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The Initial Stages of Melting of Graphene Between 4000 K and 6000 K

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Abstract

Graphene and its analogues have some of the highest predicted melting points of any materials. Previous work estimated the melting temperature for freestanding graphene to be a remarkable 4510 K. However, this work relied on theoretical methods that do not accurately account for the role of bond breaking or complex bonding configurations in the melting process. Furthermore, experiments to verify these high melting points have been challenging. Practical applications of graphene and carbon nanotubes at high temperatures will require a detailed understanding of the behavior of these materials under these conditions. Therefore, we have used exclusively reliable *ab initio* molecular dynamics calculations to study the initial stages of melting of freestanding graphene monolayers between 4000 and 6000 K. To accommodate large defects, and for improved accuracy, we used a large 10 x 10 periodic unit cell. We find that the system can be heated up to 4500 K for 18 ps without melting, and 3-rings and short lived broken bonds (10-rings) are observed. At 4500 K, the system appears to be in a quasi-2D liquid state. At 5000 K, the system is starting to melt. During the 20 ps simulation, diffusion events are observed, leading to the creation of a 5775 defect. We calculate accurate excitation energies for these configurations, and the pair correlation function is presented. The modified Lindemann criterion was calculated. Graphene and nanotubes together with other proposed high melting point materials would be interesting candidates for experimental tests of melting in the weightless environment of space.

Graphical Abstract

We have studied the early stages of melting of the freestanding graphene lattice using accurate density functional theory.

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Supporting Information

Short movies of parts of the molecular dynamics simulations for graphene at 4000, 4500, 5000, and 6000 K are available. We include a movie of the formation of a single isolated 5775 defect at 5000 K. We include top and side views of snapshots from the last frame of each simulation. RMSD and bond orientational order plots are also included. Additional computational details are listed. A plot of the Lindemann criteria vs. temperature is included. We also show a single atom on top of the lattice with a vacancy defect. We also show flat separated 57 and 75 defects.

Introduction

Graphene is a truly remarkable material, with many extreme and useful properties. The fascinating history has been described in the Nobel lectures by Nosolev and Geim.^{1, 2} Many practical uses have been developed for this material. Freestanding graphene monolayers have been mounted on point to provide pressure sensors and to make freestanding resonators and devices.^{3, 4} Graphene or its analogues may have the highest melting point of all known elemental substances, and deserves further experimental and theoretical study of its high temperature properties. Due to its high thermal stability, graphene may also be useful in high temperature electronic devices.^{5, 6, 7} Recently, a light bulb was demonstrated using a filament fabricated from reduced graphene oxide and single-walled nanotube (CNT) paper.⁸ These RGO-CNT paper ribbons routinely reach 3000 K before failure, with some samples exceeding 3300 K, higher than any other carbon nanomaterial. Recent results on nanofabricated freestanding graphene ribbons show very effective light emission up to temperatures of ~2850 K.⁹

Graphene, refractory metals and alloys, and some oxides are materials that have exceptionally high melting points. These materials have applications in high temperature processing and environments. For example, tantalum hafnium carbide (Ta_4HfC_5) is a refractory compound with a very high melting point of 4263 K.^{10, 11}

Hong *et al.* have developed a new statistical method to quickly predict the melting points of materials.¹² They have made several remarkable predictions of new high temperature alloys using density functional theory to test the co-existence of solid and liquid phases. They recently identified a novel $\text{HfN}_{0.38}\text{C}_{0.51}$ alloy with a remarkable predicted 4398 K melting point.¹³ We note that the bulk crystal graphite does not melt at room pressure, but instead sublimates at roughly 4000 K (we note that the triple point for graphite is 0.01 GPa, 4200 K, where solid-liquid-vapor coexist).¹⁴

There have also been several studies of the melting point of graphene. Fasolino and coworkers have made extensive studies of the melting of freestanding graphene and predict a remarkable melting point for graphene of 4510 K.¹⁵ (This high melting point has not yet

been verified experimentally.) They find that in graphene, there are neither observations nor predictions of stable single pentagons or heptagon defects (disclinations). Dislocations (pentagon-heptagon pairs) have been observed in the special case of graphene on a substrate at grain boundaries by Coraux *et al.* using scanning tunneling microscopy.¹⁶ Los *et al.* find a 4.6 eV formation energy¹⁷ of a Stone-Wales (SW) defect made of two adjacent pentagon-heptagons (57) pairs is much lower than the formation energy of two well separated 57 pairs as occurring in small angle grain boundaries.¹⁸ Zakharchenko *et al.* conclude that “the relative stability of SW defects makes them play a crucial role in the pre-melting behavior of graphene and prevents them from splitting into two 57 defects and further, and by this to follow the Kosterlitz, Thouless, Halperin, Nelson, and Young (KTHNY) scenario.”¹⁹ Considering the work of other groups, Galashev *et al.* reviewed the properties of graphene at high temperatures in 2010.²⁰ In 2007, Zhang *et al.* studied the melting properties of C nanotubes, and predicted a very high melting point of 4800 K for perfect tubes.²¹ In 1994, Kim and Tomanek estimated a melting point for individual fullerenes of 4000 K.²²

In a large Monte Carlo simulation with 1000 atoms using the reactive bond order potential LCBOP-II,¹⁷ Los *et al.* find that the graphene sheet transforms into a sort of quasi-2D liquid phase consisting of entangled and interconnected chains remaining roughly within the quasi-2D plane of the previously solid sheet.¹⁵ We note that the use of a relatively simpler theoretical method allows for longer simulation times and/or a larger number of atoms in the cell, or more Monte Carlo frames. (Furthermore, Monte Carlo simulations can examine equilibrium states in the canonical NVT or isobaric NPT ensembles but do not use the dynamics.) However, the theoretical methods used by the Fasolino group are not reliable for broken bonds and the complex bonding situations encountered during melting and pre-melting. Eventually, the chains start to disentangle and extend to 3D space, with a diverging simulation box in NPT simulation at zero pressure. They suggest a two-step scenario via an intermediate quasi-2D liquid phase which implies that the melting temperature of graphene is in fact the temperature at which the 2D solid and the quasi-2D liquid phases are in equilibrium.¹⁵

They state that when liquid nuclei start to form in the solid sheet, the liquid phase remains connected with the solid sheet at the edges of the nucleus, constraining it to stay within quasi-2D configurations. Fasolino's group also examined the formation of the 5775 defect, and found that it can be created in a perfect graphene layer by rotating a single bond by 90°, followed by a geometrical relaxation of the system. Furthermore, they predicted that the 5775 defects should induce significant bending and strain into the lattice.¹⁵

In light of the fact that graphene and analogues such as carbon nanotubes have such remarkably high predicted melting points, and considering the potential high temperature applications for graphene and analogs (including lighting and structural), we believe that detailed and reliable information on the initial stages of melting of graphene is important. Therefore, we have used accurate *ab initio* density functional theory molecular dynamics simulations to study the initial stages of melting of freestanding graphene at temperatures between 4000 and 6000 K. At these high temperatures, high energy excitations and the initial stages of melting were observed within 6 to 20 ps. Molecular dynamics movies, detailed energy calculations of excitations, and correlation functions will be presented.

Computational Methods

We carried out Born-Oppenheimer *ab initio* molecular dynamics simulations, using a 10×10 graphene lattice (200 atoms) with periodic boundary conditions. At 0K, the optimized graphene unit cell would be $24.6 \times 24.6 \times 20.0$ Å. We used an expanded unit cell of $25.5 \times 25.5 \times 20.0$ Å, to accommodate some expansion as the temperature is raised (3.7% linear expansion). Therefore, the starting bond lengths were approximately 1.49 Å. This will minimize the pressure during the NVT simulation between 4000 K and 6000 K. The 20 Å spacing in Z between layers ensures good isolation between layers. DFT-D and Tkatchenko–Scheffler (TS) methods were used in CASTEP²³ in Materials Studio 2016. Molecular Dynamics (MD) simulations in the constant number, volume, temperature (NVT) ensemble were carried out for 12 to 20 ps with a time step of 2 fs. Based on our previous experience with molecular dynamics simulations, this step size was designed to allow accurate calculations, but also provide the maximum simulation time possible. Note that a typical motion of 0.1 Å or less for individual atoms was observed for each 2 fs step at 4000 K (and the fact that the system can be heated to 4500 K while maintaining the lattice confirms the choice of time step). Constant pressure NPT simulations were also carried out, but CASTEP was unable to maintain the pressure within reasonable limits (variations of ± 0.5 GPa and more due to small cell size, parameters, or CASTEP itself), so constant volume NVT simulations were used in this study. The NPT runs were used to choose an appropriate and lowest pressure expansion for the overall lattice based on results of 4000K. The extended Lagrangian method was used in CASTEP, to improve the results. The isolated low energy excitation structures were optimized with variable unit cell at 0K to provide accurate energies at low pressures.

The first 8 ps were run at 4000 K, and then this starting point was extended to between 12 and 20 ps for each of the temperatures. Detailed computational parameters are listed in the supplemental information (SI). The 4000 K simulation was started from the ideal 0K graphene lattice, although in an expanded unit cell to accommodate the expansion of the system at elevated temperatures. For each simulation, an equilibration time of roughly 12 ps was used. Data were acquired after equilibration, and so the first 8, 12, 14, 14.8 ps were skipped in the 4000, 4500, 5000, and 6000 K simulations, respectively. Materials Studio was used to create the initial structures and visualize the results. The R computing environment²⁴ and Python programming environment were used for plot generation and data analysis of the Root Mean Square Displacement (RMSD), pair correlation function, and bond orientation correlation function. The RMSD was calculated using the differences between an initial data frame (after equilibration), and subsequent frames in each simulation.

The pair correlation function for our quasi-2D system $g(r)$ was calculated, where σ is the two-dimensional atomic density, N is the total number of atoms, and δ is the delta function.

$$g(r) = \frac{1}{2\pi r \sigma N} \left\langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle \quad (1)$$

The large vacuum space between layers assures good isolation of the freestanding quasi-2D layer. The diffusion coefficient D was calculated using $\langle r^2 \rangle = 4Dt$. The bond orientation correlation function was calculated. First, all bonds were identified by locating the nearest neighbors for each atom in each frame (atoms within $1.38 \times 1.48 \text{ \AA} = 2.05 \text{ \AA}$). Each bond centroid was calculated, along with the 2D bond angle of each bond relative to the X-axis (ignoring the Z coordinate of each atom). Then, a modified distribution function, $g_3(r) = \langle \cos(3\theta) \rangle$, was created where θ is the difference between two bond angles, and r is the full 3D distance between two bond centroids. The factor of three ensures that the three-fold symmetry of the 0 K optimized honeycomb structure, produces a result of one. Note that at 0K, the system occupies the ideal honeycomb ground state with all atoms in rings of 6 atoms, which we will call 6-rings in this paper. We will also refer to rings with other numbers of atoms as N-rings.

For comparison with the previous work, we have calculated the modified Lindemann criterion.¹⁹

$$\gamma_n = \frac{1}{a^2} \left\langle \left| r_i - \frac{1}{n} \sum_j r_j \right|^2 \right\rangle \quad (2)$$

Where $a = 1/\sqrt{\pi\rho_0}$, ρ_0 is the 2D particle density at $T = 0\text{K}$, r_i is the position of the i th atom and the sum over j runs over the n atoms closest to atom i . We will use $n = 12$ as in the previous work.

Results

In Figure 1, we show snapshots from the final frames of the MD simulations at 4000 K, 4500 K, and 5000 K. At 4000 K, after 12 ps, we observe the surface has smooth oscillations and the lattice is maintained. A few 3-rings (i.e. 3 atoms bonded together in a triangular arrangement temporarily), due to next neighbor atoms oscillating towards each other temporarily, are observed (an image of this arrangement and the energetics will be discussed below). No net diffusion is observed at 4000 K in the simulation period.

At 4500 K, the surface is displaying more out of plane long range oscillations, but the lattice is still maintained over the simulation time of 18 ps. Either the surface has not melted yet, or it is in a superheated state (longer simulation times would be needed to address this question). At 4500 K, the system appears to be in a quasi-2D liquid state, although our simulation is only for a brief 18 ps, which is too short to be definitive. We note that this observation of a quasi-2D liquid state is consistent with the previous work at larger sizes and longer time scales.¹⁵ We note that 4510 K is the previously predicted melting point of periodic freestanding graphene.¹⁵

At 5000 K, the surface is now in the initial stages of melting after 20 ps. The surface is substantially rougher, but most of the atoms are still in 6-rings. One 5775 defect has nucleated and two diffusion events have occurred. More details of these processes, including

energetics are discussed below. We encourage the reader to view the movies of parts of these MD simulations in the SI.

At 6000 K, the system has already melted after 7 ps, although it has not reached equilibrium yet. Figure 2 shows the last frame of this simulation. The C atoms are now coming out of the plane and forming 1D double-bonded chains. At the last frame, the system consists of primarily double bonded chains, loosely coupled together. Since the typical bond energy for a 1D double bonded C chain is 6.2 eV, which is less than the typical bond energy in graphene 7.5 eV at 0 K), we conclude that at 6000 K the system will continue to evolve.

These results demonstrate that freestanding graphene exhibits increasing oscillation and Z-motion as the temperature is raised from 4000 K to 6000 K. Additional images are shown in the SI. The lowest energy excitations are long range oscillations, which we can see clearly in Figures S1 – S9 and Figure 1.

The second lowest energy excitation is a 3-ring, as shown in Figure 3a. This defect has a relative energy of 2.44 eV, and is observed in the simulations between 4000 K and 6000 K.

A third interesting and important defect is the single broken bond, which results in a 10-ring. This is shown in Figure 3b and has a relative energy of 3.48 eV. Single broken bonds are observed rarely in the simulations at 4000 K and 4500 K, but become more common at 5000 K and above (See Table 1). In the movies of the MD simulation, we can see that when a single bond is broken, the neighboring bonds become stronger, and the defect is typically annealed out after roughly 10 fs at 5000 K.

It is interesting that the curved 5775 defect shown in Figure 4 has a relative energy of 4.78 eV. This finding generally agrees with and is 5% higher than the predictions of Fasolino et al., who calculated a relative energy of 4.6 eV for the curved 5775 defect using less reliable theory.¹⁵ At a very slightly higher relative energy of 4.80 eV, we find the flat 5775 defect shown in Figure S8. Given the close relative energies of the curved and flat 5775 defects, both versions will be observed at basically the same rate at these temperatures. (These structures were optimized with variable unit cell at 0K to provide accurate energies at low pressures).

In Figure 5, we show the pair correlation function for freestanding graphene at five different temperatures. Starting with the cold ideal lattice at 0 K, we observe the nearest neighbor, next nearest neighbor distances of 1.44 and 2.88 Å etc. These pair distances are still visible in the pair correlation plot at 4000 K, although the correlation has smoothed and been reduced substantially as the atoms move away from their ideal locations. The lattice is still maintained, but the pair correlation is dropping at larger distances. We observe a steady reduction in the pair correlation as the temperature is raised. At 4500 K significant correlation is still maintained. At 5000 K we see continued smoothing, both due to increased long and short oscillations as well as the presence of the 5775 defect which disrupts the pair correlation. At 6000 K the system is melted and on the way to becoming a gas phase, and the pair correlation drops rapidly to zero. (The data at 6000 is collected from just the last 118 fs, because this is when the system is moving into 3-dimensions).

In the supplemental information Figure S11, we include the RMSD results. We observe very little, or no *net* motion at the lower temperatures (although diffusion events were observed at 5000 K, as discussed previously). At 6000 K, the system is starting to move into three-dimensions, and more motion is observed, but the timeframe is relatively short. In Figure S12, we include a plot of the bond orientation correlation function. This shows a clear reduction of correlation as we raise the temperature from 4000 K to 6000 K. Interestingly, at 5000 K we see clear dips around 6 – 8 Å, which are caused by the presence of the 5775 defect. At 6000 K we see very low correlation as the system is converting to the gas phase. At 6000 K the nearest neighbor bond lengths are slightly reduced due to the temporary transition to 1D chains.

In Figure 6, we show the first step of the formation of a single isolated 5775 defect (from the 5000 K simulation). In this process, one carbon atom penetrates into a neighboring 6-ring. In the SI, in Figure S9, we show the final frame of this process. We see that compared to the 0 K starting lattice, two atoms have rotated, which induces the motion of several other atoms. This relative motion is shown using the relative bonds in Figures 6 and S9. (We have not re-bonded the atoms for these figures only to emphasize the net motion of the atoms). A movie of this process is available in the SI.

In Figure S10, we show two separated 57 and 75 defects. This configuration has a large 14 eV relative energy, and so it is quite unlikely for the 5775 defect to separate in this way. Thus, the unbinding of 57 defects is not the driving force for the melting transition in graphene.

We have estimated the probability of observing different ring numbers at temperatures between 4000 K and 5000 K. The results are shown in Table 2. We see that 6-rings still dominate. At 4000 K, 3 and 5-rings are observed 0.6% of the time, with rare bond breaking events leading to 10-rings 0.015% of the time. At 4500 K, the probabilities of observing this defects are all roughly doubled. At 5000 K, 3-rings are 1.8%, while a large 5775 defect is stable and brings 5 and 7 rings up to 2.7% and 1.8%, respectively. The 10–ring is now common at 0.6%. We note that the results at 5000 K are approximate and limited by the simulation time since the 5775 defect remains present during most of the simulation. These probabilities are consistent with the Boltzmann distribution for the excitation energy of each type of defect at each temperature.

We have calculated the modified Lindemann criterion for use in two dimensions. The details are discussed in the methods section above. The results are 0.071 for 4000 K, 0.082 for 4500 K, 0.11 for 5000 K, and 1.46 for 6000 K. These numbers are comparable to the Zakharchenko results in reference 19. For example, at 4500 K, we find $\gamma_{12} = 0.082$, while the previous results find $\gamma_{12} = 0.085$. Roughly speaking, the system is expected to melt at $\gamma_{12} \approx 0.1$.

In this paper we have discussed the properties of an ideal extended periodic freestanding graphene layer at high temperatures. In an experimental setting, one would typically mount a finite sample onto a substrate in a freestanding fashion. Any real world realization of this system will contain edges or defects. We agree that the presence of isolated defects,

vacancies, or edges may lower the melting point in graphene as well. We note that Los *et al.* have studied the melting behavior of graphene discs which have open edges.¹⁵ For a disc with 8020 atoms, the melting point is 4430 K. This decreases to 4250 K for a 770 atom disc. This represents a small decrease in melting temperature compared to the 4510 K predicted melting point of the infinite periodic system.

To test the effect of an isolated defect on the melting point of the system, we ran a short 6.2 ps MD simulation at 4500 K starting with 1 atom pulled out of the 10 x 10 repeating cell, and placed on top of the lattice. This starting point is shown in Figure S13. The system appears to be in a quasi-2D liquid state. These initial results show that the adatom quickly re-entered the layer. Then, after 1 ps, the system had reached a relatively stable state with separated 57, 75, and 585 defects, which persisted to the end of the simulation. The result after 6.2 ps of annealing at 4500 K is shown in Figure S14. We conclude that the addition of adatoms or isolated vacancies may have a limited effect on the system at these temperatures, because the system is already liquid like and already has excitation of 5775 and other defects.

To minimize the potential effect of defects, the system could also be rolled up into a buckyball, spiral, or large capped nanotube shape. One could also heat sink the edges of the sample to keep them from melting prematurely. One can also imagine mixing together reduced graphene oxide and single-walled nanotubes, as was done recently to make a working light bulb from these materials.⁸

We think that graphene and carbon nanotubes, together with other proposed high melting point materials including Ta₄HfC₅, HaNC alloys would be interesting candidates for experimental tests of melting in the weightless environment of space, or freefall in a plane. Heating could be carried out either resistively or remotely by irradiation. This would permit the extremely high heating temperatures necessary, while isolating the samples in a vacuum environment without contact with other materials which might contaminate the experiment.

Summary

We have investigated the early melting behavior of the quasi-2D freestanding graphene monolayer using exclusively reliable *ab initio* molecular dynamics calculations. At 4500 K, the system survives annealing for 18 ps without destroying the lattice. We have calculated the excitation energies for the 3-ring and broken bond events, which are new to this paper. By 5000 K, diffusion events occur which lead to 5775 defects. Numerous bond breaking and three-ring events which indicate the start of melting within 20 ps. We observe the initial stages and spontaneous creation of a 5775 defect during the MD simulation. At 6000 K, the system consists primarily of 1D double bonded chains, loosely coupled together. We also calculated the modified 2D Lindemann criterion for the system.

We also tested the addition of adatoms and vacancies to the system, and conclude that these may not have a huge effect on the system at these temperatures. At 4500 K, the system appears to be in a quasi-2D liquid state. We hope that our accurate calculations will contribute to future experimental and theoretical studies of these fascinating materials at

high temperatures. We hope that future longer and larger theoretical calculations can be based on our cornerstone accurate results. We have also proposed new ideas for future experimental work. We think that there is great opportunity for novel experimental studies of these new high temperature materials including bulk alloys as well as graphene analogs and carbon nanotubes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Sections of freestanding graphene layers at temperatures of 4000, 4500, and 5000 K. We show the last frame of each simulation after 12, 18, and 20 ps, respectively. The surface shows increasing roughness as the temperature is raised. At 5000 K, the system has started to melt. Two 10 x 10 unit cells are shown.

Figure 2.

Last frame of the 6000 K simulation, side view. Atoms are moving up out of the plane and starting to fill the cell (shown in white). The system primarily consists of 1D chains of atoms, loosely coupled together.

Figure 3.

a) 0 K Optimized 3-ring with constrained bond length. b) Single broken bond held by constraints. The single broken bond has a relative energy of 3.48 eV.

Figure 4. Lowest energy structure of the 5775 defect in the periodic 10 x 10 unit cell (optimized at 0 K). We observe significant curving of the surface. The 5775 defect has been highlighted in yellow (angle view).

Figure 5. Pair correlation function for graphene at five different temperatures. We observe a smooth disappearance of the pair correlation function as the temperature is raised. At 6000 K, the system shows very little correlation.

Figure 6. Initial stage of the spontaneous formation of a 5775 defect during the 5000 K MD simulation. One C atom shown in yellow is penetrating into a neighboring 6-ring. Original bonding configuration shown.

Table 1

Detailed results for relative energies of defects in the periodic graphene lattice at 0 K.

Binding and Formation Energies	Pressure GPa	Relative E eV	Cell Size Å
Base 10x10	0.015	0.00	24.63
3 Ring	0.00	2.44	24.64
Broken Bond	0.02	3.48	24.65
5775 Curved	-0.02	4.78	24.60
5775 Flat	0.00	4.80	24.66
5775 Separated	0.00	14.25	25.19

Table 2

Probability of observing various ring numbers as a function of temperature.

Ring Number	Temperature		
	4000 K	4500 K	5000 K
3	0.6%	1.3%	1.8%
4	0.0%	0.0%	0.0%
5	0.6%	1.2%	2.7%
6	98.8%	97.8%	93.0%
7	0.0%	0.0%	1.8%
8	0.0%	0.0%	0.0%
10	0.015%	0.037%	0.6%
14	0.0%	0.0%	0.0%