

The glass state: characterizing energy landscape features

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 6507

(<http://iopscience.iop.org/0953-8984/18/28/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 12:18

Please note that [terms and conditions apply](#).

The glass state: characterizing energy landscape features

Rodney M J Cotterill and Jens U Madsen

Quantum Protein Centre, Physics Institute, Building 309, Technical University of Denmark, 2800 Lyngby, Denmark

Received 29 March 2006, in final form 1 June 2006

Published 28 June 2006

Online at stacks.iop.org/JPhysCM/18/6507

Abstract

We probed the topologies imposed on configuration hyperspace by the potential energy function—the shapes of the constant potential energy manifolds—for the glassy state of monatomic Lennard-Jones matter, by following trajectories of constant potential energy. A prominent characteristic of this model matter is well-defined regions of confinement (pockets) in configuration hyperspace. We found that there are constant potential energy hyperspace paths (tubes) between such pockets, applying even to paths linking glassy regions to crystalline regions of configuration hyperspace. Also, we found that glass and crystal pockets are interspersed. For monatomic Lennard-Jones matter at least, the transition from glass to crystal therefore does not have to involve the traversing of a potential energy barrier, as is usually assumed.

1. Introduction: the energy landscape

A glass transition occurs when a supercooled liquid becomes rigid and structural relaxations substantially disappear. The term also designates the reverse phenomenon: the reasonably sudden onset of plastic flow when a glass is heated to a sufficiently high temperature. Neither the transition from liquid to glass nor the transition from glass to liquid displays the sharpness characteristic of crystal melting.

There is a long-standing need for an explanation of the glass–liquid transition [1, 2]. In contrast, the crystal–liquid transition—melting—is well understood; it occurs when the liquid free energy falls below that of the crystal. Attempts to analyse melting *quantitatively* are admittedly hampered by the lack of a comprehensive atomic-scale theory of liquids [3], but at least the underlying thermodynamic principles are well established. The situation regarding the glass–liquid transition is more complicated, and it is not even certain that this is a thermodynamic phase transition [4].

It has been recognized [5, 6] that insight can be gained by exploring, for the states relevant to the transition, the topology of the manifolds (or high-dimensional surfaces) of constant potential energy as a function of atomic coordinates. That topology can be said to

describe an energy landscape in multidimensional hyperspace, the salient features of which have traditionally been represented by one-dimensional diagrams [6, 7]. In the diagrams, the ordinate indicates energy and the abscissa a generalized positional coordinate. Such a diagram represents an idealized global section of the energy function, and it is always stressed that it cannot faithfully reproduce all the features of the real multidimensional situation. It is, however, tacitly assumed that the indicated energy barriers would have real counterparts. Moreover, it is assumed that such barriers would have to be traversed if one (meta)stable state were to be transformed into another.

Another approach [8] to characterizing the energy landscape involves identifying saddle points (that is, stationary points where the forces on all atoms are zero but which are not local potential energy minima) and quasi-saddle points (that is, points where the sum of all the squared forces on the atoms is at a minimum). The quasi-saddle points had sums of all the squared forces on the atoms that were several orders of magnitude below the same sum in average configurations, and they have, together with the actual saddle points, been associated with passages between local minima of the potential energy, or between regions of probable occupation in the liquid state.

In a glass/liquid model with 256 atoms with a modified Lennard-Jones interaction, it was found [8] that the number of both actual saddle points and quasi-saddle points depended on temperature, and effectively vanished at temperatures below a mode-coupling temperature, which was of the order of magnitude of the glass transition temperature. This implied an intrinsic relationship between the reduction to zero of the number of saddle points (a microscopic structural feature), the mode-coupling temperature (a feature characterizing the dynamics), and the glass transition temperature (an essentially macroscopic feature).

Yet another approach to characterizing the energy landscape is based on identifying eigenmodes of the instantaneous dynamical matrix for glasses and liquids (see [9] and the references cited therein). Earlier we explored [10] this aspect of the hyperspace topology by obtaining local sections of the potential energy along all the normal modes of motion—a complete set of orthogonal eigenvectors for the dynamical matrix—for states at various temperatures.

Whereas all of these previous studies, and the present study, attempt to shed light on the energy landscape of non-crystalline states, there are important differences. The studies concerned with eigenmodes [9, 10] focus on characterizing the immediate surroundings of a single state point. The studies concerned with saddle points [8] address the issues concerned with potential energy barriers. Also, the present study is directed at the issue of access from one potential energy minimum to others along paths of constant potential energy; hence the paths do not surmount energy barriers. In addition, the spatial distribution of the thus-connected energy minima was investigated.

All of these studies typically have investigated glasses which have been produced with fairly abrupt quenches and/or compressions, and hence the glasses were not necessarily fully equilibrated. There is therefore considerable interest in relaxation phenomena in such model glasses. From the perspective of the energy landscape concept, relaxation means transition from one local minimum to another, possibly repeated sequentially. Relaxation is rather difficult to achieve in computer studies because of the limited physical time duration that can be simulated, and because of the risk of crystallization. In order to avoid crystallization, it will usually be necessary to keep the temperature low, and the probability of surmounting energy barriers then becomes very low. Relaxation of glass at low temperature is likely to be associated with trajectories in the energy landscape that avoid substantial increases in the potential energy, and this point was an important motivation for the investigation of constant potential energy trajectories presented here.

Here we report new information acquired through exploring the topology of the energy landscape for the glassy state of Lennard-Jones matter, our 240-atom model being pseudo-infinite through the use of periodic boundary conditions.

2. Computer experimental technique

Various techniques are available for computer simulation of atomic arrangements in crystals, liquids, and glasses. Two are common: Monte Carlo (MC) and molecular dynamics (MD). One MC variant [11] efficiently produces a statistical ensemble of atomic states with probabilities proportional to the Boltzmann factor—a canonical ensemble—by creating a Markov chain of states with the appropriate probabilities, each lying near its predecessor. The sequence of states in such a chain does not reflect the system's temporal evolution. MD integrates the classical equations of motion by a finite difference approximation [12], with various numerical integration schemes being available [12, 13], and thermodynamic properties are obtained by temporal averages corresponding to micro-canonical ensembles.

A third technique, potential energy contour tracing (PECT) [14], aims to explore the constant potential energy manifolds by generating trajectories of constant potential energy; it is computationally a minor modification of MD. A possible integration scheme in MD employs two coupled first-order differential equations: one specifying change of atomic positions from the corresponding velocities; the other specifying change of atomic velocities from the forces on the individual atoms, as derived from the interaction energy. Only that second differential equation is modified in PECT, the changes in velocities of the individual atoms being computed so as to keep the $3N$ -dimensional velocity vector normal to the $3N$ -dimensional force vector, where N is the number of atoms in the model. This keeps the overall potential energy constant.

PECT can be implemented in various ways. We chose to stipulate that the change in each atomic velocity is the minimum possible; this was achieved by projecting the velocity prior to the integration step onto a plane normal to the force on the atom. We furthermore chose to keep the sum of squared velocities constant. In the above projection, the velocity vector will, in general, become shorter. An alternative possibility would be to correct each atomic velocity after projection, so as to retain its original length. We preferred the first alternative because it allowed the individual atomic velocity vectors to fluctuate in magnitude, as in MD.

More specifically, the numerical integration procedure in PECT is as follows. $E_p(\mathbf{r}) = E_{\text{ref}}$ formally defines a constant potential energy contour, $E_p(\mathbf{r})$ being the potential energy function and \mathbf{r} being the $3N$ -dimensional position vector. PECT involves iterative integration to follow the evolution of \mathbf{r} , of \mathbf{F} , the $3N$ -dimensional force vector, and of \mathbf{v} , the $3N$ -dimensional (pseudo)velocity vector, along a constant potential energy contour, the individual force components being calculated through suitable differentiation of the interatomic potential function. In the present implementation, the velocity vector \mathbf{v}_1 for the next iterative step is chosen to be maximally parallel to the previous velocity vector \mathbf{v}_0 . This leads to the prescription for finding, in each iteration, the new velocity vector and thereafter the new position of the state point in a PECT simulation, namely

$$\mathbf{v}_1 = \mathbf{v}_0 - \mathbf{F}_0(\mathbf{F}_0 \cdot \mathbf{v}_0)/(|\mathbf{F}_0 \cdot \mathbf{F}_0|)$$

and

$$\mathbf{r}_1 = \mathbf{r}_0 + \Delta\mathbf{r},$$

where $\Delta\mathbf{r} = a\mathbf{v}_1$, and a is calculated for each iteration so as to keep the length $|\Delta\mathbf{r}|$ of the $3N$ -dimensional displacement vector per iteration, $\Delta\mathbf{r}$, constant. It is clear that the scalar product $\mathbf{v}_1 \cdot \mathbf{F}_0 = 0$, as desired.

PECT creates an ensemble of atomic states, each lying near its predecessor, as in MD and in the usual implementation of MC. As in the latter, the sequence of states does not represent a temporal evolution and, unlike both MD and MC, the potential energy remains constant. There being no temporal evolution, the velocities in PECT are merely *pseudo-velocities*. A PECT sequence can be started from any MD state, that is, any specification of $3N$ positions and $3N$ velocity coordinates. The PECT trajectory displays continuity with the preceding MD trajectory, but there will, in general, be a discontinuous change in velocity. It must be stressed that PECT produces just one sequence of states with constant potential energy from a given starting point. There is an extremely large number of alternative sequences, because only one $3N$ -dimensional velocity direction for each state point in $3N$ -dimensional phase space leads to an increase or decrease in potential energy. All the $3N - 1$ others lead to possible PECT sequences, inclusive of the three purely translational modes, which are anyway excluded by the usual stipulation that the average velocity is zero. Alternative PECT sequences can be created from a given state point by assigning different atomic velocities. We have, in general, performed this by exchanging velocity components of two or more atoms or even the velocities of all the atoms by a random process. The advantage of exchanging velocities is that the distribution of all the velocities remains unchanged.

All individual PECT experiments were performed at constant density of the system, but the density could of course be adjusted appropriately at the outset. We measured the total squared deviation of atomic positions, $\Sigma \Delta r^2$, from any chosen starting configuration. Also, we monitored whether the system remained in the glassy state by evaluating the caloric equation of state together with the radial distribution function [15] and by performing direct inspection of the atomic arrangement, projected on three mutually orthogonal planes.

In this study, we investigated a pseudo-infinite model of 240 atoms with interactions according to the Lennard-Jones potential (see below). This was identical to that in our earlier study [10]. The number of atoms is comparable to that (256) used in the study of saddle points [8] but, whereas the cubic computational cell of that study is primarily compatible with the face centred cubic (fcc) structure, our rectangular parallelepiped computational cell with 240 atoms was chosen to be compatible with both the fcc structure and the hexagonal close packed (hcp) structure. In both the study of saddle points and the present study, the emphasis is of course on the non-crystalline states, but it should be considered significant that the models do not exclude the crystalline states.

In fact, crystallization has been found to be relatively easy with Lennard-Jones models and, conversely, the production of stable glasses has been considered difficult. For that reason, a modified Lennard-Jones potential was employed in the study of saddle points [8]. Nevertheless, we found it entirely possible to generate stable glasses, which remain in the glassy state during extended equilibrations at low temperature.

The interactions between the 240 atoms in our pseudo-infinite model were represented by the truncated Lennard-Jones potential, $E_{LJt}(r) = \varepsilon\{(r_o/r)^{12} - 2(r_o/r)^6\} + \varepsilon_t$, for $r < 2.5r_o = r_t$, and $E_{LJt}(r) = 0$ otherwise: r is the interatomic distance, r_t is the truncation distance, r_o is the equilibrium distance for a diatomic molecule, ε_t is calculated such that the potential is continuous at r_t , and $\varepsilon - \varepsilon_t$ is the binding energy of a diatomic molecule in equilibrium; $\varepsilon_t/\varepsilon$ is approximately 0.008 18.

All computations were performed in reduced units, taking r_o as the unit of length, ε as the unit of energy, the atomic mass as the unit of mass, and Boltzmann's constant as the unit for establishing a temperature scale; other units were then derived in the usual manner. The time-step employed in the numerical MD integrations was 0.001 reduced time units; it was monitored that the implementation of the MD integration kept the total energy (potential plus kinetic) constant. In the PECT integrations, the sum of squared displacements per integration step was

kept constant at a value comparable to that of a typical low-temperature MD simulation, and it was monitored that the implementation of the PECT integration kept the potential energy constant.

A glassy structure was generated in a three-stage MD procedure: (i) adjust a 240-atom model to a temperature of 1.2 reduced units and a density of 1.15 reduced units, and leave the model in this state for 10 reduced units of time; (ii) compress the end configuration thus obtained by 10% linearly and quench (i.e. remove all kinetic energy) repeatedly during 10 reduced units of time; (iii) expand the end configuration now ensuing to a density of approximately 1.5 reduced units, adjust the temperature to 0.05 reduced units, and leave the model in this state for 10 reduced units of time. Alternative glassy structures could be generated by employing different durations in step (i). When performed with an initial configuration with random atomic coordinates, the procedure was found occasionally (say, about one time out of six) to generate crystalline states. When performed with a crystalline initial configuration, the probability of crystalline outcomes was high unless the duration of step (i) was extended to be longer than about 30 reduced units of time.

A number of glassy structures generated according to the above procedure were tested for up to 5000 reduced units of time and were found to persist in the state resulting from step (iii) without crystallizing. However, it also occasionally occurred that crystallization was observed during this test of glassy states that had originally been generated from a crystalline configuration.

The above procedure is in some respects comparable to one employed by Di Leonardo *et al* [16], specifically with respect to employing a *crunch*, that is to say, a sudden density increase of a high-temperature state. In that study, a rather slow cooling rate was employed, and a modified Lennard-Jones potential was used to suppress the crystalline state. When comparing with that study, it should be observed that it specifies a different reduced length unit, resulting in a density of 1 in that study being equivalent to a density of $2^{1/2}$ in the present study.

3. Experimental results

By monitoring the temporal variation of $\Sigma\Delta r^2$ during each PECT run, we were able to probe the accessibility of regions in configuration hyperspace. An initial increase of $\Sigma\Delta r^2$ followed by a decrease to zero would indicate that the state point had prescribed a closed loop in that hyperspace. Such a closed-loop trajectory would not be surprising if the configuration space were merely two-dimensional, but it would be rather unlikely in the high-dimensional situation in our investigation. Limited increases and decreases without such a precise return would, on the other hand, indicate that the state point had spent some time in a confined region of configuration hyperspace, which one could call a pocket. This would most likely be a curled up assembly of lower dimensionality regions of accessibility.

The temporal variations of $\Sigma\Delta r^2$ observed in the investigation did indeed reveal the presence of pockets. $\Sigma\Delta r^2$ was typically seen first to rise but then to level off, forming what could be called a plateau (see figure 1). Close inspection of the plateau revealed fine-scale variations, however. $\Sigma\Delta r^2$ was often then seen to rise again and subsequently level off to another plateau, this too displaying fine-scale variation. This is just the sort of plot that one would expect if the state point were indeed periodically visiting—and spending some time in—pockets, moving around the latter's confined manifold in each case, and later travelling on to another pocket (see below). By checking the radial distribution function corresponding to observed plateaus and by direct inspection of projected atomic positions, most of the pockets were found to correspond to the glassy state, though in some pockets the 240-atom assembly had adopted the (somewhat faulted) crystalline form.

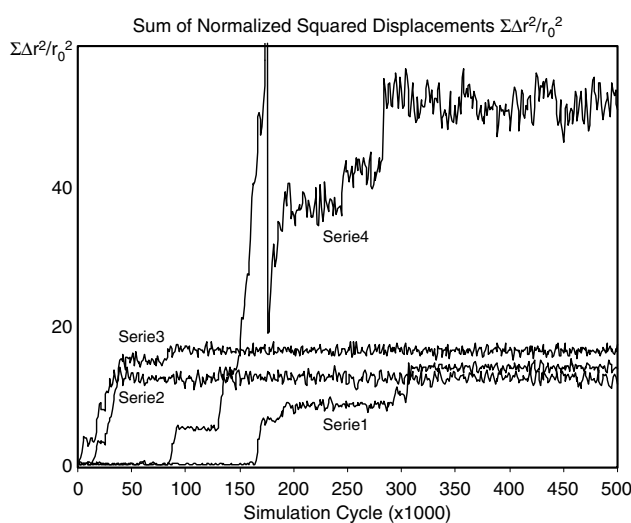


Figure 1. Evolution of the sum of squared displacements, normalized to the squared distance unit (r_0^2), for four different PECT experiments, all starting from the same glass structure; see text for discussion. Note that above 175 thousand cycles, Serie4 has been displaced downward by 35 squared distance units in order to fit inside the diagram.

As noted above, we observed the state point to make spatial excursions during the periods intervening between confinements in specific pockets, this indicating the existence of what could be called tubes. It must be stressed that the existence of pockets does not automatically imply that there would be tubes. It would be possible for the individual pockets to be completely isolated from one another by energy barriers. Energy barriers involving saddle points no doubt exist, but the surprising fact is that these do not necessarily isolate the pockets; there are alternative tube routes that, by definition, do not involve a rise in potential energy. Our purpose in the balance of this communication is to document details of the distribution of pockets and tubes, for the various states of interest in our 240-atom pseudo-infinite model.

We found that an initially amorphous state, through a succession of states generated by the PECT prescription, can make a transition to a crystalline state containing crystal defects. This implies that there exist trajectories with constant potential energy linking amorphous and (defective) crystalline states. The existence of such trajectories does not exclude the possibility that actual nucleation of crystal in an amorphous state, such as a supercooled liquid, involves scaling a potential energy barrier.

The amorphous and defective crystalline states were relatively stable. Indeed, the mere fact that it is possible to speak of an amorphous phase implies a certain degree of stability. The stability was manifested in the existence of pockets, in each of which the system could reside for a fairly large number of computational steps before making a transition to another pocket. This behaviour was in fact observed in both PECT and MD experiments. During transitions to other pockets, $\Sigma\Delta r^2$ increased almost monotonically, creating a ramp in the plot, as seen in figure 1.

It could seem surprising that these ramps almost always had positive slope and that there was seldom overall backtracking. This is probably a consequence of the high dimensionality, and it indicates that many other pockets are accessible from each individual pocket. The probability that an independent third pocket is in the general direction of a first pocket, as seen

from a second pocket in a sequence of pockets, is thus low. The rare examples of backtracking were caused by the state point oscillating between two pockets.

Several features of the pocket–tube arrangement of the potential energy manifold were intriguing. For example, the distances between neighbouring pockets (that is to say, the end-to-end lengths of the tubes) were observed to be quite small. They correspond to each atom moving through an average distance of only a fraction of the nearest-neighbour distance ($\sim r_o$) between the atoms (see table 1, below). The various glass configurations clearly lie very close to one another. Still more surprising was the discovery that this applies even to the tubes connecting glassy and crystalline states—which are thus interspersed. There has been the tacit assumption that the glassy and crystalline regions of configuration hyperspace are well removed from each other; it transpires that this is not necessarily the case, at least for the simple monatomic substance that we have studied. This accounts for the observation that crystallization is surprisingly easy. When the thermodynamic conditions are favourable, it is rapidly accomplished by the collective motions of the atoms, each of which is shifted through an almost imperceptible distance. No long-range diffusion is necessary.

In many instances, a substantial number of pockets exist within a distance of about $0.5r_o^2$ squared atomic displacements per atom from any given pocket. In a number of cases studied, indeed, the separation is as little as $0.05r_o^2$ squared atomic displacements per atom. Moreover, we found that, within these ranges, there can be pockets both of an amorphous and a (defective) crystalline nature. The typical size or width of a pocket, indicated as four times the mean square displacements within the pocket, is of the magnitude $0.005r_o^2$ squared atomic displacements per atom, but pockets as narrow as $0.002r_o^2$ and as wide as $0.02r_o^2$ squared atomic displacements per atom were observed. The number of pockets observed within the $0.5r_o^2$ squared atomic displacements per atom radius was limited in the actual experiments but, taking into account the typical generalized distance to the nearest pocket and the high dimensionality, the number of pockets within the $0.5r_o^2$ radius could be large.

Referring again to figure 1, the four graphs designated Serie1 to Serie4 represent the evolutions of the sum of squared displacements for four different PECT experiments, all starting from the same glass structure of 240 atoms in a computational cell of dimensions $4.90r_o$ by $6.79r_o$ by $4.80r_o$ with periodic boundaries; the density was thus $1.50 \text{ atom}/r_o^3$. The *pseudo-velocity* was in all cases such that the sum of squared atomic displacements per computational step was $0.004r_o^2$. The glass was quenched from the liquid state to an energy of $E_{\text{pot}} = -1689\epsilon$ using the MD technique. Serie1 and Serie4 were then at $E_{\text{pot}} = -1688\epsilon$, and Serie2 and Serie3 were at $E_{\text{pot}} = -1675\epsilon$.

Serie1 has main plateaus at $8.2r_o^2$ and $13.0r_o^2$; Serie2 at $11.7r_o^2$; Serie3 at $13.9r_o^2$ and $15.3r_o^2$; and Serie4 at $5.1r_o^2$, $68.9r_o^2$, $73.7r_o^2$, and $82.5r_o^2$; they all have additional less developed plateaus.

The states (pockets) corresponding to all Serie1–3 plateaus and to the lowest Serie4 plateau are all glassy, and the states corresponding to the highest three Serie4 plateaus (after 175 thousand cycles) are all crystalline.

The vertical variations within the plateaus represent the widths of the associated pockets and reflect the height of the energy level above the minimum energy of the pockets. The glassy Serie1 and Serie4 pockets are quite narrow, as the energy is quite close to the minimum; the Serie2 and Serie3 pockets are somewhat wider due to the higher energy. The crystalline Serie4 pockets are quite wide, because the minimum energy for a crystalline pocket is lower than for the glassy pocket. Note that the final Serie1 pocket is wider than the initial pocket, presumably because the minimum energy in that glassy pocket is also slightly lower.

The width of a pocket reflects the probability of the pocket ‘capturing’ the state point, and is thus associated with the entropy contribution of each pocket to its corresponding state. At very low energies, which in a thermodynamic perspective would correspond to low

Table 1. In the table, each plateau is identified with the Serie1 to Serie4 designation (abbreviated S1 to S4) followed by the plateau level. The table contains the distances as sums of squared displacements in units of r_o^2 between states from each combination of plateaus. Note how states, which from figure 1 might appear to be close, such as S1/13.0 and S3/13.9, are actually well apart.

Units r_o^2	S1/13.0	S2/11.7	S3/13.9	S3/15.3	S4/5.1	S4/82.5
S1/8.2	8.2	14.4	11.9	13.5	6.3	77.7
S1/13.0		22.8	21.3	22.5	14.6	90.2
S2/11.7			19.8	21.6	12.7	86.8
S3/13.9				4.4	8.6	77.4
S3/15.3					11.3	81.0
S4/5.1						74.9

temperatures, the entropy of the glass state is not necessarily higher than that of the crystal (see [17]) and certainly crystal is the stable phase compared to glass. This accounts for the fact that no transitions from crystalline to glassy pockets were observed.

The pockets associated with different plateaus are not necessarily close to one another. This also applies for pairs of plateaus lying at approximately the same level (see table 1).

4. Discussion and conclusion

When summarizing the results of this study, it should be emphasized that the PECT method primarily employed here is particularly suited to determining whether or not there exist tubes, that is to say, trajectories of constant potential energy linking pockets of preferred occupation of the system. Tubes are, of course, not the only interesting features of the potential energy landscape: two others, namely pockets themselves and saddle points, are naturally also important. Pockets are, as discussed below, also detected by PECT, whereas PECT is not well suited for detecting saddle points. The advantage of PECT over MD when investigating the potential energy landscape is primarily that, during the evolution of the system, in PECT there will not be conversions of potential energy to kinetic energy. These frequently occur in MD investigations of non-equilibrium systems, and they tend to bring the system into the equilibrium state, and far away from the conditions in which it is desired to explore the system.

A central result of this study is confirmation of the existence of pockets. The novel findings are the facts: that many of these are linked by (constant potential energy) tubes, some of which link glassy and crystalline pockets; that the distances between pockets can be remarkably short; and finally that the glassy and crystalline pockets are interspersed. They are thus not necessarily mutually removed from one another, as could be inferred from the above-mentioned energy landscape diagrams. We believe that these results shed new light on certain aspects of the glassy state, and especially on relaxation as well as devitrification—the transition from glass to crystal. The presence of tubes can be an important factor in allowing devitrification and/or relaxation to take place at temperatures well below the glass transition temperature. It is well known that window glass, for instance, can devitrify over centuries, and for obvious reasons it is difficult to study such processes experimentally.

Crystallization of the Lennard-Jones system has been found both in the present and in other studies to be relatively easy, and production of a stable glass contrariwise is relatively difficult. This has led other investigators to employ slightly modified Lennard-Jones potentials, including many-body terms suppressing crystallization [8, 16]. However, as demonstrated here, it is possible to create stable glasses with the unmodified Lennard-Jones potential according to the described procedure. It should be noted that the density of these glasses is rather high.

The results of the present study, especially the observation of adjacent crystalline and non-crystalline pockets connected with constant potential energy trajectories, is consistent with the ease of crystallization of Lennard-Jones matter.

Furthermore, the results are consistent with those of our previous study of the same 240-atom pseudo-infinite Lennard-Jones system [10], and verify some concepts presented there. In that study, we presented sections of potential energy around local potential energy minima (pockets) along eigenvectors of the dynamical matrix. In the case of a glass, we found remarkably ‘flat’ bottoms of the sections associated with the lowest-frequency eigenmodes, in contrast to the traditional parabolic behaviour. We indicated that this could be a section along the axial direction of what we now call a tube, which eventually curves away, leading to a sharp rise in potential energy, and we have now demonstrated the existence of these tubes. This behaviour was clearly seen in several eigenmodes, which of course correspond to mutually orthogonal directions.

Classical nucleation theory for non-crystalline systems held at constant temperature assumes a free-energy barrier for the onset of crystallization. Both in this study and in earlier work [18], behaviour consistent with classical nucleation theory has been observed, despite the MD technique having been used, with its acknowledged limitations. It should be noted that in MD the total (or internal) energy of the system (that is, the sum of the potential energy and the kinetic energy) is conserved. However, if a nucleation event takes place within a volume that is small compared to the computational cell, then the rest of the system can serve as an external heat reservoir at constant temperature, as is implicitly assumed in classical nucleation theory. Also, in any case, the total available kinetic energy could be adequate to bring the system over a barrier, even in circumstances when there would be a substantial reduction of the kinetic energy during the transition.

The free-energy barrier involves both total energy, usually designated U , and the product of temperature (T) and entropy (S). The Helmholtz free energy ($F = U - TS$) is appropriate for the present constant-volume experiments; the Gibbs free energy, which is appropriate for unconfined systems, would further include a product of volume and pressure. At least in elementary presentations of nucleation theory, it is customary to exemplify the free-energy barrier as a barrier in potential energy, and it is indeed fairly intuitive that such potential energy barriers should exist between relatively stable states such as those of the supercooled liquid and the crystal. The present study indicates that the free-energy barrier could be one mainly of entropy, but does not, of course, exclude the possibility of effective potential energy barrier scaling during a nucleation process. The relative probabilities of the two mechanisms remain to be investigated.

References

- [1] Anderson P W 1995 *Proc. Natl Acad. Sci. USA* **92** 6653
- [2] Binder K, Baschnagel J, Kob W and Paul W 1999 *Phys. World* **12** 54
- [3] Samios J and Durov V A 2004 *Novel Approaches to the Structure and Dynamics of Liquids: Experiments, Theories, and Simulations* (Amsterdam: Kluwer)
- [4] Debenedetti P G and Stillinger F H 2001 *Nature* **410** 259
- [5] Sastry S, Debenedetti P G and Stillinger F H 1998 *Nature* **393** 554
- [6] Angell C A 1995 *Proc. Natl Acad. Sci. USA* **92** 6675
- [7] Wolynes P G and Onuchic J N 1995 *Science* **267** 1619
- [8] Angelani L, Ruocco G, Sampoli M and Sciortino F 2003 *J. Chem. Phys.* **119** 2120
- [9] Keyes T 1997 *J. Phys. Chem. A* **101** 2921
- [10] Cotterill R M J and Madsen J U 1986 *Phys. Rev. B* **33** 262
- [11] Metropolis N, Rosenbluth A W, Rosenbluth M N, Teller A H and Teller E 1953 *J. Chem. Phys.* **21** 1087
- [12] Hockney R W and Eastwood J W 1981 *Computer Simulation Using Particles* (New York: McGraw-Hill)

-
- [13] Verlet L 1967 *Phys. Rev.* **159** 98
 - [14] Cotterill R M J and Madsen J U 1990 *Characterising Complex Systems* ed H Bohr (Singapore: World Scientific) p 177
 - [15] Pryde J A 1966 *The Liquid State* (London: Hutchinson University Library)
 - [16] Di Leonardo R, Angelani L, Parise G and Ruocco G 2000 *Phys. Rev. Lett.* **84** 6054
 - [17] Madsen J U and Cotterill R M J 1981 *Phys. Lett. A* **83** 219
 - [18] Swope W C and Andersen H C 1990 *Phys. Rev. B* **41** 7042