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Theoretical basis for the Vogel-Fulcher-Tammann equation

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The lattice model for linear polymeric glasses proposed by Gibbs and Di Marzio several decades ago is used to calculate the average relaxation time for the structure of the model as a function of temperature. Using the fact that the model exhibits the existence of a temperature T_0 for which the configurational entropy of the system vanishes, we identify this temperature with the threshold of infinitely long relaxation times. Using the analytical parameter-free expression for the specific heat for temperatures above T_0, we show that (i) there are substances for which a Vogel-Fulcher-Tammann-like (VFT) equation is accurately obeyed in the range $T > T_g$, where T_g is the experimental glass transition temperature. On the other hand, in the range $T_0 < T < T_g$ a modified VFT equation is suggested.

I. INTRODUCTION

The nature of the relaxation processes which govern the behavior of a viscous supercooled liquid as it approaches its glass temperature remains essentially unknown. Yet, it is surprising that a large number of experiments using different types of techniques devoted to the examination of the response function of the system to an external perturbation can be described by the stretched exponential function,

$$\phi(t)=\phi_0\exp-(t/\tau)^{\beta}, \quad 0<\beta<1 , \tag{1}$$

where $\phi_0=\phi(t=0)$ and τ is a parameter often interpreted as the average relaxation time of the relevant processes occurring during the glass transition. Equation (1) was first introduced by Kohlrausch[1] in his studies on viscoelasticity and later on by Williams and Watts[2] to describe dielectric relaxation. Further views on this equation as well as the attempts that have been made to derive it from various models have been recently discussed in the literature.[3-10]

Our concern here is mainly with the parameter τ which appears in Eq. (1). As has been well known for over half a century, such a parameter is a function of temperature. This dependence has also been empirically described in several ways. In 1921, Vogel[11] proposed for it a simple Arrhenius behavior later used by Tammann and Hesse[12] and independently by Fulcher.[13] This is known as the Vogel-Fulcher-Tammann (VFT) equation, namely

$$\tau(T)=\tau_0\exp\left[-\frac{\alpha}{T-T_0}\right] \quad \tau_c,\alpha,T_0>0 . \tag{2}$$

A similar empirical relation was proposed by Williams, Landel, and Ferry[10] (WLF), later modified by Narayanaswamy,[14] to account for the influence of the thermal history on the relaxation times. An account of these latter formulas applied to other relaxation processes has been given by Scherer.[15] But in spite of the success of these equations in their various contexts, very little is known about the underlying microscopic mechanisms. Very recently, careful experiments carried out on supercooled glycerol and propylene glycol using two different spectroscopies, specific-heat spectroscopy[16] and ultrasonic attenuation,[17] have revealed two interesting aspects about this puzzle. First, that for both of these glass-forming liquids the peak frequency, whose inverse value is identified with τ as a function of the temperature, may be fitted both using the VFT equation and a scaling law as arises from fluctuating hydrodynamics.[18] Experimentally, reasons are given to prefer the former over the latter one.[17] Second, the relaxation times of glycerol obtained by using five different techniques may be also fitted over nine decades of frequency with a power law and a VFT equation. The conclusion which is extracted from this work is that the relevant relaxations for such substances in the glass transition are governed by a single relaxation mechanism.

From the theoretical point of view, little effort has been spent on elucidating the temperature dependence of τ, after the pioneering work of Adam and Gibbs[19] based on a microscopic model for the glass transition proposed thirty years ago by Gibbs and Di Marzio.[20] In Adam-Gibbs' work the WLF formula was obtained and throughly compared with the then available experimental results. On the other hand, the Gibbs-Di Marzio model, which is a parameter-free model, is well known to reproduce a reasonably large number of the equilibrium properties of glasses.[21] Also, the Adam-Gibbs formulation has been recently used to justify some of the empirical equations for τ using ad hoc assumptions on the behavior of the specific-heat dependence on the temperature around the transition temperature.[22–23]

Among the most outstanding predictions of the Gibbs-Di Marzio model is the specific-heat discontinuity at the glass transition to a rather good accuracy. But also, the analytical form of this thermodynamic function is given from a critical temperature, defined in the model as that for which the configurational entropy vanishes, up to a temperature characteristic of the supercooled liquid but higher than the transition temperature. In this work we show a rather amazing property of this function, namely, if used in its full form to compute the relaxation time using the Adam-Gibbs method and without any further approximations, then in the interval $T > T_g$, where T_g is the transition temperature, one recovers an equation which is analytically different but essentially behaves as the full VFT equation. Otherwise in the interval $T_0 < T < T_g$, where T_0 is the temperature for which the configurational entropy vanishes, a modified VFT-type equation is obtained but with a temperature-dependent parameter in the exponential. Since these equations contain no free parameters one can compare them with the experimental results for available glass-forming materials. The agreement is surprisingly accurate.

To keep this paper self-contained, in Sec. II we summarize the main features of the Adam-Gibbs and Gibbs-Di Marzio results useful for our calculations, in Sec. III we give the main results and their comparison with experiment, and in Sec. IV we add some pertinent remarks on the nature of these results and provide a comparison with other work.

II. SUMMARY OF RESULTS

The following results will be stated without any proof; the interested reader may refer to the original papers where a rather clear justification of each formula is given. Adam and Gibbs compute a quantity $W(T)$, the average transition probability, as a function of the temperature which has the form

$$W(T)=D\exp(-K/TS_c)\ , \tag{3}$$

where D is a constant, K is a quantity to be defined in Eq. (4), and S_c is the molar configurational entropy of the system. Since the relaxation time $\tau(T)$ is reciprocally proportional to $W(T)$, they arrive at the expression

$$-\ln\frac{\tau(T)}{\tau(T_s)}=K\left[\frac{1}{T_sS_c(T_s)}-\frac{1}{TS_c(T)}\right]\ . \tag{4}$$

T_s is an appropriately chosen temperature and $K=2.303\Delta\mu S_c^*/k$ a quantity directly calculable from the equilibrium data of each substance and tabulated in their paper. The whole problem of obtaining the explicit form for $\tau(T)$ rests on the calculation of the term in large parentheses, and this is done using the well-known thermodynamic equation

$$S_{c_b}-S_{c_a}=\int_{T_a}^{T_b}\left[\frac{\Delta C_{P_c}}{T}\right]dT \tag{5}$$

remembering that $S_c(T_0)=0$.

In order to evaluate Eq. (5) we need an expression for ΔC_{P_c} which we draw from the Gibbs-Di Marzio model. Yet, an explanation is pertinent due to the physical nature of the VFT equation. The denominator that appears in the exponential of Eq. (2) contains the term $T-T_0$ where T_0 is the temperature that corresponds to the one at which the configurational entropy vanishes since in this model the underlying relaxation mechanisms are associated with the number of available configurations. Then, if we restore to the explicit form obtained for the specific heat by Di Marzio and Dowell,[24] [cf. Eq. (31)] we see that

$$\Delta C_{P_c}=\frac{A}{x^2}+BX-CX^2\ , \tag{6}$$

where

$$X=T/T_g\ , \tag{7a}$$

$$A=R\left[\frac{\Delta\varepsilon}{RT_g}\right]^2 f(1-f)\ , \tag{7b}$$

$$B=4RT_g\Delta\alpha\ , \tag{7c}$$

$$C=4.17B\Delta\alpha\ . \tag{7d}$$

$\Delta\varepsilon$ is the energy difference for gauche and *trans*-isomers, f is the number of bonds “flexed,” and $\Delta\alpha$ is the bulk thermal expansion coefficient. In Eq. (6) the terms that arise from the vibrational contributions to the specific heat have been ignored since they do not contribute at all to the configurational entropy.

We are, therefore, assuming here that Eq. (6) is valid throughout the temperature interval $T_0 < T < T_s$ ($T_0=T_2$ in the Gibbs-Di Marzio theory).

Inserting Eq. (6) into Eq. (5) and making use of the explicit values so obtained for $S_c(T_s)$ and $S_c(T)$ one is finally led to the result that, the so-called logarithmic shift factor is given by,

$$-\ln\frac{\tau(T)}{\tau(T_s)}=K\left[\frac{1}{T_sS_c(T_s)}-\frac{1}{T(T-T_0)\{[(A/2T^2T_0^2)+C](T+T_0)+B\}}\right]\ , \tag{8a}$$

where

$$S_c(T_s)=(T_s-T_0)\left[\frac{A}{2T_s^2T_0^2}+C\right](T_s+T_0)+B\ . \tag{8b}$$

Equation (8a) is the main result of this paper. It expresses the logarithmic shift factor as a function of temperature in the whole range $T_0<T<T_s$ and further, it contains no adjustable parameters.

III. NUMERICAL RESULTS

In Table I the values of A, B, and C are given for six typical polymeric substances. Their calculation is based upon the results obtained by Di Marzio and Dowell[24] who required the substances in evaluating the discontinuity of the specific heat at the glass transition. The particular criteria used in selecting each one of them is given in the discussion of Eqs. (32a)–(32c) of their work[24] and the ensuing results tabulated in that same paper (Table II Ref. 24). The last column in this table represents the estimated error for the difference between the experimental specific heat and that calculated theoretically according to Di Marzio and Dowell.[24]

For our purposes we now rewrite Eq. (7a) in the following form:

$$\tau(T)=\tau_0\exp\left[\frac{K}{F(T)(T-T_0)}\right]\ , \tag{9}$$

where

$$F(T)=\frac{a}{2T_0^2}\gamma+BT-\frac{CT^2}{2}\gamma \tag{10a}$$

and

$$\gamma=\left[1+\frac{T_0}{T}\right]=\left[1+\frac{T_0}{T_g}X\right]\ . \tag{10b}$$

Clearly, Eq. (9) is of the VFT form provided one can identify the temperature interval in which $F(T)$ behaves practically as a constant within the experimental error. As it turns out this behavior is readily exhibited by six substances here examined, namely, polyisobutylene (PIB), polystyrene (PS), polyvinylchloride (PVC), polymethylacrylate (PMA), polyvinylacetate (PVAC), and polymethylmethacrylate (PMMA).

The behavior of F as a function of $X=T/T_g$ for the materials quoted in Table I has been analyzed by subdividing the temperature interval into two regions, namely $1<x<1.75$ and $0.1<x<1$. In both intervals the data have been fitted to a straight line using the least-squares method. The results are shown in Tables II and III, respectively. In the former case which corresponds to temperatures larger than T_g, precisely the range in which one expects the VFT equation to hold true the behavior of $F^{-1}(T)$ is practically a constant. This implies that the model predicts a value of the constant in the exponential of the VFT equation which is equal to the constant K in Eq. (9) times the constant term in the straight line equation of Table II. This value is listed in Table IV, where in the first column an experimental value for this constant has been taken from the work of Hodge.[25] The discrepancy with K is between a factor of 5 and 10. However, the results quoted by Hodge depend on a parameter $\Delta h/R$ which is related to the annealing time.[25] The values for this parameter are given in the second column of Table IV. Thus, one could inquire on the values of the parameter $\Delta h/R$ which would lead to the values of K predicted by our model. These are given in the fourth column of Table IV. In conclusion, considering the characteristics of the Gibbs-Di Marzio model, we may assert that it predicts with rather good accuracy the behavior of the substances considered above T_g, as far as the VFT equation is concerned.

In the second case, for temperatures below T_g, the slope of the straight line is no longer a constant. In fact it differs by approximately a factor of 10 from the corresponding values above T_g.

However, the temperature dependence of the logarithmic shift factor in the temperature range $T_0<T<T_g$, where $F(T)$ varies appreciably with T may be conveniently cast into a different form. Indeed it is clear that one can write

$$\tau=\tau_0\exp\frac{KT}{G(T)(T^2-T_0^2)}\ , \tag{11}$$

where now

$$G(T)=F(T)\gamma^{-1}\ . \tag{12}$$

Equation (12) has to be understood as a proposal to describe such temperature dependence of the relaxation time below the glass-temperature T_g transitions. Due to the lack of experimental data in this region its assessment remains an open question.

The whole analysis shows then that the VFT is strictly valid in the range where $T>T_g$ ($T=T_g+50$), whereas between the temperature T_0 and the glass temperature a

TABLE I. The values of parameters A, B, C, T_g, and T_0 for six polymeric substances.

Material	A	B	C	T_g	T_0 (K)	Estim. error %
PIB	244 824	0.0133	0.000 02	202	132	7.5
PVAc	558 150	0.0133	0.000 02	305	244	4.9
PS	834 774	0.0066	0.000 005	373	311	8.5
PVC	722 454	0.0099	0.000 012	347	289	20
PMMA	857 304	0.0099	0.000 012	378	332	33
PMA	457 056	0.0133	0.000 02	276	217	

TABLE II. In the first column the least-squares fit for the function $F^{-1}(x)$ [given by Eq. (10a)] is presented for temperatures $T > T_g$. In the second column, the percentual mean error in this fitting is reported.

Material	Least-squares fit	Mean error %
PS	$F^{-1}(x)=0.0137X+0.0883$	0.33
PVAc	$F^{-1}(x)=0.0171X+0.0772$	0.22
PMA	$F^{-1}(x)=0.0137X+0.0791$	0.35
PMMA	$F^{-1}(x)=0.0189X+0.0876$	0.17
PVC	$F^{-1}(x)=0.0211X+0.0780$	0.18
PIB	$F^{-1}(x)=0.0083X+0.0656$	0.58

TABLE III. In the first column the least-squares fit for the function $F^{-1}(x)$ [given by Eq. (10a)] is presented for temperatures $T < T_g$. In the second column, the percentual mean error in this fitting is reported.

Material	Least-square fit	Mean error %
PS	$F^{-1}(x)=0.0826X+0.0314$	10.10
PVAc	$F^{-1}(x)=0.0759X+0.0294$	9.74
PMA	$F^{-1}(x)=0.0748X+0.0288$	9.76
PMMA	$F^{-1}(x)=0.0866X+0.0324$	9.86
PVC	$F^{-1}(x)=0.0800X+0.0308$	9.14
PIB	$F^{-1}(x)=0.0587X+0.0234$	10.12

modified Arrhenius-type equation is valid, but the constant term in the exponential has to be replaced by the function given in Eqs. (11) and (12). An expression similar to that given by Eq. (11) has been recently derived using the method of stochastic matrices for disordered systems.[26]

IV. CONCLUDING REMARKS

The value of this calculation relies on the fact that at least for the substances here examined the Gibbs-Di Marzio model provides a reasonable explanation of the temperature range over which the modified VFT equation as expressed by Eq. (9) agrees with experiment. Considering the fact that this model is free from adjustable parameters this result may be added to the list of accomplishments of the model in providing an adequate description for the equilibrium properties of glasses.[27] However one should not take this result as universally valid for all glass-forming supercooled liquids. Two substances recently studied, glycerol and propylene glycol, have not been included in our comparison because of the lack of appropriate data relevant to the theoretical model. In a recent study on the temperature-dependent distribution of relaxation times in glycerol using light scattering,[28] a second-order polynomial in T is taken to fit the data for $\ln\tau$ but this is done so only for computational convenience. It remains to be seen if for this substance and others Eqs. (9) or (11) hold true.

Furthermore, it is also interesting to point out that a quadratic dependence in the temperature for the relaxation time τ or for its inverse related to the diffusion coefficient has been also reported recently in the literature. Indeed, the viscosity of supercooled liquids has been reexamined using concepts developed for energy transport in random media to find the equation

$$\eta(T)=10^{14}\exp\left[T_0^2\left[\frac{1}{T^2}-\frac{1}{T_g^2}\right]\right],$$

where η is in P (poise), fits the experimental data of inorganic and organic glasses.[29] This result thus points out a T^2/T_0^2 dependence of the exponential in the expression for τ [cf. Eq. (11)]. An independent justification for these results has been also obtained from a study of the ergodic behavior in supercooled liquids and glasses[30] where, moreover, the ideas of Adams and Gibbs in which all our work is based are dominated by fluctuations of finite length within which the particles are strongly correlated.

These departures from the Arrhenius rate law behavior of the viscosity, observed as the temperature T_g is approached, are also emphasized by Angell[31] simultaneously with the virtues of the Adam-Gibbs ideas behind the temperature dependence of the structure relaxation time given in Eq. (4). Also, these same ideas have been considered from a different point of view by Mohanty.[32]

We would like to emphasize the fact that in this calculation the significance of T_0 becomes meaningful. It is usually argued that the empirical significance of this temperature is unclear.[16,17] According to our results for all those materials described by the Gibbs-Di Marzio model T_0 is precisely the temperature which corresponds to

TABLE IV. In the first and second column, the experimental VFT constants and its corresponding cooling rate are given as reported in Ref. 25. In the third and fourth column, the theoretical and the required cooling rate are presented.

Material	Experimental VFT constants	Cooling Rate $-\frac{\Delta h}{R}$	Theoretical VFT constants	Required Cooling rate $-\frac{\Delta h}{R}$
PVAc	6.8992×10^3	88×10^3	1.0578×10^3	13.4923×10^3
PVC	2.7225×10^3	225×10^3	0.3686×10^3	30.4297×10^3
PS	2.52×10^3	175×10^3	0.6141×10^3	42.6458×10^3
PMMA	6.6792×10^3	138×10^3	0.5527×10^3	11.4194×10^3

infinite relaxation time or $S_c\,(T_0)=0$.

We also like to point out that this calculation supercedes previous efforts made to derive the VFT equation from the Adam-Gibbs theory,[19,20] insofar as that no truncations have been made on the full temperature dependence of the specific-heat expression. These truncations are necessary when the original VFT equation namely, Eq. (2), is the result.

Finally, we would also like to mention other attempts made to derive the VFT equation using different models. One of the best known is based on the association of the free-volume concept which relates the relaxation time and the probability distribution of free volume with percolation theory.[12,33] According to these ideas, the theory correctly predicts the preexponential factor in Eq. (2) and that the viscosity should have the same form as τ in the region of T_g.[33] Other derivation is based on ideas related to the Landau-Ginzburg theory[34] but we shall not discuss it here.

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