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Determination of the Isoentropic Temperature in the Glass Transition

Patricia Goldstein*

Departamento de Física, Facultad de Ciencias, Universidad Nacional Autónoma de México, 04510 México, D.F.

L. F. del Castillo

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, 04510 México, D.F.

L. S. García-Colín[†]

Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, 09340 México, D.F.

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ABSTRACT: The form for the specific heat proposed by Di Marzio and Dowell based on the lattice model of Gibbs–Di Marzio for the glass transition of polymeric substances is used to find an expression for the logarithmic shift factor which through a comparison with the empirical relation of Williams–Landel–Ferry enables us to find a value for the isoentropic temperature for which the configurational entropy of the system vanishes.

I. Introduction

The Vogel–Fulcher–Tamann (VFT) equation was formulated several decades ago[1–3] to describe the behavior of the viscosity and the relaxation time of a supercooled liquid as it approaches its glass temperature T_g, namely

$$\tau(T) = \tau_s \exp\left(\frac{\alpha}{T - T_0}\right) \qquad (1)$$

where τ_s is a reference relaxation time and α and T_0 are two independent parameters taken to be nonnegative. In particular, T_0 corresponds to the temperature at which τ is infinity, thus implying the physical impossibility of configurational changes in the solid. This fact can be expressed in terms of the configurational entropy S_c of the system, i.e.

$$S_c(T_0) = 0 \qquad (2)$$

In this sense, one may refer to T_0 as the isoentropic temperature.

Several efforts have been undertaken in order to find, on the one hand, the value of T_0 and, on the other hand, theoretical expressions for the logarithmic shift factor (LSF)

$$\log a_T \equiv \log\,[\tau(T)/\tau_s] \qquad (3)$$

As far as the LSF is concerned, several empirical forms have been proposed. One of the most used expressions was introduced in 1955 by Williams, Landel, and Ferry[4] (WLF). They propose a universal form for the LSF for a great number of glass-forming substances. As for the interpretation of the isoentropic temperature from a theoretical point of view, one of the first papers in this direction was published in 1958 by Gibbs and Di Marzio[5] (GDM). Using a lattice model to describe the amorphous phases of systems formed by polymeric chains, they find some of its thermodynamic properties and the form of the entropy in terms of the parameters of the lattice. They also predict a second-order phase transition that describes in a qualitative way the same aspects of the glass transition that occurs at a temperature T_0 for which the configurational entropy vanishes. In 1965, Adam and Gibbs[6] (AG), using the GDM model, carried on a work that has two main goals: first, to find a general theoretical form for the LSF in terms of the configurational entropy of the system; second, to obtain an expression for T_0 in terms of T_g for a particular model. Several other works have been presented in this direction including those of Scherer,[7] Angell,[8–10] Hodge,[11] and others.[12,13]

The purpose of this work is to obtain an expression for the LSF, using the GDM model, which can be compared directly, without any approximation, with the WLF equation. From this comparison, we can find a new value for the isoentropic temperature.

In section II we summarize the main features of the WLF equation and the results of Gibbs–Di Marzio and Adam–Gibbs. In section III, we present our results and their comparison with experiment through the WLF equation, and finally, in section IV we provide some remarks on the nature of these results.

II. Summary of Previous Results

Williams, Landel, and Ferry[4] advanced an empirical form for log a_T for a temperature T with respect to a reference temperature T_s in terms of two constants C_1 and C_2 that reads

$$\log a_T = \frac{-C_1(T - T_s)}{C_2 + T - T_s} \qquad (4)$$

This equation may be expressed in a universal form if the value of T_s is chosen such that, for a great number of glass-forming substances, C_1 and C_2 take the same value, namely

$$C_1 = 8.86 \qquad C_2 = 101.6$$

In case another reference temperature T_s' is chosen, the form for eq 4 is the same, but with new constants C_1' and C_2' such that if

$$T_s' = T_s + \delta$$

[†] Also at "El Colegio Nacional" L. González Obregón 23, 06020 México, D.F.

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then

$$\log a_T = \frac{-C_1'(T - T_s)}{C_2' + T - T_s} \tag{5}$$

with

$$C_1' = C_1 C_2/(C_2 + \delta) \tag{6}$$

$$C_2' = C_2 + \delta \tag{7}$$

It must be noted that, in this approach, no reference is made to a temperature for which the relaxation time becomes infinite. It may be easily seen that if one defines a temperature T_∞

$$T_\infty = T_s - C_2$$

the WLF equation may be written in a VFT-like form.

As we have already mentioned before, Gibbs and Di Marzio[5] predict the existence of a temperature T_0 for which the configurational entropy vanishes, namely, eq 2. In order to find T_0, using their expression for the configurational entropy, one must solve the equation

$$((z-2)/2) \ln (V_0/S_0) + n_0/xn_x \ln [V_0^{z/2-1}/S_0^{z/2}] + \\ 1/x \ln \{((z-2)x+2)(z-1)/2\} + (x-3)/x\{\ln [1 + \\ (z-2)\exp(-(\epsilon_2 - \epsilon_1)/kT)] + f(\epsilon_2-\epsilon_1)/kT\} = 0 \tag{8}$$

where z, V_0, S_0, n_0, x, n_x, $\epsilon_2 - \epsilon_1$, and f are parameters that depend on the lattice and need not be given here.

Gibbs and Di Marzio did not actually solve this equation to find T_0, probably because they did not know some of these parameters. In fact, what they did in their paper was to present an exercise in which they propose that $T_0 = T_g$ in order to compare the consequences of this model with the experiment and to find the values of some of the lattice parameters in the case of polystyrene (PS). Nevertheless, in their final discussion they stress the fact that they cannot conclude that the value for T_0 is the same of T_g for an experiment performed in a finite time scale.

Table I
Values for *A*, *B*, *C*, *K*, T_g, and T_s Presented for the Five Polymer Substances

substance	*A*, J/(K mol)	*B*, J/(K mol)	*C*, J/(K mol)	*K*, J/mol	T_g, K	T_s, K
PIB	489 648	0.0145	0.000 02	25 907	202	243
PVC	1 444 908	0.0124	0.000 01	19 743	347	396
PMMAc	2 571 912	0.0103	0.000 01	26 389	378	435
PVAc	1 674 450	0.0165	0.000 03	13 702	305	349
PS	1 669 548	0.0093	0.000 01	6 955	373	408

In a later paper, Adam and Gibbs[6] found that the LSF may be written as

$$-\log a_T = 2.303[\Delta\mu s_c^*/k]\left(\frac{1}{T_s S_c(T_s)} - \frac{1}{T S_c(T)}\right) \tag{9}$$

where $\Delta\mu s_c^*/k$ is a quantity that may be calculated from the premises of the model (see Table I in ref 6), and the change of the configurational entropy ΔS_c may be evaluated in terms of the change of the specific heat, ΔC_p, namely

$$\Delta S_c = S_{cb} - S_{ca} = \int_{T_s}^{T_b} \Delta C_p/T \, dT \tag{10}$$

Using Gibbs–Di Marzio's idea about the existence of the temperature T_0 for which $S_c(T_0) = 0$ and taking the approximation that

$$\Delta C_p = \text{constant}$$

they find that

$$S_c(T) = \Delta C_p \ln (T/T_0) \tag{11}$$

With this result, they can express the LSF given by eq 9 in a form similar to the WLF equation (eq 4), taking a reference temperature T_s

$$-\log a_T = \frac{a_1(T - T_s)}{a_2 + T - T_s} \tag{12}$$

where

$$a_1 = \frac{2.303[\Delta\mu s_c^*/k]}{\Delta C_p T_s \ln (T_s/T_0)} \tag{13}$$

and a_2 is no longer a constant but rather a function of T, namely

$$a_2(T) = \frac{T_s \ln (T_s/T_0)}{\ln (T_s/T_0) + (1 + T_s/(T - T_s)) \ln (T/T_s)} \tag{14}$$

This last expression is then approximated to a constant a_2

$$a_2 = \frac{T_s \ln (T_s/T_0)}{1 + \ln (T_s/T_0)} \tag{15}$$

Taking the glass transition temperature T_g as the reference temperature in both their equation as well as in the WLF one, modifying the constants C_1 and C_2 by their alternative form C_1' and C_2' given by eqs 6 and 7, and setting $a_2 = C_2'$, they find the following relationship between T_0 and T_g, namely

$$\frac{T_g}{T_0} = \exp\left(\frac{T_g}{C_2'} - 1\right)^{-1} \tag{16}$$

In this manner one can compute the value of T_0 if T_g is given.

It is important to recall that T_g cannot be defined in a unique way for it depends on the way the glass-forming process is performed. Thus, in this sense, the value of T_0 computed with eq 16 is not uniquely determined. Therefore, the temperature T_0 given by this equation cannot be expected to satisfy the GDM equation (eq 2). The explicit solution for this equation, to our knowledge, remains still unsolved.

The isoentropic temperature that fulfills eq 2 cannot depend in any way on the reference temperature. If we analyze the expression for the LSF given by Adam and Gibbs, namely, eq 9, the only dependence on T_s is through the first term. The appearance of the reference temperature taken by Adam and Gibbs as T_g in eq 16 is due to the way in which they compare their expression for LSF (eq 12) with the WLF expression (eq 5). In the next section we present a different procedure to establish this comparison in which we can estimate a value for the isoentropic temperature that does not present this inconvenience.

III. Results and Comparison with Experiment

In a previous paper,[14] we showed that, using the expression for ΔC_p derived by Di Marzio and Dowell,[15] based on the lattice model of Gibbs–Di Marzio, namely

$$\Delta C_p = A\frac{1}{T^2} + BT - CT^2 \tag{17}$$

where A, B, and C are quantities defined in ref 14 and are summarized in Table I, we obtain a theoretical form for the LSF that may be expressed in a VFT-like equation

Table II

substance	WLF	$G-\mathrm{d}M-D$	m	C
PIB	$\log a_T = 0.5883 \times 10^6/T^2 - 9.8244$	$T_0 = 135$ K $\log a_T = 0.5837 \times 10^6/T^2 - 9.7917$	32	5.65
PVC	$\log a_T = 2.7743 \times 10^6/T^2 - 17.2686$	$T_0 = 289$ K $\log a_T = 2.7928 \times 10^6/T^2 - 17.4325$	33.4	5.77
PMMAc	$\log a_T = 4.2023 \times 10^6/T^2 - 21.6736$	$T_0 = 328$ K $\log a_T = 4.2335 \times 10^6/T^2 - 22.0695$	39.3	6.26
PVAc	$\log a_T = 1.7576 \times 10^6/T^2 - 14.1361$	$T_0 = 270$ K $\log a_T = 1.7700 \times 10^6/T^2 - 13.9640$	24.2	4.91
PS	$\log a_T = 2.4489 \times 10^6/T^2 - 14.5897$	$T_0 = 341$ K $\log a_T = 2.4489 \times 10^6/T^2 - 13.4699$	21	4.58

(cf. eq 9 in ref 14)

$$\log a_T = \frac{K}{F(T)(T - T_0)} \tag{18}$$

where $K/F(T)$ remains constant in the temperature range $T > T_g$.

Our concern in this section is to find the value for the temperature T_0 such that our theoretical expression for the LSF agrees with the one given experimentally by WLF for five polymeric substances, namely, polyisobutylene (PIB), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMAc), poly(vinyl acetate) (PVAC), and polystyrene (PS).

The best way to compare the WLF expression for LSF given by eq 4 and ours, given by eq 18, is through a parametrization of both in terms of $1/T^2$, since in this representation they may be adjusted to straight lines.[16] In this way, it will be only necessary to perform a comparison between their slopes.

Using the expression for ΔC_p, given in eqs 17 and 10, we evaluate the configurational entropy with respect to a temperature T_0 for which $S_c(T_0) = 0$. With this result and using eq 9, the LSF may be written in terms $1/T^2$ as

$$\log a_T = -K\left(\frac{1}{F(T_s)(T_s - T_0)} - \frac{1}{G(T)}\frac{1}{T^2}\right) \tag{19}$$

where

$$F(T) = \left(1 + \frac{T_0}{T}\right)\left(\frac{A}{2T_0^{\,2}} - \frac{CT^2}{2}\right) + BT \tag{20}$$

$$G(T) = \left(1 - \frac{T_0^{\,2}}{T^2}\right)\left(\frac{A}{2T_0^{\,2}T} - \frac{CT}{2}\right) + B\left(1 - \frac{T_0}{T}\right) \tag{21}$$

The values for A, B, C, K, T_g, and T_s are given in Table I.

On the other hand, the WLF equation may be expressed as

$$\log a_T = \frac{C_1(T - T_s)(T + T_s - C_2)}{1 - (T_s - C_2)^2/T^2}\frac{1}{T^2} \tag{22}$$

Analyzing eq 19 and 22, it may be easily seen that, on the other hand, they both depend on the reference temperature T_s so that, in order to compare them, we must take the same reference temperature in both. Here, we shall take the experimental value reported by WLF[4] for the five polymers as T_s. On the other hand, the theoretical expression given by eq 19 depends strongly on T_0.

In our analysis, we carry out a least-squares fit of both expressions 19 and 22 to represent them by straight lines. The slope of the straight line corresponding to eq 19 depends mainly on T_0, and its intercept, on T_s. Our main interest is to find the value of T_0 for which the slope of the straight line associated to eq 19 agrees best with the slope of the fit of the WLF equation.

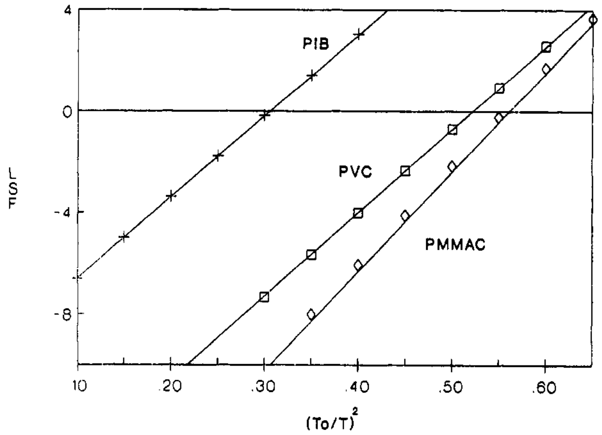

Figure 1. Comparison between the fits given in the first and second columns of Table II for PIB, PVC, and PMMAc. The solid lines represent the fits of our equation (eq 19) and the points the fit for WLF.

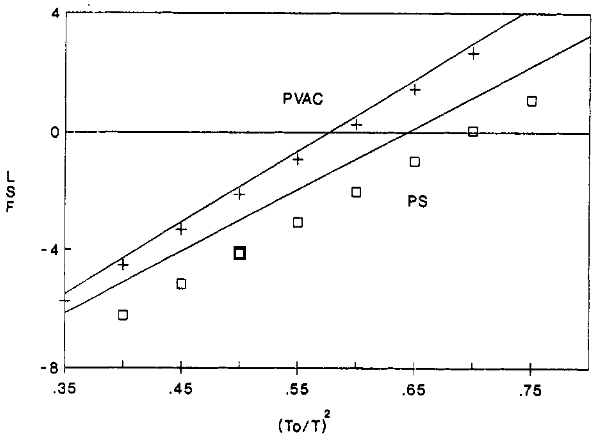

Figure 2. Comparison between the fits given in the first and second columns of Table II for PVAc and PS. The solid lines represent the fits of our equation (eq 19) and the points the fit for WLF.

The analysis for the five polymeric substances mentioned above is summarized in Table II. Notice should be made on the fact that the temperature T_0 is varied until the slopes of both agree best. In the first column the fits for the WLF equation are given, and in the second one the fits for eq 19 for the values of T_0 for which the slopes agree are presented. In Figures 1 and 2 we exhibit the plots for the LSF fits given in the first and second columns in terms of $(T_0/T)^2$. We can express the fits for eq 19 in the form

$$\mathrm{LSF} = m[T_0/T]^2 + b(T_s) \tag{23}$$

where, as we have already mentioned, m does not depend on the reference temperature, whereas this dependence is included in the intercept b. The values of m are presented in the third column of Table II.

The form of eq 23 has been considered by Bässler[16] as a universal equation obeyed by all glasses in the high-viscosity regime. This fact is in agreement with our results for the five polymers analyzed in this work. If we compare our slopes m in the representation $(T_0/T)^2$ with those proposed by Bässler, denoted as C^2, we find that PIB, PVC, and PMMAc follow his rule for the group of glasses for which $C = 6.0 \pm 0.5$ (see fourth column of Table II). However, we predict lower values of C for PVAc and PS which may represent another group of glasses not mentioned by Bässler given by $C = 4.74 \pm 0.25$. The explanation of this sort of corresponding states law is still not thoroughly completed and will be presented in a forthcoming paper.

IV. Concluding Remarks

We may assert that our result is a semiempirical one since we have obtained a theoretical expression for the LSF from a microscopic lattice model which has enabled us, through a global comparison with experiment, to determine the isoentropic temperature. This is an interesting result since there exist major theoretical difficulties to evaluate T_0.[5]

As we have already mentioned one of the few attempts to find the value for this temperature is the one given by Adams and Gibbs. Although both their work and ours are based in the same lattice model, there are several differences in the procedures. Adam and Gibbs consider that the difference of the specific heat is a constant, while we take the expression for ΔC_p that is obtained directly from GDM model. They approximate their result for log a_T to a WLF-like expression with both coefficients taken as constants and afterward compare the value for C_2' of WLF with their approximation for their coefficient a_2 in order to evaluate T_0. Instead, we take the complete result for the LSF and, without any approximation, we compare globally our expression with WLF to determine for which value of T_0 both expressions agree best.

A rather interesting property of our value for T_0 is the fact that the LSF expressed in terms of the reduced variable $(T_0/T)^2$ seems to generate (in accordance to Bässler) different classes of substances according to their behavior in the vicinity of the glass transition.

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