Comments on ‘Thermometer Effect: Origin of the Mixed Alkali Effect in Glass Relaxation’ by
Y.Yu et al. [Phys.Rev.Lett. 119, 095501 (2017)]

Vladimir Belostotsky

Institute of General and Inorganic Chemistry of RAS, Moscow, Russia *

In a recent Letter to this journal Yu et al. presented results of molecular dynamics (MD)
simulations of relaxation processes in mixed alkali (MA) glasses in response to cyclic volumetric
stress perturbations. Using Phillips’s diffusion-trapping model [1] they attempted to link
observed stretched exponential relaxation to specific processes in glasses on atomic level and,
on this basis, explain the mixed alkali effect (MAE).

Our main question is concerned with results of simulations. Authors admit that they observed
that ‘the relaxation of enthalpy and volume do not show the same trend’.

Basically, enthalpy is extensive thermodynamics state variable defined as the sum of internal
energy and product of pressure and system’s volume:

\[ H = U + pV \]

At constant pressure and temperature, enthalpy is simply proportional to volume, therefore a
situation where relaxation of volume and enthalpy do not show the same trend is impossible
even theoretically. Authors are hinting that certain microscopic ‘residual thermal excitations’ of
unspecified nature presumably affect relaxation mechanisms. However MA glasses are not
known being any kind of “heat engine”, therefore both enthalpy and volume must relax in unison
for relaxation processes in question. Experimental studies revealed that below \( T_g \) cyclic
volumetric stress perturbations induce relaxation processes connected with diffusional hops of
mobile alkali cations and reorientational motions of non-bridging oxygen (NBO) [2-9]. In MA glasses magnitude of alkali-motion-related relaxation reaches minimum at equimolar concentrations of alkalis while NBO-related process shows opposite trend. In Yu et al. work nothing even close is observed. All these raise a fundamental question of reliability of simulations and trustworthiness of results.

Equally, the discussion part of the Letter is questionable. As was shown above, the only species capable to diffuse in glass at ambient temperature are alkali cations. However, authors speculate that relaxation of compression stress in glass arising from replacement of smaller cations for larger ones, and tension stress arising from replacement of larger cations for smaller ones can occur via certain “diffusion” of local deformations (referred to as “excitations”) through glass network and their mutual annihilation. This speculation ignores the fact that local stress can involve up to several coordination shells around cation-centered polyhedra [10]. The “diffusion” of “excitations” of such size demands spatial rearrangement of relatively large volume of network which assumes viscous relaxation behavior. However, at ambient temperature, glass network exhibits brittle-elastic and not viscous response to stress. Moreover, calculated differential stress (approx. 4.7 GPa, see Fig 3d) cannot, in principle, be absorbed by rigid glass matrix without its damage which occurs via formation of pairs of structural defects, oxygen vacancies and non-bridging oxygen anions [11]. Most vividly this effect manifests itself in glasses subjected to ion exchange in molten salt both for smaller-for-larger and larger-for-smaller cation inter-replacement [12-15]. Generation of defects causes compaction of glasses which, in fact, is the real cause of the ‘thermometer effect’ [16]. MD simulations confirm that defect-induced compaction of glasses occurs regardless of means of defect introduction [17].
Authors speculate, also, that the ‘coexistence of atomic units that are under compression or tension can also explain the decrease in the mobility of the alkali atoms in mixed glasses, which results in minima in conductivity and diffusion coefficients’. Actually, it is proven that tension stress enhances ionic mobility. The theory indeed predicts cations’ mobility reduction under compression stress by restricting the amount of volume available [19,20], however it is established that in mixed alkali glasses ionic mobility decreases by significantly larger factor than the theory predicts [19].

Finally, Yu et al. maintain that ‘the structural origin of the MAE [is] still regarded as one of the most challenging unsolved problem in condensed matter science’, and ‘the atomic origin of the MAE itself remains largely unknown’. However, the MAE problem has been resolved with the introduction of the defect model for the mixed mobile ion effect [16,18] which provides comprehensive, consistent and generally applicable fundamental explanation for MAE in all its facets and agrees with all experimental facts.

* Retired, vladbel@erols.com

[1] J.C. Phillips, Rep. Prog. Phys. 59, 1133 (1996)

[2] V.P. Fitzgerald, J. Am. Ceram. Soc. 34, 339 (1951).

[3] K.E. Forry, J. Am. Ceram. Soc. 40, 90 (1957).

[4] J.E. Shelby and D.E. Day, J. Am. Ceram. Soc. 52, 169 (1969).

[5] B. Roling and M.D. Ingram, Phys. Rev. B 57, 14192 (1998).

[6] H. Rötger, Glastech. Ber. 19, 192 (1941).

[7] D.E. Day and G.E. Rindone, J. Am. Ceram. Soc. 45, 496 (1962).
[8] R.J. Ryder and G.E. Rindone, J. Am. Ceram. Soc. 44, 532 (1961).

[9] T.J. Higgins, P.B. Macedo, V. Volterra, J. Am. Ceram. Soc. 55, 488 (1972).

[10] A.M. Stoneham, *Theory of Defects in Solids. Electronic Structure of Defects in Insulators and Semiconductors*, (Clarendon, Oxford, 1975).

[11] D.L. Griscom, J. Ceram. Soc. Jpn. 99, 923 (1991).

[12] Y.K. Lee, Y.L. Peng, and M. Tomozawa, J. Non-Cryst. Solids 222, 125 (1997).

[13] M. Yamane, S. Shibata, A. Yasumori, T. Yano, and H. Takada, J. Non-Cryst. Solids 203, 268 (1996).

[14] F.M. Ernsberger, Proc. Roy. Soc. (London), A257 [1289], 213 (1960).

[15] S.S. Kistler, J. Am. Ceram. Soc. 45, 59 (1962).

[16] V. Belostotsky, J. Non-Cryst. Solids 353, 1070 (2007).

[17] L. Zheng, Q. An, R. Fu, S. Ni, and S.N. Luo, J. Chem. Phys. 125, 154511 (2006).

[18] V. Belostotsky, J. Non-Cryst. Solids 356, 129 (2010).

[19] M.D. Ingram, J.E. Davidson, A.M. Coats, E.I. Kamitsos, and J.A. Kapoutsis, Glastheh. Ber. Glass Sci. Technol. 73, 89 (2000).

[20] A.K. Varshneya, J. Am. Ceram. Soc. 58, 106 (1975).