

# Diamond Nanoparticle Surface Chemistry in Detonation

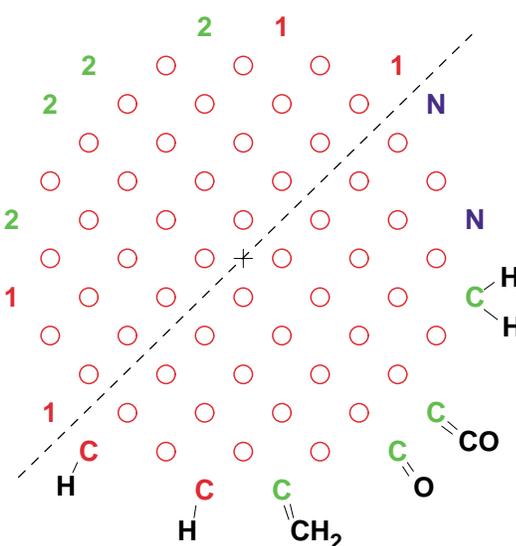
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The detonation products of a high explosive form a very nonideal and complicated mixture under extreme conditions ( $P \sim 30$  GPa and  $T \sim 3000$  K). An accurate theoretical treatment must not only handle well the extreme conditions for a single molecular fluid, but also the mixture of species and the thermodynamic chemical equilibrium composition of the products ( $N_2$ ,  $H_2O$ ,  $CO_2$ ,  $CO$ , carbon, etc.). In addition, recovery experiments show that the solid carbon is in the form of small clusters with a large fraction of atoms on the surface. In the diamond phase, the spherical clusters range from 2 - 5 nm in diameter with 20 - 30% of the atoms on the surface with energetically unfavorable dangling bonds. In this treatment, we provide for a variety of dangling bond cap groups in chemical equilibrium.

The background fluid treatment is given by a fluid perturbation theory tied to benchmark simulation methods.

A spherical diamond cluster has dangling bonds exposed over the entire surface. It is energetically unfavorable to restructure the diamond surface. Figure 1 shows a slice through the  $z = 0.5$  (lattice constant) plane for a 2.3 nm cluster. A mirror plane is indicated as a dashed line. Surface atoms with single and double dangling bonds (denoted 1 and 2) are shown in the upper left. Examples of possible surface groups are shown in the corresponding mirror sites in the lower right. Also note that the tetrahedral bonds are all out of the plane and none of the atoms in a plane are bonded to each other.

For a given radius cluster, the number and type of surface groups in the truncated lattice and the number of core atoms



**Figure 1:** The  $z = 0.5$  plane of a  $23 \text{ \AA}$  cluster. A mirror plane is indicated as a dashed line. Surface atoms with single (1) and double (2) dangling bonds in the upper left. Examples of surface groups in the corresponding mirror sites in the lower right.

without dangling bonds are counted. In order to determine the equilibrium composition of the surface, it is necessary to determine the Gibbs free energy of the cluster with arbitrary surface composition. Each surface group is treated as an additive contribution to the free energy. An Einstein model is used for the vibrational frequencies in surface group. These modes are assumed to couple weakly to the core and are estimated from similar small molecules where possible. The heat of formation of each surface group is determined by additive bond strengths. The effective volume is estimated from the geometry of similar groups in small molecules. An effective standoff distance from the geometric surface is chosen to take into account that the occupied volume (i.e., volume

excluded from the molecular fluid) is not identical to the geometric volume. Notice that a substitutional N atom

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would occupy a small volume that will become significant in the PV term at high pressure.

The surface free energy has an entropy contributions due to the counting of possible ways to occupy a set of surface sites with a given composition. This contribution to the Helmholtz free energy is similar to that of ideal mixing.

Finally, the core contributions are taken from a bulk diamond model incorporating a Debye model of vibrations and a measured cold curve.

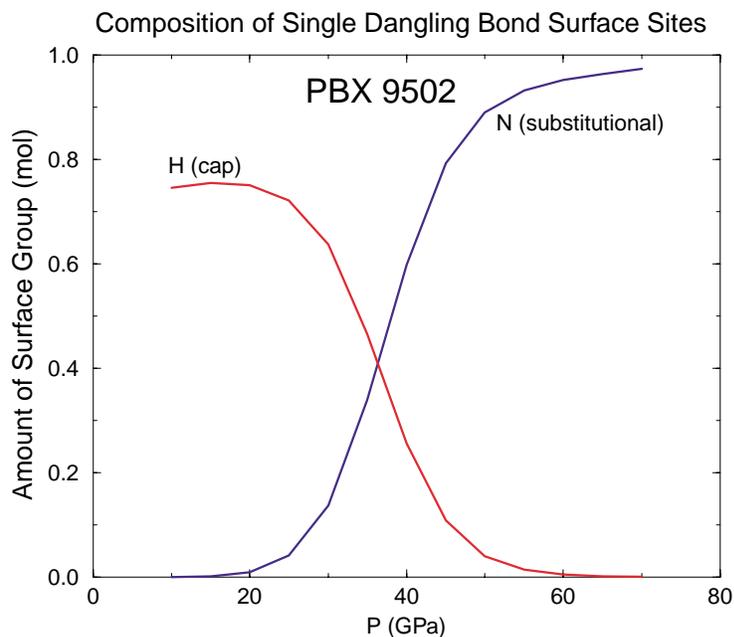
Benchmark simulation methods are used to test the various approximations used to evaluate the fluid mixture EOS. A crucial part of the simulations uses a Monte Carlo method we have developed that directly determines the chemical equilibrium composition of fluid mixtures. Accurate fluid perturbation theories and other approximations are used for spherical potentials, nonspherical potentials, nonideal mixing, and chemical equilibrium composition.

The parameters, such as intermolecular potentials, in this method were least squares fit over a limited set of data and with terms added to limit the variation of the constants where an estimate could be made of the value and uncertainty. The anomalous slope change in the overdriven Hugoniot of PBX 9502 was weighted strongly.

The present theory is in very good agreement with the data and provides a possible mechanism for this anomalous

behavior. At high pressure, the single dangling bond surface C atoms are replaced by a substitutional N atom with no dangling bonds. The PV term gives preference for the small volume occupied by this surface group. At low pressure, the lower energy of a H cap on the dangling bond dominates. The transition in surface chemistry (Figure 2) is spread over 20 GPa in pressure and  $0.5 \text{ g/cm}^3$  in density. The theory reproduces the rapid slope change around 50 GPa. In the transition region, the slope of the isentrope is very nearly constant. That implies the sound speed is also nearly constant over that region.

The chemical equilibrium treatment of surface chemistry on diamond clusters was started based on the premise that there was too large a fraction of atoms on the surface to treat the carbon as a pure bulk material. The calculations demonstrate that there can be regions with a large shift in the chemical composition on the surface. These preliminary results suggest that fitting an EOS theory to detonation velocity data is not as straightforward as it seems. Significant portions of the data could be strongly influenced by transition regions in the chemical composition.



**Figure 2: Composition of single dangling bond surface sites along a high-pressure isentrope.**