Conserving controversies of melting line of graphite and graphene

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Investigation of melting line of graphite and liquid carbon has long history. However, up to now there are still numerous controversies in the field, for instance, the melting temperatures obtained in different experiments are in very bad agreement. In the present paper we compare several models of carbon widely used in computational studies and the results of ab-initio simulations of liquid carbon. We show that the empirical models fail to reproduce the properties of liquid carbon correctly. We also discuss the "melting" of graphene.

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INTRODUCTION

Melting of graphite and the nature of liquid carbon are two long-standing problems of condensed matter physics. However, in spite of very intensive research, both problems still remain unsolved. The first attacks on the problem appeared as early as 1911 [1]. In 1923 the experimental works by Pirany were published [2]. The first theoretical calculation of the phase diagram of carbon was made by Leipunsky in 1939 [3]. Extrapolating the experimental data available at that time and introducing some assumptions (for instance, that the volume jump at melting of graphite does not exceed 5%) he managed to estimate the melting point of graphite to be \( T_m = 4000 \text{ K} \) at atmospheric pressure. Interestingly, the melting point at pressure as high as 100 kbar Leipunsky estimated to be 4240 K, i.e. the slope of the melting curve \( dT/dP \) is very small. However, all these attempts both experimental and theoretical were rather inaccurate.

The most famous experimental evaluation of the melting curve of graphite was undertaken in the work by Bundy [4]. According to his results them melting temperature is 4100 K at pressure 9 kbar, then it increases to 4600 K at 70 kbar and after that decreases back to 4100 K at 125 kbar. The presence of maximum on the melting curve of graphite was confirmed in the works by Fateeve and Vereschagin [5] and Togaya [6]. However, even if all three works report that the melting curve demonstrates a maximum the melting temperatures are very different in all these works.

Numerous experimental attempts to evaluate the melting curve of graphite were undertaken (see, for instance, Refs. and references therein). However, the problem mentioned above remained up to now: different experiments give to different melting points. The estimations of the melting temperature range from approximately 4000 up to 5000 K.

The experimental difficulties with phase diagram of carbon induced also numerous attempts to calculate it in computer simulation. The simulation of carbon mostly proceeded in frames of so called Bond Ordered Potentials (BOPs) and ab-initio methods. In the set of papers by Ree et. al (see [10] and references there) investigation a Liquid-Liquid Phase Transition (LLPT) in carbon was predicted by using the famous Brenner potential. However, the existence of the LLPT was immediately doubted by other authors who employed other empirical potentials (for example, LCBOP) and ab-initio simulations. Currently it looks to be commonly accepted that no LLPT takes place in carbon and its appearance in Brenner model is due to incorrect evaluation of torsional interactions in this model.

Several more empirical potentials were used to calculate the melting line of graphite. In Ref. [11] Long-range Carbon BOP (LCBOP) was introduced. Later on this model was modified in Ref. [12] (LCBOPI+ model) The phase diagram of this model is given in Ref. [13] In this model the melting line of graphite has a positive slope \( dT/dP \) in the whole range of pressures. The melting temperature of graphite varies from \( T = 3800 \text{ K} \) at \( P = 2 \) GPa to \( T = 4250 \text{ K} \) at \( P = 16.4 \) GPa (the graphite-diamond-liquid triple point). The properties of liquid carbon were also studied in frames of this model and no LLPT was observed.

Further improvement of this model was introduced in Ref. [14] (LCBOPPII potential). In Ref. [15] the properties of liquid carbon in frames of LCBOPPII model are studied and no LLPT was observed. The phase diagram of LCBOPPII model was calculated in Ref. [16]. It is of particular interest than LCBOPPII predicts that the melting temperature of graphite is independent of pressure and equal to \( T_m = 4250 \pm 50 \text{ K} \). The authors also calculate the specific volume of graphite and liquid carbon along the melting line and show that although both volumes of graphite \( V_g \) and liquid \( V_l \) decrease with the pressure the equality \( V_l = V_g \) holds along the whole melting line, i.e. \( \Delta V = 0 \) which according to Clausius-Clapeyron relation leads to zero slope \( dT/dP \).

Another model widely used for investigations of carbon and hydrocarbons is so-called AIREBO potential [17]. The melting curve of this model was calculated in Ref. [8] by means of moving interface method. Like in the LCBOPPII model the melting temperature of AIREBO
graphite almost does not depend on pressure. In the range of pressures from 2 up to 12 GPa the melting temperature is \( T_m = 3640 \pm 150 \) K which is slightly below the one of LCBOP-II. Also no LLPT was observed in this model.

In Ref. [19] tight-binding simulation of liquid carbon is presented. This method can be thought as something intermediate between empirical potentials and ab-initio methods in the sense of both the simulation burden and the precision of calculations. The tight-binding simulation also does not give any evidences of LLPT in carbon. The ab-initio simulations of liquid carbon also eliminate the possibility of LLPT. However, no firm estimation of melting point of graphite based on ab-initio simulation is present in the literature.

A novel approach of construction of empirical models based on machine learning methods was introduced recently. This model was implemented to amorphous carbon in Ref. [20] (GAP potential) The results obtained with this model are in close agreement with ab-initio data, but it is possible to simulate larger systems and longer times which is especially important for investigation of amorphous carbon. Although GAP model gave very encouraging results for the properties of amorphous carbon no calculations of the melting line of this model was made up to now.

One can see that the simplest empirical models of carbon, like Brenmer potential, lead to appearance of LLPT, while more elaborate models, tight-binding and ab-initio simulations do not show the LLPT. Because of this it is a common view now that LLPT is an artefact of simple models and it should not take place in real carbon. However, the conclusions on presence or absence of LLPT in carbon are usually based on two parameters: equations of state (EoS) and hybridization of atoms which is related to the number of nearest neighbors. If LLPT is present then EoS demonstrate the van der Waals loop and the hybridization experiences changes from dominant sp2 at low densities to dominant sp3 at high ones. However, the accuracy of calculations of both EoS and hybridization in ab-initio simulations are doubtful too. For instance, in Ref. [18] a comparison of EoS calculated in several works by ab-initio MD is given. The agreement between different publications is rather poor. Moreover, the best agreement is achieved between the results of the author of [18] and the paper [21] in spite of the fact that in the former publication the simulations are performed at \( T = 6000 \) K while in the later one at \( T = 7000 \) K. The situation with hybridization is very similar. The results obtained in Ref. [18] at \( T = 6000 \) K are in better agreement with the results of GAP model at \( T = 5000 \) K [20] than to other ab-initio studies at the same temperature [18]. The fact that making temperature 1000 K higher or lower changes the results less then application of other functional in DFT calculations make the precision of the results of DFT calculations doubtful.

Although the modern empirical models of carbon, tight-binding and ab-initio simulations do not demonstrate LLPT in carbon, a question of origin of almost zero slope of the melting line of graphite still remains the one. There are just a few other substances with the slope of the melting line below 5 K/kbar in a wide range of pressures. A possible explanation of this phenomena can be given in frames of regular solution theory as it is implemented to the investigation of maxima on the melting line [22]. However, in this case an LLPT should take place. Another possibility is existence of smooth structural crossover in liquid which can be also called as smooth LLPT. Unlike "real" LLPT in the case of smooth crossover there is no density jump, but the structure of the liquid smoothly changes. In this case some unusual behavior of structural characteristics, for example, the location and the height of the first peak of radial distribution functions (RDFs) can appear. Below we will also call the "real" LLPT as sharp LLPT and te crossover as smooth LLPT.

In the present paper we examine the behavior of liquid carbon in frames of empirical AIREBO model as well as ab-initio simulations. We show that AIREBO model does not describe the liquid carbon properly and therefore cannot describe the melting line. We also study the "melting" of graphene under zero pressure conditions and show the inconsistency of the results for melting of graphene with the ones for graphite.

**SYSTEM AND METHODS**

In the present study we simulate the properties of liquid carbon by means of classical molecular dynamics (MD) in frames of AIREBO model and in ab-initio MD with PBE functional.

For classical MD we use a system of 4096 in a cubic box is used. The temperature is varied from \( T_{low} = 4000 \) K which is slightly above the melting line reported in Ref. [6] up to \( T_{high} = 6000 \) K. The densities studied are from \( \rho_{min} = 2 g/cm^3 \) up to \( 3 g/cm^3 \) with the step \( \Delta \rho = 0.05 g/cm^3 \). In the case of \( T = 6000 \) K we enlarged the interval of densities up to \( 4 g/cm^3 \). The time step is set to 0.1 fs. At each point the system is simulated \( 1 \cdot 10^7 \) steps. The first half of the simulation is used for equilibrium and at the second half we perform the calculations of averages. We calculate the pressure as a function of density and temperature (EoS) and the internal energy of the system. By differentiating the internal energy along isochores we also calculate the isochoric heat capacity.

To analyze the structure of the system we calculate the radial distribution functions (RDFs, \( g(r) \)). The average number nearest neighbors is calculated from RDF: \( NN = 4\pi n \int_0^{r_{min}} r^2 g(r)dr \), where \( NN \) is the number of nearest neighbors, \( n = N/V \) is the number density of the system and \( r_{min} \) is the location of the first minimum of RDF.
The location and the height of the first maximum of RDF are also monitored.

The classical MD simulations were performed with LAMMPS simulation package [22].

In the case of ab-initio simulation we use Quantum Espresso package [23]. PBE functional is used. The energy cut off for wave functions is set to 40 Ry. The cut off for the charge density is 160 Ry. The system consists of 54 atoms in a cubic cell. Our primary interest is the RDFs of the system, in particular, the first maximum and the first minimum of $g(r)$. Because of this we do not intend to use very large systems, because RDF is not sensitive to the system size. Only $\Gamma$ point is used for calculations in the k-space. The time step is set to 20 Ry atomic units (0.986 fs). 10000 steps are made for equilibration and more 2000 steps for calculations of averages. The temperature and the density points used in QE calculations are the same that in classical MD ones. The initial configuration was extracted from the one of AIREBO model one at $T = 6000$ K and given density. After that the system relaxed in ab-initio simulation for more 2000 steps at the same temperature to ensure that no influence of the initial structure remained. The final structures of these simulations were used as initial ones for all ab-initio simulations.

**RESULTS AND DISCUSSION**

We start the discussion from the results for EoS of the system. The melting temperature of carbon modelled by AIREBO potential is $T_m = 3640 \pm 150$ K [9]. Although we simulate the system from $T_{m_{\min}} = 4000$ K up to $T_{m_{\max}} = 6000$ K most of the results are reported for $T = 6000$ K which is inside the liquid region of the phase diagram for all models and experimental studies. At the same time, this temperature is below the liquid-liquid critical point obtained in [10], therefore it is enough low to expect structural changes in liquid phase, if they exist.

Fig. 1 shows the equations of state of AIREBO model and from ab-initio simulations at $T = 6000$ K up to the density $\rho = 4g/cm^3$. Surprisingly, we are not aware of any work where the EoS of AIREBO model was calculated up to such high densities. One can see that the EoS demonstrates a van der Waals loop which means that a first order LLPT takes place in the system. However, this LLPT is different from the one obtained in Ref. [10] because it appears at strongly different densities. No peculiarities is observed in ab-initio EoS. It reminds the situation with the LLPT predicted in Brenner model: the LLPT was observed in the empirical model, but not in ab-initio simulations. We believe that this phase transition is also a property of the AIREBO model, but not real carbon. Below we justify this assertion.

Usually when sharp LLPT in liquid carbon is discussed one seeks a change in hybridization of the atoms. The hybridization is determined from the number of nearest neighbors NN. Four nearest neighbors correspond to sp3 hybridization, three - to sp2 and two - sp hybridization. The NN can be determined from RDF of the system. In Fig. 2 (a) we show the RDFs of AIREBO carbon at $T = 6000$ K and in panel (b) the NN. One can see that NN smoothly increases with density, but in the region of the loop of EoS the increase becomes very rapid and at $\rho = 4g/cm^3$ NN becomes equal to 4.

However, the RDFs of the system demonstrate more unusual features. In a simple liquid the location of the first peak of RDF is lower with density. At the same time the height of the first peak increases with the density (see, for instance, Ref. [26] for the experimental and simulation study of the location and height of the first peak of RDF in neon). However, from the inset of Fig. 2 (a) we see that the situation is more complex in the case of AIREBO model of carbon. Fig. 3 shows the height of the first peak and its location in AIREBO model of carbon. One can see that the height of the first peak $g_1$ anomalously decreases with density up to $\rho = 3.6g/cm^3$, i.e. until the LLPT in the system. The behavior of the location of the first peak of RDF $r_1$ is more simple. It decreases with density up to $\rho = 3.2g/cm^3$, then is stays nearly constant up to $\rho = 3.4g/cm^3$ and rapidly increases at the LLPT up to the density $\rho = 3.85g/cm^3$. Then it again decreases with the density. It means that except the region of LLPT $r_1$ behaves as it should be in a simple liquid.

Decreasing of the first minimum of RDF $g_1$ means that a smooth structural crossover takes place in the system. One more attribute of smooth crossover in liquid phase can be seen in the system. Isochoric heat capacity $c_V$ of solids close to the melting line is $3k_B$ per particle (Dulong-Petit law). The heat capacity of liquids close to the melting line is usually close to the same value. It can be slightly larger due to the effects of anharmonicity, how-

![FIG. 1: Equation of state of liquid carbon at $T = 6000$ K obtained by AIREBO model and in ab-initio calculations.](image-url)
FIG. 2: (a) Radial distribution functions of AIREBO model at \( T = 6000 \) K. (b) Number of nearest neighbors in the same system. NN obtained in ab-initio simulations (QE) is also given for comparison.

ever, usually it does not exceed 3.3\( k_B \) - 3.4\( k_B \) per particle. As it was shown in our recent papers \[27, 28\] smooth structural crossover leads to strong increase in the heat capacity (\( c_V > 3.5k_B \)). Fig. 4 shows the heat capacity of AIREBO carbon along three different isochores. One can see that at all these densities it exceeds 4\( k_B \) reaching as high as 4.78\( k_B \) per particle at \( \rho = 2g/cm^3 \) and \( T = 4200 \) K. Summing up unusual behavior of \( g_1 \) and high values of \( c_V \) one can claim that a smooth structural crossover takes place in the system. Importantly, the possibility of smooth LLPT in liquid carbon has never been claimed in the literature before.

We are not aware of any calculations of the melting line of diamond in AIREBO model, however, comparing it to the results of LCBOP1+, one can say that the density \( 4g/cm^3 \) should be close to the melting line of diamond or even in the metastable region below it. In this respect it looks reasonable that approaching the diamond melting line liquid carbon changes its structure from graphite-like to diamond-like. However, the RDFs of the system demonstrate at least two strange features. First of all, the first minimum is as low as almost zero which is very untypical for liquids. Interestingly, the same effect of the first minimum of RDF was obtained in Ref. \[20\] by using Tersoff potential for carbon. Such deep minima of RDFs are usually observed in amorphous state (see, for instance, the textbook \[29\] for comparison of RDFs of liquid and amorphous states. The experimental RDFs of amorphous carbon can be found in \[30\]). In AIREBO carbon such deep minimum preserves even at \( T = 6000 \) K which is about 1.65\( T_m \), i.e. far above the melting temperature. Second, there is an unusual kink at \( r \approx 2\AA \). Importantly, AIREBO includes a so called switching function, which switch on interaction if the distance between the atoms is within some cut-off distance and switch if off otherwise. The cut-off of the switching function of AIREBO model is exactly 2\( \AA \) (Table I of Ref. \[17\]) which makes us to suspect that this kink is artificially induced by the potential parametrization.

To see the origin of these effects of AIREBO RDFs we compare them to the ones obtained in ab-initio simulations. Fig. 5 shows a comparison of RDFs of liquid carbon obtained in AIREBO model and in ab-initio sim-
FIG. 4: Isochoric heat capacity of AIREBO model at three different densities.

FIG. 5: Comparison of RDFs of carbon obtained in AIREBO model and in ab-initio molecular dynamics at \( T = 4000 \) K and four different densities.

ulation at \( T = 4000 \) K which corresponds to the temperatures slightly above the melting line in the case AIREBO. One can see that at this temperature the agreement between AIREBO and ab-initio RDFs is relatively good. The main difference is in the second peak of RDF. However, at high density the kink of AIREBO RDF starts to appear, while no kink is observed in ab-initio RDFs. Importantly, ab-initio RDFs at low density also demonstrate almost zero in the first minimum. However, as the density is increased, the first minimum of ab-initio RDFs increases, while in AIREBO model it stays vanishingly small at all densities.

Fig. 5 shows a comparison of AIREBO and ab-initio RDFs at \( T = 5000 \) K. One can see that while both strange features are still present in AIREBO RDFs, they are not observed in QE ones. In particular, the first minimum is finite at all densities.

Figs. 6 and 7 give a comparison of AIREBO and ab-initio RDFs at low and high densities. Once again one observes that the first minimum of AIREBO RDFs falls almost to zero, while ab-initio ones demonstrate finite values of the first minimum at all densities. Moreover, one can see that at high densities close to the melting line the location of the first maximum of QE RDFs becomes smaller then in the case of AIREBO model. Therefore, the bond length in AIREBO and QE carbon becomes different at these densities. Fig. 6 shows a comparison of \( r_1 \) and \( g_1 \) obtained in quantum simulation and in frames of AIREBO system. One can see that the agreement is very poor. Any way, one can see that the behavior of ab-initio RDFs is even more complicated then the AIREBO ones: the location of the first maximum \( r_1 \) increases with density up to \( \rho = 3.2 \text{g/cm}^3 \) and its height decreases up to \( \rho = 3.0 \text{g/cm}^3 \). Interestingly, while at \( T = 4000 \) K the difference between AIREBO and ab-initio RDFs is mostly in the second peak, at \( T = 6000 \) K the second peak of AIREBO and ab-initio \( g(r) \) are in good agreement, but the first peak and especially the first minimum are strongly different.

Many publications report RDFs of liquid carbon obtained in frames of different models. In Ref. 20 a novel potential is constructed by the methods of machine learning which the authors call GAP. The authors of Ref. 20 calculate the RDFs by this GAP potential and by Ter-
soff one. In Ref. [19] RDFs of carbon at $T = 6000$ K obtained by tight-binding simulation technique were reported. In Ref. [16] RDFs of LCBOPII carbon are calculated. The Tersoff and AIREBO empirical potentials are constructed basing on the low temperature data for graphite, diamond and hydrocarbons. LCBOPII and GAP models are fitted to ab-initio data. Tight-binding method is in some sense similar to the first-principles simulations. Comparing the RDFs of different models one can see that Tersoff and AIREBO potentials give unphysically low first minimum while the ab-initio, tight binding and empirical potentials fitted to the ab-initio data give liquid-like RDFs of liquid carbon. From this observation we can conclude that models based on the low temperature data like Tersoff and AIREBO do not describe the liquid carbon properly. It also leads to the conclusion that these models do not describe the melting line of graphite, because for precise description of a phase transition the models should give precise description of both phases. Because of this we believe that the LLPT observed in AIREBO model is an artificial effect of the model. However, for simplicity they propose to remain the term melting. The second point of interest is that the "melting" temperature of graphene appears to be higher than the one for graphite. An explanation of this observation proposed in Refs. [34] is that when graphite is heated up some atoms leave the plane and form bonds with atoms of another plane. Formation of such bridges is responsible for graphite decomposition. In case of graphene apparently no bridges can be formed. Note that for the LCBOPII model the "melting" temperature of graphene reported in Ref. [32] is $T = 4900$ K, while in Ref. [33] which is written by the same group the "melting" temperature is $T = 4510$ K. These two publications employ different methodology: while in the former a direct observation of the structural changes is taken as melting point, in the later the authors extrapolate the results to lower temperatures using the Classical Nucleation Theory.

Finally we discuss melting of graphene modeled by AIREBO potential. Graphene melting was simulated in LCBOPII model in Refs. [32, 33] and AIREBO in Refs. [34] Two interesting observations are reported in these studies. First, upon "melting" graphene forms a phase composed of linear chains. Because of this both groups which perform LCBOPII and AIREBO simulations claim that it is not a real melting, but some kind of polymerisation process or probably formation of carbine. However, for simplicity they propose to remain the term melting. The second point of interest is that the "melting" temperature of graphene appears to be higher than the one for graphite. An explanation of this observation proposed in Refs. [34] is that when graphite is heated up some atoms leave the plane and form bonds with atoms of another plane. Formation of such bridges is responsible for graphite decomposition. In case of graphene apparently no bridges can be formed. Note that for the LCBOPII model the "melting" temperature of graphene reported in Ref. [32] is $T = 4900$ K, while in Ref. [33] which is written by the same group the "melting" temperature is $T = 4510$ K. These two publications employ different methodology: while in the former a direct observation of the structural changes is taken as melting point, in the later the authors extrapolate the results to lower temperatures using the Classical Nucleation Theory.

It is important to note that there is a difference in simulation methodology of graphite and graphene melting. The most principle item is that graphite melting is al-
ways simulated under enough high external pressure. For instance, in Ref. [9] the smallest pressure is 2 GPa. In the case of graphene the simulations are performed under zero pressure. In both cases of LCBOP II and AIREBO a sample of graphene surrounded by vacuum is simulated under zero pressure. The initial temperature is 300 K and the temperature increases with constant rate during the simulation. The melting temperature is detected by the structural changes in the system in Refs. [32] and [34]. Extrapolation to lower temperatures is made in Ref. [33].

It is known that no melting is possible at zero pressure. In the case of almost zero pressure the substance should sublime, i.e., transform from crystal directly into the gas phase. Moreover, the sublimation temperature at $P = 0$ Pa is also zero. In computer simulation the pressure is never exactly equal to the desired value. Indeed, strong fluctuations always take place in simulation. Because of this one can expect that indeed small positive pressure is simulated in all cited publications. However, one can still expect that gaseous carbon appears in such simulations instead of liquid. Although the experimental studies of gaseous carbon are extremely difficult due to very high temperatures, several works report that gaseous carbon consists of clusters of several atoms. In particular, in work [31] partial pressure of clusters of different sizes is estimated. It is shown that the major contribution comes from the clusters of three carbon atoms. In this respect it looks reasonable to assume that transition from graphite into gaseous carbon (i.e., sublimation) is indeed observed in simulations.

In our work we simulate the thermal decomposition of both graphite and graphene under zero pressure upon increasing the temperature. In both cases we simulate the system at 8000 K starting from graphene or graphite. The time step is 0.2 fs. The graphene sample consist of 6400 atoms while graphite sample - 4000 atoms. The initial lattice constants are taken as the ones at ambient conditions. Fig. 9(a) shows a snapshot of a graphene after the "melting". In agreement with Refs. [32] [34] the system consist of linear chains. The first minimum of RDF is $r_c = 1.95$ Å. We divide the system into clusters. We assume that two particles belong to the same cluster if they are separated by a distance less then $r_c$. Fig. 9(b) shows the probability distribution of the size of the clusters in two systems: with initial configuration of graphene and graphite. In the case of simulation of graphite at $P = 0$ GPa and $T = 8000$ K the sample also transforms into the disordered state. The first minimum of RDF is also $r_c = 1.95$. Dividing the system into clusters we find that the majority of the atoms belong to a single cluster (3020 particles). However, other particles form linear chains. The distribution of the size of these chains is given in Fig. 9(b) in comparison with the one for the system which started from graphene. One can see that the distributions for the two cases are very similar. In particular, in both cases most of the chains consist of 3 particles which is in agreement with expectations for gaseous carbon. The largest cluster consists of 56 atoms.

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Importantly, in both cases (starting from graphene or graphite) the volume of the system continues to increase with time after as long as 150 ns of simulation. Therefore, the system is still out of equilibrium and the structure can change if we simulate the system more. We conclude from
this observation that both graphite and graphene transform into gaseous carbon being heated at zero pressure, however, the equilibration of the system is extremely long and because of this no firm conclusions can be made even after 150 ns of simulated time. One can see that the equilibration of the system is extremely slow. This can be the reason that the system "melts" at higher temperatures than usual graphite under high pressure. Experimentally the sublimation of graphite starts at about 3000 K. Extremely strong overheating of graphene in simulation should also originate from the limitations of simulation time.

The experimental estimations of the gas-liquid-graphite triple point are from about 4700 up to 5000 K and $P = 0.016$ GPa. We emphasize that in the simulation of "melting" of graphene a single sheet of carbon atoms is placed in a box of vacuum, i.e. the system is indeed three dimensional. In principle, the triple point of such a single layer can shift with respect to the one of graphite. However, there is no reasons to expect that it should be strongly different from the later. As was pointed out in Ref. [9] the melting of graphite is related to bonding of atoms with atoms of other planes. No such mechanism is possible in the case of graphene. In this case melting should be related to the breaking of the bonds. However, one should not expect that the temperature of bond breaking is too much higher then the melting point of graphene. For example, experimental observations show that already at $T = 3000$ K graphite starts to actively sublimate [35, 36].

We are not aware of any calculation of the triple point of neither AIREBO no LCBOPPII models. However, from the observation that the melting temperatures of these systems do not depend on pressure one should conclude that the temperature of the triple point should be the same that the melting temperature of graphite ($T_l = 3640$ K for AIREBO and $T_l = 4250$ K for LCBOPPII). The "melting" (sublimation) points of graphene are $T_m = 4900$ K for AIREBO and $T_m = 4510$ K for LCBOPPII. These sublimation temperatures are above the temperatures of the triple point of graphite which looks unreasonable.

CONCLUSIONS

In the present paper we discuss the melting curve of graphite and the liquid phase of carbon. We analyze the literature data on simulation of liquid carbon and graphite melting line and perform our own calculations in frames of empirical AIREBO potential and by ab-initio simulations. Basing on our own results and the literature data we arrive to the following conclusions:

i) The empirical potentials for carbon can be divided into two groups. Some of them (AIREBO, Tersoff potential, Brenner potential) are fitted to experimental data on carbon and hydrocarbons at low temperatures. These models fail to reproduce the structure of liquid carbon above the melting line. Because of this they also do not describe the melting line of graphite properly.

ii) The AIREBO potential gives an LLPT at high densities where graphite-like liquid transforms into diamond-like. However, this LLPT is not observed in ab-initio simulations and most probably it is a property of the model, but not real carbon.

iii) Both AIREBO and ab-initio simulations give unusual dependence of the location and the height of the first maximum of RDF of liquid carbon. The same effect is observed in tight-binding simulation of liquid carbon (Ref. [19]). This observation means that a smooth structural crossover in liquid carbon takes place. This smooth LLPT is also observed in ab-initio simulations. Importantly, the presence of this smooth LLPT means that the melting line should demonstrate a diffuse maximum, which is in agreement with the classical results of Bundy [4]. However, AIREBO potential fails to describe the structure of liquid carbon, and the results of ab-initio simulation of liquid carbon are also doubtful.

iv) AIREBO and LCBOPPII models predict that the "melting" temperature of graphene is much higher then the melting temperature of graphite. Although this effect is observed in simulations, it looks to be a consequence of incomplete equilibration of the system. Indeed the simulations of "melting" of graphene are performed at zero pressure where evaporation should be observed rather then melting. The structure of the phase observed in simulations of "melting" of graphene looks to be consistent with predictions for gaseous carbon. Assumption that the "melting" temperature of graphene is higher then the one for graphite leads us to a paradoxical conclusion that the condensation curve of carbon (gaseous carbon to graphite transition) has negative slope, and therefore gaseous carbon has higher density then graphite.

Summing up the four points above we arrive to a grand conclusion. The experimental investigation of the melting line of graphite and the liquid carbons lasts already almost for a century. However, the results of different experiments are in contradiction with each other. Because of this no firm conclusions can be made on the melting line of graphite and liquid carbon. Many hopes were related to simulation of phase diagram of carbon. For some time it looked that simulations do give correct description of many different properties of the system. However, as can be seen from the present work the simulations also fail to give really unambiguous view on the phase diagram of carbon. Because of this the state of art of the investigations of the phase diagram of carbon is described best of all by a famous quotation: "There are more things in heaven and earth, Horatio, Than are dreamt of in your philosophy" (Shakespeare "Hamlet").

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