

Graphite melting: atomistic kinetics resolves longstanding controversy

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Graphite is one of the most wide-spread carbon allotropes. Unique thermophysical properties of graphite result in its important role in science and engineering. However, the experimental data on graphite melting temperature still remain controversial despite the long history of investigation. The experimental results of several works cover the wide span from 3800 to 5000 K that is an essentially larger uncertainty than the errors of individual experiments. The analysis of many experiments suggested a dependence of the measurement results on heating rate; however this fact has not been explained satisfactorily.

Here we report the results of molecular dynamics (MD) calculations on the kinetics of two competing processes in graphite: the heterogeneous melting at the solid-liquid boundary and the homogeneous melting due to the spontaneous formation of liquid phase nuclei. Our MD results show an unexpectedly weak kinetics of the melting front propagation in graphite that is several orders slower than that in metals and a high stability of crystal under superheating up to 4800-5000 K (i.e. slow rate of liquid nucleation via homogeneous mechanism).

The heating of the sample in an experiment can be characterized by the heating rate $\dot{T}(t) = \text{const}$. In the case of ultrashort pulse experiments the heating rate can be more than 10^9 K/s. The surprisingly slow melting kinetics of graphite melting revealed from MD simulations allows us to make a hypothesis that at a sufficiently high heating rate the temperatures well above T_m can be reached before the moment of formation of the liquid phase amount enough for the melting detection ($T = T_m^d$).

The analysis carried out in this work shows that the homogeneous nucleation mechanism limits the sample temperatures at 4900-5000 K even at $\dot{T} \sim 10^{12}$ K/s. This upper estimate coincides with the graphene melting temperatures and with the highest experimental values of graphite melting temperature. However, at $T < 4500$ -4600 K the homogeneous nucleation rate is negligible that, taking into account the slow nature of heterogeneous melting, allows essential crystal superheatings at the timescale of milliseconds.

The results obtained can be considered as an essential argument in favor of the hypothesis that at $\dot{T} > 10^5$ - 10^6 K/s the de facto detected in pulse heating experiments “graphite melting temperatures” T_m^d corresponds to the temperatures when the decay of the superheated metastable solid graphite takes place. And therefore these temperatures are not strictly speaking the graphite melting temperatures in the thermodynamic sense T_m .