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A derivation of the Vogel–Fulcher–Tammann relation for supercooled liquids

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ABSTRACT

The non-Arrhenius Vogel–Fulcher–Tamman relation for the viscosity, η, known for about 8 decades, describes simply one of the most characteristic features of supercooled liquids. It may be written $\eta = \eta_0 \exp[U/k(T-T_0)]$. Using the Dyre et al. result demonstrating that U is proportional to the shear modulus, G, and the Interstitialcy Theory of Condensed Matter (ITCM) we derive this relation and obtain $T_0/T_g = \gamma/(\gamma+1)$ and $U = U_0/(1+\gamma)$, where U_0 is the interstitialcy diffusion energy at the glass temperature. Here, γ is a fragility softening parameter given by $\gamma = \beta T_g (dc/dT)|_{T_g}$. β is the shear susceptibility $-d\ln G/dc$, and c is the interstitialcy concentration. γ is also a fragility parameter ranging from 0 for strong materials to 3 or above for fragile ones.

1. Introduction

1.1. Definitions and macroscopic terms

One of the most characteristic and best-known features of supercooled liquids and amorphous materials is the Vogel–Fulcher–Tammann (VFT) relation for the viscosity in the supercooled liquid state [1–3], known for about 8 decades. This generic relation

$$\log \eta/\eta_0 = U_0/k(T-T_0), \quad T > T_g \tag{1}$$

where η is the viscosity, T is the absolute temperature, T_g is the glass temperature, η_0, T_0 and U_0 are constants, is remarkable for the enormous range of up to 15 orders of magnitude of viscosity spanned in the supercooled liquid state. The viscosity is defined by

$$\eta = \sigma/\dot{\varepsilon} \tag{2}$$

and a relaxation time τ by the Maxwell (1867) [4] relation

$$\tau = \eta/G_\infty \tag{3}$$

where σ is an applied shear stress, $\dot{\varepsilon}$ is the rate of change of the shear strain and G_∞ is the shear modulus at a frequency above all relaxation frequencies and below all resonant frequencies [5]. For a static longitudinal stress and strain, a factor 3 is used [6] in the denominator of Eq. (2). Log η falls from a value of 13 poise for an arbitrary, but commonly accepted definition at T_g, to -4 as $T \rightarrow \infty$.

The VFT relation, Eq. (1), is found to be a good approximation for many classes of materials (Table 1) and has been the subject of many hundreds of articles. Collections of data are given in numerous reviews [7,8] with only a few representative and illustrative examples given here.

Recent work by J. Mauro and associates contains notable similarities and differences with that given here. Both have a description of universal behavior of the viscosity, describable with three parameters (U, T_0 and η_∞). Both find that U is non-diverging at $T<T_g$ and have an exponential dependence of U on T. However, the Mauro et al. work is based on an Adam–Gibbs approach for the configurational entropy, while the present work exploits the fact that the only thermally accessible equilibrium configurations possible are interstitialcies, and so, is analytic.

The concept of fragility,

$$F = d\log \eta/dT|_{T=T_g} \tag{4}$$

introduced by Angell [9], measures the extent of deviation of η from an Arrhenius behavior with small and large deviations called strong and fragile. This is also known for typical covalent glassy materials as long and short behaviors [10]. The fragility F is also often called the steepness parameter m [11].

A normalized fragility may be defined as [12]

$$f = F/17 = m/17. \tag{5}$$

This differs by unity from a softness parameter γ defined in a microscopic Interstitialcy Theory of Condensed Matter (ITCM) [13]. In the ITCM, the interstitialcy configuration was originally defined for an FCC simple metal such as Cu. Subsequently, the definition was found to hold also for alloys and complex molecules because the interstitialcy is spread out over several atoms, averaging out the effect of differing elements. For both crystalline and glassy materials, the definition of the interstitialcy is the same: namely, two atoms residing in an interatomic

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Table 1
Examples of good glass formers with different chemical bonds. By definition, a good glass former is a liquid with very low rates of crystal nucleation and growth at all temperatures. From J.C. Dyre, "The glass transition and elastic models of glass-forming liquids," Reviews of Modern Physics 78 July–Sept (2006) 953–972.

Glass-forming liquid	Chemical bond
Silicates, borates	Covalent
$KN0_3$–$Ca(NO_3)_2$ mixtures	Ionic
Ortho-terphenyl	van der Waals
Glycerol, glycose	Hydrogen
Pd–Cu–Ni–P alloys, Cu–Zr alloys	Metallic

well normally occupied by one [14]. γ is also given as $-d\ln G/\mathrm{d}(T/T_g)$, as is the index parameter I used by Dyre [15]

$$\gamma = f-1 \tag{6}$$

1.2. The ITCM and a microscopic interpretation

In the ITCM, the shear modulus G plays a key role and is given by

$$G = G_0 \exp(-\beta c), \tag{7}$$

where β is a shear susceptibility and c is the interstitialcy concentration. With typical values of β ~20–30, a concentration of a few percent of interstitials greatly reduces G. The volume and bulk modulus are much less affected. Interstitialcies reduce the shear modulus since the interstitialcy produces an internal strain that adds to the externally applied strain. Because of the form of Eq. (7), a small increase in the interstitialcy concentration leads to a large reduction in the shear modulus. If c is expanded in a Taylor series in the liquid state

$$c-c_0 = (dc/dT)(T-T_1) + \ldots, \tag{8}$$

the first term is a good representation for $\Delta c = c-c_0$, where T_1 is any reference temperature. A convenient choice for T_1 is the glass temperature T_g so that the temperature dependence of G (in the liquid state) is given by

$$G^l = G_g \exp\gamma\left(1-T/T_g\right) \tag{9}$$

where

$$\gamma = \beta T_g (dc/dT)_g \tag{10}$$

Most supercooled liquids have fragilities which lie in the range from 17 to 68, called strong to fragile in Angell's classification. A few may have larger values. The corresponding typical range of the differing fragility parameters is then

(strong) $17<F<68$ (fragile)
$1<f<4$
$0<\gamma<3.$

1.3. Typical curves

Figs. 1 and 2 give representative curves for the temperature dependence of the viscosity in metallic alloys both in the $T>T_g$ and $T<T_g$ range. Fig. 1 is given by Taub and Walter [16].

Fig. 2 is by Khonik [17] for the metallic alloy $Pd_{40}Cu_{30}Ni_{10}Pd_{20}$.

Above the temperature T_g, which is weakly rate dependent, a rapid non-Arrhenius decrease with temperature is found.

Fig. 3 gives data collected by Anderson [18] showing the linear relation between $[\ln\eta]^{-1}$ and T for $T>T_g$ (Eq. (1)). Fig. 4 is data collected by Dyre, Olsen and Christensen (DOC) [19] for a number of materials demonstrating that the activation energy in Eq. (1) is proportional to the shear modulus G_∞ as

$$U = G_\infty \Omega$$

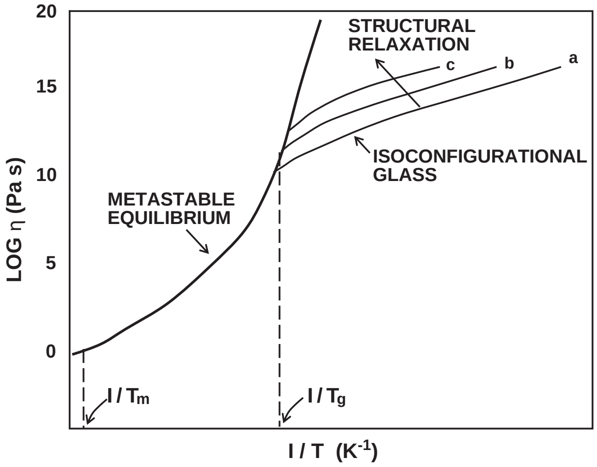

Fig. 1. From A.I. Taub and J.L. Walter, "Scaling the kinetics of flow and relaxation in amorphous alloys," Mater. Sci. Eng. 62 (1984), p. 249–260.

where Ω is a reference volume. They (DOC) interpret U as a migration energy, or work required to shove aside the surroundings, for a particle to migrate.

Fig. 4 shows viscosity as a function of inverse temperature (full symbols) and as function of $X \propto G_\infty/T$ (open symbols) for four organic liquids and one silicone oil with both x-axis variables normalized to one at $T_g (1\ P = 0.1\ \mathrm{Pas})$ (adapted from Dyre, Olsen, and Christensen [19]).

2. A derivation of the VFT relation

2.1. General aspects

We take as the basic relation for the temperature dependence of the viscosity

$$\eta/\eta_0 = \exp[U/kT] \tag{11}$$

where $U = G\Omega_0$, as in the DOC shoving model [19], with Ω as a characteristic volume of atomic dimensions. To this we add the basic relation, Eq. (7), for the interstitialcy concentration c dependency of the shear modulus. The shear modulus depends explicitly only on c and not dc/dt. The kinetics of $c(T,t)$ controls the magnitude of G and η.

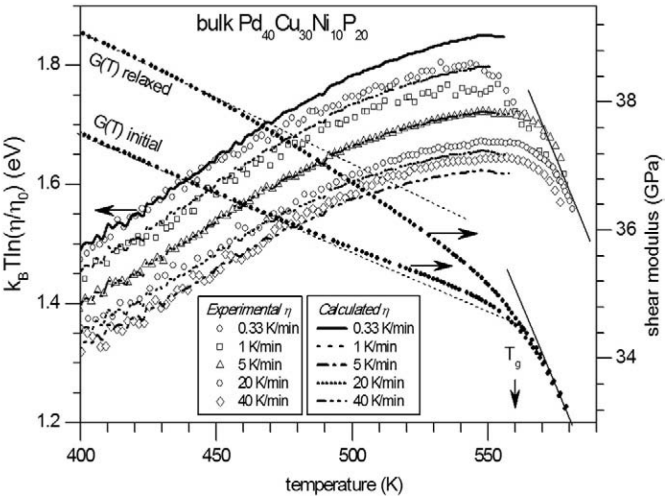

Fig. 2. From V.A. Khonik, Y.P. Mitrofanov, S.A. Lyakhov, A.N. Vasiliev, S.V. Khonik, D.A. Khoviv, "Relationship between the shear modulus G, activation energy, and shear viscosity η in metallic glasses below and above T_g: direct *in situ* measurements of G and η," Phys. Rev. B 79 132204-1–132204-4 (2009). DOI: 10.1103/PhysRevB.79.123304.