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SHORT COMMUNICATION

R. Casalini
C. M. Roland

Scaling of the segmental relaxation times of polymers and its relation to the thermal expansivity

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R. Casalini
Chemistry Department,
George Mason University,
Fairfax, VA 22030, USA

C. M. Roland (✉)
Chemistry Division, Code 6120,
Naval Research Laboratory,
Washington, DC 20375–5342, USA
E-mail: roland@nrl.navy.mail

Abstract Segmental relaxation times of polymers measured at various temperatures and pressures can be superposed as a function of temperature, using a shift factor equal to the specific volume raised to a power. The material-specific scaling exponent can be linked to the nature of the intermolecular repulsive potential for the material. We show the relationship of this scaling exponent to the thermal expansivity of the material, and how it can be used to sort out the different contributions to the temperature dependence of the local dynamics.

Keywords Segmental relaxation · Thermal expansivity · Glass transition · Fragility · Intermolecular potential

Introduction

The glass transition, most often associated with polymers, is common to all noncrystallizing liquids. An analogous phenomenon is even observed in colloidal particles. Despite this ubiquity, and the fact that controlled production of glass dates back to the mid-second millennium BC, a quantitative understanding of the factors governing vitrification still eludes researchers. Recent experimental work has shown that sufficient amounts of both thermal energy and volume must be available for segmental motion to occur near the glass-transition temperature, T_g [1, 2, 3, 4]. The combined effects of lower energy and volume contraction are responsible for the spectacular increase in relaxation times and viscosities as temperature is lowered toward T_g. To account for the strongly non-Arrhenius behavior, we have recently proposed that the intermolecular interactions be described in terms of a generalized inverse repulsive potential [5]

$$\varphi(r) = \varepsilon(\sigma/r)^{3\gamma}, \tag{1}$$

where r is the intermolecular separation, and ϵ and σ have dimensions of energy and length, respectively. The parameter γ is a material-specific constant, in principle varying from 0 (thermally activated relaxation) to ∞ (colloidal suspension of hard spheres). Attractive forces are, of course, existent, but can be relegated to a mean-field background term, serving to cohere the liquid [6]. At high densities, the liquid structure is determined mainly by the repulsions [7, 8, 9], so from Eq. (1), all thermodynamic properties can be expressed as a function of $Tr^{3\gamma}$, or in terms of the specific volume, TV^{γ}.

Recently we showed that the relaxation times of glass-forming liquids, measured as functions of both temperature and volume, can be superposed by plotting versus the quantity TV^{γ} [5]. The scaling exponent, γ, is material-dependent, reflecting the nature of the intermolecular potential (Eq. 1). That work [5] considered a number of molecular glass-formers and a few polymers. Herein, we extend the analysis to segmental relaxation times for a wider variety of polymers, and examine the implications of the scaling concerning their thermal properties.

Results and discussion

Segmental relaxation times for nine polymers, measured above T_g in the equilibrium state, are plotted in Fig. 1 in Arrhenius form, with temperature multiplied by the specific volume (for the particular condition of T and P) raised to the power γ. The exponent γ varies from 1.9 for PVE to a value as high as 5.6 for polymethylphenylsiloxane (PMPS). As apparent by inspection, there is no correlation between γ and T_g. Nor, given the very different intermolecular interactions for these different chemical species, do we expect simultaneous superpositioning of the data for all polymers. However, it is interesting to note that the relaxation times for the two oligomeric epoxies, DGEBA and poly(phenyl glycidyl ehter-*co*-formaldehyde) (PPGE), for which $\gamma = 2.8$ and 3.5 respectively, superpose in the scaled plot, even though their glass-transition temperatures differ by 77 K [10]. A similar situation pertains for the two vinyl polymers, poly(vinyl methyl ether) (PVME) and poly(vinyl acetate) (PVAc). Whether the scaling procedure more generally unifies the relaxation properties of glass-formers belonging to the same chemical class requires further investigation.

The results in Fig. 1 make clear that the segmental relaxation times are a unique function of the quantity TV^{γ}. The question arises as to the explicit form for the relationship. Equation (1) suggests activated dynamics with an activation enthalpy that depends on the specific volume; viz.

$$\tau = \tau_0 \exp\left(\frac{C}{V^{\gamma}T}\right), \tag{2}$$

in which τ_0 is a constant and C/V^{γ} is an apparent activation enthalpy. In fact, in the vicinity of T_g (τ is greater than or equal to about 1 s), the curves in Fig. 1 are linear, consistent with Arrhenius behavior.

Since the parameter γ captures the volume effect on $\tau(T,P)$, we expect it to be related to other measures how T and V govern the relaxation times. As originally proposed by Williams [11, 12, 13], the ratio of the apparent activation enthalpy at constant specific volume, $E_V = R\frac{\partial \ln \tau}{\partial T^{-1}}\big|_V$, to that at constant pressure, $E_P = R\frac{\partial \ln \tau}{\partial T^{-1}}\big|_P$, quantifies the relative contribution of temperature and volume to the segmental dynamics. The ratio E_V/E_P varies from near zero for volume-dominated dynamics, to unity for relaxation governed strictly by thermal energy. To obtain E_V/E_P in terms of the parameter γ, we take the derivatives of Eq. (2), which gives $E_V = RTV^{-\gamma}$ for the isochoric case, and$E_P = RTV^{-\gamma}(1 + T\gamma\alpha_P)$ at constant pressure (substituting in the isobaric thermal expansion coefficient, $\alpha_P = V^{-1}\frac{dV}{dT}\big|_P$). The ratio of these activation enthalpies is thus [5]

$$\frac{E_V}{E_P} = \frac{1}{1 + \alpha_P T\gamma}. \tag{3}$$

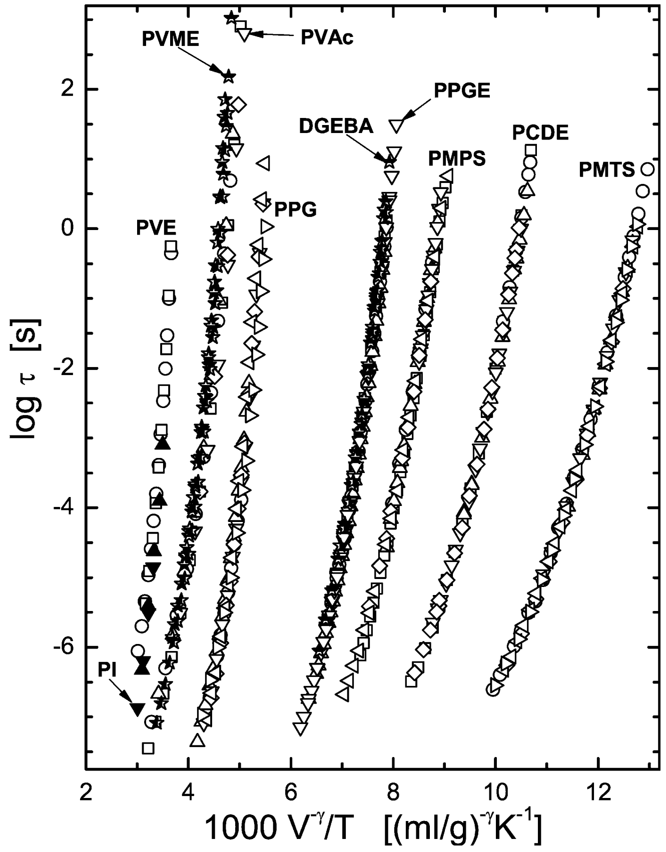

Fig. 1 Dielectric relaxation times versus inverse product of temperature and specific volume, the latter raised to the power of $\gamma = 1.9$: poly(vinyl ethylene) (*PVE*), 88% vinyl, $M_w = 3$ kg/mol, *open symbols*; $\gamma =$ 3.0: 1,4-polyisoprene (*PI*), $M_w = 11$ kg/mol, *solid symbols*; $\gamma = 2.55$: poly(vinyl methyl ether) (*PVME*), $M_w = 99$ kg/mol, *stars*; $\gamma = 2.6$: poly(vinyl acetate) (PVAC), $M_w = 170$ kg/mol, *open symbols*; $\gamma = 2.5$: poly(propylene glycol) (*PPG*), $M_w = 4$ kg/mol, *open symbols*; $\gamma = 2.8$: diglycidyl ether of bisphenol A (*DGEBA*), $M_w = 1.8$ kg/mol, *stars*; $\gamma = 3.5$: poly(phenyl glycidyl ether)-*co*-formaldehyde (*PPGE*), $M_w = 0.35$ kg/mol, *open symbols*; $\gamma = 5.6$: poly(methyl phenyl siloxane) (PMPS), $M_w = 23$ kg/mol, *open symbols*; $\gamma = 3.3$: poly[(*o*-cresyl glycidyl ether)-*co*-formaldehyde] (*PCGE*), $M_w = 0.87$ kg/mol, *open symbols*; and $\gamma = 5.0$: poly(methyl tolyl siloxane) (*PMTS*), $M_w = 35$ kg/mol, *open symbols*. For each sample, the different symbols represent different conditions of T and P

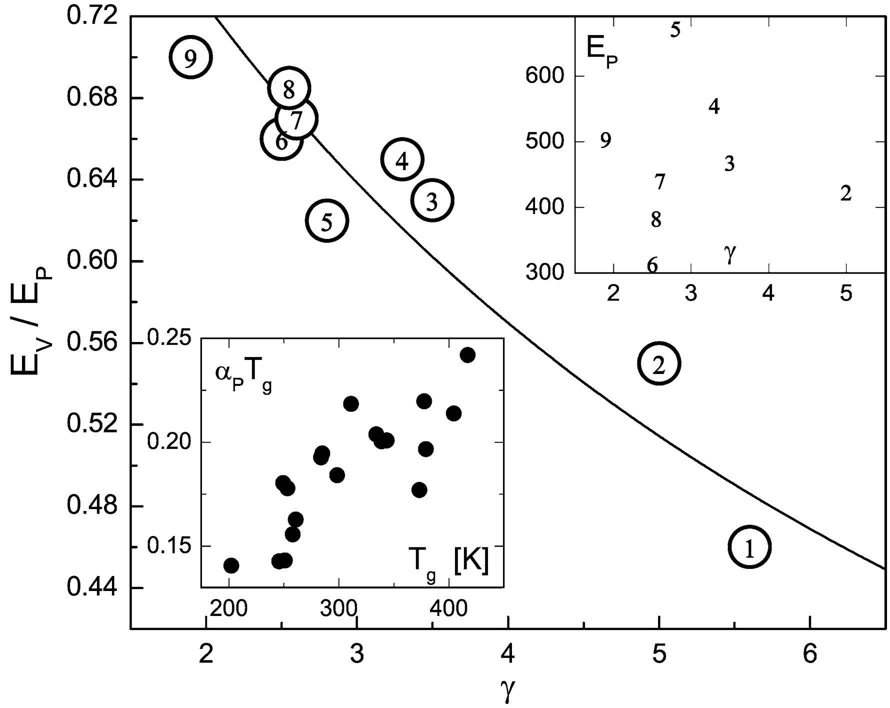

Fig. 2 Ratio of the respective slopes of the isochoric and isobaric Arrhenius plots, evaluated at $\tau \sim 1$ s, versus the scaling exponent from Fig. 1. The *solid line* is the fit to Eq. (3), yielding $\alpha_P T_g = 0.189 \pm 0.008$. The *lower inset* shows data $\alpha_P T_g$ versus T_g for 19 polymers; the average $\alpha_P T_g = 0.19 \pm 0.03$. The *upper inset* is the apparent activation energy near T_g versus the scaling exponent. PMPS (*1*), PMTS (*2*), PPGE (*3*), PCGE (*4*), DGEBA (*5*), PPG4000 (*6*), PVAc (*7*), PVME (*8*), PVE (*9*)

Then Eq. 3 predicts that the product of the thermal expansion coefficient and temperature is a constant. Analysis of data near T_g for several polymers in ref. [5] suggested $\alpha_P T_g = 0.19 \pm 0.01$.

In Fig. 2, we plot E_V/E_P versus γ for the eight polymers in Fig. 1 for which data close to T_g are available. The solid line is the regression of Eq. (3), yielding $\alpha_P T_g = 0.189 \pm 0.008$. This represents an average value for this quantity. This result is in accord with the Boyer-Spencer rule, $\alpha_P T_g \backsim 0.16$. To test this more explicitly, we collected thermal expansion coefficients and glass-transition temperatures for 18 polymers, including the eight in Fig. 2. These data are plotted in the inset in the lower-left corner of Fig. 2, where it can be seen that there is a systematic increase with T_g. The mean for all materials is $\alpha_P T_g = 0.19 \pm 0.03$.

The scaling described herein serves to linearize the relaxation data, as seen in Fig. 1 for temperatures not too far from T_g. The usual non-Arrhenius behavior of $\tau(T)$ arises from the change of the local liquid structure with temperature. This means that the heights of the potential barriers to segmental motion are changing, and thus the slope of an Arrhenius plot is not proportional to the activation energy. This problem can be circumvented by normalizing temperature by T_g. Defining the glass transition as the temperature at which τ (or the viscosity) assumes an arbitrary fixed value (around $\tau \sim 10$ s), we can quantify departures from Arrhenius behavior for materials having different T_g. This approach has become the standard method of classifying temperature-dependences [14, 15]. Following Angell [15], the steepness of the T_g-normalized curve, $\ln(10) R T_g E_p$, is referred to as the fragility. Fragility can be correlated with various other properties, such as the breadth of the relaxation function [16, 17, 18], the diffusivity of supercooled liquids [19], nonlinear behavior of glasses [20, 21, 22], and the vibrational motions [23, 24]. We have shown that for many polymers, fragility correlates with the degree to which their chemical structure engenders constraints on the motion from neighboring chain segments. Thus, for polymers with smooth, compact, flexible or symmetrical chain backbones [polyethylene, polyisobutylene, poly(dimethylsiloxane)], the segmental relaxation times have a near-Arrhenius temperature dependence (low fragility), while less flexible or polar polymers and those having sterically hindering pendant groups exhibit more fragile temperature dependences [25].

Despite these advances, the use of fragility presents conceptual difficulties. For example, the correlations developed are limited to isobaric conditions, but the changes in fragility with pressure are complex and not well understood [26, 27]. The explicit introduction of specific volume into the analysis clarifies the factors—the magnitude of the activation barrier and its change with temperature (or volume)—governing the steepness of an Arrhenius plot of $\tau(T)$. In the inset in the upper-right corner of Fig. 2, we plot the isobaric Arrhenius slopes evaluated at $\tau \sim 1$ s, versus γ. As expected in light of Eq. (3), there is no universal correlation.

However, consider the four polymers in Fig. 2 having essentially equivalent values of $\gamma = 2.6 \pm 0.15$. Their apparent activation energies are very different, and this must be due to actual differences in the respective barrier heights for local motion;i.e., E_P (actual, not apparent) rank orders as PPG < PVME < PVAc < D-GEBA. In contrast, note that poly(methyl phenyl siloxane) (PMPS) and PVAc in Fig. 2 have Arrhenius slopes which are almost equal, while γ for PMPS is twice as large as for PVAc. The relative magnitudes of γ imply that the barrier heights to local segmental relaxation are changing more rapidly with temperature for PMPS than for PVAc. This means volume effects contribute more strongly to $\tau(T)$ for PMPS, and thus PVAc must have a larger activation enthalpy, notwithstanding the equivalence of the apparent E_P. Or, in other words, a comparison of the fragility for an isochore at the $V(T_g$,0.1 MPa) with that of the isobar would show a much larger difference in the case of PMPS than for PVAc. Isobaric fragility alone cannot account for the temperature dependence of τ in this manner, because of its neglect of the volume dependence.

Summary

Arrhenius plots of segmental relaxation times for polymers measured isobarically as a function of temperature do not coincide with the corresponding isochoric curves, owing to the influence of volume. Similarly, relaxation times at a fixed temperature but different pressures are not the same. However, when all such τ are plotted versus TV^γ, the data for a given material superpose. This scaling of segmental relaxation times provides a unified view of the dynamics. The (material-specific) scaling parameter is a measure of the contribution of the specific volume or (density) to $\tau(T)$, and enables assessment of the potential-energy barriers to local rearrangements. From fitting data for several materials, we obtain $\alpha_P T_g = 0.19 \pm 0.03$ (Boyer-Spencer rule), although for individual polymers this product increases systematically with T_g.

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