

COMMENTS

Comment on “Direct determination of kinetic fragility indices of glassforming liquids by differential scanning calorimetry: Kinetic versus thermodynamic fragilities” [J. Chem. Phys. 117, 10184 (2002)]C. M. Roland^{a)} and P. G. Santangelo*Naval Research Laboratory, Code 6120, Washington, DC 20375-5342*C. G. Robertson^{b)}*ExxonMobil Chemical Company, Baytown, Texas 77522-5200*

K. L. Ngai

Naval Research Laboratory, Code 6807, Washington, DC 20375-5320

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Recently Wang *et al.* [J. Chem. Phys. **117**, 10184 (2002)] reported fragilities for various molecular liquids, as determined by calorimetry. The technique is based on measuring the change in fictive temperature with cooling rate. We point out that the same method was previously applied to polymers [Robertson, Santangelo, and Roland, J. Non-Cryst. Solids **275**, 153 (2000)], yielding good agreement with fragility values obtained by mechanical or dielectric spectroscopy. © 2003 American Institute of Physics. [DOI: 10.1063/1.1571814]

In a recent paper, Wang *et al.*¹ describe a calorimetric determination of the fragility of glass-forming liquids. The method, based on the dependence of the fictive temperature on cooling rate, offers a thermal measure of this important property of supercooled liquids. For various small molecule glass formers, Wang *et al.*¹ report good agreement with fragility values obtained from conventional techniques, such as dielectric spectroscopy or viscosity data. However, it should be noted that this method is not new. Previously, it was utilized² for polyvinylacetate, polyvinylethylene, polycarbonate, and polymethylmethacrylate, as well as for polystyrenes of various molecular weights, with the results correlating well with fragilities deduced from dielectric and mechanical spectroscopy. The only outlying data² were for polyvinylchloride, which is difficult to obtain in the completely amorphous state, and for polymer networks. By a somewhat different procedure employing thermally modulated calorimetry, Hempel and co-workers³ obtained calorimetric fragilities for several polymers and small molecule glass-formers, and likewise found agreement with kinetic fragility values.

An aim of the work of Wang *et al.*¹ is establishing a connection between kinetic fragility (a relaxation property) and thermodynamics. Toward this end, Angell^{4,5} had suggested that the magnitude of the heat capacity increment at the glass transition, $\Delta C_p(T_g)$, should correlate with the fragility of a glass former. Wang *et al.*¹ correctly point out that this idea is untenable, citing a recent compendium of data.⁶ In fact, earlier work,^{7,8} including a publication in this journal,⁹ had shown the absence of any correlation between kinetic fragility and $\Delta C_p(T_g)$.

Wang *et al.*¹ note that “the factors that determine the fragility of a given liquid or polymer remain poorly understood.” We agree that this problem is not completely solved; however, we have shown for polymers and small molecule liquids that both fragility and the breadth of the relaxation dispersion can be categorized according to the degree to which the chemical structure promotes intermolecular constraints.¹⁰ Thus, smoother, less polar, more compact, symmetric or flexible structures give rise to smaller fragilities and more narrow (Debye-like) relaxation functions. On the other hand, fragile behavior and broad dispersions are associated with inflexible structures having bulky or polar pendant groups. The underlying idea is that intermolecular cooperativity (many-body effects) governs the time and temperature dependencies (i.e., the breadth of the relaxation and its fragility).¹¹ Chemical structures which engender steric constraints or polar interactions enhance intermolecular cooperativity. One consequence is the (inverse) correlation of kinetic fragility with the value of the Kohlrausch exponent, β .¹² Another is the correlation of kinetic fragility with the rapidity of the decrease of β with decreasing scaled temperature T_B/T . T_B is the temperature at which the relaxation time crosses over from one Vogel–Fulcher dependence to another. The crossover at T_B is associated with a change in the dynamics from weakly intermolecularly cooperative [large $\beta(T)$] for $T > T_B$ to moderately or strongly intermolecularly cooperative for $T < T_B$, dependent on the magnitude of $\beta(T_g)$. The disparity between the two Vogel–Fulcher dependencies also correlates with $\beta(T_g)$ and how rapid is the change of $\beta(T)$ with T_B/T .¹³

The dominant role of intermolecular cooperativity in governing the supercooled dynamics is reflected in various other properties of glass-formers, and provides the link to thermodynamics. Conceptually, this link must be absent for

^{a)}Electronic mail: roland@nrl.navy.mil^{b)}Also at: Bridgestone/Firestone Pkwy., Akron, OH 44317-0001.

entirely noncooperative motions (i.e., Debye relaxation). As intermolecular cooperativity is enhanced, the thermodynamic contribution to the dynamics increases. This link between relaxation properties and thermodynamics is manifested in various experiments. For example, the number of molecules in the cooperatively rearranging region of the Adam–Gibbs theory,¹⁴ z^* , at T_g , as well as its T_g -scaled temperature dependence, have been shown to be correlated with the kinetic fragility.^{15–17} Similarly, positron annihilation spectroscopy experiments have shown that kinetic fragility is correlated to the T_g -scaled temperature dependence of the free volume.¹⁸ The free volume, like z^* , has a mild temperature dependence for $T > T_B$, crossing over to a more rapid variation for $T < T_B$. These results reveal how intermolecular cooperativity governs, in conjunction with thermodynamics, the relaxation properties of supercooled liquids.

The conclusion of Wang *et al.*¹ that “there remain many complexities in glassformer behavior to be rationalized” can hardly be disputed. However, we believe fruitful advances in understanding the properties of the glass transition can be gained from recognition of the central role of many-body dynamics, as evidenced by the progress made to date along these lines.

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