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Understanding the changes in ductility and Poisson's ratio of metallic glasses during annealing from microscopic dynamics

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In the paper K. L. Ngai *et al.*, [J. Chem. **140**, 044511 (2014)], the empirical correlation of ductility with the Poisson's ratio, ν_{Poisson}, found in metallic glasses was theoretically explained by microscopic dynamic processes which link on the one hand ductility, and on the other hand the Poisson's ratio. Specifically, the dynamic processes are the primitive relaxation in the Coupling Model which is the precursor of the Johari–Goldstein β-relaxation, and the caged atoms dynamics characterized by the effective Debye–Waller factor f_0 or equivalently the nearly constant loss (NCL) in susceptibility. All these processes and the parameters characterizing them are accessible experimentally except f_0 or the NCL of caged atoms; thus, so far, the experimental verification of the explanation of the correlation between ductility and Poisson's ratio is incomplete. In the experimental part of this paper, we report dynamic mechanical measurement of the NCL of the metallic glass $La_{60}Ni_{15}Al_{25}$ as-cast, and the changes by annealing at temperature below T_g. The observed monotonic decrease of the NCL with aging time, reflecting the corresponding increase of f_0, correlates with the decrease of ν_{Poisson}. This is important observation because such measurements, not made before, provide the missing link in confirming by experiment the explanation of the correlation of ductility with ν_{Poisson}. On aging the metallic glass, also observed in the isochronal loss spectra is the shift of the β-relaxation to higher temperatures and reduction of the relaxation strength. These concomitant changes of the β-relaxation and NCL are the root cause of embrittlement by aging the metallic glass. The NCL of caged atoms is terminated by the onset of the primitive relaxation in the Coupling Model, which is generally supported by experiments. From this relation, the monotonic decrease of the NCL with aging time is caused by the slowing down of the primitive relaxation and β-relaxation on annealing, and vice versa.
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I. INTRODUCTION

The correlation of plasticity or ductility of metallic glasses (MG) with the ratio of the elastic bulk modulus K to the shear modulus G was established by considering alloy compositions as a variable.[1] That is, MG with high (low) K/G ratio tends to be more ductile (brittle). The same correlation of K/G with ductility was found by examining the effects of annealing on the two quantities in a single metallic glass.[1] These correlations were confirmed by others, and had been extended to the correlation of ductility with the Poisson's ratio, ν_{Poisson}.[2,3] The latter is equivalent to that for the ratio of K_∞/G_∞ in view of the relation,

$$\nu_{Poisson} = \frac{1}{2} - \frac{3}{(6K_\infty/G_\infty)+2}, \quad (1)$$

where K_∞ and G_∞ are the infinite frequency bulk and shear modulus, respectively.

Despite the impressive empirical correlation of ν_{Poisson} with ductility, its origin is unclear because there is no obvious link between the two macroscopic quantities. In a previously published paper,[4] we have provided an explanation of the correlation based on microscopic considerations of the dynamics and relaxation mechanisms. First, ductility is linked to the secondary or β relaxation of the MG. Faster β-relaxation of the Johari–Goldstein (JG) kind[5–9] with shorter relaxation time τ_β, lower activation energy E_β, and larger relaxation strength Δ_β makes the MG more ductile. Second, faster secondary relaxation is associated with a smaller Debye–Waller factor, f_0. Third, there is a relation between f_0 and K_∞/G_∞ given from theory[4,10] by

$$f_0 = \frac{1}{\left(\frac{3}{4}\right)\left(\frac{K_\infty}{G_\infty}\right)+1}. \quad (2)$$

It follows from Eqs. (1) and (2) that larger K_∞/G_∞ or ν_{Poisson} has a smaller effective Debye–Waller factor f_0. On combining the three steps above, the correlation of ductility with

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$\nu_{Poisson}$ on varying the alloy composition was established on a microscopic basis.[4] The conclusion of the second step was arrived at by a sequence of several intermediate steps. To start with, from the Coupling Model (CM),[11–15] the ratio, τ_α/τ_{JG} at the glass transition temperature T_g, is determined by the size of the coupling parameter n, which in turn is governed by the strength and anharmonicity of the intermolecular potential. Here, τ_{JG} and τ_α are the JG β- and α-relaxation times, respectively. Results from molecular dynamics simulations on binary Lennard–Jones particles interacting with different intermolecular potentials show that increase of anharmonicity leads to larger $(1-f_0)$ as well as n, and hence also τ_α/τ_{JG} at T_g.[16]

The ratio K_∞/G_∞ or the Poisson's ratio can be measured directly,[1,17] and ductility can be assessed by the measured fracture energy. The JG β-relaxation time τ_{JG} and strength Δ_{JG} are available from dynamic mechanical measurements of some metallic glasses.[17–22] The missing link in the microscopic variables connecting ductility to Poisson's ratio[4] is the experimental values of $(1-f_0)$ or its counterpart in susceptibility, i.e., the nearly constant loss (NCL),[23–26] of alloys with different compositions or the same alloy on annealing. Without them, the theoretical explanation of the correlation of ductility with Poisson's ratio cannot be substantiated experimentally in full.

In order to supply the missing link, in this paper, we provide experimental measurements of the NCL of a single metallic glass, $La_{60}Ni_{15}Al_{25}$, and its changes by annealing at temperature below T_g. The observed decrease of the NCL with time reflects the corresponding decrease of $(1-f_0)$. This is the important result from our experimental part of the paper because such measurements have not been given before unambiguously to the best of our knowledge. The shift of τ_{JG} to longer times and the decrease of Δ_{JG} observed on annealing the same metallic glass are presented. The changes of the JG β-relaxation are similar to those found before in studies by other workers.[27–29] The fact that the observed decrease of the NCL on annealing is accompanied by concomitant increase of τ_{JG} and decrease of Δ_{JG} is shown to be a natural consequence of the evolution of dynamics with time, starting from the caged atoms dynamics which is terminated by the onset of the JG β-relaxation.[8,9,14,15,30–33] This explanation forms the theoretical part of this paper.

Before closing this section, we have to make a clarification since Ref. 10 by Novikov and Sokolov is cited when Eq. (2) was introduced. The main conclusion in this reference is the linear relation, $m = 29(K_\infty/G_\infty - 0.41)$, between K_∞/G_∞ and the liquid fragility index,[34] m, of non-metallic glass-formers. However, Yannopoulos and Johari[35] investigated the basis for this relation and found flaw in its premise because of the unjustifiable preference for an empirical variation of m with elastic properties,[10] and the linear relation no longer hold when more non-metallic glasses are considered in the same way.[35] This correlation also breaks down when metallic alloys are included as shown in several studies.[35–38] Any measure of fragility, such as the quantity m, is a measure of the apparent activation energy for viscosity with temperature scaled by T_g. It is a complex quantity determined by several factors including the change of density and entropy with T_g-scaled temperature, and the many-body dynamics controlled by the intermolecular potential. It is unsurprising that correlation of properties with fragility can break down. By contrast, in our understanding of the correlation between ductility and Poisson's ratio,[4] only pure dynamic quantities are used to provide the link and fragility is not involved.

II. EXPERIMENTAL METHODS

The $La_{60}Ni_{15}Al_{25}$ MG was prepared by arc melting pure metal in a Ti-gettered argon atmosphere. The mother alloy ingot was then re-melted and suction casted into water cooled Cu mold to get 2 mm fully glassy cylindrical rods. Rod samples used in this paper are obtained from sole mother alloy ingot and the suction casting processes utilize same Cu mold under invariable controlling parameters, to eliminate other possible influences. The glassy nature was ascertained by X-ray diffraction and differential scanning calorimetry. The glass transition temperature of the $La_{60}Ni_{15}Al_{25}$ samples is located at 461 K at a heating rate of 20 K min^{-1}. MG rods were heating treated in a high vacuum annealing furnace under 1.0×10^{-3} Pa. Annealing processes started from room temperature (RT) with heating rate of 5 K min^{-1} until reaching thermal equilibrium at 423 K, then samples were isothermally annealed at 423 K for various planned time.

To explore the annealing influence on NCL, dynamic mechanical measurements of as-cast and annealed samples were performed using a TA DMA Q800 through temperature ramp mode at a heating rate of 3 K/min. Measurement method of the complex modulus of extension or Young's modulus $E^* = E' + iE''$ used in this work has been described in previous papers.[39,40] Considering the fact that NCL from caged atoms is weak compared to other relaxation processes, and is normally observed isochronically at relatively low temperatures, cold nitrogen gas generated from controlled evaporation of liquid nitrogen is used to extend the operating temperature below room temperature. During the measurements, the strain amplitude is always lower than 10^{-3} to assure no nonlinear effects are included.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

In Fig. 1, we present the mechanical loss modulus $E''(T)$ measured at 1 Hz as a function of temperature T of $La_{60}Ni_{15}Al_{25}$ as-cast and after aging at 423 K for 1 h, 6 h, 12 h, and 24 h. Each of the isochronal spectra of $E''(T)$ has been normalized by the maximum loss of the structural α-loss peak, $E''_{\alpha-peak}$, which corresponds to the equilibrium liquid state above T_g. This operation avoids deviations from the absolute value in measurements from one aging time to another, and ensures the normalized spectra reflect the intrinsic changes on annealing of the intensities of the faster processes in the glassy state. Observed from the normalized spectra in Fig. 1 is the shift of the JG β-loss peak to higher temperatures together with reduction of its intensity on increasing the aging time, in concert with the shift of the α-loss peak to higher temperatures. The JG β-loss peak temperature, $T_{\beta p}$, increases from 364 K to 377 K, and the activation energy, E_β, increases from 98 to 110 kJ/mol, and the

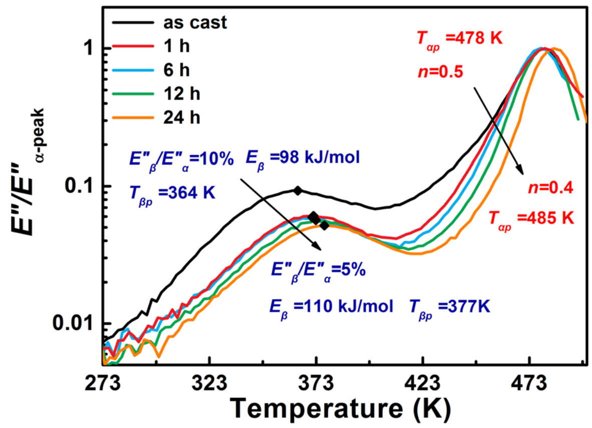

FIG. 1. Changes of the isochronal spectra of the normalized loss modulus $E''/E''_{\alpha\text{-}peak}$ as a function of temperature measured at 1 Hz of $La_{60}Ni_{15}Al_{25}$ as cast and after aging at 423 K for 1 h, 6 h, 12 h, and 24 h (order indicated by direction of the arrow). Observed is the shift of the JG β-relaxation peak to higher temperatures, the decrease in relaxation strength, and the increase in activation enery. The changes in these characteristics of the JG β-relaxation are given in the figure.

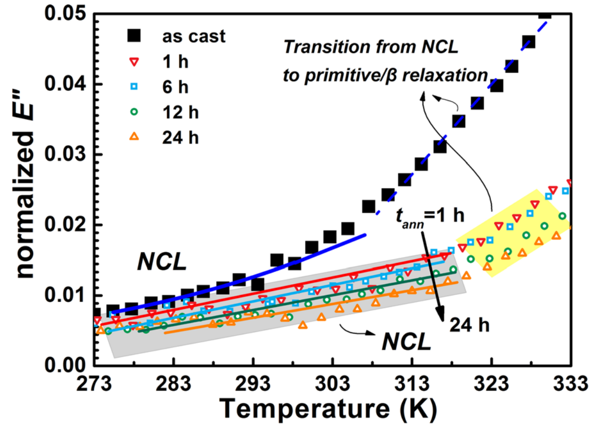

FIG. 2. Change of NCL of $La_{60}Ni_{15}Al_{25}$ glass as cast and after aging at 423 K for 1 h, 6 h, 12 h, and 24 h (order indicated by the direction of the arrow). Data shown by symbols, and the solid lines are drawn to indicate the increase of NCL with temperature. The NCL regime of the annealed glass is highlighted in grey. Decrease of the intensity of NCL with increasing annealing time is observed. Data of the annealed glass in the region highlighted in yellow represent the transition from NCL to the primitive relaxation and JG β-relaxation. Data of the as cast sample connected by the dashed blue line represents the transition from NCL to the primitive relaxation and JG β-relaxation.

relaxation strength decreases by 5%. These information are shown also inside Fig. 1.

Qiao *et al.*[27] also found on aging a similar La-based metallic glass at 433 K that the JG β-relaxation shifts to lower frequencies and its amplitude ΔG_{max} decreased with time in the isothermal loss modulus spectra. They found that the change of ΔG_{max} with aging time can be described by a stretched exponential function, the characteristic time of which provide τ_{aging} consistent with tan (δ) measurements during aging, as found before in the aging of the JG β-relaxation in a polymeric glass-former by dielectric spectroscopy.[28] By the way, the results of Ref. 28 verified the Coupling Model prediction of the relation between τ_α and τ_{JG}.

The loss at lower temperatures than the JG β-loss peak is reduced by about an order of magnitude. The data of the as-cast and annealed samples are shown better by symbols in Fig. 2. The solid lines drawn are used to guide the eye, and to indicate the weak temperature dependences of the normalized $E''(T)$ at the different aging times. The lines also show that the temperature dependences of the data are well described by

$$E''(T) = A\exp(T/T_0), \quad (3)$$

where A and T_0 are constants, which is the signature of the NCL of caged ions and molecules found before in many materials.[8,9,30–33,41,43] Fitting the experimental NCL data by Eq. (3) determines the parameters A and T_0 for different annealing times, and the values are listed in Table I, where the changes with increasing annealing time can be seen. Dynamic mechanical measurements of several other metallic glasses have shown the presence of the NCL at lower temperatures.[39–42] For the present case, the data are showing the NCL of caged atoms in $La_{60}Ni_{15}Al_{25}$. The NCL of the as-cast sample is the highest, but it is terminated at about 293 K by the onset of the primitive relaxation and at higher temperatures by the JG β-relaxation. On aging the sample, the NCL persists to higher temperatures due to the corresponding shift of the JG β-relaxation, but its intensity decreases monotonically with annealing time. The NCL regime is terminated at temperatures above approximately 323 K for the annealed sample. Mentioned in the Introduction and shown before in Ref. 4, the NCL in susceptibility is the counterpart of $(1-f_0)$, and the observation of its decrease on aging is equivalent to the verification of the corresponding decrease of $(1-f_0)$. This finding constitutes the important part of the experimental contribution from this paper. This is because for the first time, data of $(1-f_0)$ become available to verify its change on aging correlates with the shift of τ_β and the decrease of Δ_β (see Fig. 1). In turn, the changes of these microscopic parameters on aging are correlated with the reduction of ductility (i.e., embrittlement) deduced from the decrease of the fracture energy measured, and the decrease of the Poisson's ratio obtained from the bulk and shear modulus measured. Thus, the missing link of the correlation of ductility with Poisson's ratio from the experimental point of view is now provided by the data of NCL in Fig. 2. The same result also verifies qualitatively the theoretical relation of $(1-f_0)$ with either K/G in Eq. (2) or with $\nu_{Poisson}$ via Eq. (1).

IV. THEORETICAL CONSIDERATIONS

In Sec. III, the experimental results have shown that the intensity of the NCL decreases in concert with the decrease

TABLE I. Parameters obtained from the fits to Eq. (3) of the experimental NCL data shown in Fig. 2. "Annealed sample" is shortened to "AN" here.

	As cast	1 h (AN)	6 h (AN)	12 h (AN)	24 h (AN)
A ($\times 10^{-5}$)	0.892	1.80	2.32	2.70	4.90
T_0	40.6	47.0	49.2	52.5	59.1

in relaxation strength Δ_{JG} and increase of relaxation time τ_{JG} of the JG β-relaxation. In this section, we show from theory that these parallel changes of the NCL and the β-relaxation on annealing occur not by accident, but are consequence of the fundamental connection between these two processes.

Plasticity is facilitated by relaxation process. In the glassy state of metallic glass, the only effective relaxation process present and can match the rate of plastic deformation is the secondary relaxation. The structural α-relaxation is far too slow and needed not to be considered. According to the description of the evolution of dynamics with time by the CM, initially at short times, molecules (in the case of molecular glass-formers) and atoms (in the case of metallic glasses) are caged. In this caged dynamics regime, the susceptibility, $\chi''(T,\nu) = B(T)(\nu)^{-\lambda}$, originates from the dissipation of movements confined by the anharmonic potential. Its weak temperature dependence $B(T)$ is well described by $A\exp(T/T_0)$. Its power law frequency dependence with $\lambda \ll 1$ leads to the term of the NCL. The NCL is not a relaxation process with a characteristic time. It persists to lower frequencies/longer times until the atoms, or molecules leaves the cage. This primitive relaxation with relaxation time, τ_0, effectively terminates the caged dynamics regime, and the NCL dependence of the susceptibility no longer holds at frequencies lower than the onset of the primitive relaxation.[8,9,14,30–33]

Thus, the primitive frequency, $\nu_0 \equiv 1/(2\pi\tau_0)$, is an lower bound of the NCL frequency regime, or τ_0 is the upper bound of the caged dynamics time regime. This prediction has been verified by experimental data of many molecular glassformers,[8,9,14,30–33] and ionic conductors.[45–47] Isothermal frequency dependent susceptibility spectra of molecular glassformers have shown that the NCL regime is terminated by the onset of the primitive relaxation of the CM, which is the precursor of the β-relaxation of the Johari–Goldstein kind.[5–8] Glassy ionic conductors are like metallic glasses in the sense that relaxation is by translational diffusion of ions in the former and atoms in the latter. Isothermal conductivity relaxation data as a function of frequency also show the presence of NCL from caged ions dynamics at higher frequencies and are terminated by the primitive conductivity relaxation time τ_0.[44–47] Application of high electric fields to molecular glass-formers in dielectric spectroscopy has the effect of increased loss from genuine relaxation processes starting from the primitive relaxation, but no effect on the NCL was observed.[9,43] This experimental finding also provides additional evidence that ν_0 is lower bound of the NCL frequency regime. To further support the CM interpretation of NCL as the manifestation of caged molecular dynamics and termination of NCL is effected by the onset of the primitive relaxation of the CM, the precursor of the β-relaxation, we consider the experimental results obtained on hard-sphere colloidal particles suspension by confocal microscopy experiment by Weeks *et al.*[48] The mean square displacements (MSD), $\langle \Delta x^2(\Delta t)\rangle$ were obtained as a function of time Δt from 10 to 10^4 s. In a log-log plot of $\langle \Delta x^2(\Delta t)\rangle$ against Δt, the data show for the suspension with volume fraction ϕ equal to 0.56, $\langle \Delta x^2(\Delta t)\rangle$ has the power law dependence proportional to $(\Delta t)^c$ with $c \approx 0.13$ at times shorter than 200 s. During this period, effectively, the particles are all confined within cages. This is confirmed by the fact that no particle was observed to have jumped any distance of significance. The $\langle \Delta x^2(\Delta t)\rangle \propto (\Delta t)^c$ with $c \approx 0.13$ for $\Delta t < 200$ s corresponds to susceptibility with frequency dependence $\chi''(\nu) \propto (\nu)^{-c}$ with $c \approx 0.13$, which is the NCL in the caged regime. From the study of the trajectories of all particles in the suspension, Weeks *et al.* show the particles spent most of their time rattling but confined in cages formed by their neighbors. A typical particle takes average time Δt of 500 s to shift position and leaves the cage. This time is identifiable with the primitive relaxation time $\tau_0 = 500$ s of the CM, and is the time-scale for the cages to decay. This experimental result shows that the NCL extends from short times and, up to 200 s, is terminated by the primitive relaxation with $\tau_0 = 500$ s. This example is one of the best experimental demonstrations of the relation between the NCL from caged dynamic and the primitive relaxation, which is the precursor of the β-relaxation.

In the CM, the primitive relaxation is followed in time by the spatially and dynamically heterogeneous relaxation processes involving the participation of increasing number of molecules (collectively considered as the JG β-relaxation). Thus, the JG β-relaxation is spatially and dynamically heterogeneous as well as to some extent cooperative, consistent with results from simulations of metallic glass.[49] Since the primitive relaxation is part of as well as the precursor of the JG β-relaxation, there is approximate or order of magnitude agreement between the primitive relaxation time $\tau_0(T)$ and the JG β-relaxation time, $\tau_\beta(T)$, i.e.,

$$\tau_\beta(T) \approx \tau_0(T) \tag{4}$$

is predicted, and is found to be the case in many glassformers.[5–9,15,30–33,42,50]

Finally comes the terminal α-relaxation, which has the Kohlrausch time dependence for its correlation function

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]. \tag{5}$$

In the CM, there is a relation relating $\tau_0(T)$ to τ_α involving the exponent $(1-n)$ in the Kohlrausch function given by[8,11–15]

$$\tau_\alpha(T) = [t_c^{-n}\tau_0(T)]^{1/(1-n)}, \tag{6}$$

where $t_c = 0.2$ ps for metallic glasses.[51]

A. Effects of annealing on the JG β-relaxation and embrittlement

Annealing the as-cast metallic glass lowers the fictive temperature, increases the density, and decreases the configurational entropy. The well understood effect on the structural α-relaxation is the increase of τ_α with aging time t_e. From this, Eq. (6) shows that τ_0 is also increased if n (i.e., the frequency dispersion of the α-relaxation) remains constant on aging. The approximate relation (4) leads to increase of the observed value of τ_{JG}. Furthermore, the amplitudes of the displacements of atoms are reduced by the increased in density or decreased in entropy. The consequence is the reduction of the relaxation strength of the JG β-relaxation. Thus, the observed changes of the JG β-relaxation of $La_{60}Ni_{15}Al_{25}$ on aging at 423 K shown in Fig. 1 as well as from the isothermal data of Qiao *et al.*[27] can be understood rather straightforwardly. Plastic deformation requires the response from relaxation process in the material with frequency corresponding to the deformation rate, and with large relaxation strength. The prominent JG β-relaxation extended over a wide range of temperatures in the isochronal spectra of $La_{60}Ni_{15}Al_{25}$ (Fig. 1) means relaxation processes with a broad range of frequencies and large relaxation strength are available in response to plastic deformation. This connection of the JG β-relaxation with plasticity is confirmed by the experimental findings of the brittle-to-ductile transition and the JG β-relaxations follow similar time-temperature dependence in another La-based metallic glass, $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$.[18] Since by annealing our $La_{60}Ni_{15}Al_{25}$ glass the JG β-relaxation spectrum is shifted to higher temperatures/longer times, the activation energy of the relaxation time τ_{JG} is increased from 98 kJ/mol to 110 kJ/mol, and the dielectric strength is reduced (see Fig. 1); it follows that the metallic glass becomes more brittle.

B. Effects of annealing on the NCL

The increase of the density and decrease the configurational entropy with time on annealing the metallic glass necessarily tightens the cages and reduces the MSD of motion of the atoms within the cages, and hence, the NCL is decreased in intensity. The effect can be seen in another glass-forming system, namely, the suspension of colloidal particles. Earlier at the beginning of this section, we have used the data of colloidal particles suspension observed using confocal microscopy by Weeks *et al.*[48] to support the primitive relaxation of the CM acting as the terminator of the NCL of caged dynamics. Here, we cite the results from the study of aging of a concentrated colloidal glass by Courtland and Weeks[52] again using confocal microscopy. The packing fraction ϕ of the suspension studied is 0.62, which is larger than glass transition fraction at $\phi_g = 0.58$. Instead of quenching metal alloy to form a metallic glass, they started by stirring the sample, and followed the motion of several thousand colloidal particles and observe that their motion significantly slow down as the sample ages but continue to occur on all times scales. With increasing aging time t_w, Courtland and Weeks found the MSD $\langle r^2(\Delta t)\rangle$ changes according to the pattern shown in Fig. 3. The three sets of data represent three different ages of the sample, $t_w = 0\tau_{diff}$, $t_w = 100\tau_{diff}$ and $t_w = 300\tau_{diff}$, where $\tau_{diff} = 11$ s. For each sample of different ages, at shorter times, the MSD varies very slowly with time Δt as a power law, $\langle r^2(\Delta t)\rangle \propto (\Delta t)^c$ with $c \approx 0.18$ for $t_w = 0\tau_{diff}$, and $c \approx 0.13$ for $t_w = 300\tau_{diff}$. These power laws of MSD correspond in susceptibility to $\chi''(\nu) \propto (\nu)^{-c}$ with $c \approx 0.18$ and 0.13, respectively. By inspection of Fig. 3, it is clear that the NCL is reduced in intensity, and it is spread over a longer period of time before being terminated by the onset of the primitive relaxation. Each arrow indicates approximately the primitive relaxation time defined by the onset of the fractional power law of the MSD in Fig. 3.

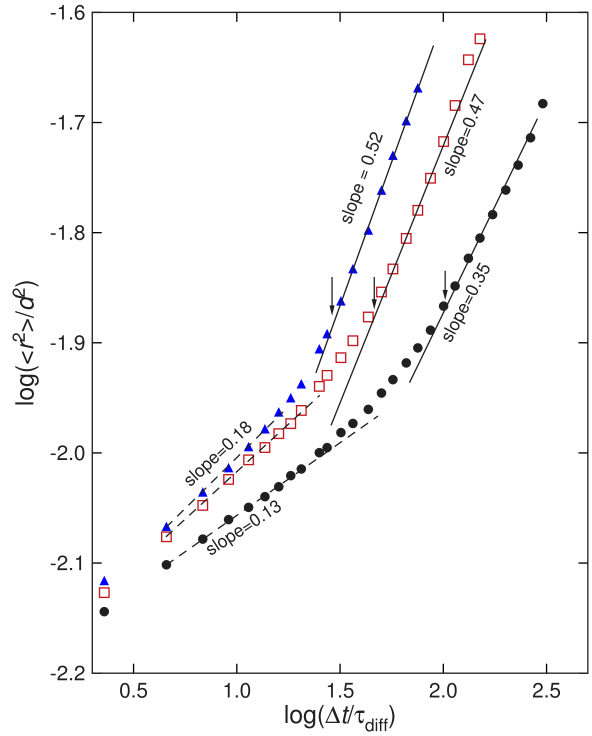

FIG. 3. Aging mean squared displacement for a colloidal glass with packing fraction $\phi = 0.62$. The three curves represent three different ages of the sample. The three sets of data represent three different ages of the sample. From top to bottom, $t_w = 0\tau_{diff}$ (closed triangles) $t_w = 100\tau_{diff}$ (open squares), and $t_w = 300\tau_{diff}$ (closed circles) where $\tau_{diff} = 11$ s. The data of $t_w = 300\tau_{diff}$ at shorter times are from the particles when they are still caged. The dashed line drawn through them has slope = 0.13.

The data from aging of colloidal glass in Fig. 3 show the concerted changes of the primitive relaxation and the NCL with time on aging the glass. This finding bears strong resemblance to the change of the NCL and the onset of the JG β-relaxation on annealing our metallic glass in Fig. 2. The general results in the two different systems are the consequences of the primitive relaxation time τ_0 in the CM acting as an upper bound of the caged dynamics regime, or equivalently the primitive relaxation frequency ν_0 being a lower bound of the NCL frequency regime. We have elucidated in Subsection IV A on aging either one of the two systems that the JG β-relaxation (led by the primitive relaxation, its precursor) is shifted to lower frequencies and is reduced in relaxation strength. Via the connection of the NCL to the primitive relaxation/JG β-relaxation, it follows as a consequence that the NCL is extended to lower frequencies and reduced in intensity.

The considerations in the above explain the reduction of the NCL intensity, or the increase of the effective Debye–Waller factor, f_0, on a microscopic dynamics basis from the connection it has with the primitive relaxation and the JG β-relaxation. The crux of the explanation is the evolution of dynamics with time changing from the NCL to primitive relaxation acting as the precursor of the JG β-relaxation, and finally to the α-relaxation, glass transition, and viscous flow. The evolution leads to connections between all the processes, which have been verified in different ways by experiments.[5–8,13–15,28–30,36–39,44] Had one viewed that these dynamic processes are independent of each other and additive in the susceptibility spectrum, none of the connections would exist and much of experimental facts cannot be explained.

The theoretical rationalization of the experimentally observed changes of the NCL, the primitive relaxation, and the JG β-relaxation given above is based on the CM. Another description of the processes in the metallic glasses is in terms of "flow units,"[39,40,53,54] the activation of which is equivalent to or correlated with the JG β-relaxation in the CM. This alternative description is based on the heterogeneous structure of the metallic glass, which engenders a distribution of local regions with different densities, viscosity, and entropy. The concept of flow units are defined as the liquid-like regions with lower elastic modulus, viscosity, and packing density. These local regions are the initial regions that undergo structural rearrangement in response to plastic deformation. The "flow units" are the local cooperative motions of atoms, which are similar to the CM view of increasing involvement of atoms with time of processes collectively called the JG β-relaxation. Thus, the flow units are the analogue of the spectrum of the JG β-relaxation, and they have the same properties and functions, as brought out in a recent paper.[40] Although further development of the flow unit model is needed, it is possible that some isolated and random activation of flow units can be identified as the experimentally observed NCL and considered as caged dynamics in the CM. Furthermore, these isolated activated events may also terminate at temperature lower than the β-relaxation peak temperature T_β and are transformed into the flow units corresponding to the primitive relaxation and JG β-relaxation of the CM.

V. CONCLUSION

Well established empirically on aging metallic glasses is the decrease of ductility accompanied by the decrease of the Poisson's ratio. The correlation of ductility with Poisson's ratio was found also empirically on varying alloy compositions. The existence of this correlation had been explained theoretically in a previous paper by invoking a string of connections between ductility, the JG β-relaxation, the caged atoms dynamics characterized by the effective Debye–Waller factor f_0 or the NCL in susceptibility, and the Poisson's ratio. There is experimental support of the explanation from measurement of all quantities in the string of connections except the data of f_0 or NCL are not available. In the experimental part of the paper, isochronal dynamic mechanical measurements of the $La_{60}Ni_{15}Al_{25}$ metallic glass, as cast and after aging at 423 K for 1 h, 6 h, 12 h, and 24 h, show the presence at lower temperatures the NCL originating from the dissipation of atoms confined within cages defined by the anharmonic interatomic potential. The intensity of the NCL decreases monotonically with increasing aging time in concert with the shift of the JG β-relaxation to higher temperatures (e.g., to longer times), and the decrease of the Poisson's ratio known from separate studies. Having measured $(1-f_0)$ or NCL by experiment in this work, we now have complete experimental support of the theoretical explanation of the correlation of ductility with Poisson's ratio. The data also verify directly the theoretical relation between f_0 and the Poisson's ratio given by Eqs. (1) and (2).

In the theoretical part of the paper, the role of the JG β-relaxation in ductility is elucidated. The shift of the JG β-relaxation to higher temperatures (e.g., to longer times) on aging the metallic glass readily explains embrittlement by annealing. In the previous paper, the connection of the NCL with the primitive relaxation or the JG β-relaxation was made by invoking results from molecular dynamics simulations of model systems and the Coupling Model relations (3) and (5) to support that longer τ_0 or τ_{JG} necessarily has smaller value of $(1-f_0)$ or NCL Based on the fact that caged atoms regime is terminated by the onset of the primitive relaxation, arguments are provided to justify theoretically that the shift of JG β-relaxation to higher temperatures on annealing lead to concomitant decrease of the NCL and vice versa.

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