



ELSEVIER

Journal of Non-Crystalline Solids 212 (1997) 74–76

 JOURNAL OF
 NON-CRYSTALLINE SOLIDS

Commentary

Commentary on ‘Strong and fragile liquids – A brief critique’

C.M. Roland *, K.L. Ngai

Naval Research Laboratory, Washington, DC 20375-5340, USA

Abstract

Recently Hodge [J. Non-Cryst. Solids 202 (1996) 164] provided a brief critique of the fragility approach to interpreting the relaxation behavior of glass-forming liquids. This classification scheme has found wide applicability, bringing out the correlation between the steepness of a liquid’s fragility curve and the breadth of its relaxation spectrum. The origin of this correlation can be gleaned from the coupling model of relaxation, which relates local chemical structure and intermolecular cooperativity. Since the latter governs both time and temperature dependencies near T_g , to a substantial extent the suggestions of Hodge [J. Non-Cryst. Solids 202 (1996) 164] concerning the origin of fragility and its correlation with non-exponentiality have been anticipated by the model.

In a recent paper in this journal [1], Hodge discussed certain features of the strong/fragile classification scheme for glass-forming liquids, making suggestions concerning the relationship of various quantities. This field of research is active, and in the extended interval between the paper’s submission and its appearance, a number of findings have been reported. In this note we examine some of Hodge’s suggestions in light of these published experimental results.

According to this scheme, relaxation behavior is considered as strong or fragile, depending on the rapidity with which the properties associated with the glassy state are modified as the temperature of a material passes through the glass transition region [2–7]. More fragile liquids exhibit a larger reduction in relaxation times with increasing temperature than do strong liquids as indicated by the curvature of the

T_g -normalized Arrhenius plots. The validity of this classification scheme has been directly verified through comparisons of polymers differing only in molecular weight. Such materials have different glass transition temperatures and different segmental relaxation times, but the shape of the segmental relaxation function is independent of molecular weight. If fragility is uniquely determined by chemical structure, then polymers differing only in molecular weight should have identical fragility curves. The demonstration of this effect for polystyrene [8], polypropylene oxide [8], poly(vinylethylene) [9,10] and polydimethylsiloxane [11] serves to corroborate the fragility concept in the classification of glass-forming liquids.

Of particular interest is the correlation between the fragility of a liquid and the non-exponentiality of its relaxation function; specifically, fragile liquids exhibit broader relaxation spectra [4–7,12–14]. Often, the stretched exponential function of Kohlrausch, $\exp[-(t/\tau)^\beta]$, is used to describe the non-exponentiality of the relaxation. There are only a few known

* Corresponding author. Tel.: +1-202 767 1719; fax: +1-202 767 0594; e-mail: roland@ccf.nrl.navy.mil.

exceptions to this correlation [15–18], at least in the absence of inhomogeneous line-broadening [19–23]. This correlation between fragility and the breadth of the relaxation spectrum is not limited to the macroscopic properties (e.g., viscosity) and macroscopic times involved in defining a ‘fragility index’, m . Analyses of the intermediate scattering function from incoherent, quasi-elastic neutron scattering and molecular dynamic simulations have shown that more fragile liquids exhibit stronger dependence of the mean square displacement, or equivalently relaxational decay, on normalized temperature, T/T_g , even through the microscopic time scale (i.e., 10^{13} – 10^{-9} s) [4,24–28]. Moreover, from dynamic light scattering, neutron scattering and molecular dynamics simulations [29–34], we conclude that (strong) liquids with larger β s lack a prominent fast relaxational process in the picosecond time regime, in contrast to (fragile) liquids with smaller β s. These recent developments indicate that among all relationships of fragility with other properties, the correlation between fragility and β is the most fundamental. This connection is evident from application of the coupling model, in which all the disparate behaviors in the macroscopic and microscopic time regimes are manifestly dependent on the coupling parameter, $n \equiv 1 - \beta$.

Hodge suggests in his recent paper [1] that the correlation between the fragility of a liquid and the non-exponentiality of its relaxation function can “be rationalized ... by appealing again to the Adam–Gibbs vision of cooperative relaxation near T_g ... larger rearranging groups would be expected to relax in a more cooperative and, therefore, more non-exponential manner”. Actually, while the Adams–Gibbs model certainly utilizes the concept of intermolecular cooperativity in describing the glass transition, the model offers no explicit prediction for the shape of the relaxation function. Hence, any correlation involving the shape (or non-exponentiality) cannot be deduced therefrom. On the other hand, the coupling model of relaxation, which is derivable from Adams–Gibbs, provides an explicit prediction for the dependence of the degree of non-exponentiality on the extent of intermolecular cooperativity [35].

Moreover, there is no need to speculate whether larger rearranging groups might relax in a more cooperative manner in order to yield non-exponential

decay. An extensive study, published in this journal [22], demonstrated how the time and temperature dependence of the glass transition dispersion are governed by the degree to which local structure engenders steric constraints on the relaxation. Specifically, smoother, less polar, more compact, symmetric, and flexible chemical structures, and those having less sterically-hindering pendant groups, experience weaker constraints on their local relaxation. As inferred from the coupling model, this condition leads to a smaller relaxation spectrum and temperature dependence. Thus Hodge’s speculation that “the correlation between fragility and the non-exponentiality parameter, β , that has been rationalized here in terms of β being a measure of cooperativity and of cooperativity being associated with large rearranging groups” has previously been experimentally verified [18,21,36], as well as given a plausible basis (see, for example, Ref. [37]).

An interpretation of the fragility property of glass-forming liquids, in terms of the topology of their potential energy hypersurface, has been proposed by Angell [2–4]. Hodge addresses this prediction, concluding that the product of the glass transition temperature and the heat capacity at T_g “is an inappropriate measure of the thermodynamic contribution to the Angell strength parameter”. We agree with this conclusion. In fact, a recent experimental study [11] established that Angell’s interpretation of the cooperativity curves in terms of the topology of the potential energy hypersurfaces cannot be correct. This study was concerned with polymers, and Angell [38] has pointed out that the heat capacity change at T_g is quite small for polymers in comparison to small molecule glass-formers. At T_g the vibrational contribution to the heat capacity change may be dominated by the chain structure, whereby the relationship between fragility and the details of the potential energy hypersurface might be obscured [38].

Summary

The fragility scheme is well established both experimentally and on theoretical grounds as a valid means to classify the relaxation behavior of liquids near T_g . The most useful aspect of this approach is the correlation apparent for virtually all homogeneous liquids between the steepness of their fragility

curve and the breadth of their relaxation spectrum. This correlation persists even at very high frequencies, where phonon motions play a significant role in the dynamics. The origin of this correlation is now understood, as experimental studies [21] have verified the predictions of the coupling model concerning the connection between chemical structure and intermolecular cooperativity. In turn, these govern both time and temperature dependencies near T_g , as well as in the microscopic time regime. Thus, to a substantial extent, the suggestions of Hodge [1] concerning the origin of fragility and its correlation with non-exponentiality have either been anticipated by theory or demonstrated by recent experiments.

Acknowledgements

This work was supported by the Office of Naval Research. The authors thank P.G. Santangelo for helpful discussions.

References

- [1] I.M. Hodge, *J. Non-Cryst. Solids* 202 (1996) 164.
- [2] C.A. Angell, in: *Relaxations in Complex Systems*, ed. K.L. Ngai and G.B. Wright (National Technical Information Service, US Department of Commerce, Springfield, VA, 1985) p. 3.
- [3] C.A. Angell, *J. Non-Cryst. Solids* 131–133 (1991) 13.
- [4] C.A. Angell, *Science* 267 (1995) 1924.
- [5] D.J. Plazek and K.L. Ngai, *Macromolecules* 24 (1991) 1222.
- [6] R. Boehmer and C.A. Angell, *Phys. Rev. B* 45 (1992) 10091.
- [7] R. Bohmer, K.L. Ngai, C.A. Angell and D.J. Plazek, *J. Chem. Phys.* 99 (1993) 4201.
- [8] C.M. Roland and K.L. Ngai, *Macromolecules* 25 (1992) 5765.
- [9] C.M. Roland, *Macromolecules* 28 (1992) 3463.
- [10] C.M. Roland, *Macromolecules* 27 (1994) 4242.
- [11] C.M. Roland and K.L. Ngai, *Macromolecules* 29 (1996) 5747.
- [12] K.L. Ngai, *J. Non-Cryst. Solids* 95&96 (1987) 969.
- [13] K.L. Ngai, R.W. Rendell and D.J. Plazek, *J. Chem. Phys.* 94 (1990) 4.
- [14] K.L. Ngai and C.M. Roland, *Macromolecules* 27 (1995) 2454.
- [15] P.G. Santangelo, K.L. Ngai and C.M. Roland, *Macromolecules* 26 (1993) 2682.
- [16] C.M. Roland, C.A. Bero, K.L. Ngai and M. Antonietti, *Mater. Res. Soc. Proc. Ser.* 411 (1996) 367.
- [17] P.G. Santangelo, K.L. Ngai and C.M. Roland, *Macromolecules* 29 (1996) 3651.
- [18] C.M. Roland, *Macromolecules* 25 (1992) 7031.
- [19] C.M. Roland and K.L. Ngai, *Macromolecules* 24 (1991) 2261.
- [20] C.M. Roland and K.L. Ngai, *J. Rheol.* 36 (1992) 1691.
- [21] K.L. Ngai and C.M. Roland, *Macromolecules* 26 (1993) 2688.
- [22] C.M. Roland and K.L. Ngai, *J. Non-Cryst. Solids* 172–174 (1994) 868.
- [23] C.M. Roland, P.G. Santangelo, Z. Baram and J. Runt, *Macromolecules* 27 (1994) 5382.
- [24] C.A. Angell, P.H. Poole and J. Shao, *Nuovo Cimento* 16 (1994) 883.
- [25] K.L. Ngai, C.M. Roland and G.N. Greaves, *J. Non-Cryst. Solids* 182 (1995) 172.
- [26] C.M. Roland and K.L. Ngai, *J. Chem. Phys.* 103 (1995) 1152; 104 (1996) 8171.
- [27] C.M. Roland, K.L. Ngai and L.J. Lewis, *J. Chem. Phys.* 103 (1995) 4632.
- [28] C.M. Roland and K.L. Ngai, *J. Chem. Phys.* 104 (1996) 2967.
- [29] M.J. Lebon, C. Dreyfus, G. Li, A. Aouadi, H.Z. Cummins and R.M. Pick, *Phys. Rev. E* 51 (1995) 4537.
- [30] A. Brodin, D. Engberg, L.M. Torell, L. Börjesson and A.P. Sokolov, *Phys. Rev. B* 53 (1996) 11511.
- [31] K.L. Ngai and C.M. Roland, *Phys. Rev. E* 55 (1997) 2069.
- [32] C.M. Roland and K.L. Ngai, *J. Chem. Phys.* 106 (1997) 1187.
- [33] P. Sindzingre and M. Klein, *J. Chem. Phys.* 96 (1992) 4681.
- [34] C.M. Roland and K.L. Ngai, *J. Time Dep. Mater.*, in press.
- [35] K.L. Ngai and R.W. Rendell, *J. Non-Cryst. Solids* 131–133 (1991) 942.
- [36] C.M. Roland and K.L. Ngai, *Macromolecules* 24 (1991) 5315; 25 (1992) 1844.
- [37] K.-Y. Tsang and K.L. Ngai, *Phys. Rev. E* 54 (1996) R326.
- [38] C.A. Angell, personal communication.