

Bauchy *et al.* Reply: In Ref. [1], based on accelerated atomic simulations [2], we argue that the mixed-alkali effect in glass relaxation is driven by the existence of stressed local instabilities in the atomic network. The preceding Comment [3] raises some criticisms of our work along four general lines.

Thermodynamics.—The author begins his Comment by arguing that “volume and enthalpy should relax in unison.” First, we would like to point out that his thermodynamics-based proof is flawed, since “absence of heat transfer” does not imply “ $T = \text{const}$ ” and vice versa—the author is neglecting the effect of the heat that is exchanged with the thermostat. Second, let us reiterate the fact that, as stated in Ref. [1], our simulations only involve energy minimization (that is, they are conducted at a temperature $T = 0$ K) while imposing a zero average stress ($P = 0$). Under these conditions, the enthalpy ($H = U + PV$) is simply equal to the internal energy (U) and is uncorrelated with the volume (V). Third, the decoupling between different modes of relaxation in glass has been observed in several studies—both in simulations [2,4–6] and experiments [7,8].

Internal friction.—The author then refers to a series of papers discussing the origin of the “internal friction” in silicate glasses (e.g., Ref. [9]), that is, their energy dissipation upon the application of an external mechanical load. Although these studies are interesting, we do not think that they are relevant to the thermometer effect. Starting from a thermodynamic equilibrium state, if a solid is subjected to a mechanical load, it must achieve a new state of equilibrium that is consistent with this load. The response of the system can be delayed if some energy barriers need to be overcome. In the case of internal friction, relaxation is driven by the elastic energy resulting from the application of a sustained load. In contrast, in the case of the thermometer effect, glass relaxation is spontaneous (with no external load) and driven by the propensity of the glass to reach a lower free energy over time. It has previously been shown that relaxation under sustained stress and spontaneous volumetric relaxation do not have the same kinetics and, hence, may not be controlled by the same atomic mechanism [8].

Atomic mechanism.—The author expresses some concerns regarding our proposed atomic mechanism of the thermometer effect. However, his reasoning is based on the fact that our mechanism would “assume a viscous relaxation behavior,” which is not correct. In our previous work [2], we showed that, upon room-temperature relaxation, no Si-O or Al-O bonds break, and that these network-forming atoms remain largely immobile (see Fig. 4 in Ref. [2]). In contrast, a fraction of Na and K atoms are able to jump from one pocket to another (see Fig. 4 in Ref. [2]). These results show that some local reorganizations of network-modifying species can indeed occur without the need for any breaking of Si-O bonds. Hence, in contrast with what is suggested in the Comment [3], such local reorganizations (i) do not “demand spatial rearrangement of

relatively large volume of network” and (ii) are not a “viscous relaxation behavior.” Our results are in agreement with recent experiments showing that room-temperature relaxation is not viscous in nature [7,10].

Origin of the mixed-alkali effect.—The author finally claims that he has already resolved the mixed-alkali effect in his “defect model” [11,12], thereby questioning the importance of our investigation. Although his work is interesting, we do not think that it is fair to claim that the mixed modifier effect has been “resolved.” His work remains a model, which, thus far, lacks direct support from experiments or simulations—which does not mean the defect model is not valuable. In addition, it is certainly an exaggeration to claim that this model explains the mixed modifier effect “in all its facets and agrees with all experimental facts.” For instance, this model does not explain the anomalous mechanical properties exhibited by mixed glasses. More importantly—to the best of our understanding—this model does not offer any clear mechanistic origin for the room-temperature volumetric relaxation observed in mixed glasses (thermometer effect). The Letter only states that “One of the direct consequences of the bond breaking and generation of defects is the compaction of glass structure.” The physical origin of this suggested relationship between defect formation and glass compaction is unclear from this previous literature. We believe that atomistic simulations offer a more robust pathway to decipher the physical nature of the atomic mechanism of glass relaxation without relying on speculations.

This work was supported by Corning Incorporated and the National Science Foundation under Grants No. 1562066, No. 1928538, and No. 1928546.

Mathieu Bauchy^{1,*}, John C. Mauro² and Morten M. Smedskjaer³

¹Physics of Amorphous and Inorganic Solids Laboratory (PARISlab), Department of Civil and Environmental Engineering, University of California Los Angeles, California 90095, USA

²Department of Materials Science and Engineering The Pennsylvania State University University Park, Pennsylvania 16802, USA

³Department of Chemistry and Bioscience Aalborg University 9220 Aalborg, Denmark

 Received 18 March 2020; accepted 22 April 2020; published 15 May 2020

DOI: 10.1103/PhysRevLett.124.199602

*bauchy@ucla.edu

- [1] Y. Yu, M. Wang, M. M. Smedskjaer, J. C. Mauro, G. Sant, and M. Bauchy, Thermometer Effect: Origin of the Mixed Alkali Effect in Glass Relaxation, *Phys. Rev. Lett.* **119**, 095501 (2017).

- [2] Y. Yu, M. Wang, D. Zhang, B. Wang, G. Sant, and M. Bauchy, Stretched Exponential Relaxation of Glasses at Low Temperature, *Phys. Rev. Lett.* **115**, 165901 (2015).
- [3] V. Belostotsky, preceding Comment, Comments on, Thermometer Effect: Origin of the Mixed Alkali Effect in Glass Relaxation, *Phys. Rev. Lett.* **124**, 199601 (2020).
- [4] T. Egami, Local dynamics in liquids and glassy materials, *J. Phys. Soc. Jpn.* **88**, 081001 (2019).
- [5] W. Song, X. Li, B. Wang, N. M. Anoop Krishnan, S. Goyal, M. M. Smedskjaer, J. C. Mauro, C. G. Hoover, and M. Bauchy, Atomic picture of structural relaxation in silicate glasses, *Appl. Phys. Lett.* **114**, 233703 (2019).
- [6] X. Li, W. Song, K. Yang, N. M. A. Krishnan, B. Wang, M. M. Smedskjaer, J. C. Mauro, G. Sant, M. Balonis, and M. Bauchy, Cooling rate effects in sodium silicate glasses: Bridging the gap between molecular dynamics simulations and experiments, *J. Chem. Phys.* **147**, 074501 (2017).
- [7] R. C. Welch, J. R. Smith, M. Potuzak, X. Guo, B. F. Bowden, T. J. Kiczinski, D. C. Allan, E. A. King, A. J. Ellison, and J. C. Mauro, Dynamics of Glass Relaxation at Room Temperature, *Phys. Rev. Lett.* **110**, 265901 (2013).
- [8] M. Potuzak, R. C. Welch, and J. C. Mauro, Topological origin of stretched exponential relaxation in glass, *J. Chem. Phys.* **135**, 214502 (2011).
- [9] J. E. Shelby and D. E. Day, Mechanical relaxations in mixed-alkali silicate glasses: I. Results, *J. Am. Ceram. Soc.* **52**, 169 (1969).
- [10] B. Ruta, G. Baldi, Y. Chushkin, B. Rufflé, L. Cristofolini, A. Fontana, M. Zanatta, and F. Nazzani, Revealing the fast atomic motion of network glasses, *Nat. Commun.* **5**, 3939 (2014).
- [11] V. Belostotsky, Defect model for the mixed mobile ion effect, *J. Non-Cryst. Solids* **353**, 1078 (2007).
- [12] V. Belostotsky, Defect model for the mixed mobile ion effect revisited: An importance of deformation rates, *J. Non-Cryst. Solids* **356**, 129 (2010).