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Translated by D. H. McNeil

Exothermic coagulation of small clusters in detonation wave fronts

A. P. Ershov and A. L. Kupershtokh

M. A. Lavrent'ev Institute of Hydrodynamics, Siberian Branch of the Russian Academy of Sciences

(Submitted January 22, 1993)
Pis'ma Zh. Tekh. Fiz. 19, 76–80 (February 12, 1993)

Ultradisperse particles (~30 Å) of carbon are created during detonation of condensed explosives. This phenomenon is of special practical interest because in a number of cases a diamond phase is produced.[1,2] In a detonation front carbon is produced in the form of isolated atoms or small groups of atoms. When these particles meet they combine (coagulate). The most interesting fact is that the dimensions of the resulting particles are essentially independent of the size of the explosive charge, which determines the time over which coagulation is possible.[1,3] Thus, particle growth is limited by some mechanism. One might expect the characteristic diameter of the particles to be determined by a transition from clusters to macroscopic particles. Various data show that this transition occurs in the range of 100 to 1000 atoms (at particle sizes of ~10-20 Å).[4]

Particles of this size also develop under other conditions (aerosols, soot). Loose structures, some of them fractal,[5] form from initial grains. This behavior is typical of detonation diamonds, as well.[6]

We have developed[6] a model for coagulation with a size limit. The limiting size at which the properties of the particles change enters the model as a phenomenological parameter. In this letter we consider the exothermic coagulation of carbon clusters in detonation wave fronts. Calculations show that the small clusters found in the detonation products undergo coagulation at relatively low temperatures. Various effects that influence particle growth are evaluated.

1. Under typical conditions for detonation synthesis the reaction products lie in the stability region for diamond. The pressure in the medium is considerably higher than on the graphitization curve, while the temperature is about 1000° lower than the melting point. Calculation leading to the formation of compact particles is possible under these conditions only if the properties of the small particles differ from those of the "monolithic" particles. For example, we might refer provisionally to reduction in the melting point owing to a large fraction of surface atoms. A reduction of this sort by hundreds of degrees has been observed experimentally in several materials.[4]

Moreover, the coagulation of small particles is exothermic.[7] As a crude estimate let us consider a cube of N particles containing $N^{2/3}$ atoms on each face. When two such clusters meet, an energy $\varepsilon N^{2/3}$ is released, where ε is the binding energy ($\approx$2 eV for carbon). At high temperatures the heat capacity is of the order of $3k$ per atom, so that the cluster is heated by $\Delta T \sim \varepsilon N^{2/3}/(3k \cdot 2N) \approx 4000 \cdot N^{-1/3}$ degrees. For $N = 1000$ we obtain 400 K, i.e., close to the shortfall from the melting point of carbon. For spherical particles the heating is essentially the same after they have recombined into a sphere. Larger particles are heated less and coagulation does not occur.

2. This primitive calculation neglects the dynamics of coagulation. When the number of atoms is small, because of statistical fluctuations there is a significant probability that a group of atoms near the contact region between the particles will take up the excess energy. The lifetime of this fluctuation may be sufficient for local reorganization of the lattice, for atoms from one particle to jump to the surface of the other, and for the establishment of a larger coagulation surface. In our words, the surface may "melt" at first and then the conditions for agglomeration may be more favorable.

Molecular dynamic calculations of cluster interactions have been done. A standard two-dimensional Lennard-Jones model was used. The calculations employed a Verlet algorithm (in its velocity form). It can be assumed that the clusters are initially separated by the distance over which the interatomic forces act and are at rest, since the velocity of their Brownian motion is low. The system of two particles is regarded as isolated, i.e., it does not interact with the surrounding medium.

The calculations showed that if the initial particle temperatures are low, then when they combine the average temperature rises because of the exothermicity, but coagulation does not occur (the clusters retain their shape). However over a fairly wide range of temperatures somewhat below the melting

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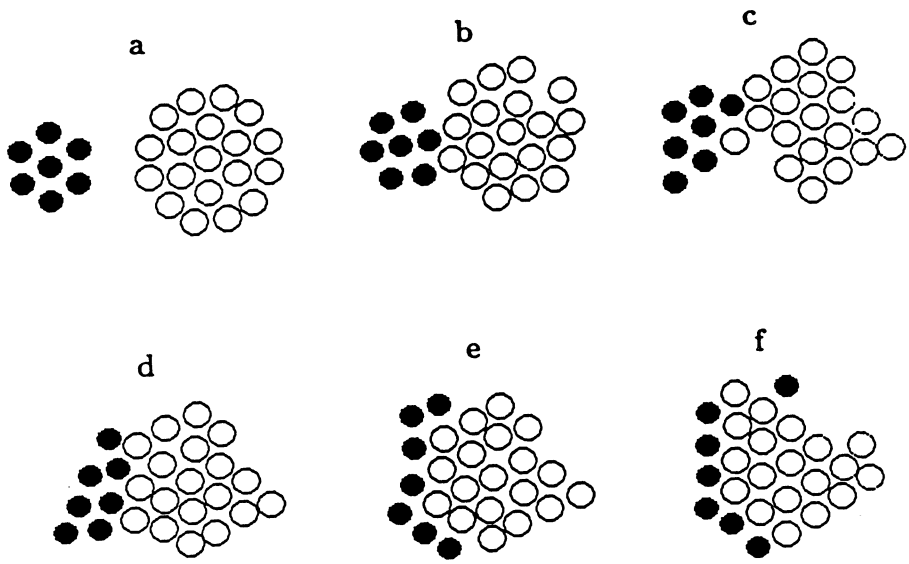

FIG. 1. The interaction of two relatively small particles (7 and 19 atoms). Times after onset of the interaction, t (ps): 0 (a), 0.5 (b), 1.1 (c), 1.5 (d), 2.0 (e), 2.9 (f).

point an interesting coagulation mechanism that resembles "wetting" is observed.

Figure 1 shows successive "snapshots" of the interaction of two small particles (7 and 19 atoms) with the correct "crystalline" shapes. The initial temperatures of the particles are 0.13ε and 0.17ε (not far from 3000 K). The smaller particle gradually spreads out to form a monolayer on the surface of the larger particle. Over a time of the order of 2 ps complete coagulation occur, with the formation of a single particle, whose surface shape is close to a two-dimensional sphere. The average temperature has increased by about 2000°. When vacancies or superfluous atoms are present on the surface, the coagulation process is easier.

The atoms on the surface of the cluster have fewer bonds with other atoms: 3-4 instead of 6 (in a planar arrangement). Relatively small fluctuations in the kinetic energy are required for them to migrate along the surface during coalescence. In this sense the surface atoms can be in a "quasimolten" state while the structure inside the particle is strictly crystalline.

It has been shown[6] that when carbon is being produced the large particles grow via the flux of smaller particles to their surface. Thus, interactions in which one of the particles is quite large are of major interest.

Figure 2 shows the interaction of a small particle (19 atoms) and a "large" particle modeled as a "wall" consisting of three layers, of which the rightmost layer is fixed. The small particle spreads out over the surface of the larger one. The average increases by more than 1000°. Note that when the average temperature of the detonation products is below the melting point, the coagulation time increases rapidly with increased cluster size because of the dominant role of infrequent fluctuations in the "wetting" effect. We can speak of a strong dependence of the coagulation kinetics on the particle size (even if the exothermicity is ignored). As the particles grow to a certain size coagulation slows down and aggregates will grow.[6] Two-dimensional regular clusters with $N \sim 100$ will merge while retaining their shapes.[8] In the three-dimensional case this corresponds to $\sim 10^3$ atoms, in accord with the estimates given above.

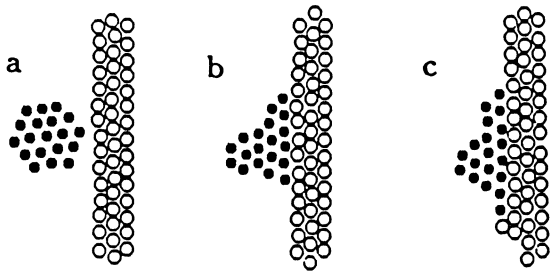

FIG. 2. Model for the interaction of small (19 atoms) and "large" (a wall) particles. Time t (ps): 1.5 (a), 6.1 (b), 7.7 (c).

The main problem with molecular dynamics calculations is the model character of the interaction. In any case the results will be mostly qualitative. Subject to this proviso, these calculations demonstrate the existence of a "quasimelting" effect that leads to the coalescence of particles at low temperatures.

3. When the particles collide there is a local pressure rise. Consider a cluster drawn to a plane surface. If a substantial fraction of the energy released, $\varepsilon N^{2/3}$, is used to accelerate the cluster, then it acquires a velocity $U \sim (2\varepsilon/mN^{1/3})^{1/2} \sim 5/N^{1/6}$ km/s. At temperatures $T \sim 4000$ K the thermal velocity is $V \sim 3/N^{1/2}$ km/s, which is much less, even for particles with dozens of atoms. For $N = 10^3$ one can already use macroscopic characteristics such as the sound speed c to estimate the pressure amplitude as $\Delta P = \rho cu/2 \sim 300$ kbar. When the particle stops the kinetic energy initially goes into compression and then thermalizes. In reality the layer closest to the wall begins to be drawn in first and then the others come in. Thus, negative pressure drops of roughly the same magnitude also appear. Tensile and shear stresses also develop because of unloading (stress release) waves.

Therefore, interacting particles are subject to loads with amplitudes of hundreds of kilobars which change sign but are positive on the average. This effect can have a major effect on phase transition. This phenomenon explain the need for a

substantial pressure margin in order to obtain a significant yield of diamond. Unfortunately, it is impossible to describe other crystalline structures in the framework of the Lennard-Jones model.

Other factors which may affect the particle interaction include heat transfer into the medium and the direct effect of impurities. The interaction with the medium is still important in the stage where the explosion products are expanding and the surrounding medium and particles undergo significant heating.[9]

We thank V. F. Anisichkin and G. V. Gadiyak for useful discussions.

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Translated by D. H. McNeill