Model for the Coagulation of Carbon Clusters at High Densities and Temperatures

A. L. Kupershtokh,[1] A. P. Ershov,[1] and D. A. Medvedev[1]　　　　UDC 539.2; 548

A two-dimensional formulation of the molecular dynamics method is used to model the coagulation of carbon particles at the high temperatures and densities corresponding to conditions behind a detonation front. When small particles interact, they coalesce in the manner of liquid drops. Particles greater than 3 nm in size adhere in faces while retaining their form. Surface atoms, however, are capable of migrating among coupled particles, thereby facilitating their bonding. Calculations reveal the existence of strong compression and rarefaction waves with amplitudes of up to 30 GPa in the interacting particles.

When condensed high explosives (HE) with a negative oxygen balance detonate, carbon is released in the form of ultradispersed particles. Interest in this phenomenon intensified when it was found that a diamond phase develops many cases [1, 2]. The first experiments' in 1963–1965 were reported by Volkov et al. [3].

The size of the particles obtained by detonation synthesis (≈ 3 nm) is almost independent of the size of the HE charge (i.e., of the time over which coagulation is possible) [1, 4]. This is because temperatures roughly 1000 K below the melting curve of carbon (Fig. 1) are reached during the explosion of typical HE. Thus, as the characteristic size at which the crystalline properties of the particles begin to predominate is reached, complete coalescence of clusters is replaced by adhesion followed by formation of rarefied aggregates. Recent experiments using HE with a higher temperature in the detonation wave have shown that the resulting particle size is much greater [5]. In this case, the detonation parameters corresponded to the liquid state of carbon. The coagulation of the liquid particles leads to the formation of coarse particles [5, 6].

The coagulation process under conditions that correspond to a stable solid phase is of undoubted interest and warrants detailed analysis. A calculation
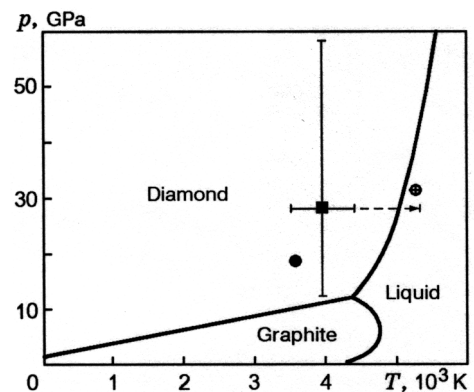

Fig. 1. Phase diagram of carbon. The parameters in detonation waves are plotted: points ●, ■, and ⊕ refer to TNT, TNT/RDX (40/60) mixture, and benzotrifuroxane [6].

of cluster growth has been made [7] employing a cutoff of particle coagulation after they reach a certain size. This results in a rather narrow size distribution of the particles after termination of the reaction. For certain values of the parameters, characteristic cluster sizes similar to those observed in experiments are obtained. The physical significance of this cutoff is understandable on a qualitative level. In particular, it reflects the reduction in the effective melting point for fine particles [8]. It is clear that in reality a transition region should be introduced, rather than a critical size.

[1]Lavrent'ev Institute of Hydrodynamics,
Siberian Division, Russian Academy of Sciences,
Novosibirsk 630090.

A more rigorous approach in place of the postulated critical particle size requires that the coagulation dynamics be examined on a microscopic level. The molecular dynamics method has been used to study the interaction of clusters [9–11]. This paper is an extension of the approach proposed in [11]. Here we present calculations which make it possible to follow the change in the adhesion mechanism for clusters as their size increases. Considerable mechanical stresses with alternating signs are identified. This effect may have a substantial effect on the phase transitions of carbon, but have not been modeled up to now. Calculations are performed of coagulation in the presence of gaseous detonation products.

COMPUTATIONAL TECHNIQUE

The calculations were done by the molecular dynamics method. In this paper a standard Lennard-Jones interparticle interaction potential

$$U(r) = 4\varepsilon\left(\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^6\right)$$

is used for the carbon atoms with the interaction radius r limited to a distance of $2.5b$. Here ε is the binding energy and b is the characteristic length. The computational results for a given potential are self-similar in the parameters ε and b. By specifying the numerical values of these parameters, one can describe the behavior of particular materials.

The interaction between the gas and carbon particles, as well as that of the gas molecules among themselves, was described by the repulsive potential

$$U = 4\varepsilon_{ij}\left(\frac{b_{ij}}{r}\right)^{12}.$$

For the parameters of the interaction between the gas and atomic carbon, we have used the usual correlations $b_{12} = (b + b_{22})/2$ and $\varepsilon_{12} = \sqrt{\varepsilon\varepsilon_{22}}$ [12].

An isolated system was modeled, i.e., the number of particles, volume, and total energy were conserved through the calculations.

The equations of motion of the particles were integrated using a Verlet algorithm in velocity form. The following dimensionless parameters were used in the calculations: temperature and energy in units of ε, time in units of $\tau = \sqrt{mb^2/\varepsilon}$, and velocity in units of $\sqrt{\varepsilon/m}$, where m is the mass of a carbon atom. The time step was limited so that the fastest particle should not move by more than 0.005 of the characteristic size (b) over a time Δt. This prevents the unphysical entry of particles into the region where the potential energy rises abruptly and ensures better conservation of the total energy during the cal-

culation, i.e., makes it more accurate. The average step size Δt in the calculations was roughly 0.005τ. The total energy was conserved to within 0.5% in the course of the calculations. In all the simulations we used a square region with periodic boundary conditions.

In this paper we examine four different variants of the initial conditions. For quasi-melting simulations, the initial configuration was a motionless, solitary cluster at the center of a cell. For the condensation calculations a chaotic mixture of carbon atoms and gas molecules was used. In modeling the interaction between a cluster and the gas, a motionless cluster was placed at the center of a cell and surrounded by gas molecules with random positions and velocities. In the stress wave calculations two clusters with zero initial velocities were separated by the interaction distance for the interatomic forces.

The temperature T was calculated from the average kinetic energy of the atoms. In the case of a cluster interacting with a surrounding gas, the motion of the center of mass of the cluster and its rotation as a whole were taken into account:

$$T = \frac{m}{(2N-3)k}\sum_i (\mathbf{v}_i - \mathbf{v}_{c.m} - \mathbf{\Omega} \times (\mathbf{r}_i - \mathbf{r}_{c.m}))^2,$$

where $\mathbf{v}_i$ and $\mathbf{r}_i$ are the velocity and coordinates of the ith atom; $\mathbf{r}_{c.m}$ and $\mathbf{v}_{c.m}$ are the coordinates and velocity of the center of mass of the cluster, $\mathbf{\Omega}$ is the angular rotation velocity, and k is the Boltzmann constant.

The following parameters were used: $m = 1.90 \cdot 10^{-22}$ g and $b = 1.54$ Å (corresponding to the bond length of carbon atoms in diamond). The energy $\varepsilon = 2$ eV was chosen as compromise between the binding energy ($6\varepsilon/2 = 6$ eV in our model and 7.4 eV in diamond) and the melting point (≈ 5000 K for carbon and $0.39\varepsilon \approx 8000$ K for a two-dimensional Lennard-Jones crystal [13]). The time scale was $\tau = 3.83 \cdot 10^{-14}$ sec and the velocity scale was $4.02 \cdot 10^5$ cm/sec. The average time step was $\Delta t = 1.9 \cdot 10^{-16}$ sec. For the gas molecules we take $b_{22} = 2.7b$ and $\varepsilon_{22} = 0.01$ eV.

The Lennard-Jones potential does not yield the crystal structure of carbon, since it gives a dense packing with an excess number of bonds. The discrepancy among the binding energies and the melting points mentioned above is one consequence of the crudity of this model. It is clear that with this potential, three-dimensional calculations will not be more accurate. On the other hand, in the two-dimensional case the volume of calculations will be much smaller for the same characteristic linear dimensions (that is, larger particles can be modeled). As in many other molecular dynamics problems, the two-dimensional

model is a natural first step. Of course, it only provides a qualitative description, but, nevertheless, does reflect many properties of the real system.

More complicated potentials capable of describing the crystalline states of diamond and graphite are known [14, 15]. For these potentials, however, the properties of the intermediate states and potential barriers between the major phases are not known with sufficient reliability. Therefore, these models cannot be applied to nonequilibrium dynamics problems in which rapid transitions between different states occur. For example, a model of C_{60} formation [15] required special fitting of the potential and additional measures to stimulate the formation of a cluster. A realistic potential would, for example, yield a phase transition, but thus far that seems to be a rather distant prospect.

There is a rigorous approach based on quantum mechanical calculations [16]. In this case, however, the volume of calculations is very large, so at present it is possible only to model the behavior of systems with a small number of atoms.

In principle, classical molecular dynamics is a qualitative approach because of the artificial character of the potential. The results given below, however, are insensitive to the imperfection of the model. Of course, this means that the purpose of this paper is to model the basic qualitative effects.

QUASI-MELTING

It has been shown [11] that the coagulation of small carbon particles is a highly exothermic process accompanied by a substantial temperature rise. The estimates in [11] gave a temperature rise of ΔT [K] $\sim 4000 \cdot N^{-1/3}$. For a cluster with a characteristic number of atoms $N = 1000$, this temperature rise is 400 K. Figure 2a–f illustrates the interaction of two small clusters. In this case, the temperature rises by roughly $0.1\varepsilon \approx 2000$ K. This temperature increase (the dashed arrow in Fig. 1) can cause the state of the cluster to move into the liquid region of the p–T phase equilibrium diagram for carbon.

In small particles the fraction of surface atoms is quite large ($\sim N^{-1/3}$ in the three-dimensional and $\sim N^{-1/2}$ in the two-dimensional case). For our calculations, this fraction is 0.1–0.2. The surface atoms have 1.5–2 times fewer neighbors than the internal atoms (3–4 instead of 6 in two-dimensions), so that their binding energies are lower. Our calculations were for the prepared thermalized, isolated clusters with zero total momentum and angular momentum and with a specified average temperature. A his-
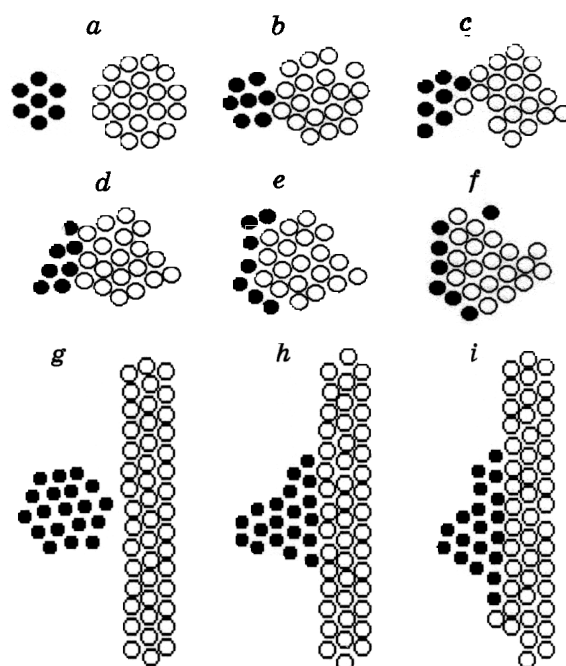

Fig. 2. The interaction of two relatively small particles (7 and 19 atoms): time after onset of the interaction $t = 0$ (a), 0.5 (b), 1.1 (c), 1.5 (d), 2.0 (e), and 2.9 psec (f) [11]. Modeling the interaction of a small particle (19 atoms) and a large particle (a wall), $t = 1.5$ (g), 6.1 (h), and 7.7 psec (i).

togram of the distribution of the average potential energy of each atom in the field of the others over the distance to the center of the cluster was obtained. Figure 3 shows the typical shape of this histogram. These calculations were averaged over 2000 time steps.

A large fraction of surface atoms results in a drop in the average binding energy per atom and in a decrease in the melting point of the cluster. A decrease in the melting temperature by hundreds of degrees has been observed experimentally in a number of substances [8] and demonstrated in numerical calculations [12, 17], as well.

For a state of thermodynamic equilibrium within a cluster, the kinetic energy of all the atoms is the same on the average. The potential barriers for atoms in the surface layer are lower than for the internal atoms. This makes possible the migration of surface atoms at temperatures too low for complete melting of the cluster. It may be said that they are in a quasi-molten state. These atoms form roughly one outer layer. The fraction of these atoms is higher for clusters with unfilled outer shells. As the temperature rises, layer-by-layer melting of clusters can occur.

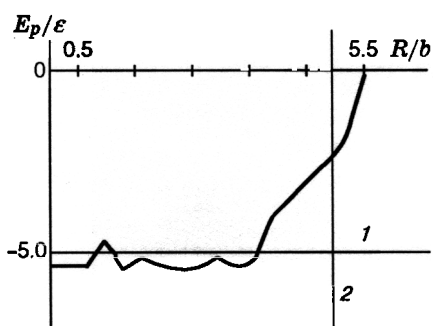The variation in the relative amount of un-

Fig. 3. Dependence of the average potential energy on distance from the center of a cluster of 61 atoms: $kT = 0.2\varepsilon$; 1) the melting limit; 2) the maximum cluster radius.
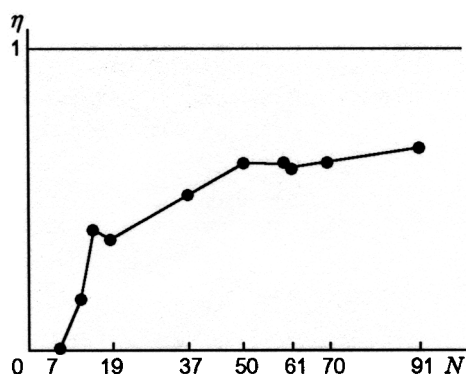

Fig. 4. The fraction of atoms in the unmelted portion of a cluster as a function of its size ($kT = 0.2\varepsilon$).

melted material with the number of atoms in the cluster is shown in Fig. 4. Small particles (7 atoms) are completely melted.

When large clusters interact, because of fluctuations surface atoms can migrate along the common surface of the particles and form a unified, more compact structure. The probability of these fluctuations is on the order of $\exp(-2\varepsilon/kT) \approx 5 \cdot 10^{-5}$ at $T \approx 4000$ K. Our calculations support that this process is very slow for large clusters and they simply become attached to facets, while retaining shape. When a large number of individual clusters of this sort aggregate, they form fractal structures. The existence of such structures in detonation products has been confirmed experimentally by small angle x-ray scattering [7].

For a plane model, clusters containing 20 particles are almost half melted. In the three-dimensional case, this corresponds to clusters with $N \approx 100$ atoms, which are heated by roughly 1000 K for an initial temperature $T_0 = 4000$ K. Then the entire cluster is in a molten state.

It has been shown [7] that when carbon is released, the large particles grow mainly through the influx of small particles to their surface. Thus, there is interest in interactions between particles, one of which is quite large. Figure 2g–i illustrates the interaction of a small (19 atoms) particle with a large particle which is modeled as a wall containing three layers, of which the rightmost layer is fixed. The small particle spreads out over the surface of the large one. Here the average temperature increases by more than 1000 K.

We have also done a series of calculations of the interaction of two clusters of different sizes with $kT_0 = 0.2\varepsilon$. It turns out that the smallest clusters with 7 atoms, which melt completely, always merge with the others and that the time for this process is independent of the size of the large cluster.

THE EFFECT OF HEAT EXCHANGE

Heat exchange with the surrounding gas plays an important role as the particles interact. We have examined the condensation of clusters from an initial mixture of carbon atoms and other (gaseous) detonation products. The initial concentration of carbon was $n_1 = 0.083/b^2$, of the gas $n_2 = 0.225/b^2$, and $T_0 = 0.1\varepsilon \approx 2 \cdot 10^3$ K. These concentrations and temperature correspond to the parameters of a detonation wave. The successive stages of the process are shown in Fig. 5. The condensation of carbon is almost complete by $8 \cdot 10^{-12}$ sec (210τ). A substantial amount of energy, representing the contribution of condensation to the overall exothermicity of the reaction, is released.

We now estimate the temperature rise in the detonation products owing to the coagulation of carbon. Let the carbon be initially in the form of atoms with a concentration n_1. An energy $\Delta E = 3\varepsilon n_1$ is released through complete coagulation. After thermal equilibrium is reached, the energy is uniformly distributed between the carbon and gaseous detonation products, whose initial concentration is n_2. Since the gas is mainly a mixture of diatomic and triatomic molecules with vibrational excitation at the characteristic pressure and temperature, the specific heat can be assumed to be roughly $5k$ per molecule. In this case, the temperature rise for constant volume is

$$\Delta T \approx \frac{n_1 \cdot 3\varepsilon}{(3n_1 + 5n_2)k} = \frac{\varepsilon}{k} \frac{1}{1 + 5n_2/3n_1}.$$

In this case, we have $\Delta T \approx 3.2 \cdot 10^3$ K for $n_1/n_2 = 0.27$. In reality, no additional temperature jumps of this magnitude are observed. This shows that the
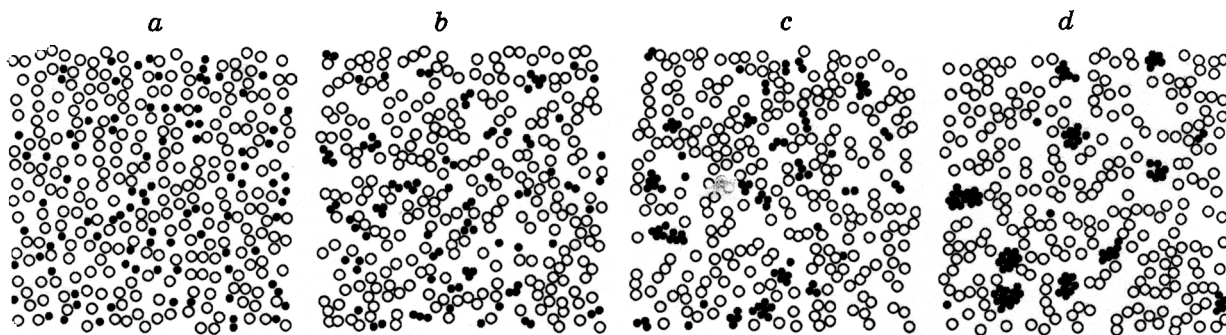
Fig. 5. Condensation of clusters from an initial gaseous mixture: time after onset of the interaction $t = 0$ (a), 1.7 (b), 3.7 (c), and 8.0 psec (d).

condensation of carbon occurs at the same time as the main chemical reaction, as a part of that reaction.

We have also studied the fluctuations in the cluster temperature owing to heat exchange with the surrounding gas. One cluster with $kT \approx 0.2\varepsilon$ was placed in the center of a cell filled with gas molecules at the same temperature. The average concentrations of the carbon and gas in the cell were the same as in the previous case. Fluctuations in the cluster temperature were studied over an interval of $7.7 \cdot 10^{-12}$ sec (200τ). The cluster remained coherent throughout the calculation, according to visual monitoring.

Figure 6 shows a typical plot of the fraction of time spent by the cluster within each temperature interval. The distribution seems close to Gaussian. Thus, we can determine the root mean square temperature deviation $\langle \delta T \rangle$.

The root mean square temperature deviation decreases with increasing particle number in the cluster as $\langle \delta T \rangle \sim 1/\sqrt{N}$. The temperature fluctuations
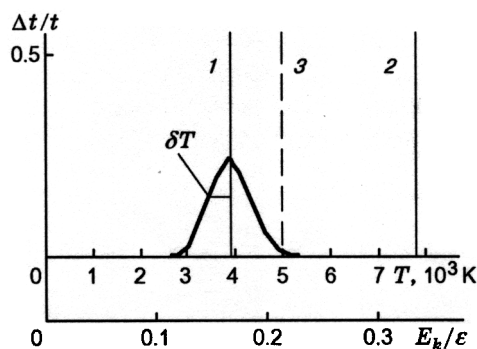

Fig. 6. The fraction of time during which a cluster of 61 atoms is at various temperatures: 1) average cluster temperature; 2) melting point for a two-dimensional model; 3) melting point of diamond at a pressure of $\sim$30 GPa.

for a typical cluster size are shown by horizontal lines in Fig. 1. The parameter $\langle \delta T \rangle$ is of the same order of magnitude as the temperature rise owing to the exothermicity of coagulation. Thus, this energy interaction with the surrounding gas must be taken into account. In the three-dimensional case the temperature rise owing to the exothermicity falls off with the number of particles $\sim N^{-1/3}$ and the temperature fluctuations, $\sim N^{-1/2}$. Thus, thermal fluctuations in the state of three-dimensional clusters should, on the whole, be significant only for the smallest particles.

STRESS WAVES DURING COAGULATION

When two initially motionless clusters interact, at first a significant portion of their energy of attraction goes into the kinetic energy of their approach. Then the particles collide and are compressed. The collision velocity [11] $u \sim 5 \cdot N^{-1/6}$ km/sec is much greater than the thermal velocity of the Brownian motion, $v \sim 3 \cdot N^{-1/2}$ km/sec. The pressure amplitude in the resulting compression wave is $p \sim 3 \cdot 10^{10}$ Pa [11].

In modeling the interaction of two particles, we computed the longitudinal stress σ_{xx} averaged over the cross section and the pressure inside each cluster $p = (\sigma_{xx} + \sigma_{yy})/2$. The longitudinal stress σ_{xx} was calculated by drawing a control surface through the center of each cluster perpendicular to the line joining their centers. The stress was calculated using the formula

$$\sigma_{xx} = \sum \Delta p_x / S \Delta t,$$

where $\sum \Delta p_x = \sum'_{i,j} \mathbf{f}_{ij} \mathbf{n}_x \Delta t + \sum''_i m_i \mathbf{v}_i \mathbf{n}_x$ is the total momentum flux through a given surface. Here $\mathbf{f}_{ij}$ is the force with which atoms i and j interact, $\mathbf{n}_x$ is the unit vector in the x direction, S is the transverse cross section, $\sum'$ is a sum over pairs of atoms
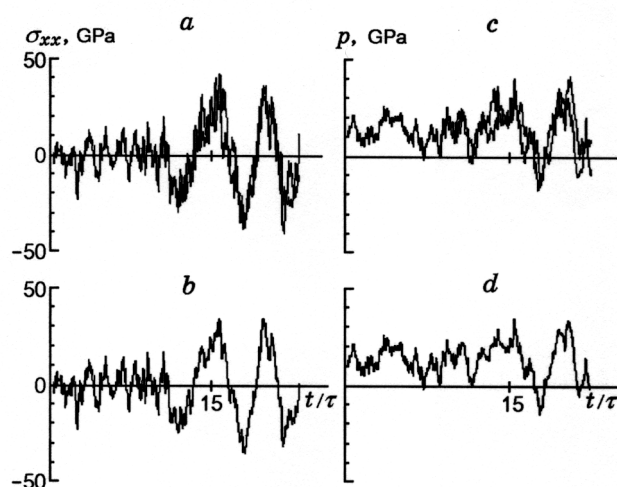
Fig. 7. Stress σ_{xx} (a and b) and pressure p (c and d) in the central region of the particles. Plots of the stresses and pressures in the left- and right-hand particles are shown in (a) and (c) and of the average over both particles in (b) and (d).

lying on different sides of the control surface, and $\sum''$ is a sum over atoms which crossed the surface in the last time step. For the pressure calculations the control surface was specified in the form of a circle whose center laid at the center of mass of the cluster and whose radius equaled the average distance of the atoms from the center. The results were averaged over 500–700 steps, which corresponds to 2–3 atomic vibrational periods.

Figure 7 shows the averaged stresses during collisions of two identical clusters containing 91 atoms each with an initial temperature $kT_0 = 0.205\varepsilon$. The clusters were initially at rest separated by the distance over which the interatomic forces act. Evidently, the clusters are initially attracted layer-by-layer and this leads to the appearance of a primary rarefaction wave. After the collision there is a compression wave which is then reflected from the back surface as a rarefaction wave. The amplitudes of both the compression and rarefaction waves are as high as 30 GPa. The pressure plots include a positive constant component, the Laplace pressure. (Since σ_{xx} was averaged over the entire cross section of the cluster, it includes both the enhanced pressure in the central region and the tension in the surface film, which compensate one another on the average.) Tension and shear stresses also develop as a result of lateral expansion.

Therefore, the interacting particles are subjected to sign-changing loads with amplitudes of tens of gigapascals. The change in the state of a cluster owing to compression waves is indicated by the verti-

cal lines on the p–T diagram (Fig. 1). This effect may explain the need for a large pressure reserve for a significant yield of diamond [18], lest the release wave bring the system into the region of the phase diagram for carbon (Fig. 1) where the diamond phase can undergo a transition to graphite. Another explanation may be a shift in the phase equilibrium diagram for small carbon particles [19]. In reality, both processes appear to be important.

CONCLUSIONS

When small clusters interact, a significant amount of energy is released, so that the particles are rapidly heated. The calculations yielded a temperature rise consistent with the theoretical estimate of [11]. In addition, atoms lying near the surface have a lower potential energy, so that we can speak of quasi-melting of the surface. Both effects act in one direction and lead to the possibility of coagulation of sufficiently fine particles at temperatures well below the melting point. For our clusters, exothermicity and quasi-melting effects are of the same order of magnitude.

The fluctuations in the cluster temperature owing to the interaction with the surrounding gas obtained in these calculations are of the same order of magnitude as the temperature rise owing to exothermicity. The signs of these fluctuations, however, can be arbitrary. In addition, the fluctuations fall off more rapidly with particle size, so their contribution to the coagulation process appears to be small.

When clusters collide, mechanical stress waves of variable sign develop with amplitudes of up to 30 GPa and may affect the phase transitions of carbon.

We have simulated the condensation of clusters from an initial gas mixture. It occurs mainly within a time on the order of a few picoseconds. The presence of a gas does not inhibit condensation. Substantial energy releases and temperature rises are observed and these reflect a contribution owing to the condensation of carbon to the overall exothermicity of the reaction.

These calculations have shown that the temperature and pressure can deviate substantially from their average values during the interaction of carbon clusters (Fig. 1). This provides a qualitative explanation of the major features of diamond particle formation right in detonation wave fronts.

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