Thermometer Effect: Origin of the Mixed Alkali Effect in Glass Relaxation

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Despite the dramatic increase of viscosity as temperature decreases, some glasses are known to feature room-temperature relaxation. However, the structural origin of this phenomenon—known as the "thermometer effect"—remains unclear. Here, based on accelerated molecular dynamics simulations of alkali silicate glasses, we show that both enthalpy and volume follow stretched exponential decay functions upon relaxation. However, we observe a bifurcation of their stretching exponents, with $\beta = 3/5$ and $3/7$ for enthalpy and volume relaxation, respectively, in agreement with Phillips's topological diffusion-trap model. Based on these results, we demonstrate that the thermometer effect is a manifestation of the mixed alkali effect. We show that relaxation is driven by the existence of stressed local structural instabilities in mixed alkali glasses. This driving force is found to be at a maximum when the concentrations of each alkali atom equal each other, which arises from a balance between the concentration of each alkali atom and the magnitude of the local stress that they experience.

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As nonequilibrium materials, glasses continuously relax toward the supercooled liquid metastable equilibrium state [1–4]. However, the dramatic increase of viscosity as temperature decreases effectively prevents viscous glass relaxation at ambient temperature [5,6]. Surprisingly, recent experiments and simulations [1,7] have shown that, for certain compositions, glass can still feature some room-temperature structural and stress relaxation. This phenomenon is known as the "thermometer effect" as, in the nineteenth century, thermometers made of mixed alkali lime silicate glass used to experience gradual changes of dimension over time, rendering them inaccurate [8,9]. This effect is usually attributed to the mixed alkali effect (MAE), which is observed in oxide glasses comprising at least two alkali oxides, A_2O and B_2O. The MAE manifests itself as a nonlinear evolution of glasses' properties with respect to the molar fraction $A/(A+B)$ [10,11].

The structural origin of the MAE and glass relaxation are still regarded as one of the most challenging unsolved problems in condensed matter science [12–14].

At low temperature (around and below the glass transition temperature), glasses typically exhibit nonexponential relaxation, which can be described by a stretched exponential or Kohlrausch–Williams–Watts function [see Eq. (1)] [15]. Various models have been proposed to explain the origin of the stretched exponential nature of relaxation [4,12]. In particular, stretched exponential relaxation has been suggested to result from the existence of some heterogeneity in the glass, wherein different regions relax following nearly exponential functions but with different relaxation times [16]. Alternatively, the stretched exponential nature of glass relaxation can be elegantly described by Phillips's diffusion-trap model, wherein some uniformly distributed "excitations" are assumed to diffuse through the network until they meet randomly distributed "traps," which annihilate the excitations [12,17]. However, this model remains largely axiomatic and the nature of the excitations and traps lacks any clear atomistic picture or any explicit link with the MAE effect. More generally, the atomic origin of the MAE itself remains largely unknown [18–22].

To reveal the atomistic origin of the MAE and stretched exponential relaxation of glass, we rely here on a recently developed accelerated simulation technique, which successfully reproduced the long-term room-temperature relaxation observed in Corning® Gorilla® Glass [1,7]. In that method, the glass is subjected to small, cyclic perturbations of volumetric stress, $\pm\sigma_0$. At each stress cycle, a minimization of the energy is performed, with the system having the ability to deform to reach the targeted stress. Note that the average stress remains zero over time and that the observed relaxation does not depend on the choice of $\pm\sigma_0$, provided that it remains subyield (see Ref. [1]). In effect, this method mimics the relaxation observed in granular materials subjected to vibrations [23,24], wherein small vibrations tend to densify the material (artificial aging), whereas large vibrations randomize the grain arrangements (rejuvenation). Similar

ideas relying on the energy landscape approach [25,26] have been applied to noncrystalline solids, based on the fact that small stresses deform the energy landscape locally explored by the atoms. This can result in the reduction of some energy barriers that exist at zero stress, thus allowing the system to jump over the barriers to relax to lower energy states. This transformation is irreversible since once the stress is removed, the system remains in its "aged" state. On the contrary, large stresses move the system far from its initial state, which eventually leads to rejuvenation [27,28]. Although previous accelerated aging techniques have sometimes been shown to yield results that do not match spontaneous aging [26], we ensured that the present protocol predicts a realistic relaxation by checking that, upon relaxation, a hyperquenched glass evolves toward the inherent configurations of the more slowly cooled supercooled liquids [1].

Here, to investigate the MAE in glass relaxation, we simulated a series of $(K_2O)_x(Na_2O)_{16-x}(SiO_2)_{84}$ (mol %) mixed alkali silicate glasses, made of 2991 atoms, with varying x. All MD simulations were performed using the well-established Teter potential [29–31] with an integration time step of 1 fs. Coulomb interactions were evaluated by the Ewald summation method with a cutoff of 12 Å. The short-range interaction cutoff was chosen as 8.0 Å. Liquids were first generated by placing the atoms randomly in the simulation box. The liquids were then equilibrated at 5000 K in the NPT ensemble (constant pressure) for 1 ns, at zero pressure, to assure the loss of the memory of the initial configuration. Glasses were formed by linear cooling of the liquids from 5000 to 0 K with a cooling rate of 1 K/ps in the NPT ensemble at zero pressure. Note that initially cooling the glasses down to 0 K allows the atoms to reach local minima in the energy landscape, to avoid any thermal contribution to the relaxation subsequently computed.

Figure 1(a) shows the relative variations of the enthalpy of the binary sodium and potassium silicate glasses (denoted Na and K hereafter) and mixed $(K_2O)_8(Na_2O)_8(SiO_2)_{84}$ glass (denoted Na + K hereafter) with respect to the number N of stress perturbation cycles applied, using a stress amplitude of $\sigma_0 = 0.4$ GPa (as used in Ref. [1]). As expected, the stress perturbations allow all glasses to relax towards lower enthalpy states. This stabilization is gradual, and about 10^4 cycles are needed for the enthalpy to plateau. As shown in Fig. 1(b), all glasses also show a gradual compaction in volume upon relaxation, which cannot be explained by elastic deformations since the average applied stress remains zero. Remarkably, the shape of the volume relaxation observed herein is fairly similar to that observed experimentally [7]. Further, as shown in the insets of Figs. 1(a) and 1(b), we observe that the magnitudes of the enthalpy and volume relaxation reach a maximum when the concentration of Na equals that of K atoms. Namely, the mixed alkali Na + K

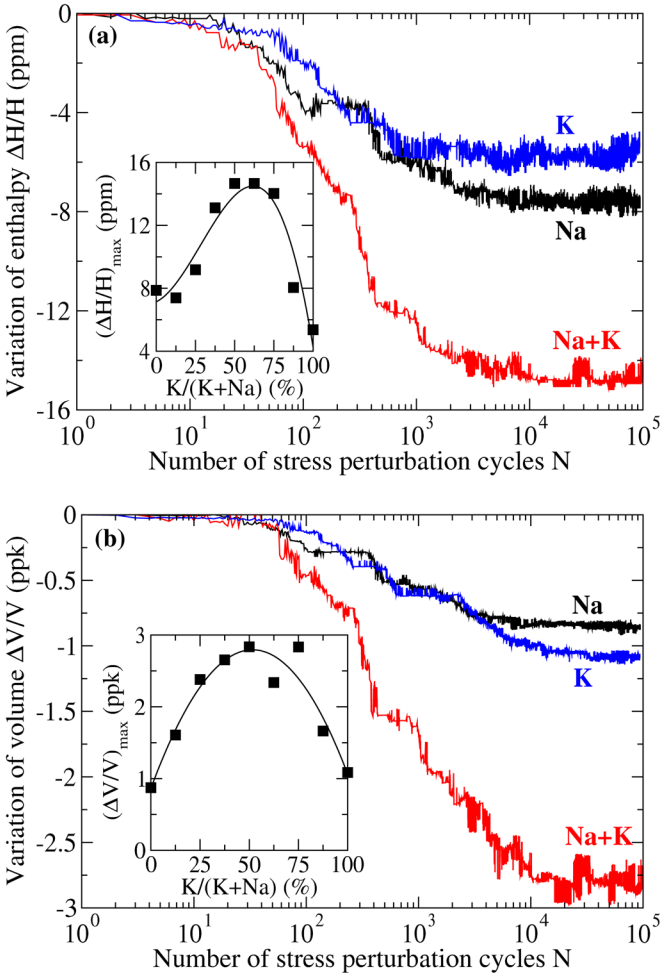

FIG. 1. Relative variation of the (a) enthalpy and (b) volume of the sodium (Na), potassium (K), and mixed alkali (Na + K) silicate glasses with respect to the number of stress perturbation cycles applied. The insets show the final absolute relative variations of (a) the enthalpy and (b) volume. Lines serve as a guide for the eye.

glass shows a final volumetric relaxation that is nearly three times larger than those of the single-alkali Na or K glasses. This is a clear demonstration that the thermometer effect is indeed a manifestation of the MAE. These results constitute, to the best of our knowledge, the first direct simulation of the MAE in glass relaxation.

We now focus on elucidating the atomistic mechanism of relaxation. Enthalpy and volume relaxation can typically be modeled using Kohlrausch stretched exponential decay functions:

$$f(N) = \exp\left[-\left(\frac{N}{N_0}\right)^{\beta}\right] \quad (1)$$

where N_0 is a typical number of stress perturbation cycles (proportional to a relaxation time [1]) and β a dimensionless stretching exponent satisfying $0 < \beta < 1$. The particular value of β is of great interest as it captures some

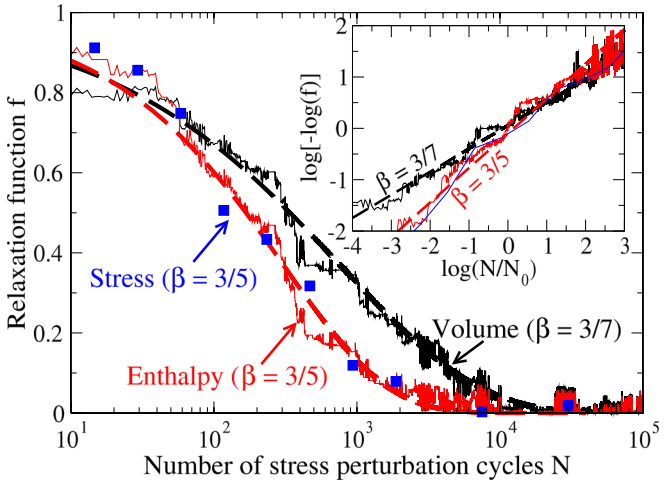

FIG. 2. Relaxation function f of the enthalpy, volume, and internal stress in the mixed sodium potassium silicate glass, with respect to the number of stress perturbation cycles N. The data are fitted with stretched exponential decay functions $f(N) = \exp[-(N/N_0)^{\beta}]$ with a stretching exponent $\beta = 3/5$ and $3/7$ for the stress or enthalpy and volume, respectively (see text). The inset shows $\log[-\log(f)]$ with respect to $\log(N/N_0)$ for the enthalpy, stress, and volume, whose slope yields β. Dashed lines corresponding to the slopes $\beta = 3/5$ and $3/7$ are added for comparison.

information about the topology of the relaxation process [17]. Indeed, Phillips's diffusion-trap model predicts a theoretical value for the stretching exponent as $\beta = d^*/(d^* + 2)$, where $d^* = \phi d$ is the effective dimensionality of the channels along which the excitations diffuse in the configurational space, d is the dimensionality of the system (i.e., 3 for structural glasses), and ϕ is the proportion of active relaxation channels [12]. Hence, when all the channels are active ($\phi = 1$), one obtains $\beta = 3/5$. When only long-range channels are active, by assuming an equipartitioning of the short- and long-range contributions ($\phi = 1/2$), the model predicts $\beta = 3/7$. It should be noted that this model only applies to perfectly homogeneous glasses, that is, featuring uniformly distributed excitations, which is rarely achieved experimentally without relying on advanced industrial-scale melting techniques like the fusion draw process [7].

As shown in Fig. 2, we observe that the computed enthalpy and volume relaxation functions indeed feature a stretched exponential decay. Interestingly, we find that enthalpy shows a stretching exponent $\beta = 3/5$, which, as mentioned previously, corresponds to the situation in which all relaxation channels are active [12]. Note that the $3/5$ stretching exponent was experimentally observed to describe the relaxation of stress in glasses [17,32], which suggests that, in terms of relaxation, stress can be an indicator of enthalpy. Further, as shown in Fig. 2, we observe that the relaxation of enthalpy and volume do not show the same trend. In contrast to the enthalpy, we find that volume features a stretching exponent $\beta = 3/7$, which corresponds to the situation in which only long-range relaxation channels are active [12]. This result agrees with experimental observations [7,17,32]. Note that previous simulations yielded a different exponent ($\beta = 1$) [1], but the glasses used in this study were not preliminary cooled to 0 K. This suggests that the presence of residual thermal excitations affects the relaxation mechanism. As shown in the inset of Fig. 2, the difference of stretching exponents can be clearly established by plotting $\log[-\log(f)]$ with respect to $\log(N/N_0)$, where the slope is equal to β. Finally, we note that, in agreement with experiments [17], the relaxation of volume appears to be slower (i.e., higher N_0) than that of the enthalpy, which is in line with the notion that the former occurs through long-range channels only.

Finally, we investigate the origin of the MAE in the context of room-temperature relaxation. First, we propose that the excitations introduced within Phillips's diffusion-trap model correspond to locally unstable atomic units. To assess this hypothesis, we first computed the coordination number (CN) of all atomic species. Although Si atoms remain fourfold coordinated with oxygen atoms in all glasses, the CN of Na and K atoms shows a variation with composition. As expected, the average CN of Na and K is around 6 and 8 for the binary Na and K glasses, respectively [33]. However, as shown in Fig. 3(a), the CN of Na decreases upon the addition of K, whereas that of K increases upon the addition of Na. This can be attributed to a mismatch between the alkali atoms and the rest of the silicate network as one moves away from the binary composition.

This miscoordinated state results in the formation of local stresses inside the atomic network, which was assessed by computing the local stress applied to each atom using the virial definition of stress [34]. The trace of the stress tensor of each atom was then averaged to obtain the local pressure applied to each atom. Although the network as a whole is at zero pressure, some bonds are under compression while others are under tension, so that they mutually compensate each other. By convention, a positive stress corresponds here to a state of tension, while a negative one refers to a state of compression. We observe that the average stress applied to Na and K atoms exhibits a clear dependence on composition. As shown in Fig. 3(b), the average stress experienced by Na atoms decreases upon the addition of K, whereas that experienced by K atoms increases upon the addition of Na. This can be understood as follows. Over-coordinated K atoms present an excess of O atoms in their first coordination shell. Because of mutual repulsion, O atoms tend to separate from each other, which, in turn, tends to stretch the K—O bonds. On the other hand, under-coordinated Na atoms show a deficit of O atoms, which, in turn, are more attracted by the central cation. This results in a compression of Na—O bonds. The total cumulative stress experienced by all Na and K atoms then

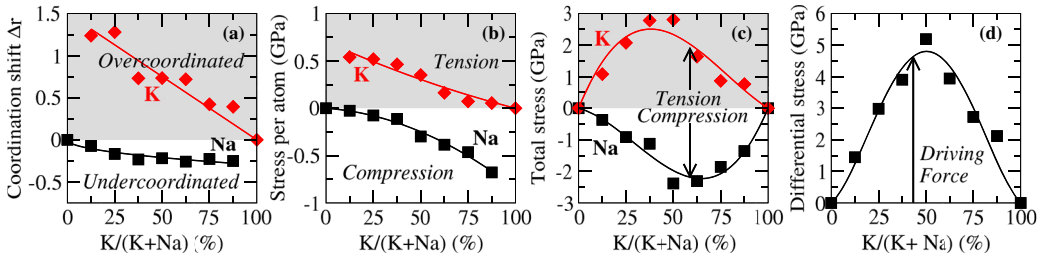

FIG. 3. (a) Shift of the coordination number of Na (K) atoms, using the binary sodium (potassium) silicate glass as a reference, with respect to the composition of the glass. (b) Average stress per Na and K atoms. A positive (negative) stress denotes a local compression (tension). (c) Total cumulative stress experienced by all Na and K atoms. (d) Difference between the total cumulative stresses experienced by Na and K atoms, which acts as the driving force for relaxation. Lines serve as guides for the eye.

arises from the balance between two competitive behaviors. (1) The absolute stress per atom experienced by Na and K species increases upon the addition of K and Na, respectively. (2) In contrast, the numbers of Na and K atoms present in the network decreases upon their replacement by K and Na atoms, respectively. Altogether, as shown in Fig. 3(c), the total cumulative stress experienced by Na and K atoms reaches an extremum when the concentration of Na equals that of K.

The mechanism of the MAE in glass relaxation can then be understood as follows. Miscoordinated species act as local instabilities (or "excitations" following Phillips's terminology). These excitations diffuse via local deformations of the atomic network, until an atomic arrangement that is locally under compression meets one that is under tension. At this point, both excitations are annihilated (or reach a "trap"), thereby relieving the initial internal stress stored in the network. As such, the driving force for relaxation corresponds to the difference between the total cumulative stress experienced by Na and K atoms, which, as shown in Fig. 3(d), is maximum when the concentration of Na equals that of K. This behavior provides an intuitive atomistic origin of the MAE, that is, the excessive volumic relaxation of glasses comprising mixed alkali atoms (i.e., thermometer effect).

This mechanism is supported by the fact that the extent of the absolute internal stress experienced by Na and K atoms decreases over time. As shown in Fig. 2, the relaxation function of the internal stress matches that of the enthalpy, both in terms of shape (same stretched exponent $\beta = 3/5$) and relaxation time (same N_0). This agrees with experiments conducted for bulk metallic glasses, wherein enthalpy and stress relaxations were found to exhibit fairly similar stretched exponents [35,36]. This demonstrates that the short-range diffusion of local internal stress controls enthalpy relaxation. In turn, volume appears to relax via some long-range reorganizations of the structure, which are made possible by the release of the internal stress, that is, when an excitation meets a trap.

The mechanism presented herein provides a clear structural origin for the low-temperature relaxation observed in glasses comprising mixed modifiers. More generally, structural relaxation is of direct relevance to the glass industry, e.g., for the processing of liquid crystal display (LCD) substrates [37]. In addition, it can be expected that the excessive internal stress observed here in mixed alkali glasses can also play a crucial role in the MAE for other properties. For instance, such local instabilities are likely to affect the propensity for atomic rearrangements under stress, which could explain the deviation from linearity observed in the hardness of mixed modifers silicate glasses [38]. 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 [11].

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