

## Observation of single transits in supercooled monatomic liquids

Duane C. Wallace, Eric D. Chisolm, and Brad E. Clements

*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

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A *transit* is the motion of a system from one many-particle potential energy valley to another. We report the observation of transits in molecular dynamics calculations of supercooled liquid argon and sodium. Each transit is a correlated simultaneous shift in the equilibrium positions of a small local group of particles, as revealed in the fluctuating graphs of the particle coordinates versus time. To the best of our knowledge, this is the first reported direct observation of transit motion in a monatomic liquid in thermal equilibrium. We found transits involving 2–11 particles, having mean shift in equilibrium position on the order of  $0.4R_1$  in argon and  $0.25R_1$  in sodium, where  $R_1$  is the nearest neighbor distance. The time it takes for a transit to occur is approximately one mean vibrational period, confirming that transits are fast.

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### I. INTRODUCTION

Long ago, Frenkel [1,2] noted that the liquid-solid phase transition has only a small effect on volume, cohesive forces, and specific heat, while the liquid diffuses much more rapidly than the solid; and from these facts he argued that the motion of a liquid atom consists of approximately harmonic oscillations about an equilibrium point, while the equilibrium point itself jumps from time to time. Goldstein [3] pictured the motion of liquid atoms as primarily controlled by thermal activation over barriers, with a distribution of barrier heights. From computer simulations, Stillinger and Weber [4,5] found mechanically stable arrangements of particles, called inherent structures. They suggested that the equilibrium properties of liquids result from vibrational excitations within, and shifting equilibria between, these inherent structures. Their simulations showed a range of energies for these structures, so when Stillinger and Weber formulated a statistical mechanics of their system they included a distribution of inherent structure potential energies [6,7]. Since then, the picture has developed of a “rugged potential energy landscape,” with a wide distribution of structural potential energies, separated by barriers having a wide distribution of heights [8–11]. Here we use the term “structure” to indicate any mechanically stable configuration of particles, corresponding to a local minimum in the many-particle potential surface.

The present study is limited to monatomic liquids, meaning elemental liquids that do not have molecular bonding. Monatomic liquids include all elemental liquid metals and the rare gas liquids, but not the molecular liquids  $N_2$ ,  $O_2$ , etc., and not polyatomic systems such as alkali halides or water. Molecular liquids have translational, rotational, and internal vibrational degrees of freedom, while monatomic liquids have only translational motion, and the potential energy surface for monatomic liquids is presumably the simplest of all liquid potential landscapes. We use the word “ion” as in metals theory, where an ion consists of a nucleus plus a rigid electron core.

The present database of thermodynamic properties of crystals and liquids, much more extensive and accurate than was available to Frenkel, suggests a potential energy surface for monatomic liquids much simpler than the rugged land-

scape picture above. Two crucial pieces of experimental information, summarized below, lead to this conclusion. First, the constant volume specific heat due only to the motion of the ions, denoted  $C_V$ , is approximately  $3k_B$  per ion. This is true for every liquid metal for which the necessary data are available (see Table I of [12] or Fig. 1 of [13]), and there is no experimental indication that this property fails for any liquid metal in the periodic table. In addition, although liquid Ar at 1 bar is somewhat gaslike [12],  $C_V$  is close to  $3k_B$  for compressed liquid Ar [13], so it is included in our list of monatomic liquids. The property  $C_V \approx 3k_B$  strongly suggests that the ions spend most of their time moving within nearly harmonic many-particle potential energy valleys.

The second piece of evidence is the entropy of melting, but before this information can be made quantitative, one must recognize two categories of melting of elements [14], namely (a) normal melting, in which the electronic structure of crystal and liquid are the same (e.g., metal to metal) and (b) anomalous melting, in which the electronic structure changes significantly upon melting (e.g., semiconductor to metal). Then the constant volume entropy of melting for the normal melting elements is found to be a universal constant, and again this property holds without exception for all the elements for which sufficient experimental data exist, including compressed liquid Ar [14–16]. Unlike the specific heat data, the entropy of melting does not compel us to an immediate conclusion, but we can construct an interpretation consistent with the data. The interpretation proposed in [12] is that the potential valleys important in the statistical mechanics of monatomic liquids are all alike, with each having the same structural potential  $\Phi_0$  and distribution  $g(\omega)$  of harmonic normal mode frequencies. On the other hand, we know from Stillinger and Weber [6,7] that a distribution of  $\Phi_0$  values can be seen in computer simulations, and we also know that crystalline valleys of different symmetry have different  $\Phi_0$  values, so in [12] we conjecture that the potential valleys fall into two classes, namely (a) symmetric valleys, which have some crystalline short-range order and hence have a distribution of  $\Phi_0$  values, and (b) random valleys, which have no order parameter and hence all have the same shape in the thermodynamic limit [same  $\Phi_0$  and  $g(\omega)$ ], and which are of overwhelming numerical superiority relative to

the symmetric valleys. Then the statistical mechanics of the liquid state depends only on the random valleys, and the universal entropy of melting is simply related to a very large universal number of random valleys. From this description of the potential surface, the Hamiltonian can be written and the partition function evaluated, and an accurate account of thermodynamic properties of monatomic liquids is obtained [12,13]. More recently [17,18], computer simulations of sodium have provided a detailed verification of this description of the many-particle potential energy surface. (That all random valleys have the same  $\Phi_0$  is shown by Eq. (3.3) of [17], and a demonstration that all random valleys have the same  $g(\omega)$  is found in Fig. 7, and in the discussion surrounding Eq. (3.7), of [17].) A similar verification, but less detailed, has been obtained for Lennard-Jones argon [19].

This description of the potential surface has two important implications for the motion of the system, called a *transit*, when it passes from one many-particle valley to another. First, because of the role of transits in establishing and maintaining equilibrium, transits must be local; i.e., each transit must involve only a small localized group of particles [12] (except for coherent quantum states, not under consideration here). Second, because the transit motion has little effect on the ion motional specific heat, transits must be sharp, i.e., of short time duration. A model of instantaneous transits has been applied to the velocity autocorrelation function and self-diffusion [20,21], and the idea that transits are correlation controlled, as opposed to thermally activated, has been applied to the glass transition [22]. The purpose of the present paper is to report the observation of individual transits in molecular dynamics (MD) calculations for monatomic systems of argon and sodium. Our procedure and results are given in Sec. II, and a comparison with previous results is given in Sec. III.

To the best of our knowledge, this work is the first observation of individual transits as they appear in the actual trajectory of an equilibrium MD system when it passes from one many-particle valley to another. A different technique, called “inherent dynamics,” which maps successive configurations of an MD calculation onto a time series of inherent structures [6,7,23], has yielded results in some ways complementary to the present study. Inherent dynamics was applied to a binary Lennard-Jones system by Schröder *et al.* [24] to show that as temperature decreases toward a cross-over temperature  $T_x$  the self part of the intermediate scattering function decays at two distinct relaxation times, a short vibrational relaxation time and a long relaxation time associated with transitions between inherent structures. Schröder *et al.* located transitions between inherent structures by monitoring the inherent structure potential, our  $\Phi_0$ , and also the real-space location of the inherent structure as functions of time. This observation demonstrates that the MD system, moving in equilibrium, will quench into different inherent structures at different times, but it does not tell us about the actual system motion during a transit. The present study is intended to provide insight into that process.

## II. OBSERVATION OF TRANSITS

We searched for transits in 500 particle systems with periodic boundary conditions. To reveal the most detailed and

precise expression of the transit process, we monitored all Cartesian coordinates of all particles as functions of time during an equilibrium MD run. As mentioned in [17], at a sufficiently low temperature, the system moves within a single random valley for as long as we can continue the MD run. In this event, the graph of each coordinate of each particle is a fluctuating signal with constant mean, where the mean value locates the particle’s equilibrium position, and the set of all such graphs constitutes an unambiguous observation that the system is moving in a single potential valley. In the present work, the temperature was chosen so that transits occur, but rarely, so that the graph of each coordinate of each particle is again a fluctuating signal with constant mean for some time, then a shift appears in the mean coordinates of several particles, and then the graphs continue as fluctuating signals with constant means. These graphs constitute an unambiguous observation that the system moves for a time within a single potential valley, then transits to a new valley, then continues to move within the new valley. Having thus isolated transits in the equilibrium MD motion, we can study their properties, such as how much time they take, how many particles are involved, and how far their equilibrium positions shift. Certain characteristics of our study should be mentioned at the outset. First, throughout each equilibrium run, those with transits and those without, the mean potential and kinetic energies of the system showed no perceptible change, hence every transit observed is between two random valleys. (Recall from Sec. I that all random valleys have the same depth  $\Phi_0$ .) Second, the mean Cartesian coordinates of every particle were constant throughout each equilibrium run, except for transits. In other words, no motion other than equilibrium vibrations and transits occurred. Finally, the graphs shown are representative of all the graphs we observed, and no selection of “best examples” was necessary.

During each equilibrium run, we identified a potential transit when the running average of any coordinate over the 5000 previous time steps moved by a distance equal to or greater than a prescribed criterion (listed below). Upon inspection, we then verified that in every case we identified, the coordinates of more than one particle moved at the same time in the manner described above, indicating a genuine transit, and every transit was from one random valley to another.

The density of our Lennard-Jones system is 0.9522 particles/ $\sigma^3$ , with corresponding nearest neighbor distance  $R_1 = 1.095\sigma$ , taken as the first maximum of  $g(r)$  in the liquid state. When applied to argon ( $\sigma = 3.405 \text{ \AA}$ ), the density is 1.600 g/cm<sup>3</sup>, the rms normal mode frequency of the random valleys is  $6.88 \times 10^{12} \text{ s}^{-1}$ , and the mean vibrational period is  $\tau = 424\delta t$ , where the MD time step is  $\delta t = 2.15634 \text{ fs}$ . (For comparison, the density of liquid Ar at 1 bar is 1.414 g/cm<sup>3</sup>.) The forces and potentials in the system are computed taking into account all pairs of particles, using the full Lennard-Jones potential. The transit criterion is  $0.1\sigma$ , or approximately  $0.1R_1$  (that is, all motions greater than  $0.1R_1$  in any coordinate averaged over time were tagged as potential transits), and the lowest temperature where transits were observed was 17.1 K, roughly comparable to the glass transition temperature.

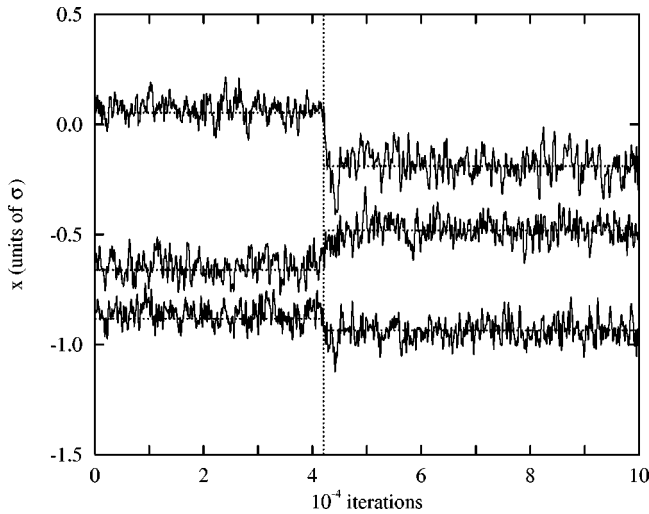


FIG. 1. The  $x$  coordinates of (top to bottom) the seventh, fifth, and second particles involved in an eight-particle transit in Lennard-Jones argon at 17.1 K. The transit time is the same as in Figs. 2 and 3.

Figures 1, 2, and 3 show, respectively, some of the  $x$ ,  $y$ , and  $z$  coordinates of an eight-particle transit in argon at 17.1 K. Only some particles are shown in each figure for the sake of clarity, and different particles are shown in different figures, but those that are shown are representative (the particle numbers are listed in the figure captions). While Figs. 2 and 3 suggest that all transiting particles move in the same direction, this is not actually the case, and the appearance results from keeping only a set of clearly distinguishable curves. (When all the curves are plotted together, the motion of individual particles is difficult to see.) The dotted lines are drawn for visual guidance. The vertical line indicates the transit time, which is the same in all three figures. The system is undergoing harmonic vibrational motion in one random valley before the transit, and in another random valley

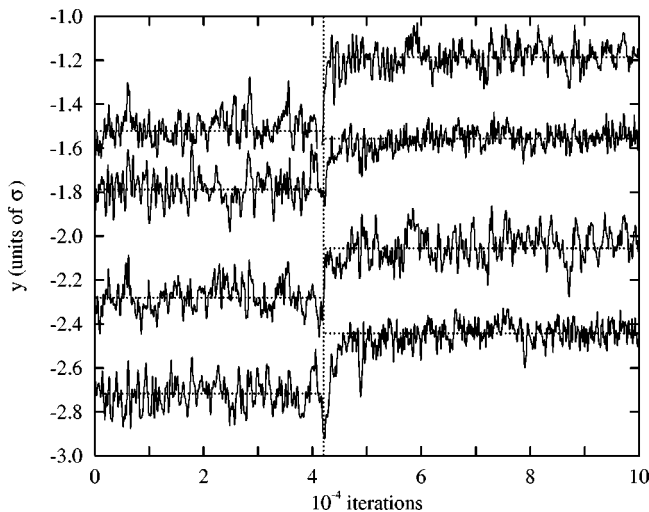


FIG. 2. The  $y$  coordinates of (top to bottom) the first, second, eighth, and sixth particles involved in an eight-particle transit in Lennard-Jones argon at 17.1 K. The transit time is the same as in Figs. 1 and 3.

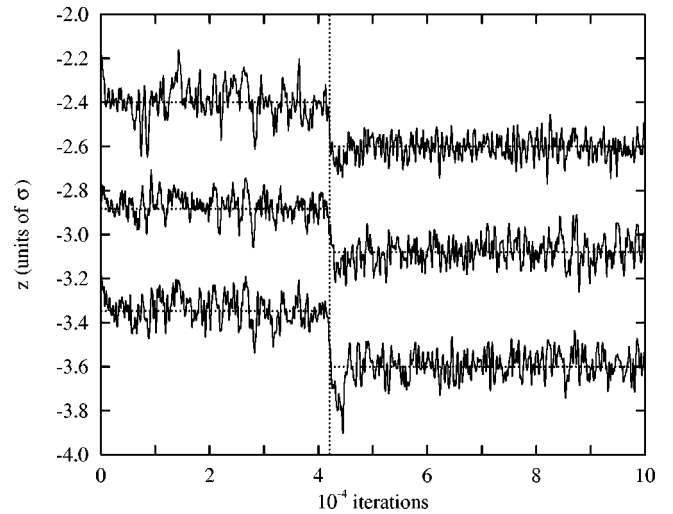


FIG. 3. The  $z$  coordinates of (top to bottom) the first, seventh, and second particles involved in an eight-particle transit in Lennard-Jones argon at 17.1 K. The transit time is the same as in Figs. 1 and 2.

after the transit. The displacement of a Cartesian component of the equilibrium position of a particle is given by the change in the horizontal dotted line. To estimate the duration of a transit for each particle separately, we draw horizontal lines approximating the upper and lower bounds of each fluctuating signal, and find how long the transiting particle is outside of both its pretransit and posttransit bounds. By this measure, many of the graphs in Figs. 1–3 show zero transit duration. A close examination reveals that the best choice for the transit time, as well as the transit duration, varies slightly even among the three coordinates of one particle. Our practice is to set the transit time precisely the same for all coordinates of all particles, and allow the transit duration to cover remaining variations. Let us denote by  $\Delta R$  the distance over which the equilibrium position of a transiting particle moves, and by  $\Delta t$  its transit duration. Then for the eight particles involved in the transit,  $\Delta R$  varies from  $0.3R_1$  to  $0.6R_1$ , with a mean value of  $0.4R_1$ , and  $\Delta t$  has an estimated mean value of  $\tau$ .

Following the eight-particle transit by a time of  $13\tau$ , another transit occurred among three entirely different particles. The coordinates of one of these are shown in Fig. 4. There is a small but measurable change in the mean of  $z$ , a nominal change in the mean of  $y$ , and a large change in the mean of  $x$ . At the transit there is a slight decrease in the  $z$  vibrational amplitude, and a noticeable increase in both the  $x$  and  $y$  amplitudes. Such changes in amplitude are common in transits we observed, but of course they must average away over many transits, because these amplitudes are all selected from a single equilibrium distribution. (Notice Figs. 1–3 also exhibit a distribution of amplitudes.) The  $x$  coordinate in Fig. 4 shows a significant precursor, unusual but not singular, extending ahead of the transit time, while the  $y$  coordinate shows only the hint of a precursor.

Our sodium system has potential energy based on pseudo-potential theory, and is described in [17,18]. The density corresponds to liquid sodium at  $T_m = 371$  K, and the nearest

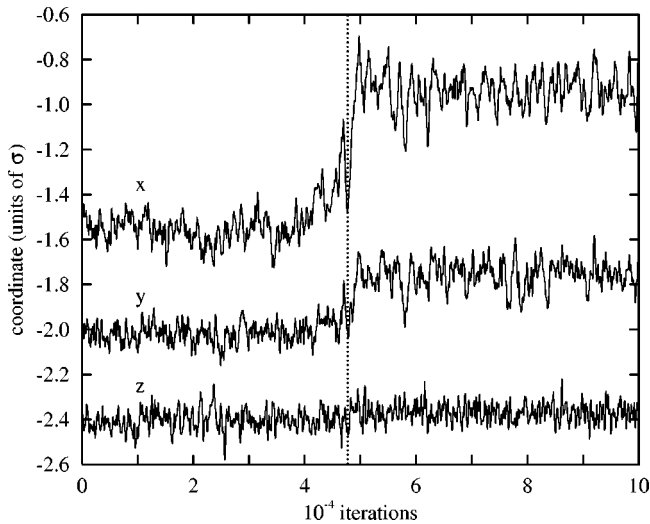


FIG. 4. The coordinates of one of three particles involved in a later transit in Lennard-Jones argon at 17.1 K. The  $y$  and  $z$  coordinates have been shifted for clarity.

neighbor distance is  $R_1 = 7.0$  bohr. The rms vibrational frequency of the random valleys is  $1.562 \times 10^{13} \text{ s}^{-1}$ , and the mean vibrational period is  $\tau = 287.25 \delta t$ , where the MD time step is  $\delta t = 1.40058 \text{ fs}$ . The transit criterion is 1 bohr, or  $0.14R_1$ , and the lowest temperature where transits were observed was 30.0 K, roughly 30% of the glass transition temperature. At this temperature we observed a transit involving 11 particles, and the set of graphs of particle coordinates versus time is qualitatively indistinguishable from the argon graphs shown in Figs. 1–3. The three coordinates of one of the transiting particles are shown in Fig. 5, and the remaining ten particles exhibit similar and equally striking graphs. Again for this 11-particle transit in sodium, every coordinate of every particle transits at the same time. The mean single-particle transit distance is  $0.25R_1$  while the group center of mass moves a distance  $0.11R_1$ , and the mean single-particle transit duration is approximately  $\tau$ . The 11 transiting par-

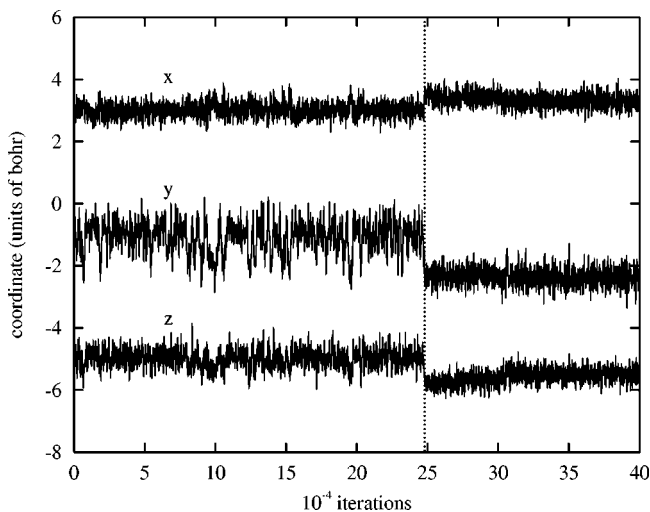


FIG. 5. The coordinates of one particle in an 11-particle transit in sodium at 30.0 K.

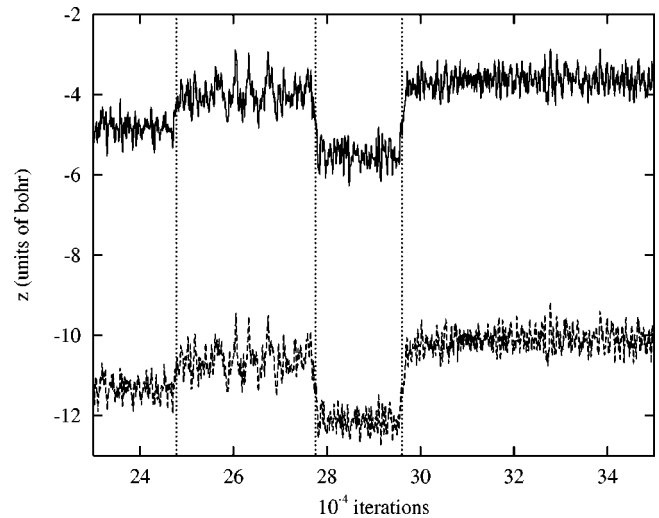


FIG. 6. The  $z$  coordinates of two sodium particles involved in three separate transits over a period of 120 000 iterations. The transit times are the same as in Figs. 7 and 8.

ticles occupy a roughly cubical volume, which contains altogether 23 particles, so that the transiting group has a rather compact shape.

Recall that in identifying each transit, we find every particle for which at least one running average coordinate moves as much as the transit criterion. Upon reducing the transit criterion by half in sodium, to  $0.07R_1$ , we found many more particles participating in each transit, but we found no new transits. This suggests there are no transits that have only very small positional shifts  $\Delta R$ , but when a transit does occur, many surrounding particles undergo small correlated positional shifts. In Fig. 5, the small shifts in  $x$  and  $z$  at approximately 310 000 iterations are associated with the transit of another group of particles.

Figures 6–8 show the Cartesian coordinates of two particles over a common time period. The transits in  $z$ , Fig. 6,

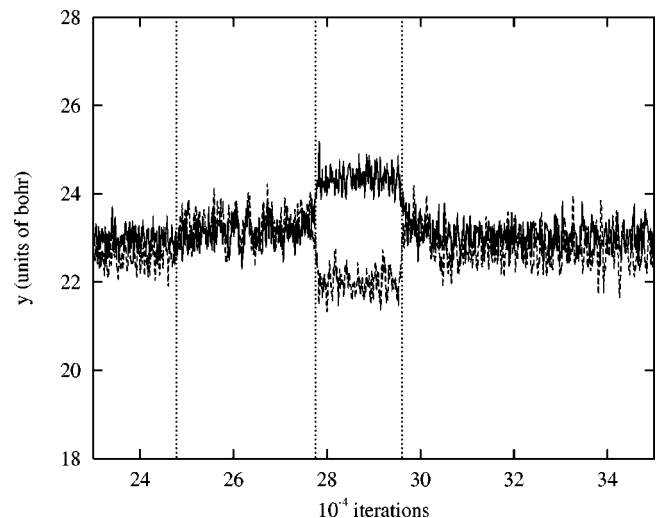


FIG. 7. The  $y$  coordinates of two sodium particles involved in three separate transits over a period of 120 000 iterations. The transit times are the same as in Figs. 6 and 8.

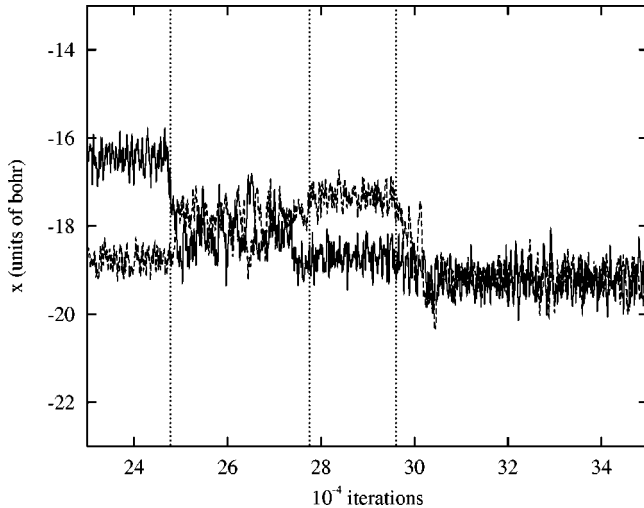


FIG. 8. The  $x$  coordinates of two sodium particles involved in three separate transits over a period of 120 000 iterations. The transit times are the same as in Figs. 6 and 7.

are sharp and perfectly correlated in time. The same holds for the transits in  $y$ , Fig. 7, but both particles show a long postcursor drift following the third transit. In the  $x$  coordinate, Fig. 8, the shift of the lower particle in the first transit lags the common transit time by  $3\tau$ , and this lag is included in our determination of the average transit width. Preceding the second transit by a time of  $12\tau$ , the lower particle is involved in a transit with a separate group of other particles. (Since the transit does not involve both particles, its time is not plotted in the figure.) This transit, at approximately 275 000 time steps, produces no discernible shift in the particle's  $y$  and  $z$  coordinates. Then at the second transit, the upper particle shows a small shift, while the lower particle shows none. Of course, both particles move significantly in  $y$  and  $z$  at the second transit (Figs. 6 and 7). Finally, both particles show a long drift following the third transit. We have not seen such a long postcursor in any other transit.

### III. DISCUSSION

For a binary soft sphere mixture, Miyagawa *et al.* [25] found correlated jumps in the rms displacement of time-averaged positions of single particles. Despite initial appearances, their results are in fact markedly different from ours. First, they averaged particle positions over a time of several vibrational periods, so that motion on a shorter time scale was not resolved. Second, they found very large jumps, around one nearest-neighbor distance, and they found that several atoms jump at successive times by permuting their positions. Wahnström [26] studied a binary Lennard-Jones mixture, and observed sharp jumps in the magnitude of the displacement of a single particle as a function of time. These jumps also do not appear to be related to the transits we observe. In Wahnström's system, the jumping particle was almost always one of the smaller particles, the jump distance was at least as large as the nearest-neighbor distance, and a jumping particle had a tendency to jump back to its original

position after a short time. It is possible that the nature of the jumps seen by Miyagawa *et al.* and by Wahnström is more characteristic of a dense gas than a liquid.

An observation of cooperative particle motion, via computer simulation, was reported by Donati *et al.* [27]. They worked with a binary mixture of Lennard-Jones particles, at temperatures well above the glass transition temperature, and observed particle positions at two different times, separated by a long period compared to  $\tau$ . Between the two observation times, groups of particles moved a distance on the order of  $R_1$  along stringlike paths, with each particle tending to move into the original position of its next neighbor along the string. In comparison, in our transits the particles move a distance noticeably less than  $R_1$ . Oligschleger and Schober [28] studied a system with a soft repulsive potential at very low temperatures, down to 2.5% of the glass transition temperature, where they observed jumps in the system rms displacement versus time. These jumps corresponded to the motion of particles in chainlike configurations, where each particle moved only a fraction of the nearest-neighbor distance. In contrast, our systems do not exhibit transits at such low temperatures. Again for a binary mixture of Lennard-Jones particles, Schröder *et al.* [24] used the technique of inherent dynamics to find transitions between inherent structures that correspond to cooperative stringlike rearrangements of groups of particles moving distances smaller than the nearest-neighbor distance (their Fig. 8). These authors also found that the distribution of displacements of the equilibrium positions in such transitions contains a large number of particles that move a very small distance (their Fig. 7). It is possible that a similar distribution applies to the monatomic systems studied here. An important difference between our transits and the motion reported in [24], [27], and [28] is that our transiting groups do not have stringlike configurations, but are more isotropic, albeit still quite irregular.

In summary, we have observed transits as they appear in the fluctuating graphs of the particle coordinates in equilibrium monatomic MD systems. Each transit is a correlated simultaneous shift in the equilibrium positions of a small local group of particles. The average shift of the equilibrium position of a single particle is around  $0.4R_1$  in our Ar system and around  $0.25R_1$  in our Na system. Occasionally a graph of coordinate versus time for a single particle will show a precursor, or postcursor, extending several  $\tau$  away from the main-group transit time. The average transit duration, for a single particle or for the entire group, is roughly  $\tau$  in either Ar or Na, and the precursors and postcursors are included in this average.

Each precursor or postcursor appears as a segment of the particle coordinate graph where the mean of the coordinate drifts for a time of several  $\tau$ . In all our calculations, no such drift occurred *except* in connection with a transit. In our view, the transit itself is the primary step of diffusive motion. Nevertheless, the precursors and postcursors, when they appear, are a part of the equilibrium diffusive motion, and it would be interesting to study further their role.

The transits we have observed are isolated events; their duration is short compared to the time between them. At higher temperatures the transits will occur at

higher rates. An important assumption of liquid dynamics theory is that the motion between random valleys is accomplished by the same kind of transits observed here, at least to a first approximation, even though the transit rate in the liq-

uid state is so high that each particle is involved in a transit approximately once in every time interval  $\tau$ . This hypothesis, as well as other more detailed properties of transits, will be investigated in future work.

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