Revising the Formulization of the Narayanaswamy Equation Using the Adam-Gibbs Theory

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ABSTRACT:

Hodge's formulization of the Tool-Narayanaswamy-Moynihan (TNM) equation from the Adam-Gibbs (AG) theory was re-evaluated. The non-linearity parameter (x) and the apparent activation energy (Δh^*) of the TMN equation were re-derived. Compared with the original derivations, the revised values of x and Δh^* were better correlated with experimental results. Of particular importance, the revised theoretical x correctly predicts the experimental trend of x for the cooling rate of polystyrene, whereas the original derivation predicted an opposite trend. Furthermore, the new derivation establishes a strong relationship between the fragility coefficient (m) and the x of a material. The relationship correlates well with the experimental values for a wide range of

materials. Ultimately, the revised equations for x and Δh^* more precisely reveal the theoretical foundation of the phenomenological TNM equation, as it relates to structural relaxation of polymeric materials.

KEYWORDS:

Tool–Narayanaswamy–Moynihan (TNM) equation, Adam-Gibbs theory, Vogel-Tammann-Fulcher (VTF) equation, fragility/fragilities

Revising the Formulization of the Narayanaswamy Equation Using the Adam-Gibbs Theory in Polymers

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Correlation between the non-linearity parameter (x) in the TNM equation and the fragility index (m) of glassy materials

1. Introduction

Almost all materials can form glasses if cooled quickly enough from their liquid states.¹ Glassy materials are as important as crystalline materials in both fundamental study and industrial applications.² For macromolecules such as polymers, this process is more obvious, even when cooling at a moderate rate. Glass state materials are in quasi-equilibrium and will relax to their equilibrium states with time, as illustrated in Fig 1. Different properties of a material will respond to this relaxation process differently, but all share a similar path with respect to temperature and time. The relaxation process is an important factor when considering the production and application of a material. For instance, supermolecular ferroelectric materials such as polyvinylidene fluoride (PVDF) have gained much attention recently due to their potential applications in the electric device and energy harvesting, *etc.*³ The relaxation of polymers is crucial to the formation of polar, ferroelectric crystal domains, as well as to the formation of other polar regions (electrets), including meta-stable dipoles and space-charge.⁴

The relaxation of a material at the non-equilibrium state toward its equilibrium state is characterized by the relaxation function, ϕ_p , which is neither exponential nor linear.⁵ The ϕ_p is defined as follows,

$$\phi_p = \frac{p(T, t) - p(T, \infty)}{p(T, 0) - p(T, \infty)}$$

where T is temperature and t is time, and therefore $p(T, t)$ is the current property of a material (e.g., volume, viscosity), $p(T, \infty)$ is the equilibrium value of the property, and $p(T, 0)$ is the initial value of the property as the temperature is brought to T .

The non-exponential behavior of ϕ_p is described by the equation,

$$\phi_p = \exp[-\xi^\beta]$$

where $0 < \beta \leq 1$, indicating the non-exponent stretch, and ξ is the reduced time that is defined as,

$$\xi = \int_0^t \frac{dt'}{\tau(t')}$$

The key element in the above expression is the characteristic parameter, τ , which depends not only on the time (t), but also the thermal history (T), that is, $\tau = \tau(t, T)$. However, τ is often expressed in terms of the thermodynamic temperature T and fictive temperature T_f . T_f was first introduced by Tool *et al.*⁶ to express the departure of a property from its equilibrium value: when a material is suddenly cooled from its equilibrium state at T_a to a non-equilibrium state at T_b , T_f is defined as,

$$p(T_b, t) - p(T_b, \infty) = (p(T_b, 0) - p(T_b, \infty)) \exp\left(-\frac{t}{\tau(T_b, T_f)}\right)$$

where $p(T_b, t)$ is the property at time t , $p(T_b, \infty)$ is the property at equilibrium and $p(T_b, 0)$ is the initial property at temperature T_b . Therefore, instead of expressing τ as a function of t and T , one can express it as a function of T_f and T , that is, $\tau = \tau(T, T_f)$.

$\tau(T, T_f)$ is the center of interest for scientists in studying the ageing of non-crystalline materials such as amorphous inorganic solids and polymers. There are several expressions for parameter τ .^{7, 8} The most widely used is the Tool–Narayanaswamy–Moynihan (TNM) phenomenological equation,^{9, 10}

$$\tau = \tau_0 \exp \left[\frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f} \right] \quad (1)$$

where Δh^* is assumed to be the apparent activation energy, T_f is fictive temperature defined as the cross point between the extension of liquid state line and the line drawn from T with the same

slope as that of glassy state line, as shown in Fig 1, and R is the universal gas constant and x is the empirical coefficient with $0 \leq x \leq 1$. Also in Figure 1, T_2 is the so called Kauzmann temperature at which the configurational entropy of the material is zero, that is, $S_c(T_2) = 0$, and T_2 will be referred in a later section of this paper.

Fig 1, Schematic diagram of a property (p) vs. temperature (T) and its relaxation at T

Because the above TNM equation is an empirical equation, the parameters h^* and x have no clear physical meaning. It is generally believed that h^* is related to the energy barrier for molecules to overcome in order to relax towards the equilibrium state, and x is the partition parameter indicating the weight of thermodynamic contribution on h^* so $(1 - x)$ indicating the weight of structural contribution to.

As pointed out by Hodge,¹¹ even though the TNM equation successfully represents the relaxation of amorphous materials in the glass transition region, it has two shortcomings: first, the equation is empirical and lacks the support from fundamental theories; second, when extended to the equilibrium state where $T_f = T$, the TNM reduces to the Arrhenius equation as,

$$\tau = \tau_0 \exp \left[\frac{\Delta h^*}{RT} \right]$$

This is inconsistent with the well-known experimental Vogel-Tammann-Fulcher (VTF) equation:¹²

$$\tau = A \exp \left[\frac{D}{T - T_2} \right]$$

where both A and D are constants.

The above two limitations motivated scientists to explore the more fundamental insights beyond the TNM equation, which is briefly outlined as follows:

The general approach is to develop the TNM equation from the basic theory of thermodynamics or statistical mechanics. For instance, Gujrati¹³ applied non-equilibrium thermodynamics to the relaxation of glassy materials. He related the parameter x in the TNM equation to basic thermodynamic quantities by separating the instantaneous temperature (T) during the relaxation into equilibrium temperature (T_e) and non-equilibrium temperature (T_n). While this analysis designates the physical meaning on the partition parameter (x) in the TNM equation, the apparent activation energy (Δh^*) in the TNM equation was still kept as a constant. However, if the structure of a material undergoes change during relaxation, the apparent activation energy might change as well, as discussed in the later part of this section. Notwithstanding, the most promising approach is applying the statistical-mechanical Adam-Gibbs (AG) theory to the glass formation proposed by Scherer and Hodge *et al.*^{14, 15} The AG theory describes the change of configurational entropy during the relaxation of polymers relaxing from a non-equilibrium state to an equilibrium state and relates the relaxation constant (τ) to the excess configurational entropy as,

$$(2)$$

where A is the pre-exponential constant, N_A is Avogadro's number, s^* is the configurational entropy for the smallest group to rearrange, $\Delta\mu$ is the activation energy for a conformational unit

to relocate, k is the Boltzmann constant and $S_c(T)$ is the thermodynamic configurational entropy.

Furthermore, $S_c(T)$ is often expressed by the equation,

$$S_c(T_f) = \int_{T_2}^{T_f} \frac{\Delta C_p(T)}{T} dT \quad (3)$$

where T_2 is the Kauzmann temperature that is a constant and $\Delta C_p(T)$ is the heat capacity contributed by the energy related to the access of new configurational states and is often assumed to be the difference between liquid and glass heat capacity, although it was argued that this is only an approximation.^{16,17,18} Different formats of $\Delta C_p(T)$ were suggested for studying different types of matter. In polymeric materials, Hodge proposed that $\Delta C_p(T)$ can be approximated by the hyperbolic function of temperature T as:

$$\Delta C_p(T) = \frac{C}{T}$$

Therefore, inserting the above $\Delta C_p(T)$ into eq (3), Hodge obtained,

$$S_c(T_f) = \int_{T_2}^{T_f} \frac{\Delta C_p(T)}{T} dT = C \left[\frac{1}{T_2} - \frac{1}{T_f} \right]$$

Further applying such $S_c(T)$ into eq (2) generates,

$$\tau = A \exp \left[\frac{N_A s^* \Delta \mu}{k C T (1/T_2 - 1/T_f)} \right] = A \exp \left[\frac{D_0}{T (1/T_2 - 1/T_f)} \right] \quad (4)$$

where the constant D_0 is defined as

$$D_0 = \frac{N_A s^* \Delta \mu}{k C}$$

When at the glassy state, both T_2 and T_f are constants and eq (4) becomes the Arrhenius equation,

$$\tau = A \exp \left[\frac{D}{T} \right]$$

with $D = \frac{D_0}{1/T_2 - 1/T_f}$.

Similarly, when at the equilibrium state, T_f is no longer a constant; rather $T_f = T$, eq (4) takes the

VTF format,

$$\tau = A \exp \left[\frac{D_0}{T(1/T_2 - 1/T)} \right] = A \exp \left[\frac{D_0}{T/T_2 - 1} \right] = A \exp \left[\frac{D_0 T_2}{T - T_2} \right] = A \exp \left[\frac{D}{T - T_2} \right]$$

where $D = D_0 T_2$.

The above VTF format was also suggested by Angell, who correlated the parameter D with the “strength” of a liquid, as either strong or fragile.¹⁹ Equation (4) is considered to be the theoretical ground on which the TNM equation is based and was called the Adam-Gibbs-Fulcher (AGF) equation by Hodge.²⁰ Therefore, the τ in the theoretical AGF equation (4) should be the same as that in the empirical TNM equation. However, when at the equilibrium state, the AGF equation induces the VTF format while the TNM equation induces the Arrhenius format.

Nevertheless, in a recent work, Dhotel *et al.*²¹ applied Differential Scanning Calorimetry (DSC) and Flash DCS (F-DSC) to study the fictive temperature (T_f) of polystyrene (PS) and poly(ethylene terephthalate)-glycol (PETg) over a broad range of heating and cooling rates. They found great consistency within the TNM model and fragility concept designated by fragility index m that was calculated from the VTF equation. *This indicates that the TNM equation should converge to the VTF equation rather than the Arrhenius equation toward the equilibrium state.*

In order to resolve this disagreement, Hodge suggested that the Δh^* in the TNM equation is a function of fictive temperature (T_f), that is, $\Delta h^* = \Delta h^*(T_f)$.²² This is physically plausible when considering Δh^* is the apparent activation energy for the rearrangement of molecules and T_f is the fictive temperature describing the configuration related to the molecular arrangement. He further developed the mathematical expressions of $\Delta h^*(T_f)$ and x :

$$\frac{\Delta h^*(T_f)}{R} = \frac{D}{(1 - T_2/T_f)^2} \quad (5)$$

$$x \approx 1 - \frac{T_2}{T_f} \quad (6)$$

These are the basic equations obtained by Hodge. When at the glassy state, $T_f = T_g$, the equation is further reduced to,

$$x \approx 1 - \frac{T_2}{T_g} \quad (7)$$

The above equations have been widely cited, including an influential paper in *Science*,⁵ however, inconsistencies in its predictive capabilities have been noted.^{23, 24} For instance, Hutchinson *et al.*²³ pointed out that the above resultant x induces an anomalous large value of T_2 . In addition, Morris *et al.*²⁴ found that the trend of x versus T_f is *opposite* to that predicted by eq (6), as further elaborated in the next section. In order to resolve these issues, we carefully examined the original derivation and found that during the derivation of the analytical formula of Δh^* with respect to T_f , Δh^* was treated as a constant,¹⁵ which was contradictory to the original assumption that Δh^* is a function of fictive temperature (T_f), as aforementioned. This is further discussed in the following “Derivation” section, along with our modifications. As a result of this discovery, we re-derived $\Delta h^*(T_f)$ and x in the TNM equation and compared the predictive capabilities to those of the original formulas.

2. Derivation

(a) Analyzing the original derivation

The original derivations were carried out under the equilibrium condition. The key derivations in the original paper²² were copied here:

Approximate relationships between the AGF and N parameters can be derived by appropriate differentiation of eq 2 and 6. In the equilibrium state

$$\Delta h^* = R \frac{d \ln \tau}{d(1/T)} = D / (1 - T_2/T)^2 \quad (8)$$

The above eq 2 corresponds to the TNM equation (1) and copied here:

$$\tau = \tau_0 \exp \left[\frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f} \right]$$

and eq 6 corresponds to the AGF equation (4) and copied here:

$$\tau = A \exp \left[\frac{D}{RT(1 - T_2/T_f)} \right]$$

The development of eq (8) was retrieved as follows:

At equilibrium state, $T = T_f$, the TNM equation reduces to

$$\tau = \tau_0 \exp \left[\frac{\Delta h^*}{RT} \right]$$

Taking the $\ln$ of both sides,

$$\ln \tau = \ln \tau_0 + \frac{\Delta h^*}{RT}$$

Differentiating the above equation with respect to $1/T$,

$$\frac{d \ln \tau}{d(1/T)} = \frac{d(\Delta h^* / RT)}{d(1/T)}$$

Only when Δh^* is independent from T can the above equation be further converted to,

$$\frac{d \ln \tau}{d(1/T)} = \frac{\Delta h^*}{R}$$

Solving for Δh^* gives the first equality in eq (8),

$$\Delta h^* = R \frac{d \ln \tau}{d(1/T)} \quad (8a)$$

Now, considering the AGF equation:

Similarly, at equilibrium state, $T = T_f$, and the AGF equation becomes:

$$\tau = A' \exp \left[\frac{D}{RT(1 - T_2/T_f)} \right] = A' \exp \left[\frac{D}{R(T - T_2)} \right]$$

Applying this result to eq (8a) yields the result eq (8):

$$\Delta h^* = \frac{d \ln \tau}{d(1/T)} = D/(1 - T_2/T)^2$$

Therefore, it is clearly seen from the above derivations that eq (8) is self-contradictory: *In order to obtain the results for Δh^* using differential definition as eq (8a), Δh^* is assumed to be temperature independent. However, if the AGF equation is applied to eq (8a), it was concluded that Δh^* is a function of T as in eq (8). Therefore, the above result is contradictory to its assumption.*

To resolve this problem, we re-envisioned Δh^* and x on the basis of the following reasoning:

Since the purpose was to find the relation between Δh^* and $T_f (= T \text{ at equilibrium})$ using the AGF equation, we abandoned the above differential definition of Δh^* in eq (8a) where the independence of Δh^* on T is required.

(b) Re-deriving the apparent activation energy $\Delta h^(T_f)$*

First, it is worth pointing out that the above eq (8) of Δh^* is same as eq (5) but with different notation. In order to keep it consistent, eq (5) derived in Hodge's other paper is used here.^{Error!}

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Actually, the derivation of $\Delta h^*(T_f)$ and x is more straightforward when the empirical TNM equation is directly compared to the theoretical AGF equation, as discussed below:

Based on the Hodge's postulation, the apparent energy Δh^* in the TNM equation is a function of the fictive temperature, that is $\Delta h^* = \Delta h^*(T_f)$. This is very physically plausible since the relaxation of a material from one state to another must involve overcoming the energy related to the current structure, which can be characterized by the fictive temperature T_f .

Similar to the Hodge's derivation, when at the equilibrium, $T_f = T$, the AGF equation (4) becomes

$$\tau = A \exp \left[\frac{D_0}{T(1/T_f - 1/T)} \right] = A \exp \left[\frac{D_0 T_f}{T - T_f} \right]$$

On the other hand, under the same condition ($T_f = T$), the TNM equation (1) becomes

$$\tau = \tau_0 \exp \left[\frac{x \Delta h^*(T_f)}{RT} + \frac{(1-x) \Delta h^*(T_f)}{RT_f} \right] = \tau_0 \exp \left[\frac{\Delta h^*(T)}{RT} \right]$$

Since the above two equations describe the same physical quantity, they should be equivalent:

$$A \exp \left[\frac{D_0 T_f}{T - T_f} \right] = \tau_0 \exp \left[\frac{\Delta h^*(T)}{RT} \right]$$

$$\ln A + \frac{D_0 T_f}{T - T_f} = \ln \tau_0 + \frac{\Delta h^*(T)}{RT}$$

Therefore,

$$\frac{\Delta h^*(T)}{R} = \left(\ln \frac{A}{\tau_0} \right) T + \frac{D_0 T_f}{1 - T_f/T}$$

Since the system is at equilibrium ($T = T_f$), the above equation can be converted to,

$$\frac{\Delta h^*(T_f)}{R} = \left(\ln \frac{A}{\tau_0} \right) T_f + \frac{D_0 T_f}{1 - T_f/T_f} = \left(\ln \frac{A}{\tau_0} \right) T_f + \frac{D}{1 - T_f/T_f} \quad (9)$$

Although the above expression for $h^*(T_f)$ is obtained from the rubbery state, it may be reasonably extended to the temperature range encompassing the entire transition state and the glassy state. Extension of the above expression makes sense, since Δh^* is the apparent activation energy related to the structure of the material and the temperature T_f is used to describe the structure of the fictitious equilibrium state when at glassy and transition states.

(c) Derivation of the non-linearity parameter x

When at the glassy state as shown in Fig 1, T_f is a constant; therefore, $\Delta h^*(T_f)$ (eq (9)) is also a constant. As noted previously, under the same condition, both the TNM equation and the AGF equation are equivalent, that is

$$A \exp \left[\frac{D_0}{T(1/T_2 - 1/T_f)} \right] = \tau_0 \exp \left[\frac{x \Delta h^*(T_f)}{RT} + \frac{(1-x) \Delta h^*(T_f)}{RT_f} \right]$$

Therefore,

$$\ln A + \frac{D_0}{T(1/T_2 - 1/T_f)} = \ln \tau_0 + \frac{x \Delta h^*(T_f)}{RT} + \frac{(1-x) \Delta h^*(T_f)}{RT_f}$$

Since x , T_f and $\Delta h^*(T_f)$ are all constants with respect to temperature (T), equating the coefficients of $1/T$ on both sides leads to

$$\frac{D_0}{1/T_2 - 1/T_f} = \frac{x \Delta h^*(T_f)}{R}$$

By applying eq (9), we obtain,

$$x = \frac{D_0}{D_0 + \left(\frac{T_f}{T_2} - 1 \right) \ln \frac{A}{\tau_0}} \quad (10)$$

Similar to the previous reasoning, when at the glassy state, $T_f = T_g$, eq (10) becomes,

$$x = \frac{D_0}{D_0 + \left(\frac{T_g}{T_2} - 1 \right) \ln \frac{A}{\tau_0}} \quad (11)$$

In summary, after revising the original derivation, we re-derived the corrected analytical formula of $\Delta h(T_f)$ and x . The results are further discussed in the next section.

3. Comparison of x with Original Results

In the TNM equation, x is the partition factor for the configurational contribution to the relaxation. As a result, from the relationship between x and T_f , we checked the validity of the nonlinearity parameter x for each derivation (original and new). The general comparative results are: (a) For the original eq (7) derivation, x decreases with a decrease in T_g , and $x \rightarrow 0$ as $T_g \rightarrow T_2$; and (b) For the new eq (11) derivation, x increases with a decrease in T_g , and $x \rightarrow 1$ as $T_g \rightarrow T_2$. The results oppose each other.

It must be noted that the Kauzmann temperature (T_2) is a thermodynamic parameter, while the glass transition temperature (T_g) is a kinetic parameter. The limit $T_g \rightarrow T_2$ corresponds to an infinitely long relaxation period that allows molecules to rearrange to their equilibrium states. In such a scenario, the thermodynamic contribution should be more prominent than the configurational contribution, indicating the first half of the TNM equation is more dominant and therefore, x should be close to 1. This interpretation is also consistent with Ingram *et al.*,²⁵ who suggested that a low x value indicates the importance of fictive temperature. From the TNM equation as eq (1), we can see that a lower x value indicates a smaller contribution from the first item, which is represented by the temperature T_f and therefore a larger contribution from the structural $(1 - x)$ component, which is represented by the fictive temperature, T_f .

The above argument only qualitatively supports the new formulation of parameter x . However, recent studies investigating Δh^* and x have allowed for a more comprehensive and quantitative evaluation of these mathematical treatments. For instance, Morris *et al.*²⁴ studied the determination of x on ageing time and claimed that “*decreases in T_f as in annealing, will cause x to increase.*” This conclusion is consistent with our derived equation of x (eq (10)), and contradictory to the original one by Hodge (eq (6)). Furthermore, more detailed research on the relaxation of standard polystyrene samples has been reported,^{26,27} and this has provided an ideal sample to quantitatively compare the two derivations. Two groups of published data were used to make quantitative comparisons with respect to: (a) the calculated Δh^* and x values versus experimental data; and (b) different trends of x with the fictive temperature (T_f) predicted by the two different equations. These comparisons are further elaborated in the following paragraphs.

Liu *et al.*²⁶ studied the enthalpy relaxation of polystyrene using both Tools-Narayanaswamy-Moynihan (TNM) and Adam-Gibbs-Fulcher (AGF) modes with consideration of the structural dependence and coupling model. The Δh^* values were calculated using equations (5) (Original) and (9) (Revised), and the x values were calculated using equations (7) (Original) and (11) (Revised), with their respective percent errors also listed. From Table 1, the revised equation (9) gives Δh^* values that are much closer to the experimental measures, with all the percent errors within 1.0 %. In contrast, the original eq (5) values possess a much higher percent error, ranging from 0.9 to 20.5 %. Similarly, revised x values are also improved and range from 0.53 to 13.3 % error in comparison to 3.22 to 37.0 % error with the original derivation. Comparisons of additional Δh^* and x values for materials other than polystyrene are shown in Fig 2, where all the experimental data were from a review paper.¹¹ It is evident from Fig 2 that both Δh^* and x values calculated from the newly revised equations more closely match the experimental values.

Table 1, Comparison of original and current Δh^* and x of polystyrene (PS)

Model	$\Delta h^*/R$ (<i>kK</i>)	T_2 (K)	x	$\ln \tau_0$	Model	T_2 (K)	D	$\ln A$	$\Delta h^*/R$ (Original)		$\Delta h^*/R$ (Current)		x (Original)		x (Current)	
									value (<i>kK</i>)	error%	value (<i>kK</i>)	error%	value	error%	value	error%
TNM	76.2	–	0.410	-199.71	AGF	225	12.1	-77.23	76.9	0.86	76.2	0.025	0.397	3.22	0.400	2.36
TNM-K1	77.0	156	0.403	-201.86	AGF-K1	167	19.4	-89.75	63.6	17.4	76.9	0.072	0.552	37.0	0.456	13.3
TNM-K2	77.6	199	0.398	-203.34	AGF-K2	195	16.1	-85.23	70.7	8.90	77.8	0.25	0.477	19.9	0.434	8.97
TNM-CM-K1	40.4	154	0.446	-116.76	AGF-CM-K1	167	9.8	-57.1	32.1	20.5	40.0	0.99	0.552	23.8	0.444	0.53
TNM-CM-K2	36.7	198	0.483	-106.87	AGF-CM-K2	199	8.06	-54.93	37.0	0.92	36.7	0.13	0.466	3.42	0.471	2.40

Fig 2, Calculated values of Δh^* and x versus experimental values¹¹

Even though the above comparisons in Table 1 and Fig 2 follow similar trends for a variety of materials, comparison of the trend of x with respect to the fictive temperature (T_f) of a same material reveal a more extreme divergence between the two derivations. This is because the revised eq (10) and the original eq (6) for x predict *opposite* trends with respect to T_f as mentioned previously. Initially, O'Reilly *et al.*²⁸ found that the x values increased as the cooling rate decreased for polystyrene samples. In a more recent study, the relationship between the cooling rate and T_f were also investigated with a polystyrene sample.²⁷ In the paper, Tropin *et al.*²⁷ reported their work on heat capacity relaxation of polystyrene with a wide range of cooling rates and obtained a correlation between the cooling rate and T_f as replicated in Fig 3. Substituting the fitting equation in Fig 3 into the two different equations (original, 6) and (revised, 10) generates the relationships between the parameter x and the cooling rate, as shown in Fig 4. It is clearly seen from these data, that the original equation for x generates a trend opposite to experiment, while the revised equation provides one consistent with experiment.

Fig 3, Relationship between the fictive temperature (T_f) and cooling rate (q)²⁷

Fig 4, Comparison between the trends of theoretical x and experimental x of polystyrene:
(a) original result, (b) current result (Experimental results are from reference²⁸)

4. Relationship between x in the TNM Equation and the Fragility of Materials

Angell *et al.* classified glass materials into “strong” and “fragile” liquids based on their deviation from Arrhenius behavior.²⁹ The quantitative parameter used to measure fragility is called the steepness index m , which is defined as,³⁰

$$m = \left. \frac{d(\log \langle \tau \rangle)}{d(T_g/T)} \right|_{T=T_g}$$

where $\langle \tau \rangle$ is the average relaxation time and is described by the VTF equation.

They further developed the relationship between the fragility parameter m and the constant D in the VTF equation as,

$$m = 16 + 590/D \quad (12)$$

From eq (10) and the VTF equation, we can obtain the following expression,

$$1/D = 1/(D_0 T_2) = \left(\frac{1}{x}\right) \frac{1}{(T_f - T_2) \ln \frac{A}{\tau_0}} - \frac{1}{(T_f - T_2) \ln \frac{A}{\tau_0}} \quad (13)$$

Substituting eq (13) into eq (12), we obtain the relation between m and x as,

$$m = 16 + \left(\frac{1}{x}\right) \frac{590}{(T_f - T_2) \ln \frac{A}{\tau_0}} - \frac{590}{(T_f - T_2) \ln \frac{A}{\tau_0}} = 16 + C_1 \left(\frac{1}{x}\right) - C_1 \quad (14)$$

Equation (14) has a clear physical meaning: as seen in the previous section and with eq (1), x is the partition parameter of thermodynamic contribution and $(1 - x)$ indicates the structural contribution. A larger x value indicates a larger thermodynamic effect and smaller structural effect in the relaxation and, accordingly, the Arrhenius part in the TNM equation becomes more prominent. On the other hand, a smaller m indicates less deviation from the Arrhenius behavior based on Angell's classification.²⁹ Therefore, the larger x value should correlate to a smaller m value for a material, as clearly expressed in eq (14). On the contrary, such a relationship cannot be obtained via the original expression of x in eq (6), where x is only determined by the ratio of T/T_f and has no explicit relationship with the parameter D .

The decrease of m with an increase in x is well documented and can be used to verify the above argument.^{31,32,33,34}

Equation (14) predicts the same trend on for m versus x as that from the relation proposed by Böhmer.³⁵ There are two theoretical limiting curves in the Böhmer equation, as shown in Fig 5. However, several materials (about 25 %) are well outside of the Böhmer's limiting curves. Also, Wungtanagorn *et al.*³⁶ did detailed analysis experimentally on m and x for several sugar samples and the results are completely beyond the region defined by the Böhmer's limiting curves. In contrast, the new curve using eq (14) presents a better fit to the data from different materials.

Furthermore, there are two interesting points worthy of mention. First, instead of two fitting parameters in a normal hyperbolic fitting equation, $m = C_1/x + C_2$, here the fitting equation eq (14), $m = 16 + C_1/x - C_1$ only has one fitting parameter C_1 . While the fitting result is still surprising, this clearly indicates the effectiveness of both Angell's model on fragility (m) and the new description on non-linearity (x). Second, from eq (14), different materials should have different C_1 constants since both T_f and T_2 are different for different materials. Nevertheless, the fitting curve and experimental data still show the clear relation between m and x , indicating that m depends much more on x than on other parameters, such as T_f , T_2 , τ_0 , etc. This is also reflected in the relatively small uncertainty of fitting parameter, $C_1 = 35.19 \pm 1.66$, which has only 5 % of uncertainty despite a wide range of materials ranging from inorganic to organic polymers. This demonstrates that the structural parameter (x) of a material is more important in determining its fragility (m) than all other thermodynamic and kinetic parameters combined, such as T_f , T_2 and τ_0 ,

Fig 5, Correlation between the non-linearity parameter x in the TNM equation and the fragility index (m) of glassy materials (All data are copied from Ref. 35. Two dashed curves are Böhmer's limiting fitting and the solid curve is the fitting from eq (14))

5. Conclusion

In this paper, Hodge's formalization of the Tool–Narayanaswamy–Moynihan (TNM) equation by applying the Adam–Gibbs theory was revised to resolve a hidden condition in which Δh^* was assumed to be constant with respect to T . New formulas for the non-linearity parameter x and the apparent energy Δh^* in the TNM equation were derived. To test the validity of these new derivations, the values of x and Δh^* from the original equations and new equations were compared against experimental results. It was found that the newly revised formulas better correlate with the experimental data. In addition, the new derivations predict the trend consistent with experiment on x versus cooling rate for a standard polystyrene sample, while the original formula predicts an inverse trend. Lastly, via the new expression, an explicit relation between the non-linearity parameter x in the TNM equation and the fragility index m in Angell's classification was established and found to apply to experimental data for a wide range of materials. Therefore, it is concluded that the new equations of non-linearity parameter x and the apparent activation energy Δh^* more precisely reveal the theoretical foundation of the phenomenological Tool–Narayanaswamy–Moynihan (TNM) equation.

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- [1] M. D. Ediger, *Science*, 287 (2000) 604 – 605.
- [2] M. D. Ediger, C. A. Angell, S. R. Nagel, *J. Phys. Chem.* 100 (1996) 13200 – 13212.
- [3] A. S. Tayi, A. Kaeser, M. Matsumoto, T. Aida, S. I. Stupp, *Nature Chemistry* 7 (2015) 281 – 294.
- [4] S. Ducharme, M. Poulsen, *Digital Commons Publications*, Paper 67 (2010)
(<http://digitalcommons.unl.edu/physicsducharme/67>)
- [5] I. M. Hodge, *Science* 267 (1995) 1945 – 1947.
- [6] A. Q. Tool, *J. Amer. Ceram. Soc.* 29 (1946) 240 – 253.
- [7] P. B. Macedo, T. A. Litovitz, *J. Chem. Phys.* 42 (1965) 245 – 256.
- [8] O. V. Mazurin, V. P. Kluyev, S. V. Stolyar, *Glastech. Ber.* 56 (1983) 1148 – 1153.
- [9] C. T. Moynihan, A. J. Easteal, M. A. DeBolt, J. Tucker, *J. Am. Ceram. Soc.* 59 (1976) 12 – 16.
- [10] O. S. Narayanaswamy, *J. Am. Ceram. Soc.* 54 (1971) 491 – 498.
- [11] I. M. Hodge, *J. Non-Cryst. Solids* 169 (1994) 211 – 262.
- [12] H. Vogel, *Phys. Z.* 22 (1921) 645 – 646; G. Tammann, G. Hesse, *Anorg. Allg. Chem.* 156 (1926) 245 – 267; G. S. Fulcher, *J. Am. Ceram. Soc.* 8 (1925) 339 – 355.
- [13] P. D. Gujrati, *Phys. Rev. E* 81 (2010) 1 – 13.
- [14] G. W. Scherer, *J. Amer. Ceram. Soc.* 67 (1984) 504 – 511.
- [15] I. M. Hodge, *Macromolecules* 20 (1987) 2897 – 2908.
- [16] M. Goldstein, *J. Chem. Phys.* 64 (1976) 4767 – 4773.
- [17] S. Sastry, *Nature* 409 (2001) 164 – 167.
- [18] L. M. Martinez, C. A. Angell, *Nature* 410 (2001) 663 – 667.
- [19] C. A. Angell, *Polymer* 38 (1997) 6261 – 6266.
- [20] I. M. Hodge, *J. Res. Natl. Inst. Stand. Technol.* 102 (1997) 195 – 204.

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- [21] A. Dhotel, B. Rijal, L. Delbreilh, E. Dargent, A. Saiter, *J. Therm Anal Calorim.* 121 (2015) 453 – 461.
- [22] I. M. Hodge, *Macromolecules* 19 (1986) 938 – 941.
- [23] J. M. Hutchinson, S. Montserrat, Y. Calventus, P. Cortes, *Macromolecules* 33 (2000) 5252 – 5262.
- [24] C. Morris, A. J. Taylor, I. A. Farhat, W. MacNaughtan, *Carbohydrate Research* 346 (2011) 1122–1128.
- [25] M. D. Ingram, J. M. Hutchinson, J. A. Pappin, *Phys. Chem. Glasses* 32 (1991) 121 – 128.
- [26] G. Liu, Y. Zuo, J. Lin, and D. Zhao, *Eur. Phys. J. E*, 37: 63 (2014), 1 – 8.
- [27] T. V. Tropin, G. Schulz, J. W. P. Schmelzer, C. Schick, *Journal of Non-Crystalline Solids* 409 (2015) 63 – 75.
- [28] J. M. O'Reilly and I. M. Hodge, *Journal of Non-Crystalline Solids* 131-133 (1991) 451- 456.
- [29] C. A. Angell, *J. Non-Cryst. Solids* 13 (1991) 131 – 133.
- [30] R. Böhmer, K. L. Ngai, C. A. Angell, D. J. Plazek, *J. Chem. Phys.* 99 (1993) 4201– 4210.
- [31] K. L. Ngai, R. W. Rendell, L. D. Pye, W. C. LaCourse, H. J. Stevens (Eds.), *The Physics of Non-Crystalline Solids*, Taylor and Francis, London, 1992, p. 309.
- [32] D. J. Plazek, K. L. Ngai, *Macromolecules* 24 (1991) 1222 – 1224.
- [33] R. Böhmer, C. A. Angell, in: R. Richert, A. Blumen (Eds.), *Disorder Effects on Relaxational Processes*, Springer, Berlin, 1994, p. 11.
- [34] C. A. Angell, *J. Non-Cryst. Solids* 131-133 (1991) 13 – 31.
- [35] R. Böhmer, *J. Non-Cryst. Solids* 172-174 (1994) 628 – 634.
- [36] R. Wungtanagorna, S. J. Schmidt, *Thermochimica Acta* 369 (2001) 95 – 116.