Search for tunnelling centres in Lennard-Jones clusters

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We report on numerical procedures for, and preliminary results on the search for, tunnelling centres in Lennard-Jones clusters, seen as simple model systems of glasses. Several of the double-well potentials identified are good candidates to give rise to two-level systems. The role of boundary effects, and the application of the semiclassical WKB approximation in multidimensional spaces for the calculation of the ground state splitting are discussed.

I. INTRODUCTION

The thermal properties of amorphous solids at low temperature \( (T \approx 0.1 \div 10 \text{ K}) \) are qualitatively different from those of the corresponding crystals (Zeller and Pohl 1971). The observed temperature dependence of the heat capacity \( (C_v(T) \propto T^3) \) and of the thermal conductivity \( (\kappa(T) \propto T^{2/3}) \) of crystalline solids at temperatures much lower than the Debye temperature is well understood in terms of a density of vibrational states (which is the only factor determining \( C_v \)) \( \rho(\omega) \propto \omega^2 \), and by assuming that phonons carry heat in the same way as particles do in a gas. On the contrary, in a large variety of amorphous or disordered solids (covalent glasses, polymers, disordered crystals, spin glasses, etc) the corresponding observed behaviour is \( C_v(T) \propto T \), \( \kappa(T) \propto T^2 \); moreover, the heat capacity is 2-3 orders of magnitude larger than in crystals, while the contrary is true for the thermal conductivity. This behaviour is so widespread and independent on structural details that any reliable explanation or model should be based on very general properties of the disordered state.

The idea that since 1972 has gained more-or-less general consensus is the so-called model of the Two-Level Systems (TLS) (Anderson, Halperin and Varma 1972; Phillips 1972, 1987). In the disordered structure the local mass distribution is rather inhomogeneous and may produce holes of different sizes; in this situation it is possible that atoms, or groups of atoms, may have two (or more) equilibrium positions available, separated by energy barriers. The energy separation between the two lowest levels in the two-well system depends on the energy mismatch of the two minima and on the tunnelling splitting. If the minima are nearly at the same energy, it is the tunnelling splitting that determines the energy difference between the two lowest levels, and depending on the potential shape this splitting can be very small. This situation produces additional possibilities of low-energy thermal excitation with respect to crystals (and so \( C_v \) increases) but, on the other hand, low-frequency, heat-carrying phonons will be scattered by the TLS by either direct absorption or relaxational phenomena (and thus \( \kappa \) decreases).

Since both the mismatch and the tunnelling splitting depend on the local details of the disordered structure, it is reasonable to assume (Anderson et al 1972, Phillips 1972) that the distribution of TLS excitations is constant, at least for small splitting, resulting in a linear \( C_v(T) \) at low \( T \) (for a derivation of both \( C_v(T) \) and \( \kappa(T) \) see the review paper by Phillips (1987)).

The microscopic nature of the TLS can only be investigated numerically because disorder prevents analytical solutions of the vibrational problem. The efforts produced so far in this direction (see for example Weber and Stillinger 1985, and references therein; Heuer and Silbey 1993, 1997, and references therein; Demichelis, Ruocco and Viliani 1997) have employed molecular dynamics simulations on samples containing from the order of 100 to the order of 1000 atoms, with periodic boundary conditions imposed. This approach has advantages and disadvantages.

One advantage is that molecular dynamics can nowadays handle rather large systems, and the use of periodic boundary conditions eliminates surface effects. One disadvantage is that in any case 1000 atoms means a simulation box having a size of 10 atoms, and with these dimensions periodic boundary conditions can introduce spurious periodicity and correlations. Moreover (and maybe more important), finding the configurations corresponding to two potential energy minima is not enough to calculate the splitting or even to decide whether the pair is a suitable candidate to be a TLS, because the splitting depends on the shape of the potential barrier that separates the minima; for example, in the case of a single particle of mass \( m \) moving along a 1-dimensional trajectory, the semiclassical WKB approximation (Froman and Froman 1965; Landau and Lifchitz 1967) gives the following expression for the tunnelling splitting in a symmetric two-well potential \( V(x) \):

\[
\delta = \frac{\hbar \omega}{\pi} D^{1/2}
\]  

(1)
Here the transmission coefficient $D$ is given by

$$D = \frac{1}{1 + \exp(2S_0)},$$

and $S_0$ is the action integral:

$$S_0 = \frac{1}{\hbar} \int_{-a}^{a} \sqrt{2m(V(x) - E_0)} dx.$$

In the last formula $E_0$ is the particle energy in one well, $a$ and $-a$ are the classical turning points, and $\omega$ is the oscillation frequency in one well.

Equation (1) provides an explicit expression for the splitting in terms of the potential and as such is very convenient for computations, but its extension to multidimensional configuration spaces is not obvious in general. The difficulty stems from the fact that in multidimensional spaces (infinitely) many different paths contribute to the dynamics, each one yielding a probability amplitude $p_i$ for the tunnelling event whose total probability is then given by

$$P = |\sum_i p_i|^2.$$

One should actually use the formalism of Feynman path integrals (Feynman and Hibbs 1965; Gillan 1987; Voth, Chandler and Miller 1989; Ranfagni, Mugnai, Moretti and Cetica 1990; Schenter, Messina and Garret 1993) to evaluate the probability. However in many circumstances the main contribution to the probability comes from the least action path (Ranfagni and Viliani 1976; Ranfagni, Viliani, Cetica and Molesini 1977; Ranfagni et al 1990), and the multidimensional problem turns into a 1-dimensional one. The conditions under which this simplification can be made are discussed at length by Ranfagni et al (1990); basically they depend on the possibility that, and on the extent to which, the wave equation can be (approximately) separated into different equations, each involving a single independent variable (Schiff 1968).

The accomplishment of this approximate separation is also important in the classical case, where the barrier is overcome by thermal activation. The one-dimensional transition rate is formally very similar to equation (1):

$$k = \frac{\omega_0}{2\pi} \exp\left(-\frac{E_b}{k_B T}\right)$$

where $E_b$ is the barrier energy and $\omega_0$ the vibration frequency in the potential well. In many dimensions, and under some assumptions concerning the existence of thermodynamic equilibrium and the absence of back- crossings, it is found that the degrees of freedom other than the single considered path introduce entropy barriers, and that the effect of the latter can be accounted for by the following substitution in the pre- exponential factor (Rice 1958; Glyde 1967; Hanggi 1986):

$$\omega_0 \rightarrow \Pi_i \omega_i^M \Pi'_j \omega_j^S.$$  

Here the $\omega^M$’s and the $\omega^S$’s are the vibrational eigenfrequencies at the minimum and at the saddle point respectively, and the prime indicates that the negative frequency at the saddle point has to be omitted from the product. We shall assume that this substitution takes proper account of entropic effects also in the tunnelling case, and shall use the WKB formula (1) along the least action path to evaluate the splitting.

From the above considerations, it appears that knowledge of the saddle points (or ”transition states” in the chemist’s jargon) is of paramount importance for the study of tunnelling or diffusion problems because a good initial guess for the least action path is one that connects the minima through the saddle point itself. The methods of molecular dynamics alone are not especially designed for their identification: finding the minima is relatively easy by means of a variety of efficient numerical methods (repeated quenching and/or viscous forces in molecular dynamics, conjugate gradients, simulated annealing, and so on), but the saddle points are much harder. As a consequence of this state of affairs, previous works were able to identify only a limited number of possible TLS.

The approach of the present paper is complementary to the traditional ones in two respects.

First of all, we consider free Ar clusters rather than systems with boundary conditions. We are aware that surface effects will be serious, but we think it is very important to have information regarding both surface-free and correlation-free systems. Furthermore, Ar clusters are interesting on their own and by increasing the number of the constituent atoms it should in principle be possible to make the cluster properties coalesce with those of the bulky solid (Buck
and Krohne 1994). So our plan is to study the evolution of tunnelling-related properties as the number of atoms in the cluster increases.

Second, for the reasons listed above, our search is primarily directed to finding large numbers of saddle points in addition to minima. As mentioned, the methods devised by Weber and Stillinger (1985), Heuer and Silbey (1993, 1997) and Demichelis et al (1997) are not specific to this task. So we will look for all kinds of stationary points on the potential hypersurface by finding the zeros of the gradient. As will be discussed in the next section, in the case of the Lennard-Jones potential this requires the solution of a non-linear set of equations. Alternative methods for systematic saddle point search are described in the review paper of Berry (1993), where numerous references to work on minima are also listed.

II. NUMERICAL PROCEDURES

A. Stationary configurations of Ar\(_N\) clusters

We consider Ar\(_N\) clusters in the range \(N = 6 \div 42\); the atoms interact via a Lennard-Jones pair potential and the total potential energy is

\[
V(x_1, ..., x_{3N}) = \sum_{ij} V_{ij} = 4\varepsilon \sum_{i>j} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]
\]

where \(\sigma = 3.405\rho A\) and \(\varepsilon/K_B = 125.2K\) are the parameter values suitable for argon.

In a free non-rigid body like a Lennard-Jones cluster there are problems with rotations. In fact, in a rigid body these (like translations) are decoupled from the vibrational degrees of freedom, and correspond to zero-frequency eigenvalues, but this is no longer true for a deformable body, because the Coriolis and centrifugal forces couple vibrations and rotations. The problem is negligible in the majority of minima because in these configurations the restoring forces are in general strong enough to quench the coupling, but it becomes severe in the saddle points: these are unstable configurations and the coupling to rotations can produce very large effects. On the other hand, if we have in mind clusters of atoms which are part of a solid, i.e. the set of atoms that undergo the largest displacements when a tunnelling transition occurs, then these clusters certainly are not allowed to rotate or translate. For this reason we have decided to eliminate 6 degrees of freedom by fixing the position of atom 1 in the origin \((x_1 = y_1 = z_1 = 0)\), while atom 2 is bound to the \(x\) axis \((y_2 = z_2 = 0)\) and atom 3 can move on the \(xy\) plane \((z_3 = 0)\). These conditions were used also by Hoare (1979) and do not influence the potential energy of the configurations, which depends solely on the mutual distances of the atoms, but definitely affect the vibrational frequencies: clusters that have the same shape (i.e. are placed in the same minimum of the configuration space) but different atoms with fixed coordinates, have also different vibrational eigenvalues. This effect becomes less and less important as \(N\) increases and, on the other hand, since the fixed coordinates are chosen randomly we do not expect that our results may be biased in any systematic way.

Let us now summarize the procedure by which we find the stationary points of Eq. (2). Writing down the partial derivatives of \(V\) is tedious but straightforward; once they are known, the non-linear set of equations:

\[
\frac{\partial V(x_1, ..., x_{3N})}{\partial x_i} = 0, \quad i = 1, ..., 3N - 6
\]

is solved by using the Newton-Raphson (NR) iterative procedure (Press, Flannery, Teukolsky and Vetterling 1986). A random configuration of atoms is created and taken as starting point for the first iteration step; the calculation requires also knowledge of the second partial derivatives. With a given initial random configuration, the procedure may or may not converge to a solution. If convergence is not achieved in a given number of iterations (in our case 5000), another initial configuration is created. When the procedure converges (typically in our case after a few thousand steps) the Hessian \(\mathbf{H}\) is diagonalized in the final configuration and the number of negative eigenvalues gives the order of the saddle point (zero-order corresponds to a minimum, while maxima are not possible for this potential). The configuration, its energy and the Hessian eigenvalues are stored and the procedure is started again with a new random configuration. In the case \(N <= 13\) the program has been run until no new stationary point was found for a few ten hours of a 160 MHz Pentium cpu time, or for a few hours of a Digital Alpha 2100 cpu time.

As noted in previous works (Hoare 1979, Weber and Stillinger 1985) the saddle points that matter really are the first order ones, because between two neighbouring minima in configuration space there always is at least a first-order saddle point, and saddles of higher order lie on average at higher energy. So, especially for larger clusters we limited the search to first-order saddles (this actually means that only first order saddle points and minima were
stored, because there is no known way of preferentially ending in either of these kinds of configurations with the NR procedure). The number of saddle points is not known but is certainly extremely large and grows enormously with \( N \). Thus for \( N > 13 \) we made no attempt at completeness and limited ourselves to collecting some thousand first-order saddles of different energy for each \( N \).

The direct search for first-order saddles, however, works well only for \( N < 7 \) because for larger clusters the number of higher-order (and higher energy) stationary points is so huge that the NR procedure very often ends up in one of them. This happens also because the initial random cluster usually has a very high potential energy, i.e. it is very distant from any of the desired configurations, and this is a well-known wrong start for NR. In order to solve this problem, before starting the NR procedure the initial random configuration is relaxed towards a minimum either by the conjugate gradient method or by a molecular dynamics calculation including a viscous force. Both algorithms are very efficient in reaching the vicinity of a minimum, that we label \( M_1 \). Once such approximate minimum is found, we repeatedly diagonalize the Hessian and move upwards in energy in the direction of the eigenvector corresponding to the minimum eigenvalue: this path leads us towards the saddle point. When the maximum potential energy along this path is reached, the system is in general sufficiently near the saddle point that the NR procedure locates it with great precision in a small number of iterations. In the majority of cases this approach singles out a first order saddle, but in a limited number of instances it may end up in a higher order one, in a minimum, or even fail to converge.

**B. Least action path**

Once the saddle point is located with precision, in order to calculate the classical action integral we move the representative point away from the saddle in the direction of the negative eigenvalue, and let it evolve either by molecular dynamics plus viscous force, or following at each step the direction of minimum eigenvalue. This is done from both sides of the saddle, and in this way we identify the two minima \( M_2 \) and \( M_3 \) that are connected by the saddle in question. It is possible that neither \( M_2 \) nor \( M_3 \) coincide with \( M_1 \).

The resulting path is often rather close to the least action path and in some cases further minimization of the action integral according to the method described by Demichelis et al (1997) produces only minor changes. In other cases, the straight path from one minimum to the other is closer to the least action path.

**III. PRELIMINARY NUMERICAL RESULTS**

**A. Stationary configurations**

In Fig. 1 we report a semilogarithmic plot of the number of minima \( g(N) \) as a function of the number of atoms up to \( N = 13 \). If one disregards the cases \( N = 2 \div 6 \) which have only 1 or 2 minima each and cannot be taken into account for statistical considerations, \( g(n) \) grows exponentially

\[
g(N) = A \exp(bN), \quad N > 6
\]  

with \( A = (3.1 \pm 0.8) \times 10^{-3} \) and \( b = 0.99 \pm 0.03 \). This is a good check that the large majority of minima have been found since \( g \) determines the extension of the configuration space where there exist stable states, \( \Gamma \), and this in turn determines the entropy of the system according to the relationship \( S = K g \ln \Gamma \): an exponential \( g \) thus produces an extensive entropy. The more-than-exponential growth found by Hoare (1979) is due to his consideration of the small clusters \( (N < 7) \) in the fitting procedure.

From Eq. (4) we obtain \( g(15) \approx 10,000 \) and \( g(18) \approx 200,000 \), so that, as mentioned, we didn’t even try to determine all minima for \( N > 13 \), but limited ourselves to finding some thousand of them for clusters of increasing size. For \( N = 15, 18 \) this was done in two different ways: (i) starting from a random initial configuration; (ii) relaxing the clusters from the first-order saddle points found in the previous step. The distributions of minima energies obtained in these two cases for \( N = 15 \) are reported in Figs. (2a) and (2b) respectively; as can be seen the distributions are practically identical, indicating that we introduce no special bias by starting the search for tunneling centres from the first-order saddle points. Similar results are obtained for \( N = 18 \). This is a very important point because this approach greatly facilitates the identification of the centres with double-well potentials (DWP) and their characterisation.

Fig. 3 shows the distribution in energy of 16,875 minima and 9,176 first-order saddle points for \( N = 29 \). The distributions look very similar, with the obvious difference that the saddles are on average at higher energy.
B. Double-well potentials

The pairs of minima separated by a first order saddle have been identified with the procedure described in the previous section. The results are summarized in Table I, where we report the total number of DWP identified, the number of symmetric \((\Delta = 0)\) and of slightly asymmetric \((0 < \Delta < 1)\) DWP, and the number of DWP that have both small asymmetry and small tunnelling splitting \((10^{-13} < \delta < 1)\). The DWP in the last column are the suitable ones to produce two-level systems; their number relative to the total DWP ranges from \(0.9 \times 10^{-3}\) for \(N = 13\), to \(3.8 \times 10^{-3}\) for \(N = 42\), and apparently grows with \(N\), though the numbers are too small to extract reliable trends. It should also be noted that the values in the last column of Table I were obtained by taking \(E_0 = \frac{1}{2} \hbar \omega_0\) in the calculation of the action integral, where \(\omega_0\) is the minimum eigenvalue of the dynamical matrix in the minimum. This procedure is right only if the direction of the least action path is the same as that of the lowest-energy eigenvector, and in general it overestimates the action integral. Therefore, these values are to be considered as lower bounds.

As regards surface effects, we find that the vast majority of the symmetric \((\Delta = 0)\) DWP involve large surface motions as indicated by the huge action integrals and the long euclidean distance; as can be seen from Table I their relative number decreases steadily with increasing \(N\) as it should; however, the abrupt fall for \(N = 29, 42\) is probably due to biased search.

Another interesting characteristic of the DWP is the so-called participation number, defined as

\[
N = \sum_i d_i^2 / d_M^2 = d^2 / d_M^2
\]

where \(d\) is the euclidean distance between the two minima in configuration space and \(d_M\) is the displacement of the atom that moves most. This quantity gives an indication of how many atoms move significantly when the system passes from one minimum to the other, and the results of its calculation in the cases \(N = 18, 29, 42\) are reported in Fig. 4 for all DWP, and in Fig. 5 for selected DWP with asymmetry \(0 < \Delta < 1\), i.e. the possible TLS. It is interesting to note that, in both figures, the maximum number of occurrences seems to have nearly reached saturation at \(N = 42\). Moreover, there seem to be no large qualitative differences between the corresponding distributions of Fig. 4 and of Fig. 5: it appears that the participation number does not depend very much on the asymmetry. A similar analysis based on the value of the barrier height gives analogous results, in the sense that DWP that are candidates to be TLS have an \(N\) distribution not qualitatively different from the whole assembly of DWP. The present results, yielding an average value of about 15 participating atoms, are in general agreement with previous values found with periodic boundary conditions (Heuer and Silbey 1993).

IV. CONCLUSIONS AND PERSPECTIVES

In this paper we have described a set of algorithms that are very efficient in finding minima and saddle points of multidimensional (potential-energy) surfaces. In particular, we have studied Lennard-Jones clusters containing up to 42 atoms and were able to find many thousand minima and first-order saddle points; among these we looked for possible two-level-systems and found several probable candidates in clusters with more than 6 atoms (see Table I), i.e. pairs of minima with total splitting in the ground state smaller than \(\approx 1\) \(K\).

To evaluate the ground state splitting one must consider both the asymmetry of the pair of minima, \(\Delta\), and the tunnelling splitting, \(\delta\). While \(\Delta\) is easily found, the calculation of the tunnelling splitting requires that the Schroedinger equation is solved in a way or another. We chose the semiclassical WKB approach; this has the advantage of providing an explicit expression for \(\delta\), but at the same time its application to multidimensional problems requires great caution (see previous discussion).

Another point that deserves further consideration is the role of boundary conditions in the simulation of the properties of small systems. Clusters suffer from surface effects, while periodic boundary conditions are likely to introduce spurious correlations. This may explain the large difference in the number of minima, DWP and candidate TLS between this work and the paper of Heuer and Silbey (1993).

Since for large enough systems boundary conditions must become irrelevant, it would be worth to check if for periodic systems the rate of growth of, for example, the total number of minima tends to approach the behaviour of Fig. 1; for this, it would be very interesting to compute (possibly) all the minima of periodic systems.

Finally, we plan to apply the present analysis to potentials suitable to experimentally available glasses.

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FIGURE CAPTIONS

Fig. 1. Semilogarithmic plot of the number of minima, \( g \), as a function of the number of atoms. The best fit gives \( g(N) \propto \exp(N) \) (see text).

Fig. 2. Energy distribution of minima for \( N = 13 \) obtained starting from: (a) an initial random configuration, (b) first-order saddle points.

Fig. 3. Energy distribution of 16,785 minima (open circles) and 9,175 first-order saddle points (full squares) for \( N = 29 \).

Fig. 4. Participation number of all DWP for \( N = 18 \) (a), \( N = 29 \) (b), \( N = 42 \) (c).

Fig. 5. Same as Fig. 4, but only for DWP with asymmetry \( 0 < \Delta < 1 \).  

TABLE I. Number of found DWP for \( N = 6 \div 42 \).
(a): DWP with \( \Delta = 0 \); (b): \( 10^{-4} < \Delta < 1 \); (c): Same as (b) but with barrier higher than minimum vibrational eigenvalue and \( 10^{-15} < \delta < 1 \).

| N  | Total No. of DWP | (a) | (b) | (c) |
|----|------------------|-----|-----|-----|
| 6  | 6                | 5   | 0   | 0   |
| 8  | 61               | 26  | 0   | 0   |
| 9  | 181              | 58  | 4   | 0   |
| 10 | 414              | 113 | 2   | 0   |
| 13 | 3416             | 588 | 41  | 3   |
| 15 | 4652             | 257 | 43  | 4   |
| 18 | 11412            | 1082| 150 | 19  |
| 29 | 9176             | 23  | 63  | 18  |
| 42 | 2878             | 12  | 31  | 11  |
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