Molecular-dynamics based insights into the problem of graphite melting

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Abstract. The experimental data on graphite melting temperature remain poorly determined despite the long history of investigations. The experimental results cover the wide span from 3800 to 5000 K that is an essentially larger uncertainty than the errors of individual experiments. In this work, we deploy the molecular dynamics method and expand our previous study of the kinetics of graphite melting comparing different carbon interatomic potentials. Here we consider the melting front propagation rate, the aspects of defect formation and single graphene layer decay. The results obtained allow us also to discuss the aspects of graphite–vapor and possible graphite–carbyne phase transitions at low pressures.

1. Introduction
Graphite is a very common material and its heat-resistant properties predetermined the wide field of its application in industry. Nevertheless, aspects of graphite behavior under high temperatures up to 5000 K still raise some fundamental questions. Experimentally obtained graphite melting points are located in a surprisingly wide range of temperatures from 3700 to 5000 K at close values of pressure [1–16]. Detailed analysis of the main experimental studies from Pirani’s [1] and Bundy’s [2] papers to recent works was made in [17].

Carbon phase diagram is of high importance for different applications (e.g. see [18–20]). Simple scaling relations (e.g. [21]) can be hardly applicable. There have been made several attempts to calculate carbon phase diagram using state-of-the-art atomistic models. In [22] and [23], the equations of state involving different carbon phases were proposed. The process of high-energy laser melting of graphite was studied using DFT in [24]. Recently the carbon phase diagram was calculated [25, 26] with an empirical potential LCBOP [27].

Another controversial question of carbon phase diagram—the problem of graphite–carbyne transition existence that anticipates direct graphite–liquid transition at low pressures—was widely discussed by Whittaker [28] and attracts a lot of interest in the search of novel materials [29].

For the experiments on the ultra-fast graphite melting (up to $10^9$ K/s) the time scales of heating and, accordingly, the processes occurring in sample, are so small that they approach the limits that can be directly calculated by the molecular dynamics (MD) method. MD method is a fundamental research tool that opens the possibility to study various systems (e.g. [30, 31]) using high performance computing [32]. MD method is known to be very prolific in studies of melting [33–38]. Thus, this method is a convenient tool for theoretical interpretation and
supplementation of the experimental data, as well as for analyzing related phenomena. In this paper, we report the results of MD simulation of graphite melting within several models of the empirical reactive interatomic potentials, which describe the change in the type of hybridization of graphite atoms with a change in the structure of their local environment. Our preliminary results were published in [39]. In [40, 41] we presented an MD-based mesoscale model and compare its results with the large set of experimental data.

2. Model and Calculation Method

2.1. Interatomic Potentials

One of the first empirical bond order potentials for carbon, REBO, was created to describe diamond [42] and was restricted by the cut-off radius of 2 Å. Its later modification, AIREBO [43], among other advantages has a component responding for the long-range interactions with the cut-off radius 10 Å. This long-range term makes it possible to model systems with significant contribution of non-bonded van der Waals interactions such as hydrocarbons and graphite. Due to its simple Lennard-Jones analytical form, the long-range component was criticized to be inaccurate at high pressures. Recently a new version of AIREBO (so-called AIREBO-M) with the Morse-type long-range component was published [44]. It provides a better agreement with experimental and ab initio data.

Figure 1. Ball-stick model represents two-phase interface in the center of the calculation cell.
2.2. Calculation methods
Calculation of the melting temperatures for various materials is of fundamental scientific interest. These calculations are conventionally carried out by finding the free Gibbs energy for each phase with the subsequent search for equilibrium. An alternative method is the two-phase simulation method [45], which implies simulation of two coexisting phases; i.e. it suggests the simultaneous presence of both liquid and solid phases in the system under consideration. At a temperature close to the expected melting temperature, the solid passes partially into the liquid phase; the subsequent shift of the equilibrium between the phases allows one to draw conclusions about the melting temperature with respect to the initial material temperature. Using two-phase method to study the graphite melting kinetics, we carried out calculations for carbon atoms behaving according to the AIREBO potential [43]. The computational cell with periodic boundary conditions had sizes of 20, 20, and 120 Å along the OX, OY, and OZ axes, respectively (during simulation, the sizes were varied depending on pressure). About 10000 carbon atoms were used in the two-phase simulation. Half of the computational cell was occupied by a graphite crystal, while the other half was filled with disordered-phase atoms (figure 1). To distinguish the ordered phase with respect to the disordered one, we used the static structural factor as an order parameter:

\[ S = \langle \cos(xk_x + yk_y + zk_z) \rangle^2 + \langle \sin(xk_x + yk_y + zk_z) \rangle^2, \]

where \( x, y, \) and \( z \) are the atomic coordinates and \( k_x, k_y, \) and \( k_z \) are the reciprocal lattice vectors corresponding to the graphite crystal structure. Averaging was performed over all atoms in the region where the structural factor was calculated. In the case of a disordered phase, the \( S \) value is close to zero, whereas for an ideal crystal it is unity. Using the structural factor, we monitored the position of the interface.

In practice, graphite is generally a polycrystalline material. Its detailed structure characterization is a very complex problem (e.g. see [46, 47]). Its structure, degree of isotropy, and density depend strongly on the preparation technique. The density may vary in the range of 1.6–2.2 g/cm\(^3\), depending on the specific grade. Highly oriented pyrolytic graphite (HOPG), which has a quasi-monocrystal structure, composed of parallel graphene plates, is generally used in experiments on graphite melting. We specifically chose HOPG for calculations as a model for describing the solid phase. One calculation corresponded to 1.5–2 ns of time in most cases. The equations of atomic motion were integrated with a step of 0.1 fs. The system was brought to the desired parameters (temperature and pressure) using a Nose–Hoover thermostat and varying the cell sizes.

3. Results
3.1. Front velocities
The melting front velocities calculated for AIREBO in [40, 41] at pressures \( P = 2 \) and 12 GPa in the range of temperatures \( T = 4100–4700 \) K are shown in figure 2. Note that the melting kinetics for graphite is slower than that for metals by about two orders of magnitude [48]. The front velocity is only about 1 m/s in the range of 4400–4700 K (the corresponding superheating is more than 600–900 K). In the temperature range of 3750–3950 K, the front velocity decreases close to zero. It is difficult to determine exactly the instant of turning of the front velocity to zero because of the slow rate of the process and, accordingly, the large calculation time. A further slow decrease in temperature revealed no tendencies to crystallization onset at times about a few nanoseconds.

To verify whether such slow rate of melting is some specific effect of AIREBO potential or not, we have performed the same calculations with another accurate bond-order carbon potential—LCBOP [27]. According to LCBOP-I model the graphite melting temperature lays in the range of 3750–4000 K [25]. The next modification of this potential, LCBOP-II, gave slightly higher value
of graphite melting temperature $T_m = 4250 \text{ K}$ [26]. Nevertheless, our calculations with LCBOP-I show the same slow melting kinetics and even higher levels of possible sample overheating: the crystal maintained its structure at temperatures $T > 5000 \text{ K}$. The relatively low velocity of the melting front may affect, in particular, the results of the experiments on heating graphite by a short (shorter than one millisecond) current pulse, where the onset of melting is determined from the change in the macroscopic sample parameters, e.g. resistivity (see [40, 41]).

For both potentials the melting front velocity has a distinct exponential dependence on temperature (figure 2), therefore in this case instead of using Broughton–Gilmer–Jackson approach [49] we apply the quasi-equilibrium model for the rate of a first-order phase change [50]:

$$v_{\text{front}}(T) = \frac{ak_BT_D}{h} \left[ \exp \left( \frac{\Delta G_m}{k_BT} \right) - 1 \right] \exp \left( -\frac{W_f}{k_BT} \right),$$

where $k_B$ is the Boltzmann constant, $h$ is the Planck constant. $\Delta G_m = L\Delta T/T_m$ is the free energy difference between solid and liquid phases ($L = 120 \text{ kJ/mol}$ is the heat of fusion). $T_m = 3650 \pm 150 \text{ K}$ was previously determined [40, 41] by thermodynamic integration technique [51]. The only remaining unknown constant $W_f$ is the energy barrier for the atom “detachment” from solid into liquid. The MD results fitting with equation (1) gives $W_f \approx 3.25 \text{ eV}$ for AIREBO and $W_f \approx 4.0 \text{ eV}$ for LCBOP-I (table 1). A visual inspection of the “detachment” events reveals their connection with the formation of the interplanar interstitial-like defects at the solid side of the melting front (see figure 1). The formation energies from 5.5 to 8.0 eV were obtained in the static ab initio calculations of different interstitial defects in graphite [52]. The value of $W_f$ is therefore quite reasonable, taking into account that it corresponds to the high temperature system with strong thermal fluctuations, basal planes oscillations and presence of the disordered phase.

In our previous works [39–41], we have suggested that the melting process in graphite is driven by the interlayer defects formation in the zone of phase contact. Figure 3 shows the decrease of the interlayer spacing with pressure for AIREBO and AIREBO-M at $T = 4000 \text{ K}$. For high pressures, the difference between the results for two potentials is almost 8%. To determine the influence of the interlayer spacing on the graphite melting kinetics we have conducted calculations with AIREBO-M similar to the described above (figure 2).

We can make a conclusion that the decrease of the interlayer spacing lowers the energy barrier for atoms to move from solid to liquid phase and accelerates the melting kinetics, possibly lowering the equilibrium melting temperature $T_m$. As expected, fitting with equation (1) gives for AIREBO-M slightly lower values of $W_f \approx 2.85–3.05 \text{ eV}$ (table 1). Since we did not obtain the exact value of the graphite melting temperature $T_m$ for AIREBO-M, we assume that it lays nearly in the same range as for the original AIREBO: 3500-3650 K (from the table below one can see that the variation of $T_m$ does not affect $W_f$ much).

For the considered variety of accurate carbon interatomic potentials (LCBOP-I, AIREBO, AIREBO-M) we obtain one and the same result: kinetics of melting process in graphite is extremely slow. Calculated values of $W_f$ also coincide well. Therefore, we are inclined to believe this effect is a real physical phenomenon that is not induces by some artificial properties of specific potential and is related to the nature of C-C bond formation and breaking.

3.2. Graphene decay

As the further investigation of interstitial defects role in the graphite melting we study the thermal decay of single graphene layer. Graphene can be considered as a graphite crystal with quasi-infinite interlayer spacing. The aspects of graphene melting were previously reported in detail in [53]; it was shown (using the Monte Carlo method and the LCBOP-II potential) that a graphene sheet successfully retains its structure upon heating to $\sim 4900 \text{ K}$. For the AIREBO
Figure 2. Temperature dependence of the melting front velocity for AIREBO, AIREBO-M and LCBOP-I potentials.

Figure 3. Graphite interlayer spacing for AIREBO and AIREBO-M potentials at $T = 4000$ K.

potential under the same conditions, we obtained that the graphene decomposition temperature is also in the range of 4800–4900 K.

Graphene decomposition is driven by formation of the clusters of Stone-Wales defects. Dynamics of graphene structure decay is shown in figure 4. During the constant rate heating
Table 1. The energy barrier for the atom “detachment” from solid into liquid \((W_f)\) for the examined potentials (for the AIREBO-M model different guessed values of \(T_m\) are shown).

| Potential   | \(T_m\) (K) | Pressure (GPa) | \(W_f\) (eV) |
|-------------|-------------|---------------|-------------|
| AIREBO      | 3650        | 2–12          | 3.25        |
| AIREBO-M    | 3650        | 2             | 2.95        |
| AIREBO-M    | 3500        | 2             | 3.05        |
| AIREBO-M    | 3650        | 12            | 2.85        |
| AIREBO-M    | 3500        | 12            | 2.97        |
| LCBOP-I     | 3950        | 4             | 4.0         |

Figure 4. Dynamics of graphene thermal decay. Heating rates are indicated near the curves.

at temperatures above 4800 K, the number of hexagonal rings begins to decrease rapidly. Decay begins at the points with the highest Stone-Wales defect concentration and results in the formation of long linear carbon chains. The similar picture was observed for LCBOP-II in [53].

We consider the temperature of graphene melting \(T = 4800–4900\) K to be the upper bound of the metastable superheated graphite [41], since graphene represents the two-dimensional crystal with no interlayer defects. Note that this value of graphene melting temperature exceeds significantly the graphite decay temperatures obtained for LCBOP in [25, 26] and our results for AIREBO; however, it coincides very well with the upper range of the experimentally measured graphite melting temperatures [41].

3.3. Liquid–liquid phase transitions

Liquid carbon was studied in the pioneering works at the dawn of the \(ab\ initio\) MD [54] that provided a certain evidence of the coordination changes in liquid carbon at 100 GPa and hence supported the liquid–liquid phase transition (LLPT) hypothesis (among similar transition we can also point out the plasma-plasma phase transition [55]). The subsequent \(ab\ initio\) studies of the carbon phase diagram showed a maximum at the diamond melting curve but did not confirm the LLPT hypothesis for the corresponding ultrahigh pressures [56, 57]. Atomistic
Figure 5. Typical picture of graphene thermal decomposition. Green balls represent $sp^2$-hybridized atoms of the original graphene structure, red—$sp$-hybridized atoms of the new polymer-like phase (see [53]).

Simulation methods became mature enough to handle the graphite melting problem as soon as the sophisticated interatomic potentials for carbon had been created (AIREBO [43] and LCBOP [27]). It was thought that LLPT between $sp^2$ and $sp^3$-hybridized liquids existing at pressures 5–8 GPa may explain the maximum on the graphite melting curve. In [58] the possibility of transition between $sp$-hybridized non-metallic and metallic liquids at $P \sim 1$ kbar was discussed. However despite considerable effort no theoretical confirmation of the LLPT in liquid carbon was found [59–61].

It is known that liquid carbon obtained in experiments at low pressures (near the triple point that is expected to be located at $P \approx 100$ atm) has a surprisingly low density. In [62] and [13] an expansion of 45–70% was detected during melting. This low-density liquid was obtained by the melting of graphite at $T_m \approx 4800$ K, i.e. according to our results by melting in highly superheated samples. Due to the low density such liquid is expected to be mostly $sp$-hybridized. It reminds us of polymer-like $sp$-hybridized structures which were observed during the modeling of graphene decay in [53] and in our work also at $T \approx 4900–5000$ K (figure 5). In [53] it was mentioned that this substance shows characteristics untypical for simple liquids. We can assume that at low pressures near the triple point graphite superheated over 1000 K may come closely to the vapor region (see e.g. classical carbon phase diagram proposed in [63]). In such case, this low-density liquid may represent some transitional substance between liquid and vapor carbon.

Carbon is known to form a large variety of allotropes, which maintain their stability deeply in the metastable zone, like diamond or fullerenes at ambient conditions. It may indicate that certain phase transitions in carbon are much slower than in other single-element materials due to the large activation energy barriers associated with C–C bond breaking, like in case of the graphite melting. This idea was highlighted by Whittaker [28] for a hypothetical graphite—
carbyne transition which he described as a multistage process that includes the formation of several types of carbyne structures (the coordination of carbon atoms was expected to change continuously from the three-fold to the two-fold type in the region $T = 2600–4000$ K in solid state). Similar situation is expected to be observed in liquid carbon: the previously discussed theoretical studies [59–61] indicate that liquid carbon above the graphite melting line changes its coordination with pressure gradually without sharp transitions from two- or three-fold to four-fold liquid. Possibly the same picture may appear at low pressures for liquid–vapor and graphite–vapor transitions leading to the formation of unusual intermediate melts like in the process of graphene decay (figure 5).

Modern ab initio methods allow us to determine more energetically preferable allotrope between the two variants with clearly defined atomistic structures (e.g. between HOPG and diamond or between two carbon nanotubes with different radius or chirality). Nevertheless for such irregular structures like carbyne or “low-density” liquid/gel the question of the stability and therefore their role on the phase diagram remains an additional challenge. From this point of view it is not surprising that due to slow kinetics and high stability of some allotropes in the metastable state many parameters of the carbon phase diagram are determined with a significant discrepancy. Perhaps, in the finite-time approximation it is more appropriate to talk about regions on the carbon $P–T$ diagram where certain phase transitions occur than about direct points of phase equilibrium (condensation being a case of particular interest [64]).

4. Conclusions
Using molecular dynamics calculations to describe graphite melting kinetics we extend here our earlier results [39–41] comparing properties of different carbon interatomic potentials (AIREBO, AIREBO-M and LCBOP-I). Due to the difference between melting temperatures obtained with AIREBO in [40,41] and LCBOP-II in [26] we can make only approximate suggestions about the exact value of the equilibrium graphite melting temperature. Nevertheless, in our calculations we observed a more interesting fact: two independent models of carbon potentials show similar surprisingly slow kinetics of graphite melting. Comparing results obtained with AIREBO and AIREBO-M we confirm our earlier results that such behavior of graphite melting is a result of the high energy barrier for the atom “detachment” from solid into liquid. Therefore, we are inclined to believe that slow melting of graphite is a real physical phenomenon that is not induces by some artificial properties of specific potential and is related to the nature of C–C bond formation and breaking. Extending the revealed slow nature of structural transitions kinetics in carbon, we consider here the hypothesis that the long-discussed carbyne phase could be an intermediate long-lived metastable structure formed in the process of vaporization of low-density carbon liquid.

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References
[1] von Pirani M S 1930 Elektrothermie: die elektrische Erzeugung und technische Anwendung hoher Temperaturen; Vorträge (Springer)
[2] Bundy F P 1963 J. Chem. Phys. 38 618
[3] Schoessow G J 1968 Phys. Rev. Lett. 21 738
[4] Fateeva N S 1971 Pisma ZhETF 13 157–159
[5] Gokcen N A, Chang E T, Poston T M and Spencer D J 1976 Determination of graphite-liquid-vapor triple point by laser heating Tech. rep. DTIC Document
[57] Correa A A, Bonev S A and Galli G 2006 Proc. Natl. Acad. Sci. USA 103 1204–1208
[58] Ferraz A and March N H 1979 Phys. Chem. Liq. 8 289–297
[59] Wu C J, Glosli J N, Galli G and Ree F H 2002 Phys. Rev. Lett. 89 135701
[60] Kum O, Ree F H, Stuart S J and Wu C J 2003 J. Chem. Phys. 119 6053
[61] Ghiringhelli L M, Valeriani C, Los J H, Meijer E J, Fasolino A and Frenkel D 2008 Mol. Phys. 106 2011–2038
[62] Savvatimskiy A I 2008 J. Phys.: Condens. Matter 20 114112
[63] Bundy F P, Bassett W A, Weathers M S, Hemley R J, Mao H U and Goncharov A F 1996 Carbon 34 141–153
[64] Amirov R H, Isakaev E K, Shavelkina M B and Shatalova T B 2014 J. Phys.: Conf. Series 550 012023