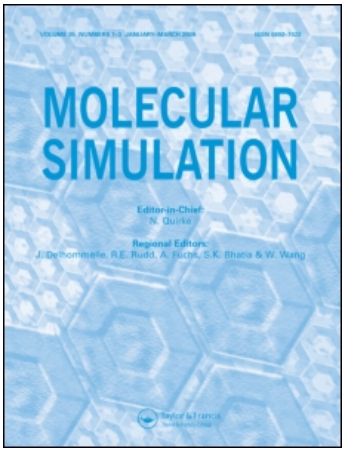

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Formation of Transient Clusters on Nanoscopic Length Scales in a Simulated One-Component Supercooled Liquid

Y. Gebremichael[a]; M. Vogel[b]; S. C. Glotzer[c]

[a] Chemical Physics Program, Institute for Physical Sciences and Technology, University of Maryland, College Park, MD, USA [b] Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, USA [c] Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA

To cite this Article Gebremichael, Y. , Vogel, M. and Glotzer, S. C.(2004) 'Formation of Transient Clusters on Nanoscopic Length Scales in a Simulated One-Component Supercooled Liquid', Molecular Simulation, 30: 5, 281 — 287

To link to this Article: DOI: 10.1080/08927020410001659376

URL: http://dx.doi.org/10.1080/08927020410001659376

Molecular Simulation, VOL. 30 (5), 30 April 2004, pp. 281–287

Taylor & Francis
Taylor & Francis Group

Formation of Transient Clusters on Nanoscopic Length Scales in a Simulated One-Component Supercooled Liquid

Y. GEBREMICHAEL[a,b], M. VOGEL[a] and S.C. GLOTZER[a,c,*]

[a]*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA;* [b]*Chemical Physics Program, Institute for Physical Sciences and Technology, University of Maryland, College Park, MD 20742-2431, USA;* [c]*Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA*

(Received March 2003; In final form November 2003)

Dense liquids above their glass transition exhibit spatially heterogeneous dynamics in which regions within the liquid exhibit enhanced or diminished mobility relative to the average on some time scale. Substantial evidence suggests that these regions are confined to nanoscopic sizes at temperatures close to the mode coupling temperature T_{MCT}, and reach well beyond the characteristic length scale over which the two-point static structure of the liquid is correlated. In this paper, we investigate the formation of clusters of mobile particles in a dynamically heterogeneous model liquid. We find that clusters are formed as a result of mobility propagation that begins from distributed locations confined within a nanoscopic local structure. This mobility is facilitated through the development of quasi-one dimensional string-like rearrangements within the nanoscopic region.

Keywords: Glass transition; Computer simulation of liquid structure

INTRODUCTION

When a liquid transforms into a glass, the structure of the glass is essentially indistinguishable from that of the liquid while the dynamical quantities, such as relaxation times, diffusivities or viscosities, change by up to 14 orders of magnitude [1–3]. The fundamental issue in glass physics is to understand the reason for such a dramatic change in dynamics without a significant variation of the structure. The emergence of spatially heterogeneous dynamics and the growing cooperativity of molecular motion have been commonly invoked to rationalize the dramatic changes in the transport properties of liquids upon cooling towards their glass transition temperature [4–7,43]. By spatially heterogeneous dynamics we mean that particles in one region of the liquid translate or rotate several orders of magnitude faster or slower than other particles a few nanometers away. Simulations have predicted that the dynamics within these regions are highly cooperative, involving larger and larger groups of particles upon cooling [8–19], and several of these predictions have now been borne out in experiments on colloidal suspensions [20,21].

Focusing on particles that, in a given time interval, move much larger distances than the average, several simulations (e.g. binary Lennard-Jones (LJ) mixtures [8,9,13,14], polymer melts [17], and water [19]) and also experiments (colloids [20]) have revealed that these mobile particles form clusters of different sizes. In particular, it was found that the average size of these clusters exhibits a peak at some intermediate time corresponding to the late-β/early-α relaxation regime of the mode coupling theory (MCT) [22–26]. Further, an increasing peak value of the average cluster size indicates that the clusters grow when the temperature is decreased. In addition, it is known that highly mobile particles within these clusters move in quasi-one dimensional string-like paths [9,18]. On the other hand, the detailed nature of the clusters and their formation is not yet well understood and the relation between clusters and strings is still elusive. In this paper, we explore these issues by monitoring individual particle trajectories for a cluster identified at the time when the mean cluster size is maximum. The paper is organized as follows. In the Second

*Corresponding author. Address: Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA. E-mail: sglotzer@umich.edu

ISSN 0892-7022 print/ISSN 1029-0435 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/08927020410001659376

Section, we describe the details of our simulation. The results are presented in the Third Section, followed by conclusions in the Fourth Section.

MODEL AND SIMULATION

The interaction between particles of the simulated one-component liquid is described by the Dzugutov pair potential [9,18]. Originally, this pair potential was developed for simple metallic liquids by optimizing its parameters to reproduce the static structure factor $S(q)$ of liquid lead measured in a neutron scattering experiment close to the melting point $T_m = 623$ K. The pair potential includes, in addition to terms describing the strong, short-range interactions and the predicted Friedel oscillation, a soft repulsive component. The latter is intended to represent the screened Coulomb repulsion between the ions. This term is considerably more long ranged than the short-range attraction so that the potential is positive beyond the first-neighbor distance. The explicit form of the Dzugutov pair potential is given by [27]

$$\begin{aligned} V &= V_1 + V_2, \\ V_1 &= A(r^{-m} - B)\exp\left(\frac{c}{r-a}\right), \quad r < a, \\ V_1 &= 0, \quad r \geq a, \\ V_2 &= B\exp\left(\frac{d}{r-b}\right), \quad r < b, \\ V_2 &= 0, \quad r \geq b, \end{aligned} \tag{1}$$

where the parameters are given in Table I.

In Fig. 1(a), we plot the Dzugutov potential together with the Lennard-Jones (LJ) potential, where the latter is shifted up by an amount of 0.419ϵ to emphasize that the two potentials have minima at the same position. It has been demonstrated [28–31] that the one-component system described by the Dzugutov potential is a good glass former [31]. Further, it is known that this potential favors local icosahedral ordering [28,29,31,32] as found in simple metallic glass formers [33,34]. In Fig. 1(b), it is shown that the static structure factor obtained from this potential exhibits a first sharp diffraction peak and a split second peak [35], which are common features of metallic glasses [33,34]. In one-component atomic systems, the nucleation of crystallites strongly competes with the glass transition and, therefore, most metallic glasses are formed from multi-component systems [36–38] where nucleation is more difficult. By construction, however, the Dzugutov potential stabilizes the one-component liquid in a metastable equilibrium supercooled state providing a time window long enough for the observation of the essential dynamical properties [29]. A structural transformation into a dodecagonal quasi-crystal is observed for long relaxation times under significant supercooling [39].

TABLE I Parameter values for the potential in Eq. (1) [27]

m	A	C	a	B	d	b
16	5.82	1.1	1.87	1.28	0.27	1.94

Our MD simulations are performed for a system of 17,576 particles and a temperature $T = 0.42$. For reference, the critical temperature of MCT is known to be $T_{\mathrm{MCT}} = 0.39$ [30]. The simulations were done under isothermal conditions for a density $\rho = 0.85$. The liquid was cooled in a stepwise manner starting from $T = 1.6$ where we allowed for equilibration at each step. The reduced units for length, temperature and time are σ, ϵ/k_{B} and $\sigma\sqrt{m/\epsilon}$, respectively. The mass m and the distance σ are set to unity.

FORMATION OF CLUSTERS

It is well established that highly mobile particles form clusters characterized by a broad distribution of sizes [8,9,13,14,17,19,20]. Here, at any time interval Δt, highly mobile particles are identified by ranking the squared displacements of all particles in this time interval and selecting the 5% of the particles with the largest displacements [8]. Then, a cluster is defined as a group of these mobile particles that are within the first neighbor shell of each other, where the first neighbor shell is defined by choosing a cutoff distance ($r = 1.5$) corresponding to the first minimum of the pair correlation function $g(r)$ [40,41]. As mentioned above, the clusters of mobile particles defined in this way depend on the choice of Δt. Specifically, a maximum of the mean cluster size is found at a time Δt_{max} which marks the crossover from the plateau regime to the diffusive regime of the mean square displacement (MSD) [17]. In Fig. 2, we show a typical example of clusters found at $T = 0.42$ for the time interval $\Delta t_{\mathrm{max}} = 102.4$ where particles in distinct clusters are colored differently. In agreement with the outcome of work on different systems [14,17,19,20], clusters of different sizes and shapes are observed for the Dzugutov liquid. Indeed, a statistical analysis which will be presented elsewhere [42] reveals that the probability distribution of the cluster size is well described by a power-law $P(n) \propto n^{-\gamma}$ with an exponent $\gamma < 2$.

In the remainder of this article, we single out one of the clusters of highly mobile particles identified for the time interval Δt_{max} and monitor the trajectories of the constituting particles. First, we demonstrate that the enhanced mobility of

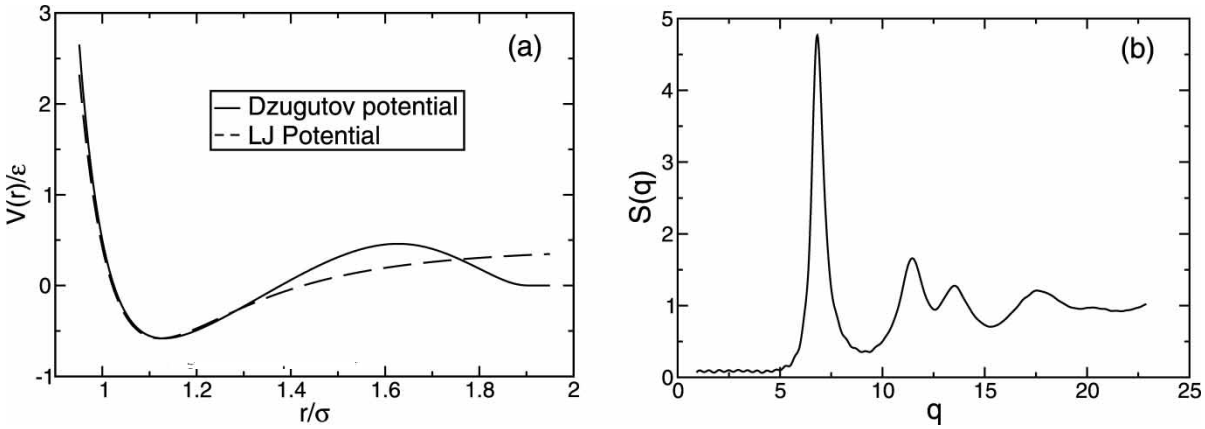

FIGURE 1 (a) The Dzugutov pair potential plotted together with the Lennard-Jones (LJ) potential. The LJ potential has been shifted by an amount of 0.419ϵ for the sake of comparison. (b) Static structure factor of the one-component Dzugutov liquid at $T = 0.42$.

the particles in this cluster is transient in nature. To quantify the time scale on which the information about the initial mobility is lost, we monitor the MSD of the selected subset of particles during successive time intervals $\Delta t_{\max}$, i.e. we compute the quantities

$$\left\langle r_n^2(\Delta t)\right\rangle = \left\langle \left[\vec{r}_j(n\Delta t_{\max} + \Delta t) - \vec{r}_j(n\Delta t_{\max})\right]^2 \right\rangle \qquad (2)$$

where $\vec{r}_j(t)$ denotes the position of the jth particle of the cluster and the brackets represent the average over the selected subensemble. The results depicted in Fig. 3 indicate that a significantly higher mobility than the average exists during the time interval where the particles have been identified as mobile ($n = 0$). On the other hand, the curves for $1 \leq n < 5$ lie only slightly above the one representing the ensemble average, and for even larger n, there is no evidence for systematic deviation from the average. Comparing the time scale of this re-equilibration with the α-relaxation time $\tau_\alpha \approx 30\Delta t_{\max}$, it becomes clear that the clusters of highly mobile particles lose their mobilities on time scales less than τ_α,

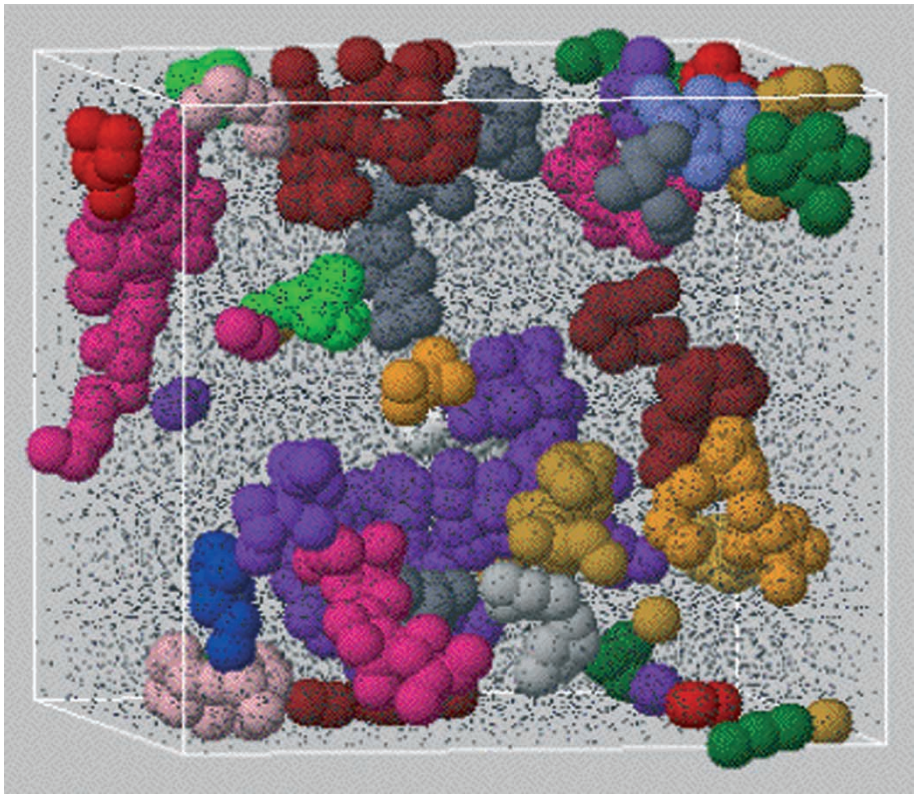

FIGURE 2 An example showing clusters formed by the 5% most mobile particles found at the time $\Delta t_{\max} = 102.4$ when the mean cluster size is maximum for $T = 0.42$. Each particle in the clusters is represented as a sphere of radius 1.0, while all other particles are assigned a radius of 0.1 in the units of the LJ length parameter σ. Particles belonging to the same cluster are colored the same. Note that all particles in the simulation are of the same size. Here only particles that form clusters are magnified for visualization, and all others are reduced in size. (Colour version available online.)

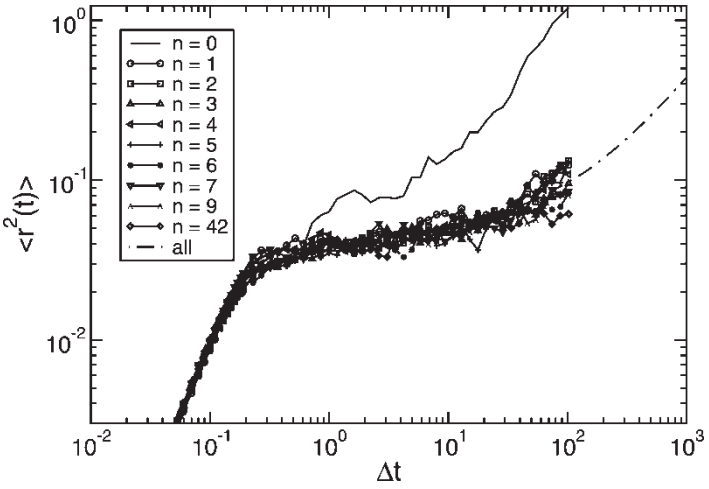

FIGURE 3 Mean square displacement $\langle r_n^2(\Delta t)\rangle$ for different time windows between $n\Delta t_{\max}$ and $(n+1)\Delta t_{\max}$, where $(n = 0, 1, 2, 3, 4, 5, 6, 7, 9, 42)$, averaged over all particles in one of the largest clusters (containing 94 particles) identified at $\Delta t_{\max}$. The dashed-dotted line shows the mean square displacement $\langle r^2(\Delta t)\rangle$ averaged over all particles in the system.

and therefore do not "dissolve" due to the structural relaxation of the bulk. Instead, the dynamical process which leads to the formation and decay of the clusters takes place on a time scale much shorter than the structural relaxation. This conclusion is consistent with the finding that the peak time of the mean cluster size $\Delta t_{\max}$ lies at intermediate times less than τ_α, in the late-β/early-α relaxation regime of the MCT.

To gain further insights into the formation of the clusters, we show snapshots of the selected cluster for different times $\Delta t < \Delta t_{\max}$ in Fig. 4. In this figure, the mobile particles at each time are colored red. Inspection of the snapshots for early times indicates a few mobile particles that are randomly distributed within the cluster. As time progresses, the mobile particles become organized in small groups which grow with time. Thus, one may speculate that

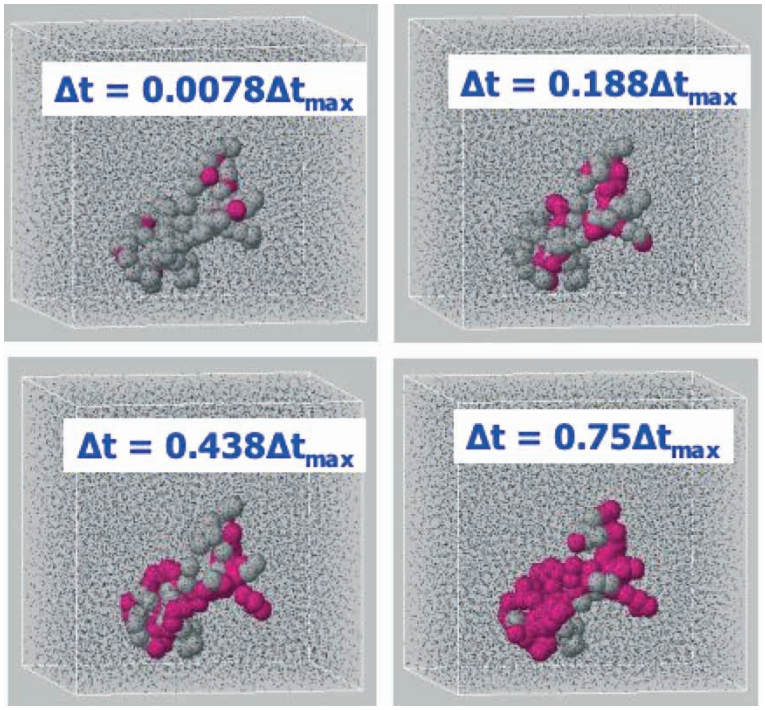

FIGURE 4 Snapshots of one of the largest clusters identified for times $\Delta t = 0.0078\Delta t_{\max}$, $0.188\Delta t_{\max}$, $0.438\Delta t_{\max}$, and $0.75\Delta t_{\max}$, as indicated on the figures. Particles belonging to the studied cluster are shown as spheres of radius 1.0. The mobility of all particles in this cluster is monitored for times $\Delta t < \Delta t_{\max}$, and at any Δt the most mobile particles are colored red. Note that all 17,576 particles in the simulation box are identical. Here only particles within the cluster are magnified for visualization, and all other particles are shown at reduced size. (Colour version available online.)

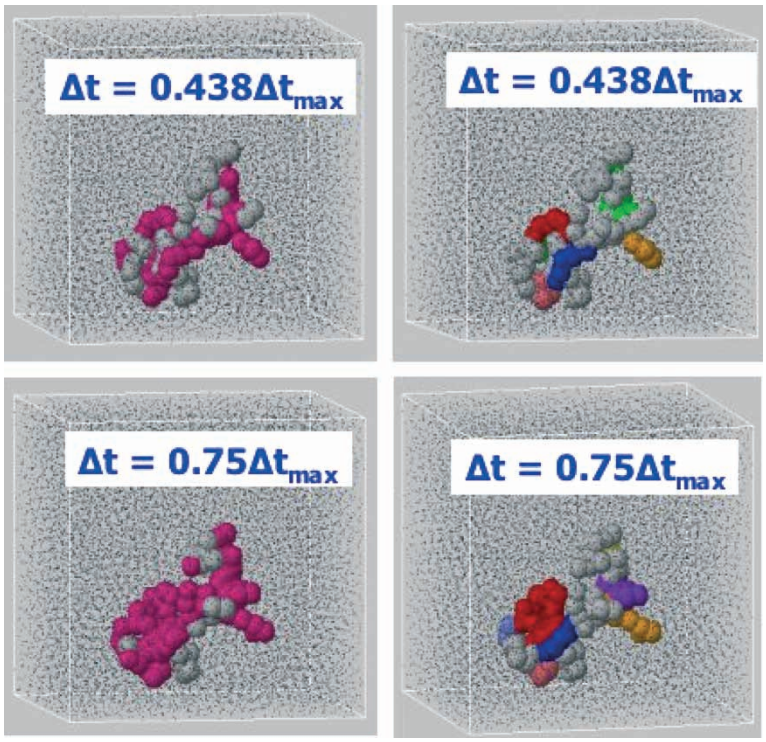

FIGURE 5 Snapshots of configurations at $\Delta t = 0.438\Delta t_{\max}$ and $0.75\Delta t_{\max}$. Particles belonging to the studied cluster are shown as spheres. On the left hand side all mobile particles at the respective time are colored. On the right side, only mobile particles involved in string-like motion are marked, where distinct strings are colored differently. (Colour version available online.)

the particles in these groups assist each other to become mobile, e.g., by moving cooperatively. This will be investigated further below. Finally, the mobile state propagates throughout the cluster.

We now focus on the groups of mobile particles identified during the formation of the cluster. In particular, we demonstrate that many of these particles are indeed involved in string-like motion, thereby establishing a relation between strings and clusters. Strings are defined as groups of mobile particles that move in quasi one-dimensional paths, replacing one another during this motion. Following Donati *et al.* [9], we construct the strings for a time interval Δt by connecting any two mobile particles i and j for which the criterion $\min[|\vec{r}_i(t) - \vec{r}_j(0)|, |\vec{r}_i(0) - \vec{r}_j(\Delta t)|] < \delta$ is fulfilled. This condition implies that one of the mobile particles has moved, and a second mobile particle has replaced its position within a radius δ. As proposed in Ref. [9], we use $\delta = 0.6$, but it has been shown in Ref. [18] that the choice of δ does not alter the qualitative features of the string-like motion, as long as δ is reasonably smaller than the hard-core radius.

In Fig. 5, we display the configurations of the selected cluster at two times $\Delta t < \Delta t_{\max}$, marking for each time two different subsets of particles. On the left hand side, all mobile particles at the respective times are colored, while, on the right hand side, only the mobile particles involved in string-like motion are marked where different colors indicate distinct strings. Note that the panels on the left hand side have already been shown in Fig. 4. Comparing the corresponding snapshots it can be immediately realized that many of the mobile particles are actually replacing each other and moving in strings. Moreover, it is evident that the lengths of the strings increase with time. These findings suggest that string-like motion is an important channel for relaxation within the highly mobile domains of a dynamically heterogeneous system. Further, one may speculate that the growth of the clusters is a consequence of the increasing string length. A more detailed quantitative analysis of string-like motion in this system will be presented in Ref. [42].

CONCLUSION

It is well established that particles in many supercooled liquids move in a correlated fashion, forming clusters whose average size peaks at a time $\Delta t_{\max}$ corresponding to the late-β/early-α relaxation regime. Here we have addressed how these clusters are formed, and how they grow and decay. To study the nature of the clusters at temperatures close to T_{MCT}, we investigated a one-component glass-forming liquid resulting from a molecular dynamics

simulation performed using the Dzugutov pair potential. We singled out one of the largest clusters identified on the basis of the particle dynamics within the time interval $\Delta t_{\max}$, and analyzed the trajectories of the constituent particles during this period. Our approach reveals that the selected cluster is formed as a result of mobility propagation starting from distributed points within the cluster. The propagation of this mobility is facilitated through the development of quasi-one dimensional string-like dynamical processes where groups of particles within the cluster move along a single path. The number of particles involved in this string-like rearrangement increases with time. These findings motivated our interest in investigating further the mechanisms involved in the formation and the growth of these strings by performing a statistical analysis. As will be shown elsewhere [42], this statistical analysis confirms that the cluster studied in the present work reflects the average properties of the clusters in the Dzugutov liquid. Further, it is qualitatively shown that string-like motion is a significant channel of relaxation in domains consisting of highly mobile particles, as demonstrated previously for LJ binary liquids [9] and a polymer melt [18].

Acknowledgements

We are grateful to the University of Michigan Center for Advanced Computing for generous access to the AMD Athlon cluster under the NPACI program.

References

[1] Jäckle, J. (1986) "Models of the glass transition", *Rep. Prog. Phys.* **49**, 171.
[2] Götze, W. (1991) "Aspects of structural glass transitions", In: Hansen, J.P., Levesque, D. and Zinn-Justin, J., eds, *Proceedings of the Les Houches Summer School of Theoretical Physics, Les Houches 1989, Session LI* (North-Holland, Amsterdam), pp 287–503.
[3] Lunkenheimer, P., Schneider, U., Brand, R. and Loidl, A. (2000) "Glassy dynamics", *Contempory Phys.* **41**, 15.
[4] Sillescu, H. (1999) "Heterogeneity at the glass transition: a review", *J. Non-Cryst. Solids* **243**, 81.
[5] Ediger, M.D. (2000) "Spatially heterogeneous dynamics in supercooled liquids", *Annu. Rev. Phys. Chem.* **51**, 99.
[6] Richert, R. (2002) "Heterogeneous dynamics in liquids: fluctuations in space and time", *J. Phys. Condens. Matter* **14**, R703.
[7] Glotzer, S.C. (2000) "Spatially heterogeneous dynamics in liquids: insights from simulation", *J. Non-Cryst. Solids* **274**, 342.
[8] Kob, W., Donati, C., Plimpton, S.J., Poole, P.H. and Glotzer, S.C. (1997) "Dynamical heterogeneities in a supercooled Lennard-Jones liquid", *Phys. Rev. Lett.* **79**, 2827.
[9] Donati, C., Douglas, J.F., Kob, W., Plimpton, S.J., Poole, P.H. and Glotzer, S.C. (1998) "Stringlike cooperative motion in a supercooled liquid", *Phys. Rev. Lett.* **80**, 2338.
[10] Yamamoto, R. and Onuki, A. (1998) "Dynamics of highly supercooled liquids: Heterogeneity, rheology, and diffusion", *Phys. Rev. E* **58**, 3515.
[11] Perera, D.N. and Harrowell, P. (1999) "Relaxation dynamics and their spatial distribution in two-dimensional glass-forming mixture", *J. Chem. Phys.* **111**, 5441.
[12] Glotzer, S.C. and Donati, C. (1999) "Quantifying spatially heterogeneous dynamics in computer simulations of glass-forming liquids", *J. Phys.: Condens. Matter* **11**, A285.
[13] Poole, P.H., Donati, C. and Glotzer, S.C. (1998) "Spatial correlations of particle displacements in a glass-forming liquid", *Physica A* **261**, 51.
[14] Donati, C., Glotzer, S.C., Poole, P.H., Kob, W. and Plimpton, S.J. (1999) "Spatial correlations of mobility and immobility in a glass forming Lennard-Jones liquid", *Phys. Rev. E* **60**, 3107.
[15] Bennemann, C., Donati, C., Baschnagel, J. and Glotzer, S.C. (1999) "Growing range of correlated motion in a polymer melt on cooling towards the glass transition", *Nature* **399**, 246.
[16] Doliwa, B. and Heuer, A. (2000) "Cooperativity and spatial correlations near the glass transition: Computer simulation results for hard spheres and disks", *Phys. Rev. E* **61**, 6898.
[17] Gebremichael, Y., Schrøder, T.B., Starr, F.W. and Glotzer, S.C. (2001) "Spatially correlated dynamics in a simulated glass forming polymer melt: Analysis of clustering phenomena", *Phys. Rev. E* **64**, 051503.
[18] Aichele, M., Gebremichael, Y., Starr, F.W., Baschnagel, J. and Glotzer, S.C. (2003) "Polymer-specific effects of bulk relaxation and string-like correlated motion in the dynamics of supercooled polymer melts", *J. Chem. Phys.* **119**, 5290.
[19] Giovambattista, N., Buldgreu, S.V., Starr, F.W. and Stanley, H.E. (2003) "Connection between Adam-Gibbs theory and spatially heterogeneous dynamics", *Phys. Rev. Lett.* **89**, 125501.
[20] Weeks, E., Crocker, J.C., Levitt, A.C., Schofield, A. and Weitz, D.A. (2000) "Three-dimensional direct imaging of structural relaxation near the colloidal glass transition", *Science* **287**, 627.
[21] Kegel, W.K. and van Blaaderen, A. (2000) "Direct observation of dynamical heterogeneities in colloidal hard-sphere suspensions", *Science* **287**, 290.
[22] Leutheusser, E. (1984) "Dynamical model of the liquid-glass transition", *Phys. Rev. A* **29**, 2765.
[23] Bengtzelius, U., Götze, W. and Sjölander, A. (1984) "Dynamics of supercooled liquids and the glass transition", *J. Phys. C* **17**, 5915.
[24] Götze, W. and Sjögren, L. (1992) "Relaxation processes in supercooled liquids", *Rep. Prog. Phys.* **55**, 241.
[25] Götze, W. and Sjögren, L. (1996) "Comments on the mode coupling theory for structural relaxation", *Chem. Phys.* **212**, 47.
[26] Götze, W. (1999) "Recent tests of the mode-coupling theory for glassy dynamics", *J. Phys.: Condens. Matter* **11**, A1.
[27] Dzugutov, M., Larsson, K.-E. and Ebbsjö, I. (1988) "Pair potential in liquid lead", *Phys. Rev. A* **38**, 3609.
[28] Dzugutov, M. (1992) "Glass formation in simple monoatomic liquid with icosahedral inherent local order", *Phys. Rev. A* **46**, R2984.
[29] Zetterling, F., Dzugutov, M. and Simdyankin, S. (2001) "Formation of large-scale icosahedral clusters in a simple liquid approaching the glass transition", *J. Non-Cryst. Solids* **293**, 39.
[30] Dzugutov, M., Simdyankin, S.I. and Zetterling, F.H.M. (2002) "Decoupling of diffusion from structural relaxation and spatial heterogeneity in a supercooled simple liquid", *Phys. Rev. Lett.* **89**, 195701.
[31] Doye, J., Wales, D., Zetterling, F. and Dzugutov, M. (2003) "The favored cluster structures of model glass formers", *J. Chem. Phys.* **118**, 2792.
[32] Dzugutov, M. (1993) "Monoatomic model of icosahedrally ordered metallic glass formers", *J. Non-Cryst. Solids* **156**, 173.
[33] Hafner, J. (1987) *From Hamiltonian to Phase Diagram* (Springer-Verlag, Berlin).
[34] Sachdev, S. and Nelson, D. (1985) "Statistical mechanics of pentagonal and icosahedral order in dense liquids", *Phys. Rev. B* **32**, 1480.

[35] Sadigh, B., Dzugutov, M. and Elliott, S.R. (1999) "Vacancy ordering and medium-range structure in a simple monoatomic liquid", *Phys. Rev. B* **59**, 1.
[36] Inoue, A., Zhang, T. and Masumato, T. (1990) "Production of amorpheous cylinder and sheet of $La_{55}Al_{25}Ni_{20}$ alloy by a metallic mold casting method", *Mater. Trans. JIM* **31**, 425.
[37] Peker, A. and Johnson, W.L. (1993) "A highly processable metallic glass $Zr_{41.2}Tr_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$", *Appl. Phys. Lett.* **63**, 2342.
[38] Bakke, E., Busch, R. and Johnson, W.L. (1995) "The viscosity of the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk metallic glass forming alloy in the supercooled liquid", *Appl. Phys. Lett.* **67**, 3260.
[39] Dzugutov, M. (1993) "Formation of a dodecagonal quasicrystalline phase in a simple monoatomic liquid", *Phys. Rev. Lett.* **70**, 2924.
[40] McQuarrie, D.A. (1976) *Statistical Mechanics* (Harper and Row, New York).
[41] Hansen, J.P. and McDonald, I.R. (1986) *Theory of Simple Liquids* (Academic Press, London).
[42] Gebremichael, Y., Vogel, M. and Glotzer, S.C. "Particle dynamics and the development of string-like motion in a simulated monoatomic supercooled liquid", *J. Chem. Phys.* (In press).
[43] Garrahan, J.P. and Chandler, D. (2002) "Geometrical explanation and scaling of dynamical heterogeneities in glass forming system", *Phys. Rev. Lett.* **89**, 035704.