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Short communication

A more realistic approach toward the differential equation governing the glass transition phenomenon

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ABSTRACT

In this contribution, the non-linear differential equation governing the glass transition phenomena of metallic glasses has been investigated analytically through a powerful mathematical tool known as the Adomian decomposition method. Unlike the previous works in this context, no simplifying assumption has been made so that the approach is more realistic. Furthermore and as a salient advantage, the method is free of discretization, linearization and perturbation. For the sake of exemplification, the resulted general solution was tested for the alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and the relevant "free volume vs. temperature" curves were obtained. In addition, as another illustrative example, the glass transition temperature for the alloy $Pd_{40}Ni_{40}P_{20}$ was estimated by the proposed scheme. The employed approach was successful to predict the glass transition temperature for the test case alloys closer to the experimental values than those of by the prior mathematical works in the literature.

1. Introduction

The glass transition in amorphous materials is encountered during differential scanning calorimetry (DSC) experiments in which a sample is heated at a constant rate. It is concurrent with a sudden rise in the specific heat followed by a maximum. Some specific alloys which undergo the glass transition are classified as metallic glasses according to a scientific terminology and an account of them, usually multicomponent systems, can be found in [1,2]. More discussion concerning the glass transition and metallic glasses is beyond the scope of this communication and the interested reader is recommended to consults the references [3,4].

In Ref. [5], van den Beukel and Sietsma managed to describe the glass transition as a kinetic phenomenon driving the change in free volume from a non-equilibrium toward an equilibrium state during the warming up. They used the famous Vogel–Fulcher–Tammann (VFT) equation for viscosity as a basis to define the equilibrium free volume. Takeuchi and Inoue [1,6] followed the work and carried out some linearizations and parameter fittings to tackle the difficulties involved in the governing non-linear differential equation.

It is the purpose of this communication to investigate the original model by van del Beukel and Sietsma in its complete form (i.e. without applying any simplifications) to be more realistic. This is fulfilled by employing a powerful analytical technique known as the Adomian decomposition method.

2. Formulation of the problem

In this section we only describe the main points of derivation of the governing equation and make reference to [5] for full details.

A rate-based expression for the change of concentration equivalents of the free volume during a DSC experiment with respect to time can be written as

$$\frac{dC_f}{dt} = -kC_f(C_f - C_{fe}) \tag{1}$$

The concentrations are related to the free volume by the following equations

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$$C_f = e^{-1/x} \tag{2}$$
$$C_{fe} = e^{-1/x_{eq}} \tag{3}$$

An Arrhenius type expression for the kinetic constant is chosen.

$$k = C_0 e^{-E/RT} \tag{4}$$

And the free volume at the equilibrium state is evaluated by a VFT-like expression

$$x_{eq} = \frac{T - T_0}{B} \tag{5}$$

As the heating is performed at a constant rate, α, during the whole process, we can write

$$\frac{dC_f}{dt} = \alpha \frac{dC_f}{dT} \tag{6}$$

Substituting Eqs. (2)–(6) in Eq. (1) and performing simple operations concludes

$$\frac{dx}{dT} = -\frac{C_0 x^2}{\alpha} e^{-E/RT} \left(e^{-1/x} - e^{-B/T-T_0} \right) \tag{7}$$

3. Basics of the ADM

The Adomian decomposition method (ADM) and its related modifications [7–11] have found widespread applications in treatment of many functional equations (i.e. linear or non-linear algebraic, differential, integral, integro-differential, etc.). Through its analytical methodology, the ADM furnishes the exact solution rapidly in most cases. As a salient advantage, the ADM is free of discretization, linearization, or perturbation. There exists a considerable deal of research works benefiting from this method (e.g. see Refs. [12–16]).

For the ease of the reader, we provide a quick review of the basic idea of the ADM in this part.

Without loss of generality, let us consider a general differential equation as follows

$$Lu + Nu + Ru = g \tag{8}$$

where L is an easily invertible linear operator, here the differential operator, N denotes the nonlinear operator, Ru symbolizes the remaining parts and g is a bounded known function. Taking the inverse operator L^{-1}, i.e. integral operator, from the both sides of Eq. (8) gives

$$u = a - L^{-1}g - L^{-1}Nu - L^{-1}Ru \tag{9}$$

with a being emerged from the integrations.

According to the ADM, the solution to Eq. (8) corresponds to a decomposed infinite series as $u = \sum_{n=0}^{\infty} u_n$ and the non-linear terms shall be replaced by a special representation of $Nu = \sum_{n=0}^{\infty} A_n$ which are famous as Adomian polynomials. These polynomials are recursively obtained from the following definitional formula,

$$A_n(u_0, u_1, \ldots, u_n) = \frac{1}{n!} \left[\frac{d^n}{d\lambda^n} N \left(\sum_{i=0}^{\infty} \lambda^i u_i \right) \right]_{\lambda=0} \tag{10}$$

By substituting the preceding summations into Eq. (9) and choosing $u_0 = a - L^{-1}g$ subsequent to a regrouping it yields

$$\begin{cases} u_0 = a - L^{-1}g \\ u_{i+1} = -L^{-1}A_i - L^{-1}Ru_i; \quad i \geq 0 \end{cases} \tag{11}$$

The forgoing recurrence simply provides the convenient solution to Eq. (8).

The convergence of the ADM has been investigated fully in [17].

4. Solution of the problem by the ADM

Let us write the Eq. (7) in its operator form equivalent as

$$Lx = -\frac{C_0 x^2}{\alpha} e^{-E/RT} \left(e^{-1/x} - e^{-B/T-T_0} \right) \tag{12}$$

with $L(\cdot) = d(\cdot)/dT$, and essentially $L^{-1}(\cdot) = \int_{T_{in}}^{T} (\cdot) dT$.

According to the described principles of the ADM, we conclude the solution in the form of the recurrence to follow

$$\begin{cases} x_0 = x_{in} \\ x_{i+1} = -\dfrac{C_0}{\alpha} \displaystyle\int_{T_{in}}^{T} A_i e^{-E/RT} \left(B_i - e^{-B/T-T_0} \right) dT; \quad i \geq 0 \end{cases} \tag{13}$$

where A_i's and B_i's stand for the Adomian polynomials pertaining to the non-linearities x^2 and $e^{-1/x}$, respectively. Unfortunately, the integral term in Eq. (13) can not be evaluated analytically. Therefore, we have to adopt a numerical scheme, like the famous Simpson's rule, to tackle the recursive computation involved for any given T.

In order to facilitate the convergence of the ADM, Wazwaz has proposed a special choice for the first component of the solution, i.e. u_0 (see Ref. [9] for more details). In this regard, in course of solving the Eq. (7), we have refined the Eq. (13) as

$$\begin{cases} x_0 = \varepsilon \\ x_1 = \delta - \dfrac{C_0}{\alpha} \displaystyle\int_{T_{in}}^{T} A_0 e^{-E/RT} \left(B_0 - e^{-B/T-T_0} \right) dT \\ x_{i+1} = -\dfrac{C_0}{\alpha} \displaystyle\int_{T_{in}}^{T} A_i e^{-E/RT} \left(B_i - e^{-B/T-T_0} \right) dT; \quad i \geq 1 \end{cases} \tag{14}$$

where $x_{in} = \varepsilon + \delta$ with ε being sufficiently smaller than δ so that the sequence produced by the recurrence Eq. (14) converges after a few iterations. By calculating the Adomian polynomial components A_i and B_i from Eq. (10) and their substitution into Eq. (14), one gets the first five terms of the solution, i.e. x, parametrically as