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Initial stages of equilibrium thermographitization of diamond

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A consistent quantum-statistical theory of equilibrium graphitization of diamond is suggested based on the truncated harmonic oscillator model. The graphitization is caused by the interaction of carbon atoms with phonons, while the essential role is played by spontaneous emission of acoustic phonons. The model allows us to carry out the analytical description of the process in a general form all the way to estimations of the observable numerical values. The values found are compatible with the computer simulation results obtained independently by several researchers. It turns out that the initial state of carbon sp^3 (diamond) is highly unstable and can, at high temperatures, spontaneously convert to sp^2 (graphite) on a time scale of 10^{-14} s. This transition is the base for graphitization. After the process has started, it slows down because of saturation effects. The temperature dependence of graphitization rates has been established. The developed theory of equilibrium graphitization can be considered as a starting point for consistent study of the later stages of graphitization, when the saturation is taken into account; as well as for the study of nonequilibrium graphitization in laser or electron beams.

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I. INTRODUCTION

Diamond is a material of unique physical properties, finding an increasing range of applications in various areas of technology and industry. One example is laser fabrication of diamond draw plates for production of thin wires or bearings that find applications in precision devices. The laser ablation taking place in this process is not sufficiently well studied. In particular, the role of the process of turning diamond into graphite is not well understood, although the fact that dark graphite deposits appear on diamonds as a result of laser ablation is well known.[1,2] Another example is making diamond components for optics and especially laser applications, and also high-current switches and other components designed to operate with intense optical beams and strong electric fields. Such components suffer slower degradation. One possible degradation mechanism of diamond components is connected with turning diamond to graphite.

Many of the diamond and diamondlike film properties are well understood. Others still need to be explored because they are particularly interesting for theory and experiment.

It is well known that the diamond form of carbon can spontaneously transit to the graphite form.[3,4] The term "graphitization" refers to the transition of carbon from the sp^3 (diamond) to the sp^2 state (one of the graphite forms). This process has been experimentally studied in detail[5–7] at different temperatures, in various buffer gases and in vacuum. It was shown that graphitization is accompanied by reducing the sample density and increasing its volume. It has been proven that some free volume is required for the graphitization onset, i.e., the graphitization takes place either near structural defects inside the sample, or at its surface. With time, the near-surface graphite/diamond interface goes deeper inside the sample, and then the entire sample turns to graphite. The duration of this transformation depends on the environment content and on the temperature. The *direct* and *catalytic* types of graphitization are usually considered.[5,6]

The direct type of graphitization is a spontaneous transition $sp^3 \rightarrow sp^2$. It takes place with appreciable rate[5,6] in vacuum or in passive gas atmospheres at temperatures over 2000 K. This type of graphitization is studied in Ref. 8 as an autocatalytic process.

A theoretical analysis of graphitization is carried out[5–7] in the so-called kinetic approximation, when the process rate was arbitrarily, "from general considerations," ascribed the Arrhenius character $R \sim \exp(-E_a/kT)$. The activation energy E_a and other parameters were chosen to match the experimental results. The diamond and graphite anisotropy had to be ignored, because taking it into account would make the task practically impossible.

In presence of water, hydrogen, oxygen, or some metals, catalytic graphitization occurs. This process can be observed near catalysis centers at 2000 K and lower.[7–9]

The above-mentioned works give an empirical description of the graphitization rather than it being consistently derived from quantum mechanics first-principles theory. Therefore a consistent theory of graphitization is needed. In spite of a large amount of experimental data on graphitization of the bulk diamond and diamondlike films, its mechanisms are not clearly understood. It appears natural, however, to consider the direct graphitization dominant, and to study it first.

The major theoretical efforts directed at the study of this type of graphitization (both at high-temperature equilibrium and at nonequilibrium, e.g., in strong laser fields) lie in the area of numerical simulation.[10–12] The simulations took advantage of the fundamental dynamics equations for an ensemble of atoms. Just like an analytical solution, this requires knowledge of the crystal geometrical and dynamic constants. The underlying physical model represented a crystalline cluster of a few hundred carbon atoms in the sp^3 state, which was tracked for several picoseconds. The simulation is limited to several dozens of elementary atomic jumps, a part of which led to transitions into the sp^2 state. The calculations have shown[10] that the graphitization becomes noticeable already after 0.1 ps from the start of the simulation. Physical explanations for such a quick graphitization onset in Ref. 10 are absent. On one hand, such a short time appears to contradict the experimental data showing that development of graphitization takes minutes or even hours. For example,[13] a 0.1 karat diamond completely turns into graphite in 10–30 min at 2200 K; and in 10–180 s at 2400 K. On the other hand, in laser fields,[12] the time of graphitization onset is less than 100 fs. Such a fast graphitization onset agrees with our estimates (shown below) for the initial stages of graphitization.

The main theoretical concepts of the "kinetic approximation" are based on the following two statements.[5–7]

First, graphitization takes place if the atom is surrounded by a sufficiently large free volume. In other words, graphitization takes place at the surface, near dislocations, vacancies, etc. Graphitization of thin films or small polycrystalline samples is particularly fast. Laser radiation can cause the formation of very small graphite "droplets" inside an ideal diamond crystal.[14]

Second, in order to participate in graphitization, an atom needs to jump over a certain potential barrier, i.e., to acquire energy exceeding the activation energy E_a (in principle, a tunneling transition with atom energy less than E_a is also possible; however, it is very unlikely for heavy particles such as carbon atoms).

In the framework of the above statements, two major graphitization mechanisms are considered. The first (i) mechanism[6,7,15] corresponds to a two-stage graphitization, i.e., a real departure of an atom from the diamond surface (in which case E_a is the sublimation or evaporation energy), and the following recondensation into the "graphite state." The second (ii) mechanism[11,16] corresponds to the one-step transition $sp^3 \rightarrow sp^2$.

There also exists a concept that diamond undergoes graphitization not atom by atom, but by small clusters consisting of several carbon atoms.[17,18]

In this paper, we suggest a graphitization model that is based on the fundamental principles of quantum statistics. This model will allow us to treat the problem analytically all the way to evaluating the experimental observables. In the present work we will only consider the initial stages of graphitization. In the following, the scope of our approach can be expanded to later times. We will follow the lines of the accepted theoretical approach and neglect the anisotropy of the diamond lattice. We will study a quantum-mechanical transition of individual carbon atoms from the state sp^3 to the state sp^2 using the truncated harmonic oscillator method. Using this method we will derive analytical expressions for mean kinetic rates of graphitization. These expressions will allow us to evaluate the graphitization rates using only the standard parameters of carbon, diamond, and graphite, without auxiliary assumptions and empirical data. The results of the evaluation agree with the simulation results very well.

The theoretical study of the initial stages of equilibrium graphitization is important for understanding of this fundamental physical phenomenon and for the further understanding of nonequilibrium graphitization caused by a particle beam or laser radiation. These types of graphitization are of major technological importance.

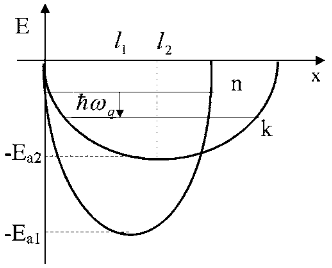

FIG. 1. Potential wells for a diamond atom (E_{a1}, l_1) and a graphite atom (E_{a2}, l_2); the arrow shows the graphitization transition from the level n to the level k accompanied by spontaneous emission of phonon $\hbar\omega_q$.

II. MODEL OF THE GRAPHITIZATION TRANSITION

In the truncated harmonic oscillator approximation discussed above, graphitization resembles the processes of defect generation, diffusion, sublimation, and impurity desorption. This allows one to expect that the same mathematical tools can be applied to graphitization as have been used for the study of those process. Following Refs. 19–22 we develop a theory for the initial stages of graphitization. We will assume that the potential confining an sp^3 carbon atom is a parabolic well with the depth E_{a1} and the width $2l_1 = a_1$, where a_1 is the diamond lattice constant (see Fig. 1). The atom performs local oscillations in its well with frequency $\omega_1 = \sqrt{K_1/M}$, where $M = 2 \times 10^{-23}$ g is the carbon atom mass and the effective spring constant K_1 can be found from $\frac{1}{2}K_1 l_1^2 = E_{a1}$. It is remarkable that the numeric value of K_1 is close to $E_l a_1$, where E_l is Young's modulus for diamond. In the well, there exist $N_{a1} = \mathrm{Int}(E_{a1}/\hbar\omega_1)$ of equidistant levels. Transitions between these levels occur with emission or absorption of phonons. If an sp^3 atom receives the energy E_{a1} it is raised to the highest level and can evaporate from the crystal surface. Then, it can recondense into the graphite sp^2 state. Therefore, we have the graphitization mechanism (i). The formal description of this mechanism is similar to that for thermodesorption of impurities, and one can use the results of Ref. 22 to determine the rate of graphitization. Additional discussion and estimates are provided below.

Besides the above studied sp^3 well, there is also an empty sp^2 well on the surface. The latter well has parameters E_{a2}, l_2, and ω_2 (see Fig. 1). Affected by the phonons, an sp^3 atom can disappear without going over the barrier E_{a1}, and a real sp^2 atom will appear instead. This is graphitization of the type (ii); here the transition can originate from any initial level n in the diamond well to any final level k in the graphite well. Such a transition is the usual quantum-mechanical transition between a given initial and all allowed final states. Since the atom sits on the surface, it always has enough free volume to expand. Due to the possibility of graphitization by transition to a final state k lying lower than the initial state n, such transition time can be very short, e.g., of the order of a half period of the diamond atom local oscillations, $\Delta t \approx T_1/2 \approx \pi/\omega_1$. A classical analog of this system is an unstable system consisting of a small weight placed on top of a smooth sphere. Substituting the typical value of the activation energy and the carbon atom mass we find $\omega_1 \sim 10^{14}\ \mathrm{s}^{-1}$ (see the estimates in Sec. VIII), and hence the graphitization onset time should be of the order of 10^{-14} s. Such a short time scale is confirmed by mathematical modeling[10–12] as well as by our estimates (see below).

III. THE HAMILTONIAN OF THE SYSTEM

The initial form of the system's Hamiltonian should describe both the diamond and graphite atoms of carbon. Therefore the unperturbed Hamiltonian should have the following form:

$$H(x) = H_1(x) + H_2(x), \tag{1}$$

where the indices 1 and 2 represent the diamond atom and graphite atom, respectively; the x axis is directed normally to the flat surface of the sample, pointing outside.

Each term in Eq. (1) has the form

$$H_i(x) = \frac{P^2}{2M} + U_i(x), \quad i = 1,2, \tag{2}$$

where $P \equiv P_x$ is the operator of the x projection of the carbon atom momentum and $U_i(x)$ is the potential energy of the atom on the surface. This potential is determined by all atoms of the sample.

The truncated harmonic oscillator approximation consists of replacing the unknown function $U_i(x)$ by the following expression:[19–22]

$$U_i(x) = -E_{ai} + \frac{1}{2}K_i x^2, \quad 0 \leqslant x \leqslant 2l_i, \quad U_i(2l_i) = 0. \tag{3}$$

Consistently with Eq. (3), the atoms can be considered as harmonic oscillators with energies

$$E_n = -E_{a1} + (n + 1/2)\hbar\omega_1 \leqslant 0, \quad \omega_1 = \sqrt{\frac{K_1}{M}}, \tag{4}$$

and

$$E_k = -E_{a2} + (n + 1/2)\hbar\omega_2 \leqslant 0, \quad \omega_2 = \sqrt{\frac{K_2}{M}}, \tag{5}$$

correspondingly for the diamond atom and graphite atom.

The eigenfunctions of the operators (3) can be represented[23] as

$$\psi_n(x) = N_n H_n(\alpha x)\exp\left(-\frac{1}{2}\alpha^2 x^2\right), \quad \alpha^4 = MK_1\hbar^{-2}, \tag{6}$$

$$\psi_k(x) = N_k H_k(\beta x)\exp\left(-\frac{1}{2}\beta^2 x^2\right), \quad \beta^4 = MK_2\hbar^{-2}, \tag{7}$$

where H_n and H_k are normalized Hermitian polynomials.

The internal degrees of freedom of atoms are not considered in the present treatment, i.e., the atoms are described as indivisible structureless particles that can only transit between states n and k.

The above description is similar to one we have used in Refs. 22 and 24 but it has important distinctions, brought about by the specifics of the graphitization process that make one consider two types of particles (sp^3 and sp^2). This substantially changes the form of the matrix elements and the necessary mathematical operations. For instance, functions (7) should be treated as the initial-state wave functions for graphitization types (i) and (ii), and also as the final-state wave functions for the type (ii). For the type (i), the final wave function should be a plane wave with a certain momentum (compare to the treatment of desorption processes in Refs. 22 and 24).

Consider the thermographitization caused by interaction of atoms with phonons. This interaction is accounted for by the displacement operator $\vec{\zeta}$,[22,24,25] introducing the creation and annihilation operators $b_q^\dagger$ and b_q of a phonon with quasimomentum $\vec{q}$, and the constant $\zeta^{(C)}$,[22,24,25] which determines the coupling of atom to various normal modes of the lattice.

To describe graphitization, it is sufficient to limit the treatment to the phonons propagating normally to the surface. Turning this perturbation on means that operators (3) are transformed as follows:

$$U_i(x) \Rightarrow U_i(\vec{i}x, \vec{\zeta}) = \frac{1}{2}K_i(\vec{i}x + \vec{\zeta})^2 \approx U_i(x) + xK_i\zeta, \tag{8}$$

where the last term describes the single-photon transitions. Two-photon transitions with amplitudes proportional to the square of the displacement from equilibrium, ζ^2, are not considered.

The complete Hamiltonian of the system has the following form:

$$H = H_0 + V(x), \quad H_0 = \frac{P^2}{2M} + U_1(x) + U_2(x). \tag{9}$$

The unperturbed Hamiltonian H_0 determines the above-mentioned eigenfunctions and energy eigenvalues. The perturbation is

$$V(x) = xK\sum_q \zeta^{(C)}(b_q e^{iqx} + b_q^\dagger e^{-iqx}). \tag{10}$$

In Eq. (10), the factor K equals $K = K_1 + K_2$, which takes into account the well-known fact that interaction with phonons is possible in the initial diamond state as well as in the final graphite state.

IV. SECOND QUANTIZATION AND INTERACTION REPRESENTATION

The following study of graphitization is convenient to carry out in terms of the second quantization. Consider the field operator

$$\Psi(x) = \sum_n A_n\psi_n(x) + \sum_k B_k\psi_k(x), \tag{11}$$

where A_n and B_k are the annihilation operators of a diamond atom in the n state and of a graphite atom in the k state, respectively. After the standard procedure of second quantization (see details in Refs. 22 and 24), the perturbation operator (10) becomes

$$V = K\sum_{n,k,q} \zeta^{(C)} B_k^\dagger A_n[\lambda(+)b_q + \lambda(-)b_q^\dagger] + K\sum_{n,k,q} \zeta^{(C)} A_n^\dagger B_k[\mu(+)b_q + \mu(-)b_q^\dagger] + \cdots, \tag{12}$$

where we omit all terms irrelevant for graphitization transitions $n \to k$ and $k \to n$.

The operator (12) includes the matrix elements of the graphitization transitions:

$$\lambda(\pm) = \int dx\ \psi_k^*(x) x \exp(\pm iqx)\psi_n(x), \tag{13}$$

$$\mu(\pm) = \int dx\ \psi_n^*(x) x \exp(\pm iqx)\psi_k(x). \tag{14}$$

Since we are presently studying the type (ii) graphitization, both $\psi_n(x)$ and $\psi_k(x)$ are real functions (6) and (7). Therefore $\psi_i^* = \psi_i$ and $\lambda(\pm) = \mu(\pm)$.

The coefficients (13) and (14) will be calculated below. Now we switch to the interaction representation by introducing the relations representing the energy conservation for the processes we study. Transition to the interaction representation is a common quantum-mechanical operation. It yields a time-dependent interaction operator

$$V(t) = K\sum_{k,n,q} \zeta^{(C)} B_k^\dagger A_n\left[\lambda(+)b_q \exp\left(\frac{i}{\hbar}\beta_1 t\right) + \lambda(-)b_q^\dagger \exp\left(\frac{i}{\hbar}\beta_2 t\right)\right] + \text{H.c.}, \tag{15}$$

$$\beta_1 = E_k - E_n - \hbar\omega_q = E_{a1} - E_{a2} + (k+1/2)\hbar\omega_2 - (n+1/2)\hbar\omega_1 - \hbar\omega_q, \tag{16}$$

$$\beta_2 = E_k - E_n + \hbar\omega_q = E_{a1} - E_{a2} + (k+1/2)\hbar\omega_2 - (n+1/2)\hbar\omega_1 + \hbar\omega_q. \tag{17}$$

The above equations pertain to the graphitization type (ii). For comparison, we write down the equation[22] responsible for the energy conservation in type (i):

$$\beta = E_k - E_n - \hbar\omega_q = \frac{P^2}{2M} + E_{a1} - (n+1/2)\hbar\omega_1 - \hbar\omega_q. \tag{18}$$

From Eqs. (16)–(18) we see that the fundamental distinctions between the graphitization types (i) and (ii) is in that the type (i) is related to overcoming the potential barrier E_{a1}, while for the type (ii) this is not necessary, although the energy difference $E_{a1} - E_{a2}$ (or $E_{a1} - E_{a2} \pm \hbar\omega_q$, to be exact) is important.

V. THE PERTURBATION THEORY, THE SYSTEM'S EVOLUTION OPERATOR, AND THE MEAN RATE OF THERMOGRAPHITIZATION

Assuming that at the initial time the system's wave function was $\psi(t_0)$, we will introduce the evolution operator $u(t,t_0)$,[26] so that $\psi(t) = u(t,t_0)\psi(t_0)$, $u(t_0,t_0) = 1$, which satisfies the Schrödinger equation in the interaction representation:

$$i\hbar\frac{\partial u(t,t_0)}{\partial t} = V(t)u(t,t_0). \tag{19}$$

Knowing $u(t,t_0)$ we can find the wave function $\psi(t)$ and the statistical operator

$$\rho(t) = u(t,t_0)\rho(t_0)u^\dagger(t,t_0), \tag{20}$$

where ρ_0 is the equilibrium (unperturbed) statistical operator. Therefore all statistical averages can also be found:

$$\langle R\rangle_t = \text{Tr}[R\rho(t)] = \text{Tr}[u^\dagger(t,t_0)Ru(t,t_0)\rho(t_0)]. \tag{21}$$

In particular the distribution function of the carbon atoms in the graphite state can be found for the time t elapsed since the graphitization onset:

$$f(k,t) \equiv \langle B_k^\dagger B_k\rangle_t = \text{Tr}[u^\dagger B_k^\dagger B_k u\rho(t_0)]. \tag{22}$$

In practice, evaluation of the trace in Eq. (22) is associated with a few known problems, including the expressing of multiparticle distribution functions via single-particle ones. This particular problem is overcome in the framework of the perturbation theory. However, this approach transforms Eq. (22) into a quantum kinetic equation describing the graphitization process, which is very difficult to solve. It is much easier to study the initial stages of the process, finding the statistical mean rate of graphitization at those stages. To do this, we will solve Eq. (19) perturbatively, keeping only the first-order terms. Then,

$$u(t,t_0) = 1 + u_1(t,t_0),$$

$$u_1 = -2\pi iK\sum_{k,n,q} \zeta^{(C)} B_k^\dagger A_n[\lambda(+)b_q\delta(\beta_1) + \lambda(-)b_q^\dagger\delta(\beta_2)] + A_n^\dagger B_k[\lambda(+)b_q\delta(\beta_2) + \lambda(-)b_q^\dagger\delta(\beta_1)]. \tag{23}$$

The operator (23) is considered on the time interval $t \to -\infty$ to $t \to \infty$, which allows us to introduce Dirac's δ functions expressing the energy conservation law for the $n \to k$ transition.

Equation (23) can be used in the framework of perturbation theory to approximately calculate the trace (22). To do this, one has to make use of Wick's theorem[27,28] and of the δ-function properties. Then from Eq. (22) we arrive at

$$\frac{\partial f(k,t)}{\partial t} = \frac{2\pi}{\hbar}K^2[1 - f(k,t)]\sum_{n,q} (\zeta^{(C)})^2 f(n,t) \times [|\lambda(+)|^2 N_q\delta(\beta_1) + |\lambda(-)|^2(N_q+1)\delta(\beta_2)]. \tag{24}$$

In Eq. (24) $f(k,t)$ is the distribution function of graphite atoms at a time t, $f(n,t)$ is a similar function for the diamond atoms, and N_q is the equilibrium distribution function of phonons with quasimomentum q.

Now we will use the approximation of short times and study the initial stages of graphitization, disregarding the reverse processes.

First of all, we notice that during the early stages of graphitization, there are very few of the sp^2 atoms, so $1-f(k,t)\approx 1$. For the same reason, the initial distribution function of the diamond atoms $f(n,t)\approx f_0(n)=f_0(E_n)$ is the usual Boltzmann distribution function normalized to the number of diamond atoms N_c of the sample surface:

$$\begin{aligned} f_0(n) &= C\exp\left(-\frac{E_n}{T}\right) \\ &= C\exp\left(\frac{E_{a1}}{T}\right)\exp\left(-\frac{\hbar\omega_1}{T}\right)\exp\left(-n\frac{\hbar\omega_1}{T}\right). \end{aligned} \tag{25}$$

In Eq. (25) we took advantage of Eq. (4) and substituted the temperature T in energy units. The normalization constant C is found from the condition

$$\sum_n f_0(n) = N_c, \tag{26}$$

which yields

$$C = N_c\left[1-\exp\left(-\frac{\hbar\omega_1}{T}\right)\right]\exp\left(-\frac{E_{a1}}{T}\right)\exp\left(\frac{\hbar\omega_1}{2T}\right). \tag{27}$$

After the simplifications we have made, the quantum-kinetic problem is reduced to a much easier problem of finding the statistical mean rate of the early stage graphitization. In this case, the total graphitization rate per atom is

$$\begin{aligned} R = \frac{1}{N_c}\sum_k \frac{\partial f(k,t)}{\partial t} &= \frac{1}{N_c}2\pi K^2 \sum_{k,n,q} (\zeta^{(C)})^2 f_0(n) \\ &\times[|\lambda(+)|^2 N_q \delta(\beta_1) + |\lambda(-)|^2 (N_q+1)\delta(\beta_2)]. \end{aligned} \tag{28}$$

Before we find the final form of the graphitization type (ii) rate, we need to calculate the factors $\lambda(\pm)$.

VI. CALCULATING THE MATRIX ELEMENTS

Calculating the matrix elements for our problem is the most mathematically intensive part of this paper. Similar calculations are encountered in Refs. 22 and 24, although presently the integrands are more complex. Since the involved transformations are so bulky, we start by a simplified description of the matrix element. For now we assume that the factors α and β are equal; see Eqs. (6) and (7). Then it follows from Eq. (13) that

$$\lambda(\pm) = N_k N_n \int_{-\infty}^{\infty} dx\, x e^{iqx} \exp(-\alpha^2 x^2) H_n(\alpha x) H_k(\alpha x). \tag{29}$$

Unfortunately, the complex exponent makes calculating (29) so difficult that an exact solution is not feasible. A similar situation arises in, e.g., absorption of light by atoms, and in similar problems. In these problems the photon wave number is considered small, and the exponential is put into a series whose first term (unity) describes the absorption in the dipole approximation. This approximation is usually accepted, although the coordinate of the atom that absorbs light can take on any values. In our case q is the phonon quasimomentum. In the first Brillouin zone $qa_1 \ll 1$, since most phonon wavelengths significantly exceed the diamond lattice constant a_1. Therefore in this work, we also will use the dipole approximation with respect to phonon quasimomenta, which simplifies Eqs. (29) and (13). This approximation also removes the distinction between $\lambda(+)$ and $\lambda(-)$. The remainder of the factor (29),

$$\lambda = \int_{-\infty}^{\infty} dx\, x \exp(-\alpha^2 x^2) H_n(\alpha x) H_k(\alpha x), \tag{30}$$

is well known from the theory of transitions between the harmonic oscillator levels:

$$\lambda = \begin{cases} \dfrac{1}{\alpha\sqrt{2}}\sqrt{n+1/2}, & k=n+1, \\ \dfrac{1}{\alpha\sqrt{2}}\sqrt{n}, & k=n-1, \\ 0 & \text{in all other cases.} \end{cases} \tag{31}$$

The result (31) can be used as a limiting case in the general description of the factor (13).

Thus we are considering the factor (13) in the dipole approximation. Recalling that α and β are essentially the inverse widths of the potential wells, we can write $\delta=\alpha-\beta$, $\delta>0$, $\delta/\beta\ll 1$ (the estimates result in $\delta/\beta\approx 0.063$). In this way a new small parameter emerges, which allows for further simplifications of Eq. (13). The first such simplification is

$$\exp\left(-\frac{1}{2}(\alpha^2+\beta^2)x^2\right) \approx \left(1-\frac{\delta}{\beta}\beta^2 x^2\right)\exp(-\beta^2 x^2). \tag{32}$$

Next, the normalization constant product can be transformed to

$$A_{kn} \equiv N_k N_n \approx \beta\left(1+\frac{\delta}{2\beta}\right)(\pi 2^k 2^n k! n!)^{-1/2}. \tag{33}$$

Finally, in the general case it can be shown that

$$H_n(\alpha x) \approx H_n(\beta x) + 2n\frac{\delta}{\beta}\beta x H_{n-1}(\beta x). \tag{34}$$

Further transformations, too extensive to be given explicitly, make use of the recurrent relation $2yH_m(y)=H_{m+1}(y)+2mH_{m-1}(y)$ to convert the terms proportional to x, x^2, x^3 to a form consisting of only Hermitian polynomial products and a constant. If we now take into account the Hermitian polynomial orthogonality, we arrive at the following expression for λ:

$$\lambda = \frac{A_{kn}}{2\beta^2}(\sqrt{\pi}2^k k!)[\delta_{n,k-1} + 2(k+1)\delta_{n,k+1}] + \frac{A_{kn}\delta}{8\beta^3}[-2(k+2)\delta_{n,k-1} + 4(k^2-1)\delta_{n,k+1} - \delta_{n,k-3} + 8(k+1)(k+2)(k+3)\delta_{n,k+3}]. \tag{35}$$

In Eq. (35), the terms with indices $k \pm 1$ correspond to transitions between the adjacent levels of the oscillators; while the terms with indices $k \pm 3$ take account of nonlinearity and correspond to jumps over two levels. It is clear that the latter processes are very unlikely and can be treated as small perturbations of the order δ/β.

Taking Eq. (33) into account, and dropping the terms of the order of $(\delta/\beta)^r$ for $r \geqslant 2$, we arrive at

$$\lambda = \frac{1}{\sqrt{2}\beta}(\sqrt{k}\delta_{n,k-1} + \sqrt{k+1}\,\delta_{n,k+1}) + \frac{\delta}{2\sqrt{2}\beta^2}[k\sqrt{k+1}\,\delta_{n,k+1} - (k+1)\sqrt{k}\delta_{n,k-1} + \sqrt{(k+1)(k+2)(k+3)}\,\delta_{n,k+3} - \sqrt{k(k-1)(k-2)}\,\delta_{n,k-3}]. \tag{36}$$

To conclude this section, we point out that calculating the value of (36) poses no difficulty thanks to δ symbols and to the small parameter δ/β.

VII. CALCULATION OF THE GRAPHITIZATION MEAN RATE

In order to calculate the mean rate of graphitization (28), we will replace the sum over the phonon quasimomenta by an integral. A standard substitution in the single-dimensional case is[25]

$$\sum_q F(q) = \frac{1}{2\pi}\int dq\, F(q). \tag{37}$$

Substituting (37) and $\zeta^{(C)}$ (Refs. 22, 24, and 25) into (28) we obtain

$$R = \frac{1}{N_c}\frac{2\pi}{\hbar}K^2 \sum_{k,n} |\lambda|^2 f_0(E_n) I(k,n), \tag{38}$$

where we defined

$$I(k,n) = \frac{1}{2\pi}\int dq \frac{\hbar}{3\rho\omega_q}[N_q\delta(\beta_1) + (N_q+1)\delta(\beta_2)]. \tag{39}$$

The term proportional to N_q corresponds to the processes accompanied by a phonon absorption, while the term proportional to N_q+1 corresponds to phonon emission, the unity representing spontaneous emission. The integral in Eq. (39) is taken over the first Brillouin zone.

Considering the acoustic phonons (diamond is a one-atomic crystal) we assume $\hbar\omega_q = uq$, where u is the speed of sound. Then the integral (39) transforms to

$$I = \frac{\hbar}{6\pi\rho u}\int \frac{d\omega_q}{\omega_q}[N_q\delta(\hbar\omega_q - E) + (N_q+1)\delta(\hbar\omega_q + E)], \tag{40}$$

where

$$E \equiv E_{a1} - E_{a2} + (k+1/2)\hbar\omega_2 - (n+1/2)\hbar\omega_1. \tag{41}$$

Integrating (40) we arrive at

$$I = \frac{\hbar}{6\pi\rho u}\left(\frac{1}{E}N_q(E) - \frac{1}{E}[N_q(-E)+1]\right), \tag{42}$$

where both terms are positive, since for various k and n there may be $E > 0$ as well as $E < 0$. It is interesting to point out that the factors $1/E$ resembles the usual energy denominators arising in description of nonresonant transitions in systems with discrete spectrum.

Substituting the derived results into Eq. (38), we can take the sum over the final states k. The complete expression for the mean rate of graphitization which comes from this summation is given in Appendix A.

Taking into account the comments from Appendix A concerning the role of spontaneous processes, and assuming $N_q \ll 1$, we will only retain one term of (A1):

$$R \approx \frac{1}{N_c}\frac{K^2}{6\rho u\beta^2}\sum_n n f_0(E_n)\frac{1}{\varepsilon_4}. \tag{43}$$

Here we need to take into account that $\omega_1 - \omega_2 = \Delta\omega \ll \omega_1$, which can be seen from Eqs. (4)–(7) and from the definition $\delta = \alpha - \beta$. Then we see that

$$\Delta\omega \approx 2\omega_1\frac{\delta}{\beta}, \tag{44}$$

which allows us to simplify Eq. (A2) for the ε_4 as follows:

$$\frac{1}{\varepsilon_4} \approx \frac{1}{\hbar\omega_1 - E_{a1} + E_{a2}}\left(1 + \frac{4(n-0.5)\hbar\omega_1}{E_{a1} - E_{a2} - \hbar\omega_1}\frac{\delta}{\beta}\right). \tag{45}$$

Neglecting the small term inside the large parentheses of Eq. (45), we derive, instead of Eq. (43),

$$R \approx \frac{1}{N_c}\frac{K^2}{6\rho u\beta^2}\frac{Z}{\hbar\omega_1 - E_{a1} + E_{a2}}, \tag{46}$$

where the sum

$$Z = \sum_n n f_0(E_n) \tag{47}$$

can be calculated exactly (see Appendix B):

$$Z = \frac{N_c}{1 - \exp(-\hbar\omega_1/T)}\exp\left(-\frac{\hbar\omega_1}{T}\right). \tag{48}$$

Taking the sum (47) and (48) in the exact form means that the contributions of all levels n to the graphitization rate are accounted for. The presence of the factor n in Eqs. (46) and (47) confirms our earlier conclusion[22] that the probability of interaction of phonons with an atom is proportional to the number of maxima of the oscillator's wave function, which increases with the level number. This confirmation appears especially valuable coming from the problem substantially different from the one considered in Ref. 22.

From Eqs. (47) and (48) we find the rate of graphitization type (ii):

$$R \approx \frac{1}{6\rho u}\frac{K^2}{a_1^2\beta^2}\frac{1}{\hbar\omega_1 - E_{a1} + E_{a2}}\frac{\exp(-\hbar\omega_1/T)}{1-\exp(-\hbar\omega_1/T)}$$

$$= \frac{n_c}{6\rho u}\frac{K^2}{\beta^2}\frac{1}{\hbar\omega_1 - E_{a1} + E_{a2}}\frac{\exp(-\hbar\omega_1/T)}{1-\exp(-\hbar\omega_1/T)}. \qquad (49)$$

Deriving Eq. (49), we assumed all linear sizes of the quantization volume equal to unity, and normalized the calculations to one atom. Thus the factor a_1^2 appeared, denoting the surface area taken by a single diamond atom. Instead of introducing this factor we could express the full rate of graphitization via the surface concentration n_c of the diamond atoms, arriving at the same value for the rate.

Equation (49) is our final result for the graphitization (ii). We will use this result for numerical estimates. Expression (49) shows the graphitization rate dependence on the main parameters of the diamond crystal. It is worth mentioning that the exponentials in (49) depend on the oscillator energy $\hbar\omega$ and not the sublimation energy E_{a1}. It is also noteworthy that in (49) we recognize Planck's formula for an oscillator with frequency ω_1:

$$N_{\omega_1} = \frac{1}{\exp(\hbar\omega_1/T)-1} \equiv \frac{\exp(-\hbar\omega_1/T)}{1-\exp(-\hbar\omega_1/T)}. \qquad (50)$$

VIII. PARAMETER SET AND EVALUATION OF THE GRAPHITIZATION RATE

The main parameters of the problem will be assumed as follows: $M=2\times10^{-23}$ g, $a_1=1.78\times10^{-8}$ cm, $a_2=2\times10^{-8}$ cm, $\rho=3.51$ g/cm^3, $u=1.75\times10^6$ cm/s, $E_{a1}=7.35$ eV $\approx1.17\times10^{-11}$ erg, $E_{a2}=7.32$ eV, $\Delta E_a=E_{a1}-E_{a2}=0.022$ eV $\approx3.52\times10^{-14}$ erg.

Then we find $K_1\approx2.95\times10^5$ cgse units, $K_2\approx2.34\times10^5$ cgse, and, according to Eqs. (4) and (5), $\omega_1\approx1.22\times10^{14}$ s^{-1}, $\omega_2\approx1.08\times10^{14}$ s^{-1}. Next, from the definition of β [Eq. (7)] we find $\beta\approx1.44\times10^9$ cm^{-1}. Therefore for our choice of parameters and for the temperature $T\approx0.172$ eV (i.e., 2000 K) Eq. (49) yields $R\approx2\times10^{14}$ s^{-1}. The estimate based on the half of the local oscillation cycle yields $R_{1/2}=2/T=\omega_1/\pi\approx4\times10^{13}$ s^{-1}, which is approximately five times smaller than what we just have found. However, if Planck's formula (50) is taken into account to determine the level populations, the mean value of $R_{1/2}$ increases by a factor 1.7, which reduces the discrepancy between $R_{1/2}$ and R to 2.9. The threefold discrepancy is considered an excellent agreement, for the given type of problem.

To evaluate the graphitization rate for type (i) we will use Eq. (36) from Ref. 22,

$$R_1 \equiv R_d \approx \frac{\sqrt{2M}K_1^2}{8a_1^2\beta^2\rho\hbar\omega_D}\left[1-\exp\left(-\frac{\hbar\omega_1}{T}\right)\right]$$

$$\times \exp\left(-\frac{\hbar\omega_D}{T}\right)\sum_n (n+1/2)\frac{\eta(\Delta\varepsilon)}{\sqrt{\Delta\varepsilon}}\exp\left(-n\frac{\hbar\omega_1}{T}\right), \qquad (51)$$

where the notation from the present work has been substituted; ω_D is the Debye frequency, $\Delta\varepsilon$ is defined in Ref. 22, and a_1^2 is the surface area per one atom.

To obtain a comprehensive comparison of Eqs. (49) and (51), we replace $n+1/2$ by just n in the latter, and also, for the order-of-magnitude estimates, replace $\Delta\varepsilon$ by $Mu^2/2$. Then the simplified Eq. (51) looks as follows:

$$R_1 \approx \frac{K_1^2}{4a_1^2\beta^2\rho u\hbar\omega_D}\left[1-\exp\left(-\frac{\hbar\omega_1}{T}\right)\right]\exp\left(-\frac{\hbar\omega_D}{T}\right)Z, \qquad (52)$$

where the sum Z is found from Eqs. (47) and (48).

Taking into account that in diamond $\omega_D\approx2\omega_1$ and substituting the numbers from the parameters list above we find Eq. (52) to yield

$$R_1 \approx 1.4\times10^{13}\ \text{s}^{-1}. \qquad (53)$$

By comparing the values found from Eqs. (49) and (52) we see that graphitization type (i) is more than an order of magnitude slower than type (ii).

IX. CONCLUSION AND DISCUSSION OF THE RESULTS

We have studied a fundamental physical problem, which is also technologically important, the unique property of diamond to spontaneously convert to graphite. The initial stages of graphitization, that is, before the saturation turns on, are studied. In contrast with the earlier research works, the selected model allows us to build a consistent quantum theory. This theory yields the mean statistical rate of the diamond-graphite transition. This rate can be compared to experimental data directly, without invoking additional assumptions and without fitting parameters. The following are the major results of our work.

We have built a quantum-kinetic model for the initial stages of the "true" graphitization of diamond, occurring without any active impurities (catalysts). Two types of such graphitization have been considered: a two-stage graphitization (i) which consists of detaching a carbon atom from the surface and then its spontaneous recrystalization in the graphite state, and a single-stage type (ii) which is related to a carbon atom transition from the sp^3 state directly to sp^2. The treatment has been carried out in the framework of first-order perturbation theory which allows one to pay special attention to the energetic of the processes.

The description is based on the concept of a truncated harmonic oscillator. This model's advantages come from its self-evidence and plausibility, as well as with the possibility to carry the analytical calculations all the way through, using this model.

The stochastic force responsible for the graphitization transition is due to the interaction of the surface carbon atoms with acoustic phonons. This interaction is considered in the dipole approximation. Since graphitization requires the high-frequency acoustic phonons, the main contribution comes from their spontaneous emission. Experimental observation of phonons near the frequency ω_1 of local oscillations of a carbon atom in its potential well may be possible. Such an experiment could confirm or elucidate the mechanisms of equilibrium thermal graphitization of diamond.

It is found that the transitions $n \leftrightarrow k \pm 3$, although allowed by the presence in the system of suitable nonlinearities, do not take place due to the relation $\max \omega_q < 3\omega_1$. However, these transitions may become quite important for nonequilibrium graphitization in laser fields.

The derived results pertain to only the initial stages of graphitization when the majority of the atoms is still in the sp^3 state. These stages are characterized by very large graphitization rates, consistently with the graphitization onset time found by mathematical modeling of the process and with the decay time of nonequilibrium state of the sp^3 graphite. In reality, the process should be substantially slowed down as a result of saturation the surface with the sp^2 atoms, and of the consequent reduction of the free volume.

It is very interesting to point out that for the initial graphitization stages, the Arrhenius factor $\exp(-E_{a1}/T)$, usually assumed in the kinetic model, is absent. Instead, similar factors appear, however, with lower activation energy. It turns out that the two-stage graphitization is an order of magnitude slower than the direct graphitization. The graphitization rates depend on all local level populations, i.e., the model accounts for graphitization transitions starting from all initial states.

The concepts and methods developed in the present work create the base for description of both the unfolded graphitization at large times, and the nonequilibrium graphitization in strong laser fields or electron beams.

APPENDIX A

Taking into account the form of the integral in (42) and taking the sum over k in (38), we can find the following expression for the mean rate of graphitization of type (ii):

$$\begin{aligned} R \approx{}& \frac{K^2}{6N_c\rho u\beta^2}\sum_n f_0(E_n)(n+1)\left(\frac{N_q(\varepsilon_1)}{\varepsilon_1}+\frac{N_q+1}{\varepsilon_2}\right) \\ &+\frac{K^2}{6N_c\rho u\beta^2}\sum_n f_0(E_n)n\left(\frac{N_q(\varepsilon_3)}{\varepsilon_3}+\frac{N_q+1}{\varepsilon_4}\right) \\ &+\frac{K^2\delta^2}{24N_c\rho u\beta^4}\sum_n f_0(E_n)(n+1)(n+2)^2 \\ &\times\left(\frac{N_q(\varepsilon_1)}{\varepsilon_1}+\frac{N_q(\varepsilon_2)+1}{\varepsilon_2}\right)+\frac{K^2\delta^2}{24N_c\rho u\beta^4}\sum_n f_0(E_n)n(n-1)^2 \\ &\times\left(\frac{N_q}{\varepsilon_4}+\frac{N_q(\varepsilon_4)+1}{\varepsilon_4}\right)+\frac{K^2\delta^2}{24N_c\rho u\beta^4}\sum_n f_0(E_n)(n+1) \\ &\times(n+2)(n+3)\left(\frac{N_q(\varepsilon_5)}{\varepsilon_5}+\frac{N_q(\varepsilon_6)+1}{\varepsilon_6}\right)+\frac{K^2\delta^2}{24N_c\rho u\beta^4} \\ &\times\sum_n f_0(E_n)n(n-1)(n-2)\left(\frac{N_q(\varepsilon_7)}{\varepsilon_7}+\frac{N_q(\varepsilon_8)+1}{\varepsilon_8}\right). \end{aligned} \tag{A1}$$

The two first terms in (A1) are the most important, while the other four should be treated as small perturbations of the order δ/β. The terms have different physical meanings and correspond to different transitions. Those depending on $\varepsilon_1 - \varepsilon_4$ correspond to transitions between the adjacent levels. Those depending on $\varepsilon_5 - \varepsilon_8$ arise from nonlinearity of the interaction with respect to the coordinate x and correspond to transitions over two levels to the third one.

The energies ε_i have the following form:

$$\begin{aligned} \varepsilon_1 &= -\varepsilon_2 = E_{a1} - E_{a2} + (n+3/2)\hbar\omega_2 - (n+1/2)\hbar\omega_1, \\ \varepsilon_3 &= -\varepsilon_4 = E_{a1} - E_{a2} + (n-1/2)\hbar\omega_2 - (n+1/2)\hbar\omega_1, \\ \varepsilon_5 &= -\varepsilon_6 = E_{a1} - E_{a2} + (n+7/2)\hbar\omega_2 - (n+1/2)\hbar\omega_1, \\ \varepsilon_7 &= -\varepsilon_8 = E_{a1} - E_{a2} + (n-5/2)\hbar\omega_2 - (n+1/2)\hbar\omega_1. \end{aligned} \tag{A2}$$

It should be taken into account that ε_i are the arguments of the phonon distribution functions $N_q(\varepsilon_i)$ and that the inequalities setting the maximum phonon energy to the Debye energy $o \leqslant \varepsilon_i \leqslant \varepsilon_{Deb}$ should hold. Positivity of ε_i is provided by the choice of the index n in the sums (A1) and means that a particular channel of graphitization is actually possible. By this reasoning, in the first two terms of (A1) only the terms with ε_1 and ε_4 are retained, while the terms with ε_2 and ε_3 are discarded.

The terms containing N_q correspond to processes with phonon absorption, i.e., to transitions to the final state k, which is higher than the initial state n. The terms with N_q+1 correspond to phonon emission and transitions to a lower level k. Since the phonons involved in the transitions between levels have relatively high energies $\hbar\omega_q \approx \hbar\omega_1$ (see the estimates), it is to be expected that the principal contribution to the graphitization transitions will be made by the processes involving spontaneous emission of phonons. Therefore to make estimates, it is sufficient to keep in (A1) only the term proportional to $1/\varepsilon_4$.

Finally, the factors $1/\varepsilon_i$ are similar to the energy denominators that appear in nonresonant processes of the first order in the systems with a discrete energy spectrum.

APPENDIX B

There are two possible approaches to evaluation of the graphitization rate. One way is to calculate the individual contributions of transitions from selected levels n. Alternatively, one can look for the total rate, taking the sum over n. In the latter case, one needs to calculate the following sum:

$$S = \sum_{n=0}^{N} n \exp(-n\gamma), \tag{B1}$$

where $\gamma = \hbar\omega_1/T$ and $N \gg 1$. Usually the summation over all initial states is a complicated problem which is seldom solved exactly. Our case, however, happens to be a lucky exception, since the sum in Eq. (B1) is relatively easily found.

Equation (B1) can be rewritten in the following identical form:

$$S = \frac{d}{d\gamma}\int d\gamma \sum_{n=0}^{N} n \exp(-n\gamma). \tag{B2}$$

Interchanging the order of the sum and the integral, we obtain

$$S = \frac{d}{d\gamma}\sum_{n=0}^{N} n\left(C_0 - \frac{1}{n}\exp(-n\gamma)\right) = \frac{d}{d\gamma}\left(C_1 - \sum_{n=0}^{N}\exp(-n\gamma)\right), \tag{B3}$$

where

$$C_1 = C_0 \sum_{n=0}^{N} n \tag{B4}$$

is a parameter that does not depend on γ, and therefore vanishes after differentiation.

Evaluating the sum in (B3) and differentiating the result, we arrive at

$$S = -\frac{d}{d\gamma}\sum_{n=0}^{N}\exp(-n\gamma) = \frac{d}{d\gamma}\left(1 + e^{-\gamma}\frac{1-e^{-N\gamma}}{1-e^{-\gamma}}\right)$$
$$= \frac{e^{-\gamma}}{1-e^{-\gamma}}\left(\frac{1-e^{-N\gamma}}{1-e^{-\gamma}} - Ne^{-N\gamma}\right) \approx \frac{e^{-\gamma}}{(1-e^{-\gamma})^2}. \tag{B5}$$

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[1] P. Whiteman and G. W. Wilson, Nature (London) **208**, 66 (1965).

[2] D. J. Bradley, M. Engwell, and H. Komatsu, Nature (London) **208**, 1081 (1965).

[3] G. Friedel and G. Ribaud, C. R. Hebd. Seances Acad. Sci. **178**, 1126 (1924).

[4] P. Libeau and M. Picon, C. R. Hebd. Seances Acad. Sci. **179**, 1059 (1924).

[5] T. Evans, *The Properties of Diamond*, edited by J. E. Field (Academic, London, 1979), Chap. 13.

[6] T. Evans and P. James, Proc. R. Soc. London, Ser. A **277**, 260 (1964).

[7] G. Davies and T. Evans, Proc. R. Soc. London, Ser. A **328**, 413 (1972).

[8] M. Seal, Phys. Status Solidi **3**, 658 (1963).

[9] C. P. Ewels, N. T. Wilson, M. I. Heggie, R. Jones, and P. R. Briddon, J. Phys.: Condens. Matter **13**, 8965 (2001).

[10] A. De Vita, G. Galli, A. Canning, and R. Car, Nature (London) **379**, 523 (1996).

[11] G. Kern and J. Hafner, Phys. Rev. B **58**, 13167 (1998).

[12] H. O. Jeschke, M. E. Garcia, and K. H. Bennemann, Phys. Rev. B **60**, R3701 (1999); Appl. Phys. A: Mater. Sci. Process. **69**, (Suppl), S49 (1999).

[13] V. R. Hoves, Proc. Phys. Soc. London **80**, 648 (1962).

[14] V. N. Strekalov, V. I. Konov, V. V. Kononenko, and S. M. Pimenov, Appl. Phys. A: Mater. Sci. Process. **76**, 603 (2003).

[15] F. P. Bundy, W. A. Bassett, M. S. Weathers, R. J. Hemley, H. K. Mao, and A. F. Goncharov, Carbon **34**, 141 (1996).

[16] C. Pantea, J. Qian, G. Voronin, and T. Zereda, J. Appl. Phys. **91**, 1957 (2002).

[17] H. P. Bovenkerk, F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, Nature (London) **184**, 1094 (1959).

[18] F. P. Bundy, H. P. Bovenkerk, H. M. Strong, and R. H. Wentorf, J. Chem. Phys. **35**, 383 (1961).

[19] G. S. De, U. Landman, and M. Rasolt, Phys. Rev. B **21**, 3256 (1980).

[20] J. W. Gadzuk, Phys. Rev. B **44**, 13466 (1991).

[21] J. Zhang, J. Chem. Phys. **96**, 4729 (1992).

[22] V. N. Strekalov and D. V. Strekalov, Phys. Rev. A **65**, 062901 (2002).

[23] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968).

[24] V. N. Strekalov and D. V. Strekalov, Phys. Rev. A **63**, 032901 (2001).

[25] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).

[26] W. H. Louisell, *Radiation and Noise in Quantum Electronics* (McGraw-Hill, New York, 1964).

[27] G. Wick, Phys. Rev. **80**, 268 (1950).

[28] C. Bloch and C. de Dominicis, Nucl. Phys. **7**, 459 (1958).