Free Volume on T_f

Figure A-1 provides a schematic illustration of the temperature dependence of the volume, V, of a glass-forming liquid. V_l is the volume of the equilibrium liquid and V_c is the core volume of the atoms, exclusive of interatomic volume. The free volume is defined by $V_f = V - V_c$. If V_l is extrapolated through the glass-transition region, $V_l = V_c$ at temperature T_1, so $V_f(T_1) = 0$. The
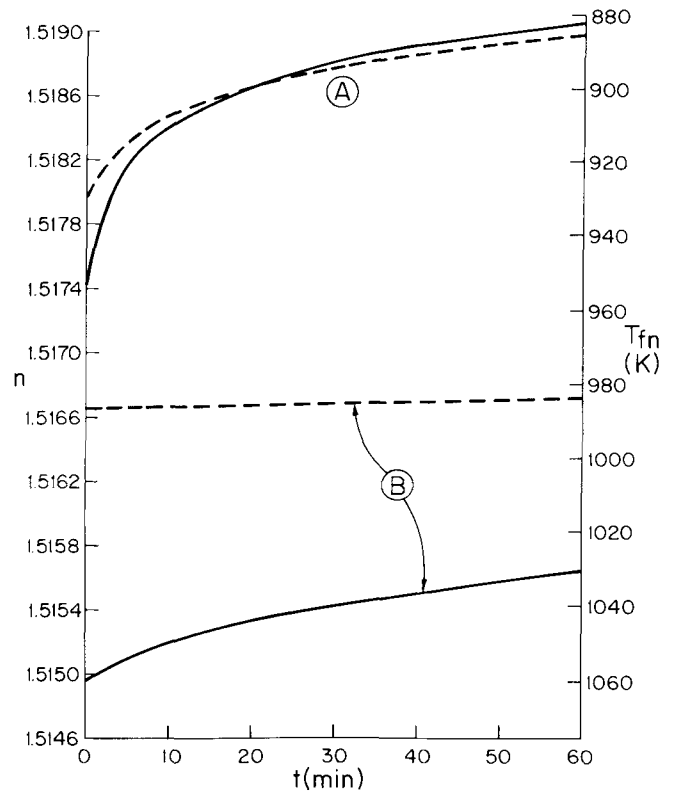

Fig. 13. Same as Fig. 12, except $q_c = -10^4$ and $-10^6°C/s$ and $T_H = 400°$ and $300°C$, respectively.

volume thermal expansion coefficient is defined by $\alpha = (1/V)(dV/dT)$; the corresponding values for the liquid, glass, and core volume are, respectively, $\alpha_l(=\alpha_{vl}/V)$, $\alpha_g(=\alpha_{vg}/V)$, and $\alpha_c(=\alpha_{vc}/V)$.

The volume along the liquid curve can be found by integrating

$$\int_{V_1}^{V_l} \frac{dV}{V} = \ln\,(V_l/V_1) = \int_{T_1}^{T} \alpha_l\, dT' \tag{A-1}$$

so

$$V_l = V_1 \exp\left[\int_{T_1}^{T} \alpha_l\, dT'\right] \tag{A-2}$$

Since the integral is small,

$$V_l \approx V_1\left[1 + \int_{T_1}^{T} \alpha_l\, dT'\right] \tag{A-3}$$

Similarly, the core volume may be written

$$V_c \approx V_1\left[1 + \int_{T_1}^{T} \alpha_c\, dT'\right] \tag{A-4}$$

so the free volume is

$$V_f \approx V_1 \int_{T_1}^{T} (\alpha_l - \alpha_c)\, dT' \tag{A-5}$$

and

$$V_f/V_c \approx \frac{\int_{T_1}^{T} (\alpha_l - \alpha_c)\, dT'}{1 + \int_{T_1}^{T} \alpha_c\, dT'} \approx \int_{T_1}^{T} (\alpha_l - \alpha_c)\, dT' \tag{A-6}$$

Assuming that $\alpha_g \approx \alpha_c$,

$$V_f/V_c \approx \int_{T_1}^{T} \alpha_s\, dT' \tag{A-7}$$

where $\alpha_s \equiv \alpha_l - \alpha_g$.

Equation (A–7) applies along the equilibrium liquid curve. To describe the free volume of the nonequilibrium liquid, we note that the volume, V, may be written (see Fig. A–1):

$$\ln \left[V/V_l(T_f) \right] = \int_{T_f}^{T} \alpha_g \, dT' \tag{A–8}$$

so

$$V \approx V_l(T_f) \left[1 + \int_{T_f}^{T} \alpha_g \, dT' \right] \tag{A–9}$$

Substituting Eq. (A–3) into Eq. (A–9), and neglecting the second-order term in α, we find

$$V \approx V_1 \left[1 + \int_{T_1}^{T} \alpha_l \, dT' + \int_{T}^{T_f} \alpha_s \, dT' \right] \tag{A–10}$$

Using Eq. (A–4) and assuming $\alpha_c = \alpha_g$, we find from Eq. (A–10) that

$$V_f = V - V_c \approx V_1 \int_{T_1}^{T_f} \alpha_s \, dT' \tag{A–11}$$

so

$$V_f/V_c \approx \int_{T_1}^{T_f} \alpha_s \, dT' \tag{A–12}$$

Fig. A–1. Temperature dependence of volume of glass-forming liquid: V_l is volume of equilibrium liquid, with slope α_{vl}; V_c is core volume of atoms, with slope α_c; $\alpha_{vg} = dV/dT$ below glass transition; T_f is fictive temperature of glass at temperature T; free volume is zero at T_1.

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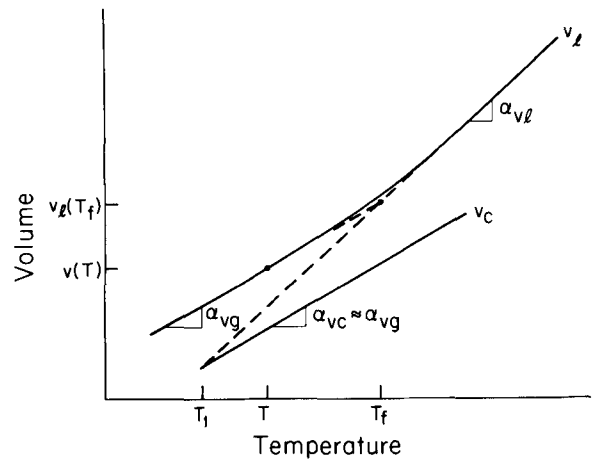
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