Physics of Complex Systems, 2024, vol. 5, no. 4
www.physcomsys.ru

Condensed Matter Physics.
Phase equilibria and phase transitions

UDC 538.9
EDN JFGSTK
https://www.doi.org/10.33910/2687-153X-2024-5-4-172-176

Melting and sublimation of graphene and silicene

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For citation: Fomin, Yu. D., Tsiok, E. N., Ryzhov, V. N. (2024) Melting and sublimation of graphene and silicene. *Physics of Complex Systems*, 5 (4), 172–176. https://www.doi.org/10.33910/2687-153X-2024-5-4-172-176 EDN JFGSTK

Received 9 September 2024; reviewed 26 September 2024; accepted 26 September 2024.

Funding: The study did not receive any external funding.

Abstract. This study involves molecular dynamics simulations aimed at investigating the crystal structure collapse of graphene, graphite and silicene. It shows that in the case of graphene and graphite, crystal structure collapse is related to the sublimation of the sample. At the same time, when a silicene sample is heated at constant volume, it comes into the liquid–gas two-phase region of the phase diagram. The difference in the crystal structure collapse of graphene and silicene is caused by the differences in the pressure of the liquid–gas–crystal triple point.

Keywords: molecular dynamics simulations, graphene, silicene, sublimation, liquid–gas–crystal triple point

Introduction

It is believed that the ground state of all systems should be some kind of a crystal structure. However, when this crystal is heated, the ordered structure collapses, and the system becomes disordered. Importantly, the collapse of the crystal structure proceeds via either melting or sublimation phase transition depending on the pressure in the system: if the pressure is above the one in the liquid–gas–crystal triple point, the crystal melts. Otherwise, it sublimates. Therefore, depending on the triple point location, different processes can govern the collapse of the crystalline structure.

Nowadays there is a strong interest in two-dimensional materials such as graphene and silicene. These materials are expected to give numerous advantages for different technological applications. Therefore, the issue of their thermal stability is also of great importance.

Melting of graphene was studied in a number of papers. A Monte Carlo study of graphene melting was reported in Ref. (Zakharchenko et al. 2011). It was observed that at very high temperatures (about 4,900 K) carbon atoms start to form linear chains that can decompose from the graphene sheet. The authors made a conclusion that at $T_m = 4{,}900$ K graphene melts in a kind of polymer gel.

The same group of authors improved these findings in Ref. (Los et al. 2015), extrapolating them to lower temperatures using classical nucleation theory. As a result, they concluded that the melting temperature of graphene is $T_m = 4{,}500$ K.

Another attempt to address this issue was undertaken by Orekhov and Stegailov in Ref. (Orekhov, Stegailov 2015). Based on molecular dynamics simulations with the well-recognized AIREBO model

(Stuart et al. 2000), they concluded that the melting temperature of graphene is $T_m = 4{,}900$ K, which is consistent with Ref. (Zakharchenko et al. 2011). They did not employ the extrapolation procedure like the one used in Ref. (Los et al. 2015); therefore, one might expect that $T_m = 4{,}500$ K is a more reliable result. Since the melting point of graphene is extremely high, we are not aware of any experimental work on the topic. All available results are based on molecular simulation methods.

The melting temperature of silicene was also evaluated in a number of computational works.

Ref. (Bocchetti et al. 2014) reported on the Monte Carlo simulation of the melting of a silicene sheet. The Tersoff potential (Tersoff 1989) with two sets of parameters was implemented: the original ones (Tersoff 1989) and the ones from Ref. (Agrawal et al. 2005). The melting temperature of silicene was estimated to be 3,600 K in the former case and 1,750 K in the latter.

Non-equilibrium molecular dynamics simulation of the melting of silicene with the Tersoff potential was performed in Ref. (Das, Sarkar 2018). The melting temperature was estimated to be 1,201 K.

Non-equilibrium molecular dynamics simulation of the melting of silicene in the framework of the Stillinger–Weber potential (Stillinger, Weber 1985) was carried out in Refs. (Min et al. 2018) and (On 2020). The melting temperature was reported to be 1,500 K in the former publication and 2,500 K in the latter.

It is seen from the discussion above that the estimation of the melting point of silicene ranges from 1,200 K up to 3,600 K, which is definitely unsatisfactory.

In the present paper, we perform a molecular dynamics simulation of the crystal structure collapse of graphene and silicene, showing that they experience different phase transitions: sublimation in the case of graphene and transition into the two-phase region in the case of silicene.

Systems and methods

We performed molecular dynamics simulations of graphene, graphite and silicene.

In the case of graphene and graphite, the AIREBO potential (Stuart et al. 2000) was utilized. The graphene sample consisted of 6,400 carbon particles in a layer surrounded by vacuum. In the case of graphite, a 4,000-particle sample in a rectangular box was used. Periodic boundary conditions were used. The time step was set to 0.2 fs, and the whole simulation run was 2 ns. The temperature was set to 8,000 K. The pressure was fixed at 1 bar. For the crystal structure that collapsed during the simulation time, a system of linear chains (clusters) was obtained. The particles were considered to belong to the same cluster if the distance between them was less than 1.95 Å.

In the case of silicene, the Stillinger–Weber potential (Stillinger, Weber 1985) was employed. The system consisted of 20,000 silicon atoms surrounded by vacuum. Periodic boundary conditions were used. The time step was set to 1 fs, and the whole run was 10 ps. The system was simulated at constant volume and at several different temperatures. Two characteristics of the system were monitored during the simulation time: the average potential energy per particle and the thickness of the silicene film, which was defined as the difference between the z coordinates of the highest and the lowest particles in the system. When the time dependence of these quantities experienced a jump, the crystal structure collapsed.

Results and discussion

The case of graphene and graphite

Firstly, we performed a molecular dynamics study of the crystal structure collapse of graphene and graphite. As stated above, both systems are simulated at a very high temperature of $T = 8{,}000$ K, which is definitely above the melting or sublimation points. The snapshots of the configurations after the structure collapse of graphene and graphite are given in Fig. 1 (a) and (c) respectively. It is seen that the final configurations consist of linear chains of different length (linear clusters). We calculated the distribution of cluster sizes, which is given in Fig. 1 (b). It is seen that the probability distribution of cluster sizes perfectly coincides for both initial structures. Moreover, the probability distributions have a high peak at the chain length of three atoms.

According to the experimental data (Leider et al. 1973), gaseous carbon consists mostly of three atoms' clusters. Comparing it to our results, we conclude that gaseous carbon is obtained after the collapse of the crystal structure. Therefore, sublimation takes place in the case of graphite and graphene.

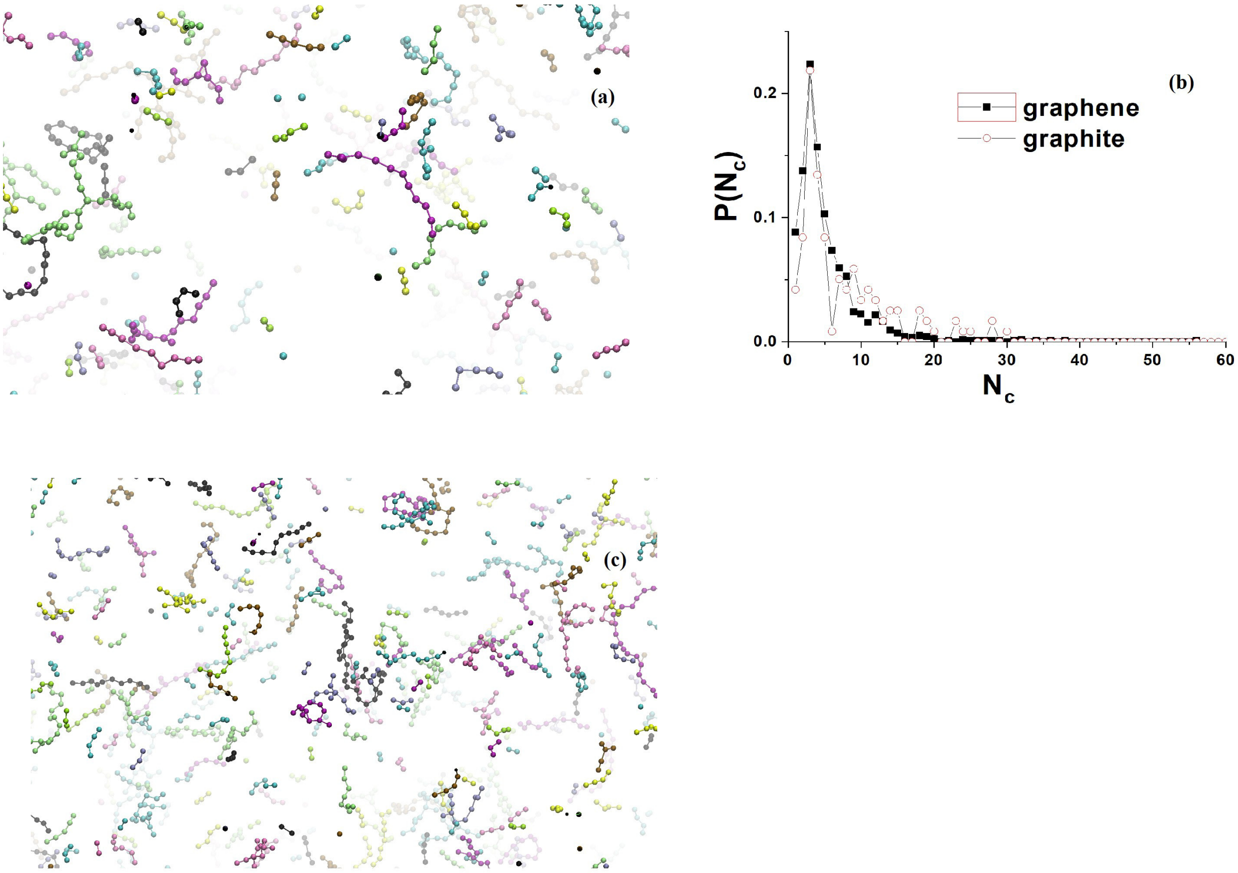

Fig. 1. (a) The snapshot of a system with the initial structure of graphene after the crystal structure collapse. (b) The probability distribution of the size of the clusters of carbon atoms in the systems with the initial structures of graphene and graphite after the crystal structure collapse. (c) The same as (a), but with the initial structure of graphite

The case of silicene

In the case of silicene we simulated the system at different temperatures and monitored its potential energy and the thickness of the sample. Fig. 2 (a) shows time dependence of the potential energy per particle of silicene at different temperatures. At room temperature, the silicene layer has buckled configuration at thickness 5 Å, but at the same time it retains its defect-free honeycomb shape. The potential energy does not change during the whole simulation time.

With temperature rising to 850 K, the potential energy increased slightly, which may be due to the formation of defects because of thermal instability, which leads to a growth in the thickness of the system. The potential energy and thickness of the system do not change during simulation at T = 850 K.

However, as soon as the temperature reaches T = 875 K, after a while there is a sharp drop in potential energy, which means that the structure of the system has changed dramatically. Apparently, the low-energy state of the system is thermodynamically more favorable than the initial defective one at T = 875 K. However, the energy still continues to decrease slightly over time, and the thickness of the system grows continuously, that is, silicene does not reach thermodynamic stability during simulation. The snapshots of the system at T = 850 and 875 K are shown in Fig. 2 (b) and (d) respectively. It is seen that the sample remains crystalline at the former temperature, but is disordered at the latter. At the same time, the system remains condensed at T = 850 K, since it has finite thickness, i. e. its atoms do not occupy the whole available volume.

We are not aware of any evaluation of the location of the gas–liquid–crystal triple point of silicon. However, the pressure of a saturated vapor is available (Babichev et al. 1991). The melting temperature of silicon at ambient pressure is 1,673 K. The pressure of the saturated vapor of silicon at 1,673 K is about 5 bar, which is very close to the ambient one. It means that although we do not know the exact position

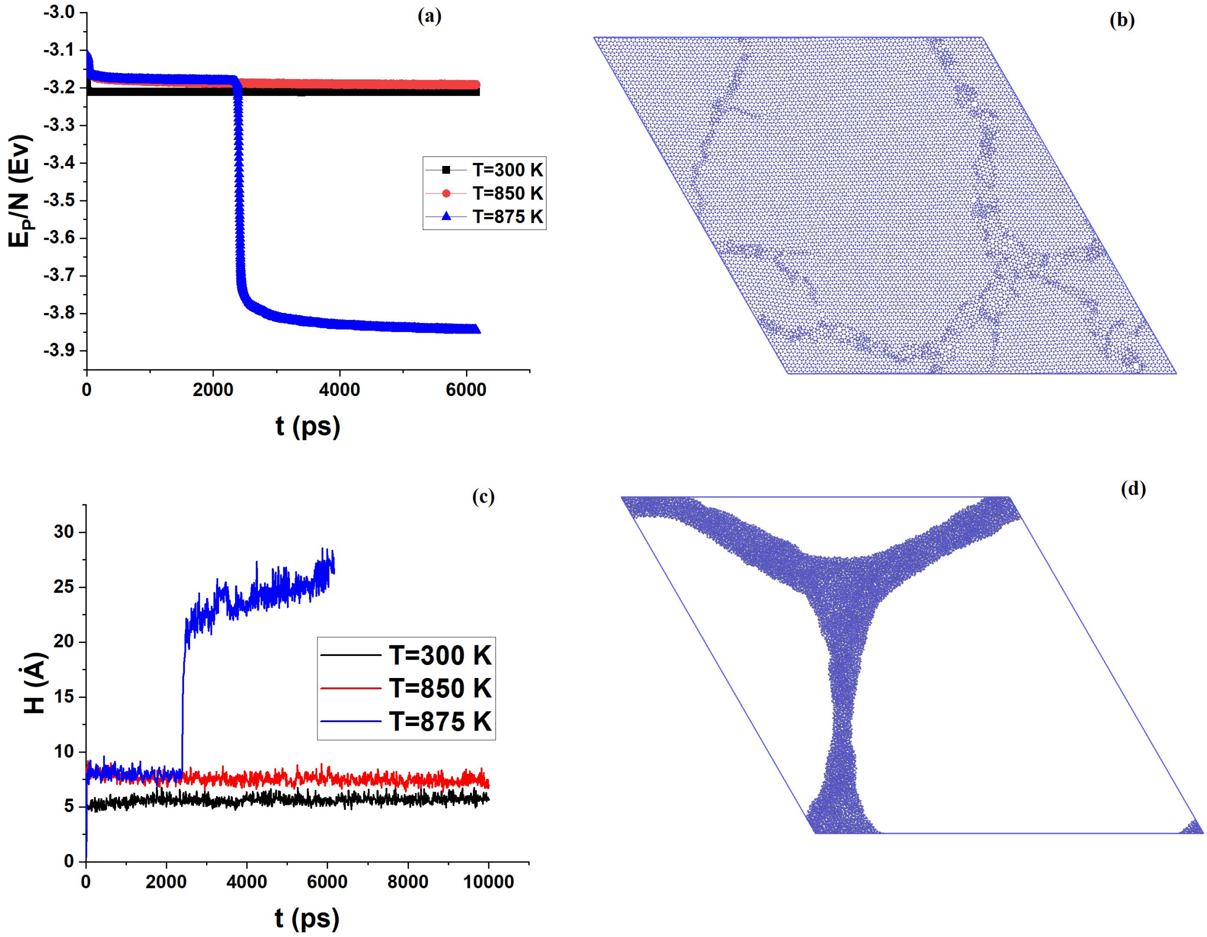

Fig. 2. (a) The time dependence of the potential energy per particle in the system of silicene at different temperatures. (b) The snapshot of the system at $T = 850$ K. (c) The time dependence of the thickness of the system at different temperatures. (d) The same as (b) at $T = 875$ K

of the triple point, it is not far from the $P = 1$ bar and $T = 1.673$ K. Therefore, it is possible that the heating of silicon at ambient pressure will cause melting rather than sublimation.

This conclusion is illustrated in the snapshots, which show the final structures of the systems at $T = 850$ and 875 K. In the case of $T = 850$ K, the system remains in the state of a strongly defective silicene layer, but the two-dimensional lattice is still retained. At the same time, at $T = 875$ K, the silicene layer breaks due to the formation of voids. Strongly compressed silicon atoms form a Y-shaped ‘island’. Such structures appear in molecular simulations in liquid–gas two-phase regions: since the density of the gas phase is much smaller than the one of a liquid, the gaseous regions look like voids. We conclude that the heating of the silicene sample leads to a transition into the liquid–gas two-phase region, i. e. it is neither melting nor sublimation, but something in-between.

Conclusions

In the present paper, we have performed molecular dynamics simulations of the crystal structure collapse of graphene, graphite and silicene. It is shown that in the case of graphene and graphite, the crystal structure collapse is related to the sample sublimation. At the same time, when the silicene sample is heated at constant volume, it comes into the liquid–gas two-phase region of the phase diagram. The difference in the crystal structure collapse of graphene and silicene is caused by the differences in the pressure of the liquid–gas–crystal triple point: while in the case of carbon the pressure of the triple point is very high (P_{tr} =16 MPa), the pressure of the triple point of silicone is close to the ambient one.

Conflict of Interest

The authors of this work declare that they have no conflict of interest.

Author Contributions

Yu. D. Fomin performed the simulations and wrote the manuscript, and E. N. Tsiok and V. N. Ryzhov analyzed the results and wrote the manuscript.

Acknowledgements

The authors are grateful to V. V. Brazhkin for his interest in the work and useful discussions of various aspects of the subject. The work was partially performed using the equipment of the Interdepartmental Supercomputer Center and with computing resources of the federal collective usage center "Complex for Simulation and Data Processing for Mega-science Facilities", both affiliated with the National Research Center "Kurchatov Institute".

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