

# Unified approach to atomic transport phenomena in metallic glasses from the bond deficiency perspective

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Atomic bond deficiency (BD) is considered to be a structural defect that facilitates atomic transport in metallic glasses (MGs) and deeply undercooled liquids. A small displacement of an atom from the second to the first-nearest-neighbor position of a BD cage is regarded as the elementary process which involves cooperative movements of multiple adjacent atoms and hence requires existence of a cluster of BD defects. Such a local configuration is defined as the most basic transport unit. Diffusion, structural relaxation, and inelastic shear flow are all attributed to cooperative responses of different numbers of the transport units. Some long-standing unsolved puzzles for three major transport phenomena are clarified, including (1) the fractional Stokes-Einstein relationships between diffusion and flow, and between diffusion and structural relaxation, (2) the great variety of the activation parameters of shear flow, and (3) the bimolecular kinetics of structural relaxation.

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## I. INTRODUCTION

Atomic transport mechanisms in metallic glasses (MGs) are the controlling processes for diffusion, structural relaxation, crystallization, liquid-glass transition, and inelastic deformation (flow) at temperatures around the glass transition. The macroscopic behaviors are often manifestations of various mass transport processes at the atomic scale under different kinds of driving forces. Chemical diffusion, e.g., diffusion during crystallization, is driven by chemical-potential gradients. Plastic deformation is a consequence of atom transport under externally applied stress. Structural relaxation, usually measured in terms of change in shear viscosity, is driven thermodynamically from a less stable state to a more stable one, leading to significant changes in many properties including volume, shear modulus, ductility, and Curie temperature. While well-defined structural defects (vacancies, interstitials, and interstitialcy) are considered to be the facilitators for atomic transport processes in crystals,<sup>1</sup> it is suggested that the various atom transport processes in MG and deeply undercooled liquid (DUCL) are also thermally activated ones which are facilitated by some kind of defects or local carriers.<sup>2</sup> However, what kinds of defects these are and how they function are still, largely, open questions. The complexity arises from the “undefined” amorphous characteristics of atomic structures in MG and DUCL. It is believed that both chemical and topological short-range ordering (CSRO/TSRO) remain while the long-range ordering is absent, as indicated in diffraction investigations using x rays, electrons, and neutrons. The SRO can mostly be characterized in a statistical meaning according to the diffraction data and modeled based on the efficient atomic-cluster packing mechanism. Even if one or multiple kinds of local configurations with such SRO can be identified in the simplest situation, the great variety of atomic interactions (including strengths and effective ranges), in the usually multicompo-

nent metallic glass formers, make it difficult to characterize any structural defects or deviations from the optimum configuration(s), not to mention how the structural defects work for the transport processes. The analysis of the pertinent experimental observations is oftentimes based on the free-volume (FV) model<sup>3</sup> or on its extended version where the free-volume fluctuations with sufficient extra volume at atomic sites function as the transport defects.<sup>4</sup> The FV theory is basically a mechanism of a single atom jumping, which in many aspects is a remnant of crystal vacancies. There are quantitative evidences indicating a more complex picture of atomic transport processes in MG/DUCL.

(1) Diffusion<sup>5</sup> and flow<sup>6,7</sup> can be multiple atom processes; furthermore, the associated activation parameters, as measured, can differ greatly. The energies, particularly associated with flow, can range from that for single atom movement (between two atomic sites like a crystal vacancy) to values higher than the cohesive energies; the elementary volume involved in diffusion and flow can range from an atom size<sup>4</sup> to a few hundred atoms.<sup>8</sup>

(2) The diffusion and shear flow are observed to be related in a way that can be more complicated than a simple Stokes-Einstein relationship (shear strain rate  $\propto$  diffusivity) indicated in the FV model. Measured diffusivities are significantly greater than would be expected from measured flow viscosities.<sup>9,10</sup> It was suggested that the structural defects that facilitate atomic diffusion would be different<sup>11,12</sup> from those for flow in order to account for the discrepancies. Based on the FV model, the analysis of the flow, diffusion, and anelastic relaxation observed during glass structural relaxation<sup>12–14</sup> would lead to a “mysterious”<sup>12</sup> square-root relationship between the concentrations of two kinds of supposed defects, that is,  $n_f \sim (n_d)^{1/2}$ , where  $n_f$  and  $n_d$  represent the densities (per atom) of the flow carriers and diffusion carriers, respectively.

(3) Similarly, structural relaxation<sup>15,16</sup> is observed to be many orders of magnitude slower than what would be ex-

pected from a simple diffusion process;<sup>10</sup> furthermore, structural relaxation, measured as a change in viscosity, indicates a puzzling bimolecular annihilation<sup>17,18</sup> reaction rather than a monomolecular one indicated in the FV (vacancylike) model.

There are theories, other than the FV, and computer modeling that attempt to account for these observations. Molecular-dynamics (MD) simulations of diffusion indicate chainlike motion of multiple atoms that leads to an effective displacement on the order of the nearest-neighbor (NN) distance at low temperatures.<sup>19</sup> The shear transformation zone (STZ) model<sup>20,21</sup> is a multiple atom mechanism suggested for inelastic flow. The STZ, a cluster of local atoms, is regarded as those areas that are ready to accommodate a local inelastic shear transformation (referred to as LST in the following) through a configurational change. The diffuse movement of the STZ is considered to yield a uniform local shear strain ( $\sim 0.1$ ). The STZ model is apparently complementary, to some extent, with the FV concept since a small local area with a larger free volume can more readily have shear responses to an applied stress and hence can be regarded as a STZ. However, the atomic configurations of STZ are not defined and, hence, connection of the flow with atomic diffusion is apparently beyond the discourse of the STZ model. On the other hand, MD studies in Cu-Zr (Ref. 22) indicate that there are a variety of ordered clusters, e.g., icosahedra, with high symmetry and high population coexisting with some fragmented regions with low symmetry and population, and changes in the “full icosahedra” are related to the variation in elastic shear modulus and Poisson ratio, slowing down of structural relaxation around the glass transition, initiation of plastic flow, and strain localization. Further in amorphous silicon, MD simulations showed that among solidlike material there exists liquidlike material which may function as the “fertile sites” for plastic relaxation.<sup>23</sup> MD simulations<sup>21,24</sup> of metallic glasses indicated those fertile sites or STZs can be visualized as elongated zones (consisting of a group of atoms) that are more susceptible than its neighbors to a shearing transformation in some direction. The directional response to stress can be treated as a two-state model transition between jammed and flowing states.

In a recent paper,<sup>25</sup> diffusion in some binary MG/DUCL was inspected from the perspective of the atomic bond deficiency (BD) concept. The atomic cages with BD were considered as small structural defects<sup>26</sup> that facilitated small displacements of diffusing atoms. The process must involve cooperative movements of neighboring matrix atoms and, hence, requires the presence of multiple BD defects. This concept of the “BD defect facilitated cooperative movement” (will be referred to as BD-COM) of multiple atoms explains major distinct features of diffusion in MG/DUCL as compared with that in crystalline counterparts, including (1) much more pronounced atomic size effects of the diffusing element on the activation energy, (2) the much larger slope of the logarithm of the pre-exponential factor as a linear function of the activation energy, (3) sometimes vanishing isotope effects, and (4) sometimes, small pressure effects. With a cluster of the BD defect identified as the carrier, or facilitator, of atomic transport, this small displacement (BD-COM) concept is different from the so-called T1 plastic rearrangement events in the mechanical response of foams<sup>27</sup>

and it also differs from the bond-exchange mechanism<sup>28</sup> or the coordination variation-induced flow.<sup>29</sup> In the present effort, an attempt is made to establish this BD-COM of the local configuration as the most basic process of the most basic structural unit for various atom transports in MG/DUCL. From this perspective, the goal is to identify what particular atomic configurations are (in terms of the basic structural units) and to examine how they yield an effective displacement to efficiently respond to the different kinds of driving forces for diffusion, shear flow, and structural relaxation. It is aimed to address, semiquantitatively, those puzzling experimental results, which are listed above, at the atomistic level. Section II starts with a description of BD as characteristically small defects in MG-DUCL (Sec. II A). The BD-COM is established as the most basic atomic transport process of the most basic units, and when applied to diffusing atoms, they are elementary diffusion carriers (Sec. II B). In Sec. II C, diffusion dipoles are introduced as local configurations that respond to shear and generate LST and hence function as shear flow carriers. It leads to a fractional, rather than simple, Stokes-Einstein relation between shear flow and self-diffusion, as observed in experiments. A broad diversity of diffusion dipoles is inspected and, hence, a variety in activation parameters is thus explained. In Sec. II D, structural relaxation and its relation to diffusion is then examined which results in bimolecular annihilation of diffusion carriers. Differences between this model and other theories are discussed in Sec. III. Finally, some concluding remarks are given in Sec. IV.

## II. BOND DEFICIENCY DEFECTS AND ELEMENTARY PROCESSES OF ATOMIC TRANSPORTS

While TSRO/CSRO (Refs. 2 and 30) are retained in MG and DUCL, the translational freedom of atoms is severely suppressed with the atomic cages freezing,<sup>31</sup> and hence, atomic movement is restricted, rather than free, similar to the situation in crystalline solids. This solidlike feature distinguishes MG/DUCL from regular and slightly undercooled liquids and supports the concept of structural defects that can be thermally inherent and have substantial or nontrivial migration barriers in the otherwise ordered and stronger matrix.<sup>25,32</sup> These local “easy-going” configurations, potentially the carriers for various atomic transports, can be either chemical or topological deviations (disordering) from the optimal arrangements with lowest configurational energies. In the following, the topological aspect will be the focus while the weak-bonding effect resulting from variations in partial coordination is assumed to be a secondary effect and therefore neglected.

### A. Bond deficiency defects

According to a previous study,<sup>26</sup> the atomic BD is referred to as a deviation from the coordination number  $Z_0$ , the optimum atomic structure with both TSRO and CSRO. Such a local configuration is defined as containing a BD defect with a deficiency  $\delta = (Z_0 - Z)/Z_0$  (usually  $\sim 0.1$ ). The cost of BD defects is small with respect to volume and energy—about

one fifth of those for vacancylike defects in the modified “FV” model. BD represents characteristic structural disordering in amorphous structures with translational-symmetry absence and the SRO-only constraint. The BD defects originate from two possible sources—those thermally inherent and those geometrically required for atomic packing. Also owing to the short-range only constraint in the amorphous structure, those BD defects are considered to facilitate a characteristically small atomic movement, that is, the displacement from the second-NN to the first-NN positions of a BD cage—effectively with a displacement  $l_d$  much shorter than the interatomic distance. The density  $n_{th}$  of those thermally inherent BD defects depends on temperature [or more exactly, fictive temperature  $T_f$  (Ref. 33)] and on their formation energy  $h_{BD}$  which is a function of the bond strength  $h_{ij}$ , chemical composition  $x_i$ , and the critical BD value  $\delta_c$  (on the order of magnitude of 0.1) for enabling a specific atomic displacement.<sup>26</sup> Assuming geometrically required BD defects are independent of those thermally inherent ones, the total density  $n_{BD}$  of the effective BD defects,

$$n_{BD} = n_{tp}(\delta_c) + n_{th}(T_f, h_{ij}, x_i, \delta_c), \quad (1)$$

where the BD defects are characterized by the critical BD value  $\delta_c$  for a given element in an alloy at a given temperature (or  $T_f$ ) and  $n_{tp}$  are those geometrically required ones. It is noted that all the densities defined in the text are in the unit of per atom.

### B. Transport unit (as diffusion carrier)

Because of the small “free” volume associated with BD defects, the adjacent matrix atoms must be involved for the completion of the effective displacement of a transport atom. This is illustrated in Fig. 1(a). The local configuration that contains the required number  $k_T$  of BD defects with a BD value  $\geq \delta_c$  (Ref. 26) for the cooperative movements of multiple atoms can be regarded as the most basic structural unit [will be referred to as a transport unit(s) or TR-U, singular and plural] and the BD-COM can be regarded as the most basic process for any atomic transport or rearrangements. For atomic transport under different driving forces, this most basic process can be characterized as the relocations of the BD cages (BD defects) involved for the BD-COM—the only distinguishable ensuing configurational change. Atomic mobility of each element in alloys is obviously different depending on the surrounding atomic interactions. It is reflected in the critical value  $\delta_c$  which is mostly dependent on the relative atomic size  $d_T$  of the transport element.<sup>26</sup> The density of the TR-U that potentially generate the specific atom effective displacements is then

$$n_T = [n_{BD}(d_T)]^{k_T}. \quad (2)$$

More specifically, the completion of this thermally activated process requires (1) the presence of a number  $k_T$  of BD defects, clustering at the designated positions for the BD-COM, and (2) the vibrational displacement of the atoms to be large enough to overcome an energy barrier.<sup>25</sup> The energy barrier can be regarded as the elastic strain energy associated with severely and nonuniformly deformed zones of the volume  $V_T$

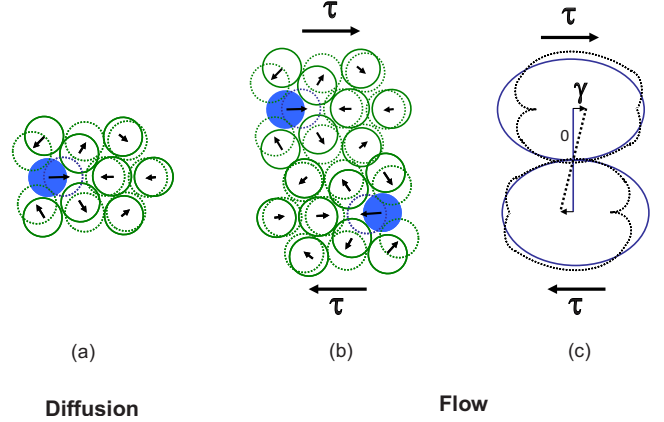


FIG. 1. (Color online) Schematic drawings of configurations and how changes occur during the elementary processes for local atomic rearrangement—the most basic atomic transport process, e.g., (a) in self-diffusion and [(b) and (c)] for flow under a shear stress  $\tau$  in amorphous structures with BD defects. The initial configurations are represented by the solid-sided circles and the final by the dot-sided circles and the atoms with the most effective displacement are filled circles. The atom’s migration occurs between the first-NN and second-NN positions involving the cooperative movements of adjacent atoms which hence requires the multiple BD defects (not explicitly shown). The arrows denote the displacement vectors of the atoms. The continuum model (c) approximately depicts the severely deformed zone from two ellipsoids (blue solid line) to two apple-shaped zones (black dot line) corresponding to the cooperative atomic movements.

as an inclusion in the elastic matrix. The inclusion is subject to the strain that is proportional to a critical displacement of the transport atoms and the strain-energy associated parameter  $c_M$  (a multiple of “local” elastic constants of the matrix). The rate of the BD-COM (per atom) in a sample along any direction is

$$\Psi_T = n_T \cdot f_T, \quad (3)$$

where  $f_T$  denotes the frequency of a TR-U completing BD-COM that depends on the migration energy (and is hence related to elastic constants).<sup>25</sup>

The atomic movements (in terms of TR-U) are thermally intrinsic in MG/DUCL and they proceed at random but only those that respond to reduce the driving forces, e.g., the chemical-potential gradient during diffusion, the mechanical potentials during inelastic flow, or the configurational enthalpy (and system volume) during structural relaxation are counted as “effective.”

The BD-COM mechanism of a single TR-U, leading to a small effective displacement of a diffusing atom, has been regarded as an elementary process of diffusion.<sup>25</sup> The small displacement of the diffusing atom (with an atomic size different from the “matrix” atoms) is driven by a chemical-potential gradient for chemical diffusion. In other words, this single TR-U with BD of critical  $\delta_c$ , which depends on the size of diffusing atoms, is a diffusion carrier. The critical  $\delta_c$  and, hence, the density  $n_D$  of the diffusion carriers depend on the relative atomic size  $d_D$  (ratio over the mean atomic size



of matrix) of the diffusing element and other factors,<sup>25</sup> that is,

$$n_D = n_T(d_D) = [n_{BD}(T_f, h_{ij}, x_i, d_D)]^{k_T}. \quad (4)$$

The effective rate of transport for diffusion along the designated path is

$$\Psi_D = \alpha_D f_D n_D, \quad (5)$$

where  $\alpha_D$  is a constant combining both the geometrical factor and correlation factor for consecutive jumps of atoms along the designated path, and  $f_D$  is the frequency of the diffusion carriers completing the BD-COM. The diffusivity  $D = \Psi_D l_d^2$  can thus be obtained. According to the calculation of trace diffusion in three binary MG, when compared to experiments, the effective number  $k_T$  of diffusion carriers, was shown to range from 4 to 10.<sup>25</sup>

### C. Flow carriers

The movements of TR-U, as exhibited in self-diffusion, are thermally intrinsic in MG/DUCL. It proceeds at random with or without an externally applied stress. Inelastic flow of the solidlike MG/DUCL around the glass transition is also a thermally activated event of atomic transport under shear loading. It is thought to be a result of biased accumulations of shear transformations of certain local configurations, or LST(s), that are embedded in the “stronger” elastic matrix. Because of the formless feature, the configurations that most efficiently respond to shear stresses, or accommodate shear strain, should not necessarily be the same as those local configurations (TR-U) for the thermally intrinsic atomic movement (e.g., those for diffusion).

#### 1. Diffusion dipoles and relationships between diffusion and flow

Identification of the LST unit, or the flow carrier, is essentially to recognize certain local configurations that respond to a shear stress by generating nontrivial shear strains under structural constraints. It is natural to initially consider a TR-U, the most basic easy-going unit. This will then give rise to a simple Stokes-Einstein relation between the shear flow and atomic diffusion, that is, the rate of shear strain  $\propto$  diffusivity. However, it become clearer in the following analysis that the BD-COM of the individual TR-U (e.g., for self-diffusion) gives rise to only trivial, if not zero, shear strain. In other words, the diffusion carriers (single TR-U) individually have relatively insignificant responses to the shear stress. Instead, a pair of adjacent TR-U, if positioned favorably, e.g., perpendicular to the loading direction, and moving cooperatively in the opposite direction can generate a significant shear strain. Figure 1(b) [and Fig. 1(c)] illustrates such a pair of TR-U; when a shear stress  $\tau$  is applied, it can have a shear strain response, or generate a LST  $\gamma_0$ ,

$$\gamma_0 = 2l_d/l_{T-T} = 2l_d/(V_T)^{1/3}, \quad (6)$$

where  $l_{T-T}$  is the distance between the centers of the two TR-U and, in this case, equals the diameter  $(V_T)^{1/3}$  of the TR-U with volume  $V_T$ . The elementary process involved for

the LST is similar to that for self-diffusion and the flow carriers—a pair of TR-U appropriately positioned and moving in opposite directions—can be termed as “diffusion dipoles.” The density of the flow carriers depends on the relative atomic size  $d_F$  of the contributing element(s),

$$n_F = [n_T(d_F)]^2 = [n_{BD}(T_f, h_{ij}, x_i, d_F)]^{2k_T}. \quad (7)$$

With the activation volume  $2\gamma_0 V_T$ , the work by the external stress required for shear to cross over the saddle point is then  $2\tau\gamma_0 V_T = 4\tau l_d V_T^{2/3}$ . The process can be thermally activated forward and backward along the loading direction with the rate

$$\Psi_F = f_F \exp(\pm 4\tau \cdot l_d \cdot V_T^{2/3}/kT), \quad (8)$$

where  $f_F$  denotes the frequency of a flow carrier completion,  $k$  the Boltzmann constant, and  $T$  the temperature.

The effective diffusion-dipole shear responses within a sample result in a biased accumulation of BD-COM and, hence, give rise to the macroscopic shear strain rate

$$\begin{aligned} \frac{d\gamma}{dt} &= (\alpha_F/2) n_F \gamma_0 f_F (\Psi^+ - \Psi^-) \\ &= \alpha_F n_F \gamma_0 f_F \sinh\left(\frac{4\tau \cdot l_d \cdot V_T^{2/3}}{kT}\right), \end{aligned} \quad (9)$$

where  $\alpha_F$  is a constant that accounts for the geometrical factor of diffusion dipoles. Under low stress and/or high temperature, i.e.,  $2\tau\gamma_0 V_T \ll kT$ , the shear deformation becomes Newtonian viscous,

$$\frac{d\gamma}{dt} = \tau \cdot \frac{\alpha_F f_F \cdot n_T^2 \gamma_0^2 V_T}{kT}. \quad (10)$$

The viscosity  $\eta = \tau/(d\gamma/dt)$  that is independent of the stress or strain rate can be accordingly calculated. Both diffusion and flow processes involve the BD-COM of similar configurations, and they proceed through atomic vibration with large amplitudes to overcome the similar energy saddle surface (migration energies, which depends on the surrounding elastic constants and the critical vibration amplitudes<sup>25</sup>) even though different numbers of atoms or local volumes are involved, which indicates  $f_F \sim f_D$ . It then leads to a relationship between self-diffusivity  $D$  and Newtonian flow  $\eta$ , a fractional Stokes-Einstein relation, according to Eqs. (5) and (10),

$$D\left(\frac{\eta}{kT}\right)^{1/2} = \left(\frac{\alpha_D f_D}{2\alpha_F^{1/2} f_F^{1/2}}\right) \frac{l_d}{V_T^{1/6}} = \alpha' \frac{l_d}{V_T^{1/6}}, \quad (11)$$

where  $V_F = 2V_T$  and  $n_D = n_T$  are used for self-diffusion of the controlling element ( $d_T = d_D$ ) and  $\alpha' = \alpha_D f_D / (2\alpha_F f_F)^{1/2}$  is a constant for the given diffusion dipole. This diffusion-dipole mechanism of Newtonian flow explains the puzzling observations of  $n_D \sim (n_F)^{1/2}$  for flow and Fe diffusion in a FeNiB glass<sup>12,14,16</sup> and agrees well with the observation of  $\eta D^2 = \text{const}$  for flow and interdiffusion in Pd-Si/Pd-Si-Fe multilayers at constant temperatures.<sup>13</sup>

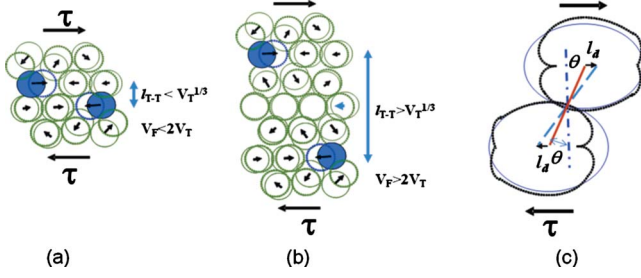


FIG. 2. (Color online) (a) A reduced diffusion dipole with reduced distance  $l_{T-T}$ , reduced volume involved and larger shear transformation  $(l_{T-T}/V_T^{1/3})\gamma_0$ ; (b) an extended diffusion dipole with increased distance  $l_{T-T}$  and smaller shear transformation  $(l_{T-T}/V_T^{1/3})\gamma_0$ ; (c) an inclined diffusion dipole with center-to-center distance  $l_{T-T}=V_T^{1/3}$  but smaller shear transformation  $\gamma_\theta = \arcsin(\sin \theta + \gamma_0) - \theta$ .

## 2. Varieties of responding configurations

In addition to the perfectly positioned diffusion dipoles as described above because of the formless feature of MG/DUCL, different configurations can respond to the applied shear stress. In terms of the most basic TR-U, there are four kinds of intrinsic varieties of potential shear-responding configurations.

One type of variety results from the configuration of two TR-U(s) with different interTR-U distances  $l_{T-T}$ . As shown in Figs. 2(a) and 2(b), each pair of TR-U (diffusion carriers) can be aligned with the distance  $l_{T-T}$  either larger or smaller than  $V_T^{1/3}$  and, hence, the flow carriers can have varied volumes (or number of atoms) involved  $[=(1+l_{T-T}/V_T^{1/3})V_T]$  and varied shear transformations  $\gamma_0=2l_d/l_{T-T}$ . Correspondingly, the density  $n_F$  of flow carriers can be different from that in Eq. (7) as

$$n_F = [n_T(d_T)]^m \quad (12)$$

where the exponent  $m=(1+l_{T-T}/V_T^{1/3})$ . The activation volume will be  $2\gamma_0 m V_T = 4(l_d/l_{T-T})m V_T$  and the Newton's viscous flow rate will be

$$\frac{d\gamma}{dt} = \tau \cdot \frac{(\alpha_F f_F) \cdot n_F^m \gamma_0^2 V_T}{kT}. \quad (13)$$

For the extremely reduced diffusion dipoles,  $l_{T-T}/V_T^{1/3} \ll 1$ , that is,  $m \rightarrow 1$ , the standard Stokes-Einstein relation for the self-diffusion and shear flow is approached as

$$\eta D = \left( \frac{\alpha_D f_D}{4\alpha_F f_F} \right) \frac{kT}{(V_T/l_{T-T}^2)} = \alpha'' \frac{kT}{(V_T/l_{T-T}^2)} \quad (14)$$

with the characteristic length  $V_T/(l_{T-T})^2$ , which covers the situation for simple metallic glasses as discussed in Refs. 2 and 9. It is noted that the reduced diffusion dipole is a case similar to the flow defect concept suggested in Ref. 2.

The second variety is due to shear responses of TR-U pairs that are not exactly perpendicular to the loading direction, rather with an inclining angle  $\theta$  as shown in Fig. 2(c). The corresponding shear transformation depends on the inclination  $\theta$

$$\gamma_\theta = \arcsin(\sin \theta + \gamma_0) - \theta, \quad (15)$$

which is small for the TR-U pairs with a large inclination  $\theta$ . There is also a variable orientation for the displacement with respect to the loading direction, which similarly results in the reduced LST of those varied flow carriers.

The third variety is for shear responses from different elements in binary or multicomponent systems. For elements of large atomic sizes, although their effective displacement  $l_d$  is large, they have a lower density of working TR-U for their larger critical BD value  $\delta_c$  [as indicated in Eq. (1)].

The last one but equally important is due to the existence of multiple preferred cages with relatively low configurational energies in real alloy systems,<sup>22,34</sup> resulting from the complexity of atomic interactions (atomic size difference and interaction strength variation). They may include both stable and “metastable” cages with different  $Z_0$  and BD formation.

These intrinsic varieties of the responding configurations have two immediate implications: (1) there is a distribution of the activation parameters of shear flow in a given alloy system and (2) the activation parameters of shear flow is sensitive to the chemical composition since the shear flow depends on the controlling configurations, or dominating diffusion dipoles, characterized by BD formation energies and the number of involved atoms (number of required BD) which in turn is a function of the atomic size of the controlling element(s) (and hence  $\delta_c$ ) and the interaction (bonding strengths) among atoms. It is also, generally, consistent with the observation that there is a wider variation in activation parameters for flow than there is for diffusion in a metallic glass.<sup>5</sup> To account for the all the varieties—distribution of the cage volume, dipole orientation, and the multiplicity of the preferred cages, obviously, requires very complicated statistical treatments. Nevertheless, one would expect Eqs. (6)–(11) could hold when the major quantities are regarded as the average parameters.

## D. Annihilation of BD defects for structural relaxation

Structural relaxation is an ordering process thermodynamically driven from a less stable to a more stable state in MG/DUCL. It was believed to be a phenomenon corresponding to the annihilation of excess FV in MG and DUCL through a small number of diffusive steps of those FV defects.<sup>4</sup> The FV model, without consideration or identification of the FV sinks in a MG, infers a monomolecular reaction for FV annihilation. However, the isothermal measurements of MG particularly below  $T_g$  showed a striking linear increase in shear viscosity with time.<sup>15</sup> This suggested a bimolecular process<sup>17,18</sup> of defect annihilation during structural relaxation. In analogy with the excess atomic vacancies in crystals that can aggregate and collapse in the form of vacancy disks to produce dislocations<sup>35</sup> (rather than being absorbed in grain boundaries), it is argued<sup>2</sup> that how the structural defects are annihilated in a MG also depends on the collapsibility or “shrinkability” of the configuration formed by the “clustering” defects. There are open questions for MG/DUCL including (1) what are those “removable” defects that can lead to “structural relaxation” or “ordering” with a

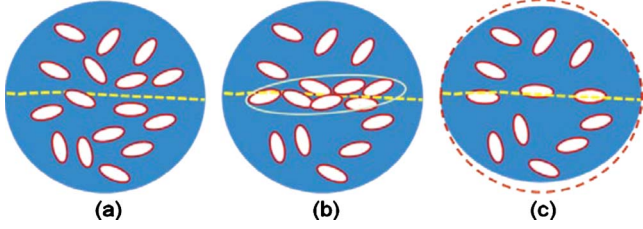


FIG. 3. (Color online) Annihilation process of BD defects: (a) randomly distributed BD defects in a group of diffusion carriers; (b) Aggregation of BD through relocations (requiring diffusion carriers), resulting in a BD condensed region; (c) shrinkage of the BD condensed region, resulting in elimination of some BD defects involved.

concomitant reduction in volume and enthalpy? and (2) where can they be eliminated?

Similar to vacancies in crystals, the BD defects are stable, ubiquitous, and volume and energy consuming (although much smaller) in MG/DUCL. The structural relaxation of MG/DUCL (but not regular liquids) can be considered to be an ordering process—the elimination of excess BD defects through BD collapsing inward with respect to the specimen boundary since their diffusion rate is not sufficient for their migration to and escape from the surfaces similar to vacancies in crystals.<sup>36</sup> Individual BD defects (defected cages) have stable configurations and their relocation must involve the BD-COM of a number of adjacent atoms which requires multiple [e.g., 4–10 (Ref. 25)] BD defects. In other words, the relocation of individual BD defects is thermally inherent and is facilitated by TR-U although leading to no annihilation. With an excess amount of BD defects and, hence, an excess amount of TR-U, when TR-U aggregate to generate critically loose space in a given local volume, the local configuration becomes unstable and tends to collapse or shrink leading to elimination of some of the BD defects involved. As illustrated by the sketches in Fig. 3, this process of BD-defect elimination may proceed in two steps: (1) aggregation and positioning of BD defects to form the critically loose configuration through self-diffusion jumps or TR-U (BD) relocations and (2) collapse of the loose local configuration. Obviously, the rate-controlling first step is the one that requires a number, say of  $j_{ann}$ , of diffusion jumps. The consequence of the collapse is the elimination of only some BD defects due to the geometrical constraint. Assume a TR-U aggregate configuration is collapsible which leads to elimination of a number  $i_{BD}$  of BD defects when its overall extra FV is larger than a critical volume. The critical excess FV is that of a number  $i_c$  of atomic sizes, that is, containing  $i_c/(2\delta_c)$  number of BD where  $2\delta_c \cdot V_a$  is the volume cost per BD. The BD-defect annihilation rate is then

$$\begin{aligned} \dot{n}_{BD,ann} &= \frac{i_{BD}}{j_{ann}} (n_{BD})^{i_c/(2\delta_c)} \Psi_D \\ &= \frac{i_{BD}}{j_{ann}} (n_T)^{i_c/k_T(2\delta_c)} \Psi_D, \end{aligned} \quad (16)$$

where the second equality is based on Eq. (2). The annihilation of the diffusion carriers, or the TR-U, is in a rate

$$\dot{n}_{T,ann} = k_T n_{BD}^{k_T-1} \dot{n}_{BD,ann} = \frac{k_T i_{BD}}{j_{ann}} (n_T)^{i_c/k_T(2\delta_c) + (k_T-1)/k_T} \Psi_D. \quad (17)$$

Considering self-diffusion is involved in the annihilation process, and  $i_c \sim 1$  and  $\delta \sim 0.1$ ,<sup>26</sup> for  $k_T$  [taking the number of BD defects to be between 4 and 10 (Ref. 25) or more], this leads to  $\dot{n}_{D,ann} = \frac{k_T i_{BD}}{j_{ann}} (n_D)^\beta \Psi_D$  with  $\beta$  ranging from 2.0 to 1.4 or less (but always larger than 1). The upper-limit case indicates the bimolecular annihilation ( $\beta \sim 2.0$ ) as suggested in the analysis of experimental data.<sup>16,17</sup> The annihilation rates of the self-diffusion carriers (or effective TR-U) as shown would be much slower than expected from the pure diffusion process considering  $n_D < 10^{-2}$  and  $(k_T i_{BD}/j_{ann})$  is comparable with  $\alpha_F$  in Eq. (5). This is, again, in agreement with the experimental observation mentioned in Sec. I.

### III. FURTHER DISCUSSION

In the analysis above, a distinction of MG/DUCL is made from regular or slightly undercooled liquids, and the solid-like properties of MG/DUCL are addressed by assuming that they contain structural defects with mobilities restricted by nontrivial migration barriers. The BD defects are considered to be defects exhibiting characteristics similar to atomic vacancies in crystals, although they are much smaller in their formation energies and volumes. The typically *small* displacement (second NN  $\rightarrow$  first NN) of an atom (which involves cooperating movements of multiple adjacent atoms) is regarded as a thermally activated LST for the most basic configuration of transport (termed TR-U). The LST is confined by the more ordered and stronger (elastic) surroundings. Although the single-step movement of individual TR-U can lead to chemical or self-diffusion, it generates insignificant shear strain contributions. It is like a crystal vacancy which does not accommodate shear strain.<sup>37</sup> On the other hand, it could be argued that, similar to crystal vacancies, multiple consecutive and correlated movements of a TR-U can generate shear strains when there are pre-existing inhomogeneities, such as, sinks and sources of BD defects throughout the specimen, somewhat similar to grain boundaries for vacancies during Herring-Nabarro creep<sup>38</sup> or Coble creep<sup>39</sup> in crystals. This defect source-sink concept was suggested<sup>11</sup> to explain diffusion-flow relations observed in some experiments but was later strongly argued against by some quantitative analyses.<sup>40</sup> Another model extended from the theories for crystals is the interstitialcy model<sup>41</sup> based on a simple observation that “the most characteristic, if unusual, signatures of close-packed metallic liquids, glasses, and irradiated crystals are essentially the same.”<sup>42</sup> These conceptual entities are obviously hard to be defined since specified atomic sites are vague and undefined in the “formless” structures of MG/DUCLs.

These considerations, instead, validate the LST concept where both STZ theory<sup>20</sup> and the present diffusion-dipole model are based on for shear flow. However the diffusion-dipole model, or a BD-COM model as extended here, is different from the STZ model in some critical aspects, in-



cluding (1) the diffusion-dipole model considers the atomic configuration, that is, well-defined structural defects (BD), and the shear flow is related to the more basic atomic transport of individual TR-U (and, hence, the flow-diffusion relationship is demonstrated); (2) cooperative and nonuniform atomic movements, rather than a collective and uniform movement as associated with the STZ, are considered; and (3) the local shear transformation of the elementary volume diffusion dipoles is smaller (typically 0.02 versus 0.1 for STZ).

The concept of topological disordering within the first NN or bond configurations serving to mediate mass transport was also suggested for nonmetal materials.<sup>43</sup> For instance, it was shown that motion of broken bonds can lead to flow in silica<sup>44</sup> and amorphous Si and Ge.<sup>45</sup> It was proposed<sup>29</sup> that a local change in the coordination number of a glass constituent, that is, a change in distribution of low-density regions, may also result in flow in nonpolymeric melts. As mentioned above, along with these models, the coordination shift<sup>29</sup> and the bond switch<sup>28</sup> also consider a small displacement. In the current model, the fundamental feature is the existence and function of the structural defects (BD) as carriers for both diffusion and shear.

The wide spread of the activation parameters (energies and volumes), particularly for flow, observed in experiments has been explained by the great varieties of responding local configurations (e.g., diffusion dipoles for flow) in the last section. In practice, structural relaxation during various thermomechanical procedures can also have significant contributions to the wide distribution<sup>2</sup> as reported.

In the analysis of the bimolecular reaction during structural relaxation, the CSRO is neglected although it is noted that in structural relaxation the two subprocesses TSRO and CSRO can be involved (e.g., Ref. 46).

Plastic deformation processes of MG/DUCL will involve changes in density of the diffusion dipoles as flow carriers. The changes include both generation of those flow carriers through the work of an external applied stress and annihilation of the carriers during structural relaxation. The further work that takes those effects into account, which is in progress, will allow for more detailed and more quantitative comparison with STZ and CSM models.

#### IV. CONCLUSIONS

In this work, atomic transport in MG/DUCL was considered to proceed through characteristically small atomic dis-

placements facilitated by characteristically small structural defects—BD defects that must involve cooperative, rather than collective, movements of multiple atoms. BD defects can be thermally inherent and geometrically required, which cost much less energy and volume than vacancylike free-volume defects. Under the SRO-only constraint of an amorphous structure, the small atomic displacement is for an atom to move from the second-nearest-neighbor position to the first-nearest neighbor of the BD cages. The basic process of a local configuration was referred to as TR-U which is thermally intrinsic with or without applied driving forces.

Diffusion, structural relaxation, and inelastic flow were all attributed to the cooperative response of different numbers of the basic transport units under various driving forces. The TR-U containing BD defects with a characteristic BD value—a function of the atomic size of the diffusing element—was presented to be responsible for diffusion. The configurations responding to a shear stress resulting in a shear flow were diffusion dipoles, which are essentially a pair of TR-U that are positioned closely and move cooperatively in opposite directions. It is the diffusion dipole that yields the shear transformation which is inversely proportional with the distance between the two. This leads to a fractional Stokes-Einstein relation between diffusion and flow with a much smaller density (around  $n_D^2$ ) of carriers for flow than those for diffusion, agreeing with the experimental observation. It also, partly, explained the observed great variety of the activation parameters, particularly associated with inelastic flow.

Structural relaxation was treated as the annihilation of BD defects through shrinkage of the loose regions with aggregate BD defects. The controlling step was considered to be the aggregation of the BD defects that involved multiple TR-U. The arrangement generated a sufficient extra “loose” volume in the region for them to shrink, resulting in elimination of some of the aggregate BD defects. Assuming the critical volume is the atomic size, the annihilation rate would then be close to that of the bimolecular reaction observed in experiments.

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