Stringlike Cooperative Motion in a Supercooled Liquid

Claudio Donati,[1] Jack F. Douglas,[1,2] Walter Kob,[3] Steven J. Plimpton,[4] Peter H. Poole,[5] and Sharon C. Glotzer[1,2,*]
[1]*Center for Theoretical and Computational Materials Science, NIST, Gaithersburg, Maryland 20899*
[2]*Polymers Division, NIST, Gaithersburg, Maryland 20899*
[3]*Institut für Physik, Johannes Gutenberg Universität, Staudinger Weg 7, D-55099 Mainz, Germany*
[4]*Parallel Computational Sciences Department, Sandia National Laboratory, Albuquerque, New Mexico 87185-1111*
[5]*Department of Applied Mathematics, University of Western Ontario, London, Ontario N6A 5B7, Canada*
(Received 27 October 1997)

Extensive molecular dynamics simulations are performed on a glass-forming Lennard-Jones mixture to determine the nature of the cooperative motions occurring in this model fragile liquid. We observe stringlike cooperative molecular motion ("strings") at temperatures well above the glass transition. The mean length of the strings increases upon cooling, and the string length distribution is found to be nearly exponential. [S0031-9007(98)05583-5]

PACS numbers: 61.20.Lc, 61.43.Fs, 64.70.Pf

The concept of cooperative molecular motion [1,2] is commonly invoked to rationalize dramatic changes in the transport properties of liquids as they are cooled toward their glass transition [3]. In the heuristic Adam and Gibbs model [1] of supercooled liquids, relaxation occurs through "cooperatively rearranging regions" which grow with decreasing temperature. A more rigorous treatment of collective motion in liquids by Zwanzig and Nossal emphasizes the occurrence of momentum density excitations whose lifetime grows as the temperature is lowered [4]. Mode-coupling theory (MCT) [5] attributes the slowing down of particle motion at low temperatures to "backflow" collective particle motion which eventually causes a structural arrest of the liquid dynamics. However, there has been no direct experimental observation of these kinds of cooperative motion.

Computer simulations offer advantages over experiments on real liquids for the investigation of collective particle motion. In molecular dynamics the position and velocity of all the particles are known at all times. As a consequence, correlation functions quantifying the motion of particular subsets of particles can be readily determined. Recent experiments [6,7] and simulations [8,9] have identified dynamical heterogeneity in supercooled liquids and spin glasses [10]. It is natural to suppose that cooperative motion might be associated with this dynamical heterogeneity. A well studied Lennard-Jones (LJ) system, recently introduced to study the dynamics of simple supercooled liquids, provides a particularly good model to test for cooperative motion, since its properties have been well characterized [11] and evidence for dynamical heterogeneity has already been identified for this model [9].

In this Letter, we test whether cooperative molecular motion occurs in this model fragile glass-forming liquid. We find that molecular motion indeed becomes increasingly collective upon cooling. However, the regions involved in this motion are not compact, as usually supposed [1,12], but instead form stringlike structures. The average string length increases with decreasing temperature, and the string length distribution is nearly exponential.

We performed extensive molecular dynamics simulations of a three dimensional binary mixture (80:20) of 8000 LJ particles where the interaction parameters [13] are chosen to prevent demixing and crystallization [11]. Ten temperatures T between 0.550 and 0.451 above the fitted mode-coupling temperature $T_c \approx 0.431$ [11] are studied. We emphasize that this temperature range is well above the glass transition, so that our system is readily equilibrated. Physical aging effects, which complicate

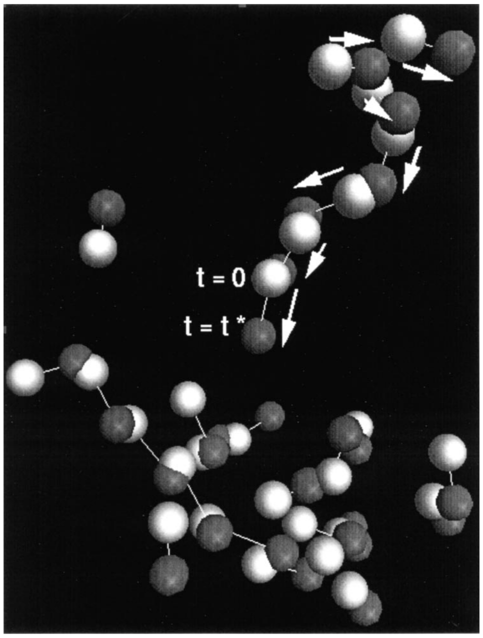

FIG. 1. Mobile particles in a subregion of the simulation box shown at two different times. Light spheres: particles at $t = 0$. Dark spheres: same particles at a later time. The white segments connect the same particles at the two times. White arrows mark the path followed by some of the particles.

lower temperature simulations [14], are not relevant here. Data for up to 25 ns (4×10^6 time steps) for the lowest T following equilibration are stored for each T. Details of the simulation are given in [9,15].

Previous simulations in the supercooled region [9] showed that a small fraction of the particles undergoes large displacements on time scales long compared to the average collision time, and short compared to the structural relaxation time [16]. In the following, we define these particles as "mobile" using the same definition as given in Ref. [9]. Figure 1 shows a snapshot of these mobile particles in a subvolume of the liquid at our lowest T. The light spheres correspond to the mobile particles at $t = 0$, while the dark ones correspond to the same particles at a later time. We see that at any given time the mobile particles are spatially correlated [9]. Viewing the mobile particles at two different times as in Fig. 1 reveals a cooperative motion along stringlike paths. Collective motion was recognized in previous simulations of glass formation, but the nature of the motion was not studied quantitatively; see e.g., [17]. This kinetic structure is even clearer in an animation of the particle dynamics [18].

To quantify the nature of this correlated motion, we calculate the distinct part of the van Hove correlation function [19] $G_d^m(r,t)$ between mobile particles, which measures the time-dependent density of mobile particles at a distance r from the position of an arbitrarily chosen mobile particle at $t = 0$. If the particle motion is correlated so that the position of the original mobile particle is occupied with high probability by another mobile particle at later times, then $G_d^m(r,t)$ should develop a strong maximum about $r = 0$. This effect is evident in Fig. 2, which presents $G_d^m(r,t)$ at different t for the lowest T. At $t > 0$ the height of the nearest-neighbor (NN) peak decreases, and a peak at $r = 0$ develops and grows with time, reaching its maximum value near a characteristic time $t \sim t^*$ [9,16]. No significant peak at $r = 0$ exists for the distinct part of the van Hove correlation function calculated between mobile and the remaining relatively immobile particles, showing that the relative motion between mobile and less mobile particles is quite different.

We further quantify the collective particle motion by examining the angular correlation between the motion of two neighboring mobile particles. Figure 3 shows a contour plot of the probability distribution of the displacement vector $\vec{\delta r}_i(t^*) = \vec{r}_i(t^*) - \vec{r}_i(0)$, projected onto the plane defined by $\vec{\delta r}_i(t^*)$ and $\vec{r}_{ij} \equiv \vec{r}_i(0) - \vec{r}_j(0)$, where j denotes a mobile particle within the NN shell of a mobile particle i. The vector $\vec{r}_{ij}$ points in the direction of the positive x axis. The contours divide the range of values of the probability into 20 intervals so that the probability inside the innermost contour centered on $(0.7, 0.0)$ is at least 20 times higher than the probability outside the outermost contour [20]. The distribution has been calculated using all mobile particles that have at least one other mobile particle in their NN shell. If more than one mobile NN particle exists in the proximity of a reference mobile particle, then the averaging for the data in Fig. 3 includes all distinct pairs of NN mobile particles. In the absence of any correlation between $\vec{\delta r}_i(t^*)$ and $\vec{r}_{ij}$, the contour plot should have a rotational symmetry about the origin. Instead, the pronounced asymmetry of the contour plot in Fig. 3 shows that it is much more probable for a mobile particle to move in the direction of another mobile particle than in any other direction. This asymmetry, as well as the area under the peak at $r = 0$ in Fig. 2, increases with decreasing temperature. It is this dynamical correlation that appears to cause the stringlike morphology of clusters of mobile particles.

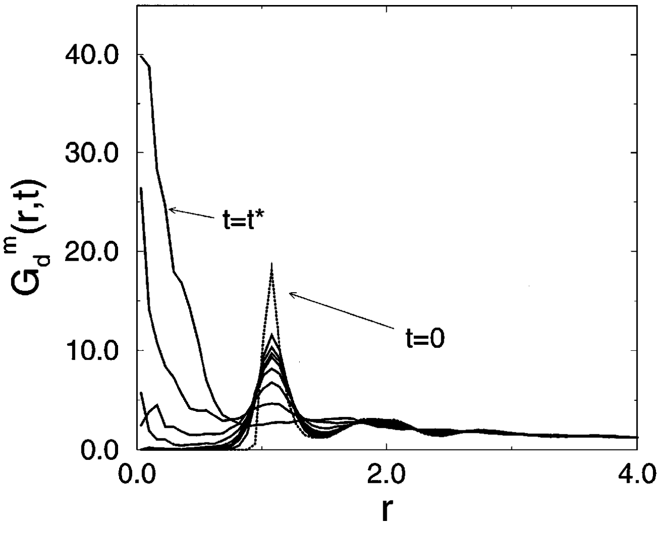

FIG. 2. Distinct part of the van Hove correlation function $G_d^m(r,t)$ between mobile particles at various t.

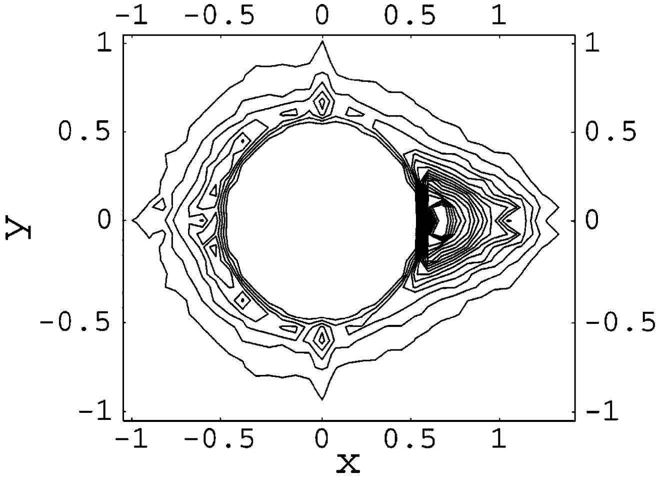

FIG. 3. Contour plot of the probability distribution of the vector $\delta\vec{r}_i(t^*)$ in the plane defined by $\delta\vec{r}_i(t^*)$ and $\vec{r}_{ij}$. The vector $\vec{r}_{ij}$ defines the positive x axis. The increment between any two contours is 5% of the total range. The distribution vanishes by definition in the circular central region.

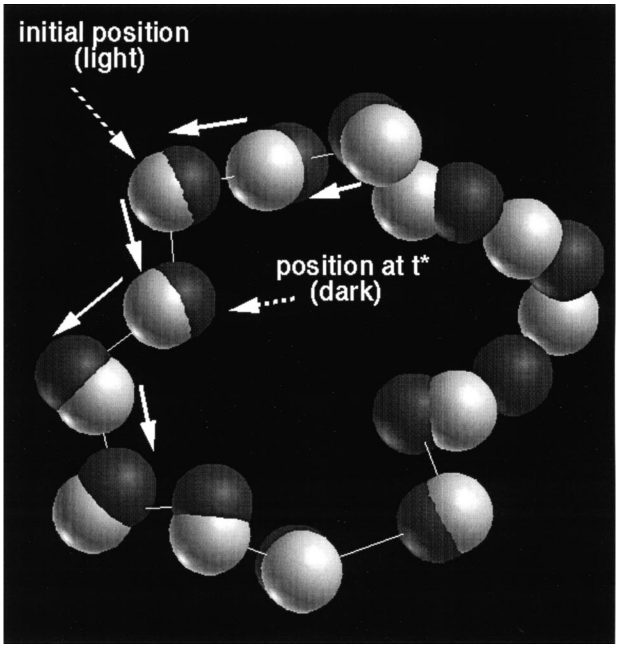

FIG. 4. A large loop of 13 mobile particles exhibiting correlated stringlike motion at $T = 0.451$. Line segments connect identical particles at successive times as in Fig. 1. The arrows show the path of some of the particles. The size of this cluster corresponds to approximately 1.48 nm for *o*-terphenyl, when the size of the molecule is taken as the van der Waals radius 0.37 nm [7].

To measure the number of particles involved in the stringlike cooperative rearrangements, we define strings by connecting two mobile particles i and j if $\min[|\vec{r}_i(t^*) - \vec{r}_j(0)|, |\vec{r}_i(0) - \vec{r}_j(t^*)|] < \delta = 0.6$ [21]. This condition implies that one of the mobile particles has moved, and a second mobile particle has occupied its position. Figure 4 [18] shows a representative string which has a looplike form. Most of the strings have free ends, but loops occur with modest frequency. The average length and size of the strings increase as T decreases; their mass n distribution $P(n)$ is shown in Fig. 5 for three different T. The semilog plot reveals that $P(n)$ is approximately exponential, i.e., $P(n) \sim \exp(-n/\langle n\rangle)$, where the average "string length" $\langle n\rangle$ increases with decreasing T (see inset). For small n, the average radius of gyration R_g of the strings appears to grow linearly with $\langle n\rangle$, while for large n, an exponent near $1/2$ is observed, similar to discrete random walk chains. Observations similar to Fig. 5 have been found in studies of the equilibrium polymerization of linear chain polymers [22].

By analogy with equilibrium polymerization [22], the fraction of mobile particles involved in strings defines an "order parameter" for describing the changing population of mobile particles. This fraction increases from 0.51 for the highest T studied to 0.75 for the lowest T, although the total fraction of all particles that are mobile (0.055 ± 0.005) changes little over the T range investigated. That is, an increasing fraction of mobile particles participates in strings as the system is cooled. Notably, these collective motions would be difficult to detect in equilibrium scattering experiments [23].

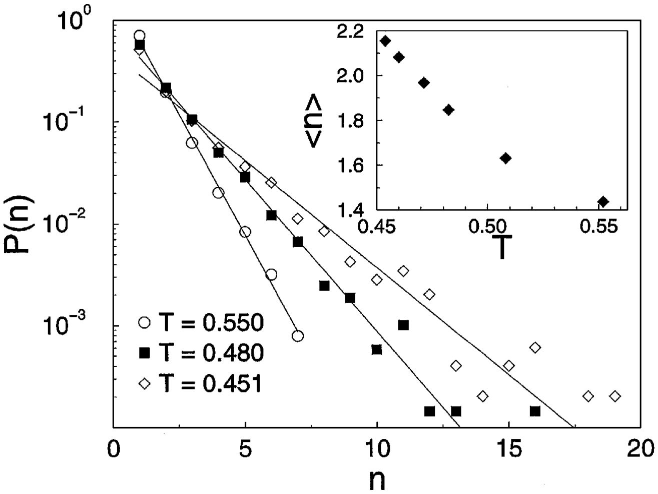

FIG. 5. Probability distribution $P(n)$ of string lengths n for various T. Inset: First moment $\langle n\rangle$ of $P(n)$ vs T.

The original motivation for invoking cooperative motion in glasses was to rationalize the large growth of the apparent activation energy for transport in supercooled liquids [1,24]. Stringlike collective motion provides a natural structure to identify with this increasing activation energy. A simple possibility would be that the activation energy increases in proportion to the average number of particles n in the string (see Fig. 5) [1,25]. A preliminary comparison of the change of the apparent activation energy of supercooled liquids such as *o*-terphenyl shows a change in activation energy similar to what we observe for $\langle n\rangle$ over a corresponding temperature range [26].

Our simulations demonstrate that long lived, highly cooperative, collective particle motion can be observed at temperatures significantly higher than T_c of MCT. The existence of stringlike structures in liquids should have important implications for theories of dense liquids [5], relaxation of liquids in constrained geometries [27], fluid viscoelasticity above T_g [28], and physical aging below T_g [3]. In particular, the relationship between strings and "floppy modes" and the boson peak [29] merits further investigation.

We acknowledge useful conversations with Ray Mountain of NIST. P. H. P. acknowledges the support of NSERC (Canada). W. K. is partially supported by Deutsche Forschungsgemeinschaft under SFB 262.

---

*Corresponding author (sharon.glotzer@nist.gov).

[1] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[2] F. R. Blackburn, M. T. Cicerone, G. Hietpas, P. A. Wagner, and M. D. Ediger, J. Non-Cryst. Solids **172–174**, 256 (1994).

[3] For a summary of phenomenology and theory on glasses and supercooled liquids, see, e.g., recent issue of Science **297**, 1945 (1995); M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13 200 (1996).

[4] R. Zwanzig, Phys. Rev. **156**, 190 (1966); R. Nossal, Phys. Rev. **166**, 81 (1968).

[5] W. Götze and L. Sjogren, Chem. Phys. **212**, 47 (1996).

[6] K. Schmidt-Rohr and H. W. Spiess, Phys. Rev. Lett. **66**, 3020 (1991); J. Leisen, K. Schmidt-Rohr, and H. W. Spiess, J. Non-Cryst. Solids **172–174**, 737 (1994); A. Heuer, M. Wilhelm, H. Zimmermann, and H. W. Spiess, Phys. Rev. Lett. **75**, 2851 (1995); M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **103**, 5684 (1995); F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, Z. Phys. B **88**, 195 (1992).

[7] M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, J. Chem. Phys. **102**, 471 (1995).

[8] M. Hurley and P. Harrowell, Phys. Rev. E **52**, 1694 (1995); A. I. Mel'cuk, R. A. Ramos, H. Gould, W. Klein, and R. Mountain, Phys. Rev. Lett. **75**, 2522 (1995); T. Muranaka and Y. Hiwatari, Phys. Rev. E **51**, R2735 (1995); R. D. Mountain, in *Supercooled Liquids: Advances and Applications* (American Chemical Society, New York, 1997), p. 122; D. Thirumalai and R. D. Mountain, Phys. Rev. E **47**, 479 (1993).

[9] W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **79**, 2827 (1997).

[10] P. H. Poole, S. C. Glotzer, A. Coniglio, and N. Jan, Phys. Rev. Lett. **78**, 3394, (1997); S. C. Glotzer, N. Jan, T. Lookman, A. B. MacIsaac, and P. H. Poole (to be published).

[11] W. Kob and H. C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994); W. Kob and H. C. Andersen, Phys. Rev. E **51**, 4626 (1995); **52**, 4134 (1995); W. Kob and S. J. Plimpton (unpublished).

[12] M. T. Cicerone, P. A. Wagner, and M. D. Ediger, J. Phys. Chem. B **101**, 8727 (1997).

[13] The Lennard-Jones interaction parameters $\epsilon_{\alpha,\beta}$ and $\sigma_{\alpha,\beta}$ are given by: $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, $\sigma_{BB} = 0.88$. Lengths are defined in units of σ_{AA}, temperature T in units of ϵ_{AA}/k_B, and time t in units of $\sqrt{\sigma_{AA}^2 m/\epsilon_{AA}}$. Both types of particles are taken to have the same mass.

[14] W. Kob and J. L. Barrat, Phys. Rev. Lett. **78**, 4581 (1997).

[15] C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer (to be published).

[16] Particle mobility was defined in Ref. [9] in terms of the distance traveled by the particle after some time interval. The particles which travel farther than a certain distance r^* after a characteristic time t^* are defined as mobile, where t^* is calculated via the non-Gaussian parameter α [see, e.g., A. Rahman, Phys. Rev. **136**, A405 (1964)] and is on the order of the late-β relaxation [5] of the intermediate scattering function.

[17] J. L. Barrat, J. N. Roux, and J. P. Hansen, Chem. Phys. **149**, 197 (1990); H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. **86**, 3879 (1988); G. Wahnström, Phys. Rev. A **44**, 3752 (1991); J. N. Roux *et al.*, J. Phys. Condens. Matter **1**, 7171 (1989).

[18] For an animation of a looplike string, see http://www.ctcms.nist.gov/~donati/movie.html

[19] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

[20] Although mobile particles have a much greater probability to move towards other mobile particles, the motion is not perfectly correlated, so the maximum in Fig. 3 occurs at $(0.7, 0)$ rather than at $(1, 0)$.

[21] δ is chosen to be less than the hard-core radius of a particle. Results are insensitive to the choice of δ, provided that δ is chosen smaller than σ_{AA}.

[22] Y. Rouault and A. Milchev, Phys. Rev. E **51**, 5905 (1995); S. C. Greer, Adv. Chem. Phys. **94**, 261 (1996); R. Bellissent, L. Descotes, and P. Pfeuty, J. Phys. Condens. Matter **6**, A211 (1994).

[23] R. L. Leheny, N. Menon, S. R. Nagel, D. L. Price, K. Suzuya, and P. Thiyagarayan, J. Chem. Phys. **105**, 7783 (1996).

[24] D. Lancaster and G. Parisi, J. Phys. A **30**, 5911 (1997); J. P. Sethna, Europhys. Lett. **6**, 529 (1988).

[25] Stringlike excitations involving correlated atomic motions in liquid ^{4}He were suggested long ago by Feynman [R. P. Feynman, Phys. Rev. **90**, 1116 (1953); **90**, 1291 (1953); **94**, 262 (1954)] in his model of superfluids; see also, D. M. Ceperley and E. L. Pollock, Phys. Rev. B **39**, 2084 (1989).

[26] E. Rössler, Phys. Rev. Lett. **65**, 1595 (1990).

[27] B. Jerome and J. Commandeur, Nature (London) **387**, 589 (1997).

[28] J. F. Douglas and J. B. Hubbard, Macromolecules **24**, 3163 (1991). This paper introduces a model of stress relaxation in fragile glass-forming liquids based on the assumption of string excitations having an exponential length distribution; see also, J. F. Douglas, Comput. Mater. Sci. **4**, 292 (1995).

[29] S. D. Bembenek and B. B. Laird, J. Chem. Phys. **104**, 5199 (1996); V. N. Novikov, JETP Lett. **51**, 80 (1990).