Journal of Non-Crystalline Solids 357 (2011) 404–410

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

The defect diffusion model, scaling, E_V^*/H^* and monomer volume and correlation lengths for glass-formers

J.T. Bendler [a], J.J. Fontanella [b,*], M.F. Shlesinger [b,c], M.C. Wintersgill [b]

[a] BSC, Inc., 3046 Player Drive, Rapid City, SD 57702, USA
[b] Physics Department, U.S. Naval Academy, Annapolis, MD 21402, USA
[c] Office of Naval Research, ONR Code 30, 875 N. Randolph St., Arlington VA 22203, USA

ARTICLE INFO

Article history:
Received 19 January 2010
Received in revised form 29 June 2010
Available online 21 August 2010

Keywords:
Dielectric relaxation;
High pressure;
Scaling;
Correlation length

ABSTRACT

Four topics are treated within the framework of the defect diffusion model (DDM). First, it is shown how the relationship between E_V^*/H^* (ratio of the apparent isochoric activation energy to the isobaric activation enthalpy) and monomer volume for polymers that has been pointed out by Floudas and co-workers [G. Floudas, K. Mpoukouvalas and P. Papadopoulos, J. Chem. Phys. 124 (2006) 074905] is predicted. Next, it is shown that in the DDM, scaling arises because the critical temperature can be represented approximately by a power law. Consequently, in the DDM scaling is always approximate and significant departures from scaling, as is observed in the case of hydrogen bonded materials for example, are matters of degree. It is also shown how the connection of scaling with E_V^*/H^* is a natural consequence of the DDM. Finally, DDM calculations of the defect correlation length are carried out and compared with experimental dynamical correlation lengths measured using the 4D3CP solid state NMR method.

1. Introduction

The effects of volume and temperature on the properties of glass-forming liquids are topics of current interest [1–4]. In order to separate these effects, the ratio of the apparent isochoric activation energy, E_V or E_V^*,

$$E_V = E_V^* = \left(\frac{\partial \ln x}{\partial (1/T)}\right)_V \tag{1}$$

to the isobaric activation enthalpy, E_P or H^*

$$E_P = H^* = \left(\frac{\partial \ln x}{\partial (1/T)}\right)_P, \tag{2}$$

where x is a transport property such as electrical relaxation time, viscosity or ionic conductivity, is often considered. This ratio can be written

$$\frac{E_V^*}{H^*} = \left(\frac{\partial \ln x}{\partial T}\right)_V \Big/ \left(\frac{\partial \ln x}{\partial T}\right)_P. \tag{3}$$

Many experimental evaluations of this ratio have been reported [3,5] and the authors have recently derived an expression for the ratio based on the defect diffusion model (DDM) [6,7]. In a recent paper, Floudas et al. have established a connection between E_V^*/H^* and the monomer volume, V_m, for polymers [3]. They find that as V_m increases, in general E_V^*/H^* decreases. This trend is accompanied by significant deviations. In the present paper, it is shown that this connection is accounted for by the DDM. A second experimental observation related to E_V^*/H^* is known as scaling. Specifically, it has been found that for many glass-forming liquids $\ln(x)$ scales at least approximately with $1/(TV^\gamma)$ and that scaling is related to E_V^*/H^*. A review of the work until 2005 is given in Ref. [5]. In the present paper, it is shown how the phenomena related to scaling are natural consequences of the DDM. Finally, the DDM is used to calculate correlation lengths and the results are compared with experimental dynamical correlation lengths measured using the 4D3CP solid state NMR method [8–12].

2. Theory

The basic assumptions for the DDM are that a super-cooled liquid contains mobile single defects (MSDs), immobilized clustered single defects (ICSDs) and normal liquid molecules. In the case of fragile liquids, one may consider defects as persistent packets of free volume, MSDs being mobile defects with greater than average free volume and ICSDs having less than average free volume. Defects are persistent in that they are conserved, neither created nor destroyed, and simply converted thermodynamically between MSDs and ICSDs with changes in pressure and temperature. Transitory molecular configurations with instantaneous free volumes higher or lower than average are not permanent "defects" in this sense, but rather contribute to the high

---

* Corresponding author. Tel.: +1 410 293 5507; fax: +1 410 293 5508.
E-mail addresses: jbendler@usna.edu (J.T. Bendler), jjf@usna.edu, fontanel@comcast.net (J.J. Fontanella), shlesing@usna.edu (M.F. Shlesinger), mwinter@usna.edu, mwinter@comcast.net (M.C. Wintersgill).

0022-3093/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2010.07.031

frequency background fluctuations of the molecular properties of the fluid. MSDs and ICSDs are associated with regions where the density is smaller and larger than average, respectively. Consequently, MSDs are large and ICSDs are small [13]. Because ICSD-rich regions of the fluid are rigid regions and MSD-rich regions are mobile, dynamic heterogeneity is an essential aspect of the DDM picture of super-cooled liquids. Finally, all of the physical properties of a fragile super-cooled liquid are influenced by the tendency of the MSDs to cluster (i.e., to form ICSDs/rigid regions) as temperature decreases or pressure increases.

In the DDM the concentration of MSDs, c_1, is given by [7]

$$c_1 = c\exp\left(-\frac{\beta_{KWW}B^* T_C^{0.5\eta}}{(T-T_C)^{0.5\eta}(1-\delta)}\right). \tag{4}$$

This leads to the following equation for the dielectric relaxation time

$$\tau_{DDM} = c^{-1/\beta}\tau_o \exp\left(\frac{\Delta_o}{k_B T}\right)\exp\left(\frac{B^* T_C^{0.5\eta}}{(T-T_C)^{0.5\eta}(1-\delta)}\right). \tag{5}$$

Δ_0 is the *smallest* barrier opposing a defect hop. The exponential containing Δ_0 together with the prefactor τ_o, give the shortest pausing time for the jump of a defect [14,15]. As usual, the Arrhenius term will be omitted so that the working equation is

$$\tau_{DDM} \approx c^{-1/\beta}\tau_o \exp\left(\frac{B^* T_C^{0.5\eta}}{(T-T_C)^{0.5\eta}(1-\delta)}\right). \tag{6}$$

In Eqs. (5) and (6), c is the total concentration of defects (i.e., the fraction of lattice sites occupied by a defect), τ_o is the shortest time for the jump of a defect, and β_{KWW} is the Kohlrausch–Williams–Watts or stretched exponential parameter associated with the relaxation function [16,17]

$$\phi(t) = A\exp\left(-(t/\tau_{DDM})^{\beta_{KWW}}\right). \tag{7}$$

$(1-\delta) = V(T,P)/V_o$ and $V(T,P)$ is the volume of the liquid at pressure P, and absolute temperature T, and V_o is a reference volume at $P=0$ at a given reference temperature. For consistency with the notation given in other papers in the literature, for the remainder of this paper, $V(T,P)/V_o$ will be referred to simply as V. η is an integer (1, 2 or 3) describing the dimensionality of the correlation volume [18]. If $\delta=0$ and $\eta=3$, a 3/2 power law results. Materials such as poly(propylene glycol) are successfully described by $\eta=3$ [13]. If, on the other hand, the correlation volume grows in a two-dimensional manner, with $\eta=2$, then Eq. (6) reduces to the standard Vogel equation [19], (assuming that volume is not strongly dependent upon pressure or temperature i.e. $\delta=0$). For example, glycerol is best described by $\eta=2$ [13]. A correlation length, $\xi_{j,DDM}$, corresponding roughly to the distance beyond which the defects do not interact, is given by [14,18]

$$\xi_{j,DDM}(T) = L_j\left(\frac{T_C}{T-T_C}\right)^{0.5}. \tag{8}$$

T_C is the critical temperature at which all defects would be clustered ICSDs if the glass transition did not intervene. The critical temperature, T_C, depends on pressure, i.e. $T_C = T_C(P)$. (See also Eq. (13) below where a simple Bragg–Williams lattice model for T_C is discussed.) The correlation length of Eq. (8) plays a central role in the DDM analysis, and, in particular, in the derivation of the VTF-like temperature laws such as Eq. (6) [20,21]. As will be shown, this quantity appears to be associated with experimental dynamical correlation lengths. As the temperature falls, more defects become immobile, locked into clusters and thus unavailable to promote relaxation. Only mobile single (uncorrelated) defects (MSDs) remain effective in producing relaxation, and this depletion of MSDs with falling temperature leads directly to Eq. (6).

Another parameter in the exponent of Eq. (6) is

$$B^* = -\frac{L_1 L_2 L_3 \ln(1-c)}{d_o^3 \beta_{KWW}}. \tag{9}$$

d_o is the average distance between neighboring sites at $P=0$ and at a given reference temperature. The three indices on the "direct" correlation lengths L_j allow for anisotropic defect–defect interactions. If the interactions are isotropic, then $L_1 = L_2 = L_3 = L$.

As has been pointed out [7], Eq. (6) is only applicable between T_B (or T_{LL}) and T_g. It is not valid below T_g because rigidity percolates below T_g and the motion of the MSDs is thereby restricted. In addition, Eq. (6) is not expected to apply to temperatures above T_B (or T_{LL}) which is on the order of 1.2 T_g. For temperatures above T_B, we assume that jamming caused by the ICSD-rich regions is greatly diminished and sufficient free volume becomes available to allow new relaxation processes in addition to those controlled by MSD hopping diffusion. Consequently, the properties of the liquid will vary differently with temperature and pressure above and below T_B but the changes in behavior are likely to be continuous and small. In fact, property changes near T_B are often subtle, being observable primarily via the temperature dependence of a property rather than as a discontinuous change in a property itself [22].

As shown elsewhere [7], if the isothermal compressibility, κ_T, and isobaric volume thermal expansion coefficient, α_P, are defined in the usual manner,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{10}$$

and

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \tag{11}$$

the assumption that $T_C = T_C(P)$ leads to

$$\left(\frac{E_V^*}{H^*}\right)_{DDM} = \frac{1-\frac{\alpha_P}{\kappa_T}\frac{T}{T_C}\left(\frac{\partial T_C}{\partial P}\right)_T}{1+\frac{\alpha_P(T-T_C)}{0.5\eta}}. \tag{12}$$

(An approximate version of Eq. (12) was given in an earlier note [6].) Eq. (12) has been used to predict the ratio E_V^*/H^* and its temperature dependence for several materials [7] and good agreement between theory and experiment is found.

An interesting form of Eq. (12) is obtained using a simple Bragg–Williams treatment of a (defect) phase separation transition (for nearest-neighbor pair interactions with equal occupancy of A and B sites). It has been pointed out that the critical demixing temperature is given by [23]

$$T_C = \frac{z|\Delta h|}{4k_B} = \frac{z(|\Delta\varepsilon + P\Delta v|)}{4k_B} \tag{13}$$

where z is the lattice coordination number, k_B is Boltzmann's constant, and $\Delta h = \Delta\varepsilon + P\Delta v$ is the decrease in enthalpy resulting from the formation of a defect pair:

$$\text{defect} \quad + \quad \text{defect} \quad \leftrightarrow \quad (\text{defect})_2 \tag{14}$$

where $\Delta\varepsilon$ is the decrease in pair energy and Δv is the decrease in volume.

From Eq. (13) one finds

$$(\partial T_C/\partial P)_T \approx z|\Delta v|/4k_B \tag{15}$$