Effect of the cooling rate in the thermally driven differential mutation method

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Abstract. The thermally driven differential mutation algorithm is an evolutionary algorithm dealing with the structural optimization of large amorphous systems represented by empirical potentials. It is a hybrid algorithm that combines a differential mutation evolutionary algorithm with a metropolis selection criterion and a cooling schedule inspired by simulated annealing. In this manuscript, the influence of the cooling rate on the quality of obtained amorphous graphene structures is discussed.

1. Introduction
The thermally driven differential mutation algorithm (thDM) [1] is an algorithm that combines an evolutionary differential mutation algorithm [2, 3] with a selection criterion inspired by simulated annealing. The method is applied to the structural optimization of amorphous graphene starting from unbiased random initial configurations. In general, the success of evolutionary algorithms is dependent on the size and diversity of the population covering the possible solution space [3, 4]. This has been addressed by refeeding the optimization run with new structures [4, 5, 6, 7] or by starting with a large population size, then reducing the population and resupplying with new candidate structures when needed (for references see [4]). The thDM circumvents this requirement by allowing thermally restricted increases in energy which enable the structures to climb over energy barriers and explore a wide range of the configuration space. In fact, it has been demonstrated at the structural optimization of amorphous graphene [1] that with just a very small population size of only six systems high-quality minimum energy structures can be achieved. The optimization starts at a temperature that is higher than the melting point of the material allowing the atoms to easily break bonds and rearrange. As the temperature is lowered the ability of the systems to escape local energy basins decreases until they eventually become trapped. The temperature is lowered according to

\[ T^{l+1} = T^l \exp[-\gamma l], \]

where \( \gamma \) is the cooling factor and \( l \) the cooling step with \( T^0 = T_0 \), \( T_0 \) is the starting temperature. To some extent, it is to be expected that the thDM will be dependent on the rate of cooling. This can be easily seen by considering the limit \( \gamma \to \infty \). After the initial equilibration at the starting temperature, which is too high to recognize the fine structure of the potential energy landscape, the systems will attain structures corresponding to the nearest energy traps and be unable to escape. It is to be expected that this instantaneous freezing will result in rather poor outcomes.
structures. For a finite $\gamma$ the same is not to be expected. In this article, the effect of the cooling rate at the structural optimization of amorphous graphene will be examined. The obtained structures are puckered 3-dimensional surfaces of amorphous graphene. Predominantly amorphous graphene structures have been obtained by creating Stones-Wales defects [8, 9] on pristine graphene structures. The resulting structures were 2-dimensional [10, 11, 12]. Only Li and Drabold [13, 14] showed that from these 2-dimensional structures 3-dimensional structures can be obtained that are lower in energy than the originating 2-dimensional structures while maintaining the same ringstructure.

2. Method

The thermally driven differential mutation algorithm is an algorithm dealing with the structural optimization of large atomic systems whose constituents interact via empirical potential energy functions. Initial values are specified for the temperature $T_o$, the number of systems $m$, the number of atoms per system $N_p$, the confining volume, the cooling rate $\gamma$, $C_r$ a value relating to the probability of mutation, and the weighting factor $F$. The systems $\zeta_1, \ldots, \zeta_m$ are initialized by placing the $N_p$ atoms at random locations within the confined volume. The optimization routine works in the following way:

For every system $\zeta_k$ (the index $k$ denotes the target system) two base systems $\zeta_n$ and $\zeta_m$ are randomly selected. From each of the base systems $\zeta_n$ and $\zeta_m$ one atom is drawn, denoted by $\vec{r}_i$ and $\vec{r}_j$ (with $\vec{r}_i \in \zeta_n$ and $\vec{r}_j \in \zeta_m$), and their difference $\Delta \vec{r} = \vec{r}_i - \vec{r}_j$ is calculated. This difference is then added to an atom $\vec{r}_o$ from the target system via the weight factor $F$, i.e. $\vec{r}_o = \vec{r}_o + F \Delta \vec{r}$ (where $\vec{r}_o$ denotes the mutated target atom). This procedure is repeated such that at least the position of one of the atoms from the target system $\zeta_k$ has to be mutated and others are selected for mutation with a probability equal to $C_r$. The positions of atoms which are not selected for mutation are carried unchanged into the trial system $\hat{\zeta}_k$. Once the trial system has been obtained, the potential energy of the trial system $U(\hat{\zeta}_k)$ is compared to the energy of the target system $U = U(\zeta_k)$. If $\Delta U = U - U$ is less than or equal to zero, the trial system is accepted, otherwise a random number is drawn from a uniform random number distribution and compared to the Boltzmann factor in energy. If $\text{rng}[0,1] < \exp[\beta \Delta U]$ (where $\beta = 1/k_B T$ is the Boltzmann constant) the new configuration is accepted, otherwise the target system is carried unchanged into the new population.

This procedure is repeated for all the systems at the set temperature $T^l$, with $T^0 = T_o$ being the initial temperature. Once sufficient equilibration is reached the temperature is lowered according to eq. (1), and the procedure is repeated. This itself repeats until some stopping criterium is reached.

3. Numerical Results

Interactions between the atoms were represented by a bond-order potential introduced by Albe and Erhart [15]. This potential represents bond distances and bond angles. To speed up the calculation a center approximation was used in the calculation of the bond angle contribution. This approximation only takes into account the changes in the bond angle for which atom $i$ is at the center and not those for which atom $i$ is at one of the sides

To initialize the optimization routine, for each of the $m = 6$ systems $\zeta_1, \ldots, \zeta_6$, 300 atoms were placed in a confined volume of dimensions $28.098\,\text{Å} \times 28.098\,\text{Å} \times 1.4\,\text{Å}$. The two long sides make up the x- and y-coordinate, the shorter side is the z-direction. The optimization was started at a temperature of $T_o = 5800\,K$, and the systems were allowed to evolve and interact in x- and y-direction via periodic boundary and minimum image conditions. To prohibit the formation of three-dimensional bulk structures, in z-direction only periodic boundary conditions were used.

1 A detailed discussion can be found in ref. [1]
For different choices of the parameter $\gamma$, the thermally driven differential mutation routine was employed with approximately 53000 trial displacements per atom at each temperature. The parameter $F$ was allowed to vary within the boundaries $(0, 0.004]$, and $C_r$ was set to 0.05, allowing on average 16 site mutations on the location of the atoms of the mutant systems. At a temperature of $90K$ the thDM was stopped, and the systems were then locally relaxed using a standard gradient method [16]. For this step, the center approximation was omitted (i.e. now the full Erhart-Albe potential [15] was used) and the systems were allowed to freely evolve in the $z$-direction without restriction in their height, i.e. without periodic boundary conditions. Periodic boundary and minimum image conditions were maintained in $x$- and $y$-direction. The results can be seen in figs. (1) to (4).

Figure 1. Top view of lowest energy structure for $\gamma = 0.005$. The bonds of 5-ring structures are drawn in blue, 6-ring in gray, 7-atom rings in green and 8-atom rings in red.

Figure 2. Average energies (black dots) and lowest energies (blue triangle) of the obtained structures for different cooling rates $\gamma$. The bars represent the standard deviation.

As an example, fig. (1) shows a top view of the lowest energy structures obtained for $\gamma = 0.005$. The bonds between the atoms are colored corresponding to the number of atoms forming the rings. 5-atom rings are colored blue, 6-atom rings gray, 7-atom rings green and 8-atom rings are colored red.

Fig. (2) shows for different cooling rates $\gamma$ the average and lowest energy of the obtained structures. The energies are represented with respect to the energy of an ideal graphene sheet, i.e. $\Delta U = U - U^g$, where $U$ represents the energy of the systems and $U^g$ represents the energy of the pristine 2-dimensional graphene sheet. As can be seen from fig. (2), overall slower cooling rates produced on average energetically lower structures. On average, the structures for a cooling rate of $\gamma = 0.005$ were 3.95% above the energy of graphene. Very low energy structures were also obtained for cooling rates of $\gamma = 0.010$ and 0.015 with only 4.03% and 4.06% (respectively) above the energy of graphene. Note that a cooling rate of $\gamma = 0.005$ requires 42 cooling cycles, whereas $\gamma = 0.010$ and 0.015 require only 30 and 25 cooling steps (respectively) thus allowing to obtain reliably low energy structures with significantly less computational effort. Fast rates of $\gamma$ led to higher energy structures. E.g., for $\gamma = 0.100$ and 0.150 the structures were on average 4.99% and 4.85% (respectively) higher than graphene. Fig. (2) also shows the lowest obtained energies. While overall slow rates of cooling produced lower energy structures, the lowest structure was obtained for a cooling rate of $\gamma = 0.015$ indicative of the randomness of the mutations.

2 The average was taken over all the systems, i.e. $\langle \Delta U \rangle_i$.
Figure 3. **Left:** Distribution of rings of the lowest energy structures for the different cooling rates $\gamma$. **Right:** Average distribution of the rings for the different cooling rates $\gamma$. The distribution shows only up to 11-atom rings.

Fig. (3) shows the distribution of rings of the structures for the different cooling rates $\gamma$. Corresponding to fig. (2), the averaged values (right) and the lowest structure (left) are shown. As can be seen, accounting for more than 44% (on average) of all ring structures 6-atom rings had the highest occurrence at all the cooling rates $\gamma$. The highest formation of 6-ring structures of 60% occurred at a cooling rate of $\gamma = 0.015$ for the lowest energy structure. A high probability of occurrence was also found for 5-atom rings, followed by 7-atom and 8-atom rings. As can be seen in the right figure of fig. (3) for average values a clear pattern emerged. The probability of 6-ring structures was highest for slow cooling rates and decreased with increasing values of $\gamma$. Interestingly, while the number of 6-ring structures decreased for faster cooling rates, the number of 5-ring structures increased (e.g. from 27% for $\gamma = 0.005$ to 30% for $\gamma = 0.150$). A similar pattern for the lowest energy structures was not observed. The number of 7-ring and 8-ring structures on average seemed to be unaffected by the different choices of the parameter $\gamma$. For $\gamma = 0.005$ no ring structures greater than 8 occurred. Rings with more than 10 atoms only occurred for faster cooling rates. Note, the inset of the right figure of fig. (3) only shows the distribution of up to 11 membered rings. A single 12-atom ring occurred for $\gamma = 0.140, 0.155$ and 0.100, and the systems obtained for $\gamma = 0.150$ also had one 14-atom ring.

Fig. (4) shows the distribution of the bond angles measured with a resolution of 2°. As can be seen from the figure, the highest occurrence of angles was around the 120° angle confirming that 6-ring structures predominantly assumed hexagonal shapes. The average distribution [right fig. in fig. (4)] of the hexagonal bond angles, followed also very closely the distribution of the rings. The occurrence of angles close to 120° was highest at slow cooling rates and reduced with faster cooling rates. Except for the lowest energy structure at $\gamma = 0.055$ heptagon angles were not distinctly visible. This behavior was discussed in detail in ref. [1].

4. Conclusion

The thermally driven differential mutation algorithm is an algorithm that combines a differential mutation evolutionary algorithm with simulated annealing. Mutated structures are accepted or rejected based on a Metropolis criterion. For this purpose, a temperature is introduced and stepwise lowered following a cooling schedule. This article investigated the effects that the cooling rate has on the quality of the obtained structures of amorphous graphene. While due to the randomness of mutations individually the systems can obtain very low energy structures at
Figure 4. Left: Distribution of the bond-angles of the lowest energy structures for the different cooling rates $\gamma$. Right: Average distribution of the bond-angles for the different cooling rates $\gamma$.

modest rates of cooling, the results showed that for slower rates of cooling the systems reached on average energetically lower configurations. These configurations are dominated by 6-ring hexagonal structures with internal angles close to 120°. For faster rates of cooling the obtained systems have on average higher energies. The occurrence of high membered rings at only large values of the cooling parameter $\gamma$ indicates that fast cooling rates lead to the formation of large ring-structures which are energetically less favorable than 5-, 6-, 7- and 8-ring structures.

5. References

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