# Local Structure of Liquid Carbon Controls Diamond Nucleation

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(Received 23 May 2007; published 2 August 2007)

Diamonds melt at temperatures above 4000 K. There are no measurements of the steady-state rate of the reverse process, i.e., diamond nucleation from the melt, because experiments are difficult at these extreme temperatures and pressures. Using numerical simulations, we estimate the diamond nucleation rate and find that it increases by many orders of magnitude when the pressure is increased at constant supersaturation. The reason is that by increasing the pressure the local coordination of the liquid changes from threefold to fourfold, and we show that the free-energy cost to create a diamond-liquid interface is lower in the fourfold than in the threefold liquid. We speculate that this mechanism for nucleation control is relevant for crystallization in many network-forming liquids. We conclude that homogeneous diamond nucleation is likely in carbon-rich stars and unlikely in gaseous planets.

DOI: 10.1103/PhysRevLett.99.055702 PACS numbers: 64.60.Qb, 07.05.Tp, 81.05.Uw, 96.15.Nd

Most liquids can be cooled considerably below their equilibrium freezing point before crystals start to form spontaneously in the bulk. This is caused by the fact that microscopic crystallites are thermodynamically less stable than the bulk solid. Spontaneous crystal growth can only proceed when, due to some rare fluctuation, one or more microcrystallites exceed a critical size (the "critical nucleus"). An estimate of the rate at which critical nuclei form in a bulk liquid can be obtained from classical nucleation theory (CNT) [1]. This theory relates $R$, the number of crystal nuclei that form per second per cubic meter, to $\Delta G_{\mathrm{crit}}$, the height of the free-energy barrier that has to be crossed to nucleate a crystal:

$$R = \kappa e^{-\Delta G_{\mathrm{crit}}/k_B T}. \qquad (1)$$

Here $\kappa$ is a kinetic prefactor, $T$ is the absolute temperature, and $k_B$ is Boltzmann's constant. The nucleation rate depends strongly on the height of the nucleation barrier. CNT predicts the following expression for the height of the nucleation barrier:

$$\Delta G_{\mathrm{crit}} = c \frac{\gamma_{\mathrm{LS}}^3}{\rho_S^2 |\Delta\mu|^2}, \qquad (2)$$

where $\gamma_{\mathrm{LS}}$ is the liquid-solid surface free energy per unit area, $\Delta\mu$ is the difference in chemical potential between the solid and the supercooled liquid, and $\rho_S$ is the number density of the crystalline phase. The factor $c$ depends on the shape of the nucleus, e.g., $c = 16\pi/3$ for a spherical nucleus. As the nucleation rate depends exponentially on $\Delta G_{\mathrm{crit}}$, a doubling of $\gamma_{\mathrm{LS}}$ may change the nucleation rate by many orders of magnitude. In general, the kinetic prefactor $\kappa$ in Eq. (1) can be estimated quite well [2].

Because of the extreme conditions under which homogeneous diamond nucleation takes place, there have been no quantitative experimental studies to determine its rate. Moreover, there exist no numerical estimates of $\Delta\mu$ and $\gamma_{\mathrm{LS}}$ for diamond in supercooled liquid carbon. Hence, it was thus far impossible to make even an order-of-magnitude estimate of the rate of diamond nucleation.

In this Letter, we calculate the diamond nucleation rate $R$ in liquid carbon at two state points $\{P = 85\ \mathrm{GPa}, T = 5000\ \mathrm{K}\}$ and $\{P = 30\ \mathrm{GPa}, T = 3750\ \mathrm{K}\}$ (points $A$ and $B$ in the carbon phase diagram shown in Fig. 1). At both state points, the liquid is supercooled by $(T_m - T)/T_m \approx 25\%$

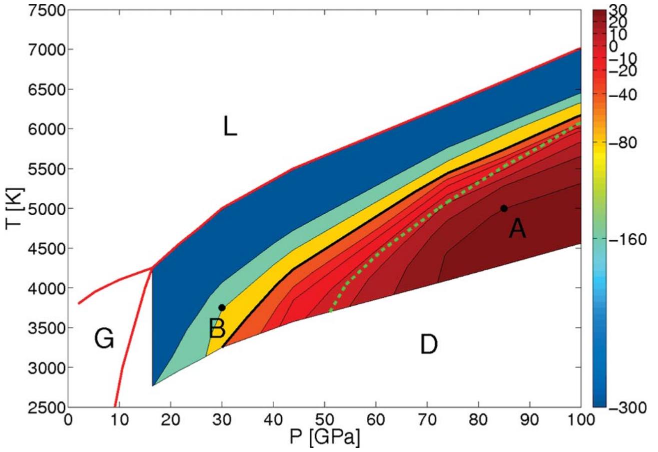

FIG. 1 (color). The figure shows part of the carbon phase diagram from and the isonucleation rate zones. The solid red lines represent the coexistence lines from Ref. [3], bordering the liquid (L), graphite (G), and diamond (D) stability regions. $A$ is at $P_A = 85$ GPa, $T_A = 5000$ K, and $B$ at $P_B = 30$ GPa, $T_B = 3750$ K. In the text, we give estimates for the nucleation rate at $A$ and $B$. Along the green dashed curve, the ratio of threefold and fourfold coordination in the liquid is 1:1. The color code used in the plot: numbers on the right indicate the order of magnitude of the nucleation rate (in $\mathrm{m}^{-3}\,\mathrm{s}^{-1}$). The continuous black curve indicates the boundary of the region where the nucleation rate is negligible ($<10^{-40}\ \mathrm{m}^{-3}\,\mathrm{s}^{-1}$).

below the melting curve of diamond, with $T_m$ the melting temperature and $T_m^A = 6600$ K and $T_m^B = 5000$ K, respectively. Simulations studies of the diamond melting curve have been reported for pressures up to 400 [3], 1400, and 2000 GPa [4]. The last two studies were carried out by using "*ab initio*" molecular dynamics. However, it would be prohibitively expensive to study nucleation using such an approach. We therefore use a semiempirical many-body potential that has been fit to experimentally measured and *ab initio* calculated properties of carbon solid phases and the liquid [5]. We use this model to study diamond nucleation in a system of 2744 particles in the "low-pressure" ($P < 100$ GPa) region of the phase diagram. In this pressure range, the calculated melting lines of Refs. [3,4] are in reasonable agreement. In particular, all the three calculations predict a melting temperature of about 7000 K at 100 GPa.

In order to estimate the crystal-nucleation rate, we first determine the top of the free-energy barrier $\Delta G_{\mathrm{crit}}$, i.e., the free energy required to form a critical nucleus. For high barriers, the spontaneous formation of a critical nucleus is a rare event. We therefore use biased Monte Carlo (MC) sampling [6] to compute the probability that a critical nucleus forms. From this probability we can then directly derive the free energy of this nucleus. For state point $A$ we find that the barrier height equals $\Delta G_{\mathrm{crit},A} = 25 k_B T$ corresponding to a critical nucleus size of $N_A = 110$ [7]. Knowing $\Delta G_{\mathrm{crit}}$ and the kinetic prefactor (see Ref. [2]), we estimate the crystal-nucleation rate to be $R_A = 10^{30}\ \mathrm{s}^{-1}\,\mathrm{m}^{-3}$. When we tried to follow the same procedure to compute the diamond nucleation rate at state point $B$ (30 GPa, 3750 K), we failed to reach a critical nucleus that was small enough to fit in a system of 2744 particles. We therefore had to resort to an indirect way, based on CNT, to estimate $\Delta G_{\mathrm{crit}}$. CNT assumes that $\Delta G(N)$, the Gibbs free-energy difference between a metastable liquid containing an $N$-particle crystal nucleus and a pure liquid, is given by $\Delta G(N) = S(N)\gamma_{\mathrm{LS}} - N|\Delta\mu|$, where $S(N)$ is the area of the interface between an $N$-particle crystallite and the metastable liquid. In order to determine the number of particles in a crystallite, we use a spherical-harmonics based criterion (see, e.g., Ref. [8]) that allows us to distinguish particles in a liquidlike environment from those in a crystal (diamond or graphite). The surface area $S(N)$ is given by $a(N/\rho_S)^{2/3}$, where the factor $a$ depends on the geometry of the nucleus. From our simulations, we can only determine the product $a\gamma_{\mathrm{LS}}$: it is this quantity and the degree of supersaturation ($\Delta\mu$) that determine the nucleation rate. In order to calculate $\Delta\mu$, we compute the temperature dependence of the molar enthalpy difference ($\Delta h$) between the supercooled fluid and the stable crystal at equal pressures. From $\Delta h$, $\Delta\mu$ is evaluated by thermodynamic integration from the melting point [9]. We find $|\Delta\mu_A/k_B T| = 0.60$ and $|\Delta\mu_B/k_B T| = 0.77$, respectively.

From the calculated $\Delta G_{\mathrm{crit},A}$ and the number density of the solid ($\rho_A = 0.191$ Å$^{-3}$), we can estimate the surface free energy per unit area at state point $A$ using Eq. (2). Assuming that the critical nucleus is effectively spherical, we find $\gamma_{\mathrm{LS},A} \approx 0.27 k_B T/\text{Å}^2 = 1.86\ \mathrm{J/m^2}$. We stress that, in what follows, we do not make use of this estimate; rather, we always employ the combination $a\gamma$ that follows directly from the simulations.

In state point $B$ we could not follow the same procedure, as a system of 2744 particles is too small to accommodate a critical nucleus. In order to estimate $\gamma_{\mathrm{LS},B}$, we therefore prepared a rodlike crystal in a system with a slab geometry (a flattened box containing $N \sim 4000$ particles, with lateral dimensions that are some 4 times larger than its height). The crystal rod is oriented perpendicular to the plane of the slab. It spans the height of the simulation box and is continued periodically. The cross section of this crystal rod is lozenge shaped, such that its [111] faces are in contact with the liquid [10]. We used umbrella sampling to determine the Gibbs free energy of such a crystallite as a function of its size, both at state points $A$ and $B$. In this way we estimate the ratio of the surface free energies at $A$ and $B$. We find that $a\gamma_{\mathrm{LS},B}/a\gamma_{\mathrm{LS},A} = \gamma_{\mathrm{LS},B}/\gamma_{\mathrm{LS},A} \sim 2.5$ (the $a$ factors are the same since the shape of the rod nucleus is approximately the same at the two state points). Since we know $\gamma_{\mathrm{LS},A}$ from the height of the nucleation barrier in state point $A$ for a spherical nucleus, we deduce the corresponding $\gamma_{\mathrm{LS},B}$ for a spherical nucleus. Using our estimate, $\gamma_{\mathrm{LS},A} \approx 1.86\ \mathrm{J/m^2}$, we find $\gamma_{\mathrm{LS},B} \approx 0.68 k_B T/\text{Å}^2 = 3.5\ \mathrm{J/m^2}$. As $\Delta\mu$ and $\rho_B$ are known ($\rho_B = 0.17$ Å$^{-3}$), we can now use CNT to estimate $\Delta G_{\mathrm{crit}}$ in state point $B$. It turns out that, mainly because $\gamma_{\mathrm{LS},B}$ is 2.5 times larger than $\gamma_{\mathrm{LS},A}$, the nucleation barrier in $B$ is more than 10 times higher than in point $A$, thereby hugely suppressing the nucleation rate ($R_B \sim 10^{-80}\ \mathrm{s}^{-1}\,\mathrm{m}^{-3}$). We can estimate the size of the critical (spherical) nucleus at $B$ to be around $N_B = 1700$ particles. Thus, one would need a system of at least 17 000 particles to contain a critical nucleus and avoid spurious interactions among its periodic images. Such a system size is beyond our present computational capacity. In contrast, in the slab geometry we find that the free energy of a lozenge-shaped crystal goes through a maximum at a size of ~340 particles, which is much less than the system size (4000 particles).

To understand the microscopic origin for the large difference in nucleation rates in state points $A$ and $B$, it is useful to compare the local structure of the liquid phase in both state points. It turns out that the liquid structure in state points $A$ and $B$ is markedly different (see also Refs. [11,12]): liquid carbon is mainly fourfold coordinated at state point $A$ (20% threefold and 80% fourfold), while at the lower temperatures and pressures of point $B$, the coordination in the liquid resembles that of the graphite and is mainly threefold coordinated (5% twofold, 85% threefold, and 10% fourfold). Apparently, it is less favorable to create an interface between a diamond and a graphitic liquid than between a diamond and a fourfold coordinated liquid. The destabilizing effect of the graphitic liquid on the diamond nuclei is most pronounced for small nuclei (large surface-to-volume ratio). In fact, in state point *B*, nuclei containing less than 25 particles tend to be graphitic in structure, with a small number of fourfold coordinated particles linking the different graphite planes. Nuclei containing up to 60 particles show a mixed graphite-diamond structure, whereas larger nuclei have a diamond bulklike structure, but the surface remains graphitic in nature (see Fig. 2). The unusual surface structure of the diamond nucleus is an indication of the poor match between a diamond lattice and a threefold coordinated liquid.

There are many network-forming liquids that, upon changing pressure and temperature, undergo profound structural changes or even liquid-liquid phase transitions [13]. Our simulations on carbon indicate that such a change in the local coordination in the liquid has dramatic consequences for the rate of crystal nucleation. Experiments on a completely different class of materials, viz., liquid metals [14], suggest that the local structure, in particular, local icosahedral packing, may interfere with direct nucleation of crystals. What is interesting about the present simulations is that we show that the ease of homogeneous crystal nucleation from one-and-the-same metastable liquid can be tuned by changing its pressure, and thereby its local structure.

The thermodynamic conditions we discuss are relevant for experiments that study nucleation in compressed, laser-melted carbon. In addition, homogeneous nucleation of diamond may have taken place in carbon-rich white dwarf [15]. It has also been suggested that diamonds could also have formed in the carbon-rich middle layers of Uranus and Neptune [16]. The present work allows us to make a rough estimate of the conditions that are necessary to yield appreciable diamond nucleation on astronomical time scales.

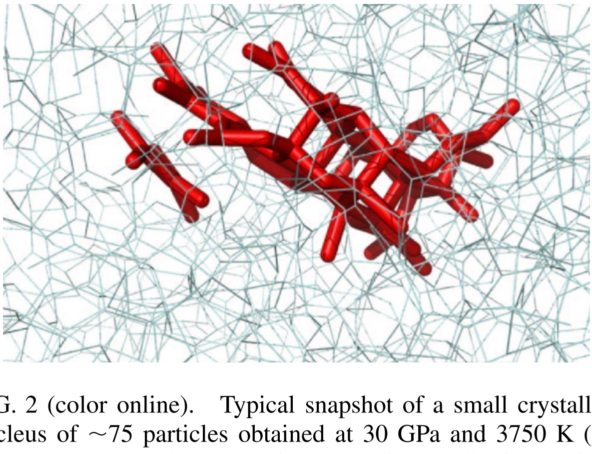

FIG. 2 (color online). Typical snapshot of a small crystalline nucleus of ~75 particles obtained at 30 GPa and 3750 K (*B*), surrounded by mainly threefold coordinated liquid particles (gray lines). The nucleus contains both three- (left part) and fourfold (right part) coordinated particles.

Neither white dwarfs nor planets consist of pure carbon. Nevertheless, it is useful to estimate an upper bound to the diamond nucleation rate by considering the rate at which diamonds would form in a hypothetical environment of pure carbon. To this end we use our numerical data on the chemical potential of liquid carbon and diamond and our numerical estimate of the diamond-liquid surface free energy to estimate the nucleation barrier of diamond as a function of temperature and pressure. We then use CNT to estimate the rate of diamond nucleation [17]. The results are shown in Fig. 1. The figure shows that there is a region of some 1000 K below the freezing curve (continuous red line) where diamond nucleation is less than $10^{-40}$ m$^{-3}$ s$^{-1}$. If the rate is lower than this number, not a single diamond could have nucleated in a Uranus-sized body during the life of the Universe. As can be seen from the figure, our simulations for state point *B* are outside the regime where observable nucleation would be expected. However, this figure provides just an upper bound to the rate of diamond nucleation. In practice, the carbon concentration is somewhat less in carbon-rich stars (~50%) [15], and much less (1%–2% [16]) in Uranus and Neptune.

In Fig. 3, we show the effect of dilution on the regime where diamond nucleation is possible. To simplify this figure, we do not vary pressure and temperature independently but assume that they follow the adiabatic relation that is supposed to hold along the isentrope of Uranus [18]. We make the assumption that nucleation takes place from an ideal mixture [19] of C, N, O, and H [20]. Not surprisingly, Fig. 3 shows that dilution of the liquid decreases the driving force for crystallization to the extent that no diamond phase is expected for *C* concentrations of less than

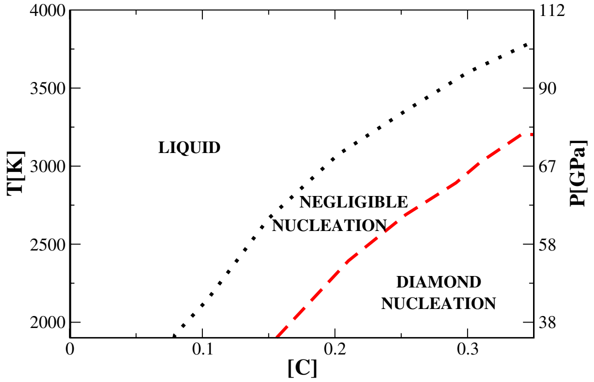

FIG. 3 (color online). Diamond nucleation boundaries as a function of carbon concentration: the rate is zero (no thermodynamic driving force to nucleation) in the top region (liquid), it is negligible ($<10^{-40}$ m$^{-3}$ s$^{-1}$) in the middle region, and non-negligible ($>10^{-40}$ m$^{-3}$ s$^{-1}$) in the bottom-right region. The nucleation rate is negligible when it corresponds to less than one nucleus per Uranus-sized planet over a period of $10^{10}$ yr. As pressure and temperature are related along the Uranus isentrope (see [16]), the left *y* axis indicates the temperature and the one on the right gives the corresponding pressure.

8%. As before, there is a wide range of conditions where diamonds could form in principle, but never will in practice. Assuming that, for a given pressure, the width of this region is the same as in the pure *C* case (almost certainly a serious underestimate), we arrive at the estimate in Fig. 3 of the region where nucleation is negligible (i.e., less than one diamond per planet per life of the Universe). From this figure, we see that quite high carbon concentrations (over 15%) are needed to get homogeneous diamond nucleation. Such conditions do exist in white dwarfs, but certainly not in Uranus or Neptune. Hence, our simulations indicate that it is extremely unlikely that diamonds could ever have nucleated from the carbon-rich middle layers of Uranus and Neptune.

We gratefully thank D. J. Stevenson, E. Tosatti, S. Iacopini, E. Sanz, P. R. ten Wolde, and H. L. Tepper for helpful suggestions, and gratefully acknowledge J. Los and A. Fasolino, whose MC code [5] was adapted for our calculations. The work of the FOM Institute is part of the research program of FOM and is made possible by financial support from the Netherlands Organization for Scientific Research (NWO), partly through Grant No. 047.016.001.

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[8] We used a local order parameter as introduced in Ref. [6]; rather than the 6th order harmonic, we found that a 3rd order harmonic can capture the correct symmetry for both graphite and diamond lattices.

[9] In detail, $\Delta(\beta\mu) = \int_{\beta_{\text{coex}}}^{\beta_1} \langle [h^S(\beta) - h^L(\beta)] \rangle_{P,\beta} d\beta$, where $h^S(\beta)$ $[h^L(\beta)]$ is the specific enthalpy of the solid (liquid) and the integration path is an isobar from the coexistence temperature $[\beta_{\text{coex}} = 1/(k_B T_{\text{coex}})]$ to the temperature of the selected state point.

[10] The [111] planes are the most stable for the diamond lattice. Note that when graphite and diamond structures compete at 30 GPa (see Fig. 2), the [0001] graphite sheets transform into [111] diamond planes. We can write the size ratio of lozenge-shaped and spherical critical nuclei at the same state point as $N_{\text{crit}}^{\text{sph}}/N_{\text{crit}}^{\text{loz}} = 8\pi\gamma\sin\theta/(3\rho_s|\Delta\mu|h)$, where $\gamma$ is the lozenge-shaped nucleus interfacial free energy, $\theta$ the angle between two adjacent sides (70.05°), $\rho_s$ the solid density (0.17 Å$^{-3}$), $\beta|\Delta\mu| = 0.77$ in $B$, and $h$ the slab height (10 Å). Our numerical results indicate that a spherical critical nucleus is about 5 times larger than a rodlike nucleus in the (unphysical) periodic slab geometry.

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