A graph theoretical approach to fluctuating networks in glass-forming liquids: A molecular dynamics study with applications of the pebble game algorithm

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Abstract. The network structures fluctuating in space and time are studied in glass-forming liquids of silica (SiO$_2$) and silicate (Mg$_2$SiO$_4$), by carrying out molecular dynamics (MD) simulations and then applying the graph theoretical algorithm of a "pebble game". The pebble game algorithm was developed in Thorpe and coworkers' studies on the percolation of rigidity to form amorphous solids and, although its exactness is proved only in two dimensions, it has been demonstrated to apply to three-dimensional networks. In liquid silica and silicates, the network connections are extended with amounts of network-forming Si, O atoms, and infinitely-percolating clusters emerge over an extensive range of compositions. The search along a network for free "pebbles", attached virtually to the constituent atoms to represent their degrees of freedom of motions, shows that one infinitely-percolating cluster contains some rigid clusters. These rigid clusters in liquid states fluctuate in space and time because of the alteration of connections at high temperatures, in contrast to those solidified below glass transition temperatures, and these fluctuations are responsible for the slow structural relaxations. The pebble game analyses thus give insights into the internal structures in infinitely-spanning networks, beyond surveys by the conventional theory of percolation, and reveal the behaviors of rigid clusters playing the dominant role in the slow structural relaxations in glass-forming liquids. We discuss these results especially by taking focus on varieties in network structures, such as the composition-dependent degrees of connectivity and structural transformation under high pressures.

1. Introduction
The high abilities to form glasses of various inorganic materials, e.g. silica (SiO$_2$), have their origins in network structures. Three-dimensional networks are infinitely spanned by Si-O connections in liquid or vitreous silica. The connections impose constraints on motions of the network-forming atoms and, correspondingly, fluctuations to relax strains in networks are constrained. Viscous flow relaxations in network liquids are especially suppressed, because these relaxations undergo the thermal activation of altering connections and rearranging atoms. In lowering temperatures, fluctuations are converged to infinitesimal motions and the random configurations of atoms under constraints are readily "frozen in.” An intuitive understanding thus ascribes glass transitions to stiffening of liquids, or, inhibiting fluctuations for fluid relaxations at low temperatures [1].

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The degrees of connectivity in network structures depend strongly on chemical compositions of glass-forming liquids. If one- or two-valent cations are added to silica to form silicates such as MgSiO$_3$ and Mg$_2$SiO$_4$, these cations are coordinated to dangling O atoms and intercalated amongst networks for the local charge neutrality. The degrees of connectivity are therefore reduced with amounts of intercalated cations. The decreasing degrees of connectivity induce the decrease in shear viscosities by several orders of magnitude. Long shear relaxation times, tens nanoseconds or longer in highly-connected network liquids, correspondingly decrease in ill-connected network liquids and approach normal relaxation times of the order of 0.1 picosecond. The transitions from "strong", highly-connected networks to "fragile", ill-connected networks are responsible for the distinct temperature-dependences of shear viscosities, Arrhenian in highly-connected network liquids and non-Arrhenian in ill-connected network liquids [1]. The network connectivities thus play the dominant roles in slow structural relaxations, and consequently in glass-forming abilities.

In addition to depending strongly on chemical compositions, network structures undergo transformations under high pressures, and thereby their structural relaxations are affected. Highly-connected network liquids especially exhibit enigmatic behaviors, viz. decreasing shear viscosities under high pressures [2, 3]. High-pressure transformations enhance structural relaxations in highly-connected networks because some fractions of regularly network-forming, 4-fold Si atoms are compacted to irregularly network-forming, 5-fold atoms and catalyze the alteration of Si-O connections [3, 4]. These spatial and temporal fluctuations of network connections are intrinsic in glass-forming liquids and determine the behaviors of their structural relaxations.

The time-dependent configurations of atoms in network liquids can be obtained from molecular dynamics (MD) simulations. The network structures are readily identified from these configurations and, if their degrees of connectivity exceed the percolation thresholds, major parts of these networks are occupied by singly-connected clusters which percolate infinitely over three-dimensional space [5]. Besides their single connectedness, these infinitely-percolating networks are comprised of finite domains having different flexibilities or rigidities in structural relaxations, because of spatially and temporally fluctuating connections. These domains are ill identified, however, in a conventional framework of the percolation theory. The connectedness of flexible or rigid domains can rather be explored by employing the theory of rigidity percolation, which was addressed pioneeringly in Thorpe’s studies on ascribing glass transitions to the percolation of rigid domains under the constraints of covalent bondings [6]. To identify the topology of constraints determining the rigidity percolation, the protocols are specified by the algorithm of a "pebble game" [7, 8, 9, 10, 11, 12, 13, 14] in a framework of graph theory.

This article reports the preliminary results of a graph theoretical approach applying the pebble game algorithm to network structures in glass-forming liquids. MD simulations were carried out at first to generate highly-connected network structures in liquid SiO$_2$ (silica) and ill-connected network structures in liquid Mg$_2$SiO$_4$ (Mg-olivine) at high temperatures and high pressures. The methodology of these simulations is described in Section 2. The pebble games are then played on these network structures to identify their flexibilities or rigidities under the constraints of Si-O connections. Section 3 is devoted to describing the pebble game algorithm, which specifies the feasible protocols to identify the edges (or, connections) as the constraints on motions of domains in a network, and thereby to enumerate the degrees of freedom of domain motions. This algorithm was exploited originally to apply to two-dimensional networks [7, 8, 9, 10], according to its rigorous proof in two dimensions by graph theory, whilst recent studies have empirically verified its applicability in three dimensions [11, 12, 13, 14]. In Section 4, the applications of the pebble game algorithm to network liquids are discussed. The results of these applications reveal that, in network liquids, the rigidities differ by the degrees of connectivity, and that these different rigidities are consistent with the different behaviors in
slow structural relaxations, \textit{viz.} large and small shear viscosities of highly- and ill-connected network liquids, respectively, and their decrease and increase under high pressures.

2. Molecular dynamics simulations
The $NVE$ (or, microcanonical) ensembles of network structures were generated by carrying out MD simulations on liquid SiO$_2$ and Mg$_2$SiO$_4$ at high temperatures $T \simeq 2200$-$3300$ K and high pressures $P \simeq 0.1$-$10$ GPa. Temperatures $T \simeq 1.1 \times T_m$ were elevated along the elevation of melting temperatures $T_m$ under high pressures. The finite numbers of the constituent atoms (512 Si, 1024 O of SiO$_2$, and 512 Mg, 256 Si, 1024 O of Mg$_2$SiO$_4$) were confined to the cubic boxes with the periodic boundaries, and neither external degrees of freedom nor constraints were imposed to the systems conserving the numbers $N$ of atoms, volumes $V$, and energies $E$. The box sizes $L \simeq 24$-$28$ Å were fixed to serve the densities under the relevant temperatures and pressures. The constituent atoms were assumed to be the rigid ions (\textit{i.e.} the firm couplings of cores and valence electrons) interacting in a framework of classical mechanics by the Born-Mayer-Huggins pairwise potentials with Matsui’s empirical parameters [15]. The Ewald method [16] was applied to sum the long-range Coulombic interactions over all pairs of atoms in the fundamental box and its replicas, whilst the short-range interactions of Born-Mayer repulsion and van der Waals dispersion were truncated at some separations of atoms. The equations of motion of atoms were integrated numerically by Verlet’s central difference algorithm [17] with the time-step increment $\Delta t = 1$ fs over 102400 time-steps, corresponding to the uppermost time $t_{\text{max}} = 102.4$ ps, and their positions and velocities were accumulated at intervals $\Delta t' = 100\Delta t = 0.1$ ps. Prior to thus achieving equilibria, temperatures were controlled by scaling the velocities of atoms. The time series of the atomic configurations fluctuating in equilibria were generated consequently and, according to the ergodic hypothesis, these time series are equivalent to $NVE$ ensembles.

3. The pebble game algorithm
An intuitive understanding speculates that a larger number of edges cause the larger rigidity in a network whilst, if edges are overabundant, not all of them independently impose the constraints on motions of incident vertices and thereby some of them are redundant. This speculation is verified in a framework of graph theory by Laman’s theorem [18]. We assume generic networks hereafter, which have no special symmetry such as parallel edges or collinearly connected edges [7, 8, 9, 10]. Laman’s theorem states that a generic network of two dimensions ($d = 2$) contains no redundant edge if, and only if, none of its subgraphs violates $b \leq 2n - 3$ ($n, b$ are the numbers of vertices and edges of a subgraph), or equivalently, if and only if no subgraph contains larger numbers of edges than the rest of subtracting the degrees of freedom of trivial motions of a rigid body ($d(d + 1)/2 = 3$) from those of all vertices in a subgraph ($dn = 2n$). If overall subgraphs are naively enumerated, however, their number increases divergingly with the size of their parent network and, inevitably, the search over them is not tractable in large networks.

To implement Laman’s theorem by circumventing the diverging numbers of combinatorial countings, Jacobs and Hendrickson proposed the algorithm of a ”pebble game” [9, 19]. Their algorithm deals with the virtual objects, pebbles, by which the degrees of freedom are visualized in a two-dimensional generic network. Two $ (= d$) pebbles are attached to each vertex and represent its inherent degrees of freedom of two-dimensional unconstrained motions. Free pebbles are located on vertices, and one free pebble contributes one degree of freedom to those of motions of the distinct domain containing its attached vertex. Those other than free pebbles are, on the other hand, assigned to independent constraints and have no contribution to the degrees of freedom of domain motions. One independent edge is covered by one pebble, by consuming one free pebble complementarily from one of its incident vertices. Each domain contains at least three $ (= d(d + 1)/2$) free pebbles of a rigid body. The domains containing more than three free pebbles have larger degrees of freedom of motions and are, therefore, more flexible than rigid
bodies. The flexible domains are thus defined by the underconstrained domains consisting of $n$ vertices and less than $2n - 3$ edges. The domains containing only three free pebbles are rigid, on the other hand, and each rigid domain contains $2n - 3$ independent edges. The rigid domains containing just $2n - 3$ edges are isostatic, and all of their edges are independent constraints. If more than $2n - 3$ edges are contained in a rigid domain, its excess edges other than $2n - 3$ independent constraints are redundant constraints. The rigid domains containing redundant edges are overconstrained. The redundant edges are not covered by pebbles, because all pebbles are either free on vertices or assigned to independent edges. The underconstrained, isostatic, and overconstrained domains under the independent and redundant constraints are thus identified throughout a two-dimensional generic network. The protocols to search over all edges and to rearrange pebbles do not consume so huge computational efforts as combinatorial countings of subgraphs, and consequently, along these protocols, the computations amenable rigorously to Laman’s theorem are feasible.

Besides its exactness in two dimensions, no rigorous extension of the pebble game algorithm is proven in three dimensions. This is because the sufficient condition in Laman’s theorem (or, the part of ”only if” in its statement) is broken in three dimensions [19]. Jacobs conjectured that the pebble game algorithm applies to three-dimensional bond-bending networks, because the angular constraints on bond-bending rule out the ”double banana graph”, an infamous counterexample to Laman’s theorem in three dimensions [11]. His conjecture is analogous to the molecular framework conjecture [20] on applying Laman’s theorem to the flexibilities of framework molecules. Some works have, in fact, applied the pebble game algorithm successfully to macromolecules such as proteins [12, 13]. Furthermore, no failure has been reported in its tentative applications to both bond-bending and non-bond-bending networks in three dimensions [14].

The pebble game algorithm specifies the same protocols in three dimensions ($d = 3$) as in two dimensions, except for attaching three ($= d$) pebbles to each vertex and fixing six ($= d(d+1)/2$) free pebbles of a rigid body in each domain [11, 12, 13, 14]. A three-dimensional pebble game is executed along the following protocols:

(i) Initially, locate all vertices without edges, and attach three free pebbles to each vertex.
(ii) Add one edge, $e_{ab}$ connecting vertices $v_a$ and $v_b$, and try to cover $e_{ab}$ by one pebble;
    (a) Collect three free pebbles to each of $v_a$ and $v_b$, and fix these six free pebbles on $v_a$ and $v_b$ temporarily.
    (b) Search for a seventh free pebble to be located on one of the vertices which are connected to $v_a$ or $v_b$ by the edges added in the preceding protocols, without rearranging the six free pebbles on $v_a$ and $v_b$.
        • If a seventh free pebble is found and is located on a vertex connected to $v_a$ (or $v_b$), then identify $e_{ab}$ as an independent constraint, and cover $e_{ab}$ by consuming one of the three free pebbles on $v_a$ (or $v_b$).
        • Otherwise, identify $e_{ab}$ as a redundant constraint. Furthermore, identify $v_a$, $v_b$, $e_{ab}$, and the vertices and edges which were trailed in the failed search for a seventh free pebble, as some parts of an overconstrained domain.
(iii) Iterate Protocol (ii) until all edges are added.

In these protocols, the search for a free pebble which can be located on a vertex $v_x$ is executed by rearranging the pebbles in the sequences of connected edges starting from $v_x$, under the definitions of attaching three pebbles to each vertex and covering each independent edge by one pebble. From a pebble game along these protocols, the flexible and rigid domains are identified in a three-dimensional network, and their degrees of freedom under the independent and redundant constraints are obtained.
Figure 1. The average numbers $N_F$ of floppy modes (asterisks), $N_E$ of edges (circles), and $N_R$ of redundant constraints (triangles) in liquid SiO$_2$ (red lines) and Mg$_2$SiO$_4$ (blue lines) at various pressures $P$.

4. Rigidity in network liquids

The network structures in liquid SiO$_2$ and Mg$_2$SiO$_4$ consist of the vertices and edges which are defined by the network-forming Si, O atoms and the Si-O connections, respectively. Playing the pebble games on these networks, the flexible and rigid domains are identified with their degrees of freedom of unconstrained motions, or the numbers of "floppy" modes which in glassy states are excited at no (or negligible) energy cost [6, 7, 8]. The time averages of the fluctuating numbers of floppy modes, $N_F$, of a network-forming atom are shown in figure 1. The average numbers of edges $N_E$ and redundant constraints $N_R$ are additionally shown.

The results in figure 1 show the smaller values of $N_F$ in highly-connected networks of liquid SiO$_2$ than those in ill-connected networks of liquid Mg$_2$SiO$_4$, and therefore indicate the larger rigidities in highly-connected networks than in ill-connected networks. These results further show that $N_F$ in liquid SiO$_2$ is insensitive to pressure whereas $N_F$ in liquid Mg$_2$SiO$_4$ decreases under high pressures, and these behaviors are consistent with the decreasing and increasing shear viscosities respectively of liquid SiO$_2$ and Mg$_2$SiO$_4$ under high pressures, as predicted in Takéuchi’s recent studies [2].

As a consequence, the pebble games in network liquids reveal that their rigidities differ by the degrees of connectivity, and that these different rigidities reflect the different behaviors in structural relaxations. Takéuchi’s future works will advance from these preliminary results, by exploring the dynamics of flexible and rigid network domains to determine their behaviors in slow structural relaxations, especially under high pressures: This will be discussed elsewhere.

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