Lennard-Jones Energy Minimisation

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Contents

1 Introduction

The model molecular energy minimisation problem involves the geometric configuration of a cluster of atoms in two dimensions, each connected by rigid bonds of unit length, such that the total potential energy yielded by the sum of individual Lennard-Jones potentials is globally minimised. The total potential energy of the cluster is given by

$$V(r) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(r_{ij}^{-12} - 2r_{ij}^{-6} \right)$$

Where r is the euclidean distance between a pair of atoms and N is the number of atoms in the chain.

The energy minimisation problem is historically difficult because of the exponential relationship between the locally stable structures and the number of atoms, N, in the molecule. That is, as the size of the cluster increases, the number of local minima increases exponentially such that when N approaches 100, there exist more than 10^{140} minima [1]. It is therefore necessary to employ sophisticated search algorithms in order to make larger input sizes attainable.

Section 2 will discuss some of the research that has already taken place in this area. Section 3 will detail the algorithm proposed by this paper.

2 Literature Review

Genetic algorithms have been applied [2], [3] successfully in order to extend the range of input size N that is reachable through structural optimisation. This population based approach emulates the Darwinian process of natural selection, and works by performing crossover operations on pairs of candidate configurations with selection probabilities based on their fitness, producing new child nodes which contain genetic material from both parents. With every crossover operation there is a small chance of subsequent random mutation of the child configurations, the purpose of which is to promote genetic diversity within the population and prevent premature convergence. Over many generations the population converges towards a global minimum as each configuration communicates information about the global search space through the crossover operation. This method has been successful in producing results that were previously unseen in literature for certain input sizes.

Judson *et al.* compare the performance of GAs with simulated annealing, a stochastic global optimisation technique in which Monte Carlo steps are taken and new states are accepted if they are fitter, or with a probability based on a function of a temperature value [2]. When applied to the molecular conformation problem, they found that the GA method and the SA method, both applied as global meta-heuristics in conjunction with gradient-based local optimisers (conjugate gradient), similarly outperformed purely stochastic methods [2]. Judson *et al.* classify points on the model energy surface as being in one of

three states: knotted and of high energy, unknotted and of low but not minimal energy, and unknotted with globally minimised energy [2]. They applied both GA and SA in order to make the transition from the first state to the second state before applying local optimisation to descend to the bottom of the basin.

Genetic operators for the two dimensional bonded Lennard-Jones problem have since been further developed with successful results [3], proving the GA approach to be a viable global optimisation technique. Pullan [3] proposes three genetic crossover methods and four mutation operators and applies these in a parallel genetic algorithm to find global minima for most values of $N, 2 \leq N \leq 55$, as well as a minimum for $N = 61$ which was previously unseen in literature.

This two stage hybrid method has been successful, but Judson *et al.* also suggest the possibility of adding a third optimisation stage which is intermediate between the global and local gradient methods [2]. It is thought that a non-gradient optimisation method such as the simplex method may provide a means of stepping over barriers into possibly deeper minima surrounding those found by the global method in the first phase.

More recently, the Conformational Space Annealing Method [4] has been developed as a global optimisation algorithm that has produced very good results when applied to the problem of an unbound cluster of atoms with Lennard-Jones relationships. This algorithm combines concepts of Monte Carlo with minimisation, genetic algorithms, and simulated annealing. While this technique has not been applied to the bonded variant of the Lennard-Jones conformation problem as discussed here, it demonstrates that a hybrid approach combining SA and evolutionary population based algorithms may be a viable technique in a similar problem domain.

3 Proposed Algorithm

As discussed in section 2, global meta-heuristics such as the genetic algorithm, have been used successfully as a means of navigating the global search space and avoiding local minima that are caused by knots in the configurations [2], [3]. These methods use the global optimiser to find unknotted potential candidate configurations and then refine them using gradient-based methods. Judson *et al.* have suggested a three stage system in which a non-gradient optimiser such as the simplex method may be used as an intermediate stage between the global and local-gradient optimisation in order to traverse barriers into potentially deeper basins [2].

As simulated annealing has been found to be successful when combined with evolutionary algorithms in similar problem domains [4], this paper will explore its use as an intermediate non-gradient method such that the proposed algorithm has three levels: (1) global meta-heuristic, (2), intermediate non-gradient optimisation and (3) local gradient-based optimisation.

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