MINIMUM-ENERGY CONFIGURATIONS OF ATOMIC CLUSTERS:
NEW RESULTS OBTAINED BY SIMULATED ANNEALING

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The classical potential energy surfaces for clusters of up to 25 atoms, interacting under two-body Lennard-Jones forces, have been searched for global minima using the simulated annealing method. This is a Monte Carlo technique which simulates a process of slow cooling in order to avoid trapping in local minima. Two recently reported improvements over older work have been reproduced and a new minimum for 24 atoms has been found. The simulated annealing procedure yields low-lying energy states whose distribution depends on the cooling rate.

1. Introduction

Calculations of molecular conformations, based on energy minimisation, are often faced with the problem of multiple minima. Local minima on the potential energy surface can be found efficiently with current search techniques, most of which are based on a gradient method [1]. The potential energy surface can be partitioned in a number of catchment regions, each one associated with a local minimum All points in the same catchment region lead to the same minimum by application of a gradient optimiser. When the number of degrees of freedom gets larger, the dimensionality of the potential energy surface increases and it is often observed that the number of local minima seems to grow exponentially with the problem size. In order to find the global minimum two approaches are possible. The first one consists of generating a large number of random initial configurations and applying a local optimiser to each one of these. This method becomes too time consuming as the number of degrees of freedom increases. Moreover, in order to have a sufficiently high probability of finding the global minimum, a rather large number of initial guesses have to be made, and even then minima in narrow catchment regions may be missed [2]. Alternatively, one appeals to physical intuition, usually under the form of a set of growth rules, to generate configurations which are

likely to lead to the global minimum, but this procedure tends to miss low-symmetry solutions. Obviously, energy minimisation in the presence of several minima is an extremely complicated problem. The complexity of this problem is remarkable, when one realises that nature seems to be able to solve it very efficiently. Each time a crystal is grown or a molecule synthesised, the energy minimisation is solved by what could be called an analog computation. It is this observation which led Kirkpatrick et al. [3] to develop the simulated annealing method which will be described in section 2.

The structure and stability of small aggregates of atoms is an active field of research, both theoretically and experimentally [4]. These objects, intermediate between atoms and solids, have peculiar properties, such as the predominance of fivefold symmetry, photoyield enhancement, Coulomb explosions, magic numbers, etc. Apart from their intrinsic interest, cluster studies are important in nucleation theory, catalysis and astrophysics. The existence of magic numbers, corresponding to extremely stable sphere packings, was first established for Xe clusters [5]. It was observed that clusters consisting of $N = 13, 19, 23, 25, ...$ atoms showed up more prominently in the mass spectrum than neighbouring cluster sizes.

Computer modelling has usually assumed that the interaction between rare-gas atoms could be

described by a two-body Lennard-Jones potential. Three-body interactions have been considered [6], but do not appear to affect the ground-state geometry, although their influence on the total energy cannot be neglected. Before observation in a time-of-flight mass spectrometer the clusters are ionised by a pulsed electron beam and it could therefore be that the magic numbers reflect the stability of positively charged clusters rather than neutral ones. This possibility has been investigated in several studies (see ref. [7] and references therein).

Extensive calculations of the morphology and statistical properties of rare-gas clusters have been performed by Hoare and co-workers [8–12]. Originally, this work focused on polyhedral growth sequences [8–10], and ref. [8] contains a list of minimum energy configurations within the different growth schemes, which has been the basis for comparison with later work. Later an almost exhaustive search of the potential energy surface was made for the smaller clusters ($N \leqslant 13$) [11,12]. The possibility of a polyicosahedral growth scheme was investigated by Farges et al. [13–15]. This model of interpenetrating icosahedra led to the prediction of a new structure consisting of 23 atoms [14] with an energy lower than the configuration found by Hoare and Pal [8]. In the course of a quantum Monte Carlo calculation, Freeman and Doll [16] discovered a new (classical) 17-particle structure, lower in energy than the one reported in ref. [8]. The energy difference is marginal and no particularly stable structure results.

In summary, in the size range considered in this Letter ($4 \leqslant N \leqslant 25$), the best minimum-energy configurations, known so far, are those obtained by Hoare and Pal [8], except for the cases $N=23$ [14] and $N=17$ [16]. It should also be pointed out that the magic number $N=25$, observed by Echt et al. [5], cannot be explained in terms of the stability of a neutral cluster. However, calculations for charged clusters predict that the formation of a molecular dimer ion produces a very stable 25-atom structure [7]. The present work is the first in which a thorough search of the potential energy surface of larger clusters ($N>13$) has been made. This has led to several new local minima, and in one case ($N=24$) a structure with an energy lower than that given by other authors was found. In all other cases (including $N=17$ and 23) the previous best results were reproduced. It is

likely that these structures correspond to global minima, although this has not been proved.

2. Method and results

Originally formulated for discrete optimisation problems, the simulated annealing method [3] is easily extended to deal with continuous ones as well [17–19], and it is this version that will be briefly described here (an alternative implementation using Langevin molecular dynamics has been proposed by Biswas and Hamann [20]). Structural optimisation involves the minimisation of the potential energy $E(r_1, ..., r_N)$, which is a function of the positions of the particles r_i, $i=1, ... N$. The simulated annealing method uses the Metropolis prescription [21] to decide whether or not to accept a random step Δr_i, $i=1, ..., N$. If the associated energy change

$$\Delta E = E(r_1, ..., r_i + \Delta r_i, ..., r_N)$$
$$- E(r_1, ..., r_i, ..., r_N) \tag{1}$$

is negative or zero, the step is accepted, otherwise it is accepted with a probability

$$p = \exp(-\Delta E/T), \tag{2}$$

where T is the temperature (in reduced units). In this way potential energy barriers can be surmounted (at sufficiently high temperatures), i.e. the algorithm is not confined to a single catchment region. In the process of annealing, the system is started in a random initial configuration at a sufficiently high temperature. Several series of steps are attempted and then the temperature is reduced by a certain factor χ_T (typically 0.75–0.9). This process is repeated until no further improvements have been made over a number of iterations.

In the present work the initial temperature was taken from a short preliminary simulation and the step length adjusted so that between 25% and 50% of the steps were accepted. The algorithm was found to give a larger fraction of low-lying states when more steps were attempted at lower temperatures and to this end the number of steps per particle was taken to be proportional to $1 - \log T$, a choice that performed satisfactorily in practice. The factor χ_T by which the temperature was reduced was 0.9. As soon

as the energy dropped below a certain value (also taken from a preliminary simulation) a gradient optimiser was called. Finally the whole process was repeated a number of times for each cluster size N, to increase the probability of detecting the global minimum. It is important to note that these calculations are not simulations of the freezing of clusters. To this end, the cooling, characterised by χ_T and the number of attempted steps, would have to proceed even more slowly. The freezing process could be monitored by looking at the specific heat [3,18], defined as

$$C(T) = T^{-2}(\langle E^2 \rangle - \langle E \rangle^2) , \qquad (3)$$

where the angular brackets denote an average over all attempted steps. A large value of C signals a change in the state of order of the system and can be used as an indication that freezing has begun. In the author's experience, it is computationally more efficient (especially for the larger clusters) to use several runs with a relatively fast cooling as described above (in conjunction with a gradient optimiser) rather than perform a true Monte Carlo simulation of freezing, even if one is only interested in the global minimum. An additional advantage of using a fairly fast cooling rate is that the algorithm will find low-lying local minima as well. In many physical problems one is not merely interested in the ground-state configuration but also in nearby excited states. By fixing a certain cooling rate and a threshold value, below which a local minimisation is performed, one selects in fact an energy range in which the algorithm will search for minima. A final feature of the present calculations is that for the smaller cluster sizes ($4 \leqslant N \leqslant 13$) one of the atoms was kept in a fixed central position, to eliminate translational degrees of freedom, and for the larger ones ($14 \leqslant N \leqslant 25$) 13 atoms were kept in a central icosahedral environment, during the annealing part of the calculation. The latter calculations were checked against simulations where all atoms (except the central one) were allowed to move and turned out to be in full agreement.

This algorithm has been used to search the potential energy surfaces of atomic clusters held together by two-body forces derived from a Lennard-Jones potential

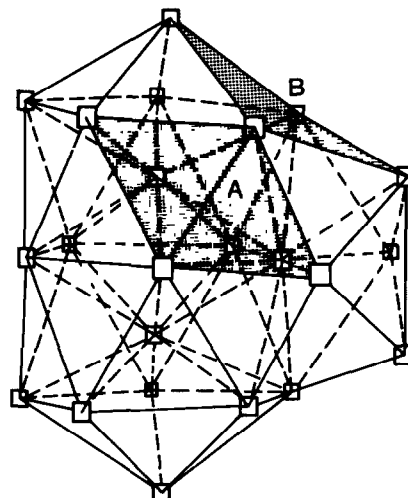$$V(r) = r^{-12} - 2r^{-6} . \qquad (4)$$

Fig. 1. Twenty-three-atom cluster consisting of three interpenetrating icosahedra. The structure contains two types of fourfold hollow sites, two of which are shaded and labelled A and B.

This potential has a minimum energy of -1 at a distance $r=1$, which determines the energy and length units that will be used subsequently. In the size range $4 \leqslant N \leqslant 25$ only one new minimum has been found that improves the previous best result ($N=24$). It turns out that the corresponding structure is an intermediate step between two known growth schemes. This new minimum and a local one very close in energy will be discussed subsequently, as well as some properties of the freezing process. Several new low-lying local minima have been found and these results together with more details of the annealing scheme will be given elsewhere.

The polyicosahedral growth scheme of Farges et al.[13–15] starts from a primitive icosahedron containing a central atom and twelve surface atoms. On each one of the five tetrahedral sites, surrounding a particular vertex, a new atom is added and finally a sixth atom is placed on top to create a pentagonal cap. In this way a 19-atom structure consisting of two interpenetrating icosahedra is obtained (see fig. 1 in ref. [14]). Alternatively, this can be viewed as three pentagonal bipyramids each one sharing an apex with its nearest neighbour. If this procedure is repeated once, a 23-atom model consisting of three interpenetrating icosahedra is obtained (fig. 1). Unlike the 19-atom structure, which also belongs to the pen-

tagonal growth sequence considered by Hoare and Pal [8], this model with 23 atoms does not fit in the simple polyhedral schemes. The structure possesses a threefold rotation axis and a mirror plane perpendicular to it, hence it contains three further mirror planes.

This 23-atom structure was obtained by the simulated annealing algorithm, even when all atoms except a central one were allowed to move. Its binding energy is 92.844, which is to be compared to 90.647 for the dodecahedral model considered by Hoare and Pal [8]. For 24 atoms two minima close in energy were found: the binding energies are 97.349 and 97.313 respectively. Both improve on a tetrahedral model with an energy of 96.514, obtained by Hoare and Pal [8]. The corresponding structures are shown in fig. 2 and turn out to consist of the previously discussed 23-atom cluster with an additional surface atom in a fourfold site. The model in fig. 1 contains only two types of non-equivalent fourfold hollow sites (shaded). The highest binding energy corresponds to an atom in the site labelled A: the local coordination of the two sites (before relaxation) is the same, but an atom in the A site will be closer to the centre of gravity of the structure, hence the small energy difference. The nearest-neighbour distances are: 0.975, 1.036, 0.972, 1.036 for an atom in the A site, and 0.975, 1.030, 0.975, 1.030 for an atom in the B site. Finally for 25 atoms the simulated annealing algorithm found the structure shown in fig. 3. Its energy is 102.37, and it has previously been obtained by Hoare and Pal [8] within the tetrahedral growth scheme. As can be seen, that model can be derived from the 24-atom one by adding an atom in one of the fourfold hollow A sites. The bonding distances are: 0.955, 0.997, 1.007 and 1.108 to the nearest neighbours and 1.092 between the two extra atoms.

The most difficult part of a simulated annealing calculation is the determination of the cooling schedule. A cooling rate that is too slow is time consuming, while a fast cooling rate will lead to final states that are bad approximations of the actual ground state. In the present case, where one wants to find the absolute minimum and not some nearby local one, the matter is even more complicated. In order to analyse the influence of the cooling schedule on the final state, a number of simulations have been performed for 13-atom clusters, taking the number of attempted steps
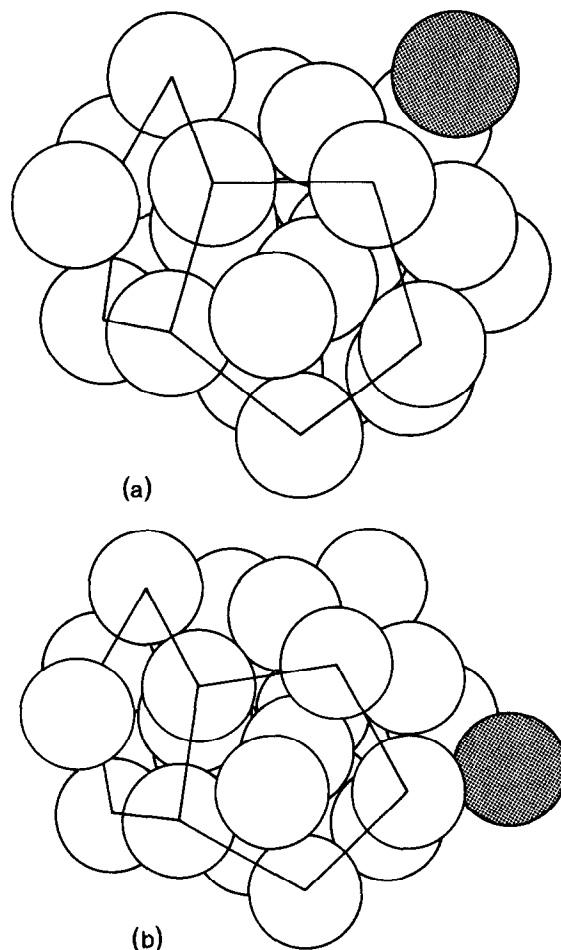

Fig. 2. Twenty-four-atom clusters found in the present work. They consist of the $N=23$ model with an additional atom (shaded) in one of the fourfold hollow sites. The two pentagonal caps are also outlined. (a) An additional atom in an A site, binding energy 97.349, (b) an additional atom in a B site, binding energy 97.313.

per particle at each temperature equal to $N_c(1-\log T)$, where $N_c=200$ and 2500, χ_T being fixed at 0.9. In the first case three out of thirty runs produced the icosahedral structure, whereas in the second case four out of five runs gave this result. Although these numbers are insufficient to give good statistics, they indicate how the likelihood of detecting the global minimum increases with decreasing cooling rate. For the icosahedral structure the freezing temperature is known to be $T_f=0.2438$ from molecular dynamics simulations [22]. When the cooling proceeds too quickly one expects the system
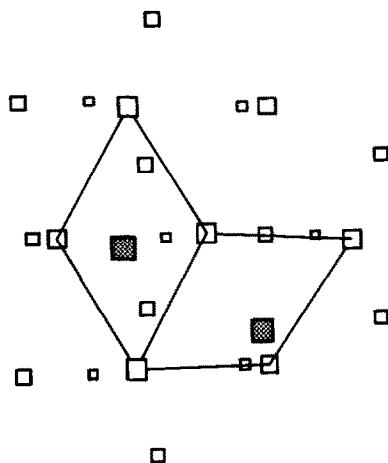
Fig. 3. Twenty-five-atom cluster obtained by adding a further atom to an A site. The basic structure is the same as in fig. 1, but it has been rotated slightly to bring the two extra atoms (shaded) to the foreground.

Fig. 4. Specific heat as a function of temperature for (a) $N_c = 200$, and (b) $N_c = 2500$, where the number of attempted steps per particle at each temperature is $N_c(1 - \log T)$. The units are determined by the parameters of the Lennard-Jones potential (see text).

to behave like an undercooled liquid and freeze at a temperature below T_f. To illustrate this point, fig. 4 shows typical results for the two values of N_c. As N_c is increased from 200 to 2500 the main peak in the specific heat (calculated according to (3)) shifts from 0.10 to 0.24, which is consistent with the fact that the system is better equilibrated at the slower cooling rate. Clearly the number of iterations is too small to provide a proper description of the thermodynamics – the slow convergence of simulations in this temperature range is well known [22] – but the results confirm the physical picture.

3. Conclusions

The simulated annealing method has been used to determine low-lying minima on the potential energy surfaces of atomic clusters with up to 25 atoms. Two new minima have been found for a 24-atom cluster; both structures are an intermediate step between a previously obtained 23-atom model (in the polyicosahedral growth scheme) and a 25-atom one (in the tetrahedral growth scheme). All previously known optimal results have been reproduced, as well as a number of local minima, some of which are new and will be discussed elsewhere. This illustrates that simulated annealing is a powerful method for molecular
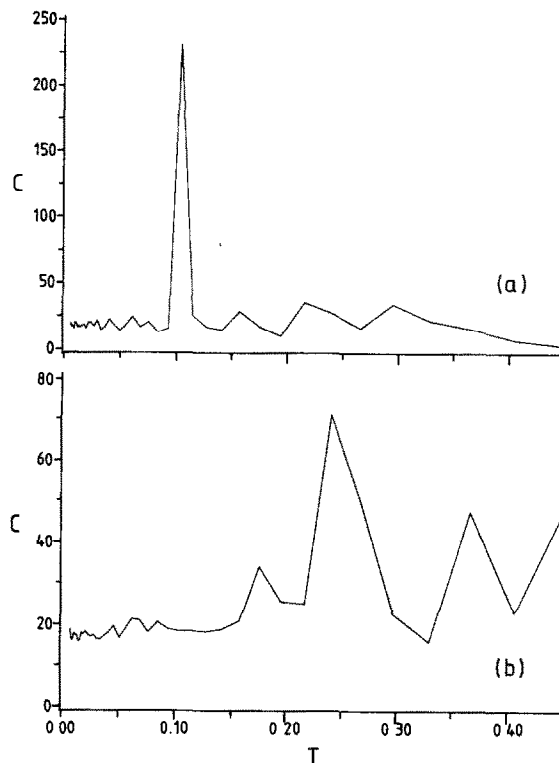
geometry optimisations; it would be interesting to apply it to other complicated packing problems [23]. The method is not restricted to two-body forces, but can be extended to deal with fully quantum-mechanical Hamiltonians, along the same lines as in Car and Parrinello [24].

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