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Citation: *J. Chem. Phys.* **136**, 084506 (2012); doi: 10.1063/1.3686750

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Molecular dynamics and kinetic study of carbon coagulation in the release wave of detonation products

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(Received 10 October 2011; accepted 1 February 2012; published online 29 February 2012)

We present a combined molecular dynamics and kinetic study of a carbon cluster aggregation process in thermodynamic conditions relevant for the detonation products of oxygen deficient explosives. Molecular dynamics simulations with the LCBOPII potential under gigapascal pressure and high temperatures indicate that (i) the cluster motion in the detonation gas is compatible with Brownian diffusion and (ii) the coalescence probability is 100% for two clusters entering the interaction cutoff distance. We used these results for a subsequent kinetic study with the Smoluchowski model, with realistic models applied for the physical parameters such as viscosity and cluster size. We found that purely aggregational kinetics yield too fast clustering, with moderate influence of the model parameters. In agreement with previous studies, the introduction of surface reactivity through a simple kinetic model is necessary to approach the clustering time scales suggested by experiments (1000 atoms after 100 ns, 10 000 atoms after 1 μ s). However, these models fail to reach all experimental criteria simultaneously and more complex modelling of the surface process seems desirable to go beyond these current limitations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3686750>]

I. INTRODUCTION

The detonation of CHON explosives with a negative oxygen balance (e.g., RDX or TATB) produces soots which contain a large variety of carbon particles (graphitic ribbons, nanodiamonds, nano-onions, etc.) and modify significantly the way the detonation energy is released. Two phenomena contribute to slow down the energy release: the kinetics of carbon coagulation and the gradual release of heteroatoms enclosed in the core of carbon clusters. Besides, the carbon clusters interact with the gaseous detonation products and modify their chemical and thermodynamic equilibrium properties.¹ Therefore the description of the kinetics of carbon cluster coagulation is crucial to describe the time-dependent properties of the detonation products.

Experimental data on the time evolution and final state of the solid carbon phase along the full detonation/expansion process are scarce in terms of structure, size, and kinetic/thermodynamic history. Besides numerous postmortem analysis of the carbon soots which usually contain up to a few ten mass-percent of nanodiamonds with 5 nm diameter (corresponding to about 10 000 atoms), one can mention a SAXS experiment² on TNT and mixed TNT/RDX which suggests that carbon clusters with diameters larger than 2.8 nm (i.e., about 1000 atoms) may form in the reaction zone ($t \sim 100$ ns), while further aggregation may proceed in the expansion wave for a few microseconds, in agreement with various references.^{3,4}

Several previous studies dealt with the kinetics of carbon cluster coagulation,⁴⁻⁸ based on the Smoluchowski the-

ory developed in 1916 to describe coagulation kinetics in viscous media.^{9,10} In 1987, Shaw and Johnson⁵ mentioned such a study applied to the coalescence of carbon in a detonation wave, using a dilute atomic carbon gas in a constant viscosity medium as a starting point. The output data were used to estimate the energy release during the aggregation process. The thermodynamic properties (pressure, temperature, and density) were set to the Chapman-Jouguet values throughout the calculations, neglecting their time evolution during the full expansion process, reaction zone + release of gaseous products on the order of a few microseconds, having a non-negligible impact on viscosity thus on aggregation kinetics. Besides, more recent studies showed that detonation waves lead to the initiation of carbon cluster formation inside the reaction zone,^{11,12} contrary to the basic assumption of a dilute gas of carbon atoms. In 1994, Mal'kov presented a similar study using empirical values for the mean volume of clusters and viscosity as a function of time, yielding reasonable orders of magnitude for carbon cluster formation.⁶ Finally between 1998 and 2002, Ree, Vieceili, and Glosli^{4,7,8} published several studies on the kinetics of carbon coalescence, using the same approximations as Shaw and Johnson.⁵ Starting with similar initial conditions, they found that pure aggregation kinetics yield mean cluster sizes of 10 000 atoms after 100 ns, when experiment suggests values close to 1000 atoms. Therefore, they improved the Smoluchowski model with a fragmentation term designed to slow down the kinetics, which they interpreted as a process of surface evaporation of atomic or dimer fragments.

These experimental and theoretical observations suggest that the previous Smoluchowski models may be improved in terms of properties of the viscous fluid with respect to real detonation gas expansion: indeed the thermodynamic

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properties of the detonation gas vary substantially during the release process which has some impact on viscosity. Besides, the size of the clusters appears explicitly in the model and should therefore be modeled consistently, and their initial structure is far from mono-atomic for many carbon-rich explosives such as TATB: Zhang *et al.* used molecular dynamics simulations with the ReaxFF potential¹¹ to show that clusters formed right after the shock front can contain as many as 145 atoms, including many H-N-O heteroatoms as impurities. Finally the evaporation mechanism suggested by Glosli, Viecelli, and Ree was not observed in recent molecular dynamics simulations of carbon clusters under detonation conditions,^{13,14} and therefore alternate mechanisms need to be proposed when too fast kinetics is obtained for pure aggregation processes.

In this paper, we present a combined molecular dynamic (MD) and kinetic study of the carbon clustering process under time-dependent thermodynamic conditions relevant for the expansion of the gaseous products of carbon rich explosives. First we use MD simulations in the NVT ensemble in order to assess (i) the Brownian motion behavior of carbon clusters in a high temperature, high pressure viscous media and (ii) the usual approximation that two encountering clusters undergo coalescence with a 100% probability under those conditions. We describe the coalescence mechanism of nano-onion clusters, with particular emphasis on the influence of pressure, temperature, mass, and mass-mismatch effects on final topologies. Then we use the Smoluchowski model to evaluate the kinetics of formation and the impact of the evolution of the thermodynamic properties in the detonation gas expansion. We discuss on the relevance of various surface processes (evaporation, reactivity, etc.) to balance the too fast aggregation kinetics yielded by the original Smoluchowski model.

II. MOLECULAR DYNAMICS SIMULATIONS

A. Simulation details

We used the molecular dynamics code STAMP developed at CEA and the LCBOPII empirical potential for carbon.¹⁵ Previous studies showed that LCBOPII provides good descriptions for a large variety of carbon systems under high temperature and pressure, typically up to 10.000 K and 100 GPa.^{13,14,16,17} All the simulations were run in the NVT ensemble using a Langevin thermostat with a friction parameter of 10^{14} s^{-1} and periodic boundary conditions whenever external pressure was applied. The equations of motion were integrated with a Velocity-Verlet scheme and a time step of 0.5 fs, yielding good conservation of the total energy over long simulation times in the NVE ensemble (several hundreds of picoseconds). All the simulations were stopped when the energy of the system was converged, reaching times of the order of a nanosecond.

We studied the coalescence processes under thermodynamic conditions close to the Chapman-Jouguet (CJ) point of TATB ($P \sim 30 \text{ GPa}$ and $T \sim 3000 \text{ K}$), a high explosive that produces substantial amounts of solid carbon residues. Temperatures up to 6000 K were used to account for local thermodynamic inhomogeneity of the surrounding det-

onation gas,¹⁸ and some simulations were run in vacuum to evidence the pressure effects. Although the structure of nanocarbons has never been observed during the explosive process itself, the postmortem analyses of detonation carbon soot show 3 main types of nanocarbons, nano-onions, nano-diamonds, and nano-graphites, which proportions vary with the explosive and experimental conditions.^{19–22} However, a previous study¹⁴ showed that nano-onions, consisting of concentric piles of nearly spherical fullerenes with increasing diameter, are likely to be the most stable structures for carbon clusters containing up to a few thousand atoms, making them good candidates for a model of detonation soot. Therefore, we designed a set of samples using an initial 1000-atom nano-onion that was progressively peeled off to obtain smaller clusters of 44/127/226/426/634 atoms, respectively. Each cluster was equilibrated at 3000 K, the lowest temperature used in this study, resulting in a decrease of the number of internal layers for clusters of 226 atoms and above. For each cluster pair, three constant temperature simulations were run (3000 K, 4000 K, and 6000 K). The final state of the 3000 K cases was used as the starting point for the 4000 K cases, while the 6000 K cases were run independently starting from liquid cluster pairs obtained by individual equilibrations. Simulations with pairs of clusters of equal and unequal masses were run: in the following parts of this paper they are referred to as “symmetric” and “asymmetric,” respectively.

The initial configuration of each system was set such that the surface-to-surface distance between two carbon clusters was inferior to the LCBOPII long-range cutoff (6.0 Å), while preserving an overall attractive interaction. We found that surface-to-surface distances ranging from 2.5 to 4.0 Å were reasonable, yielding cluster separations short enough to avoid insertion of the LJ fluid, while large enough to avoid the repulsive part of the LCBOPII potential. In order to mimic the high pressures achieved in the detonation products of high explosives, the carbon clusters were immersed in a cubic simulation cell containing a Lennard-Jones (LJ) fluid of argon: the thickness of the rare gas layer around the clusters was at least 1 nm in all directions, resulting in simulation cell sizes ranging from 30 Å to 60 Å. The LJ parameters provided in Table I are the same as those used in previous simulations of the nucleation and growth of carbon clusters under thermodynamic conditions close to the CJ point of nitromethane.¹³ Using a rare-gas pressure bath neglects the influence of the reactivity of the clusters with the hot mixture of detonation gas. Multi-species potentials such as ReaxFF (Ref. 23) have the capability to model this type of reactive medium; however, we preferred to use the LCBOPII potential with a LJ bath because (i)

TABLE I. Interaction parameters Ar-Ar and C-Ar. The Ar-Ar parameters are taken from Ref. 24. We combined these parameters and the C-C parameters used in Ref. 13 to calculate the C-Ar parameters, using usual Lorentz-Berthelot rule.

	ϵ (J)	σ (Å)	Cutoff radius (Å)
Ar-Ar	1.654×10^{-21}	3.405	10.0
C-Ar	1.0×10^{-21}	3.800	10.0

experiments suggest that coagulation occurs mainly beyond the reaction zone of the detonation wave,² (ii) we focus primarily on the carbon/carbon interactions for which LCBOPII is one of the best known potentials in this thermodynamic regime, and (iii) the computational cost of simulating large systems with a fully reactive potential would have been prohibitive. Although the simulations were not run in the NPT ensemble, we checked carefully that the pressure remained reasonably constant in the course of each NVT trajectory.

B. Results

1. Brownian motion assessment

In order to assess the possibility of non-Brownian behavior of the carbon clusters in a high viscosity medium, we ran a first set of simulations imposing various orders of magnitude of collisional velocities to the clusters: we found these initial velocities vanished before the formation of any inter-cluster bond due to the interaction with the surrounding argon bath, implying that the carbon clusters formed in the detonation gas undergo Brownian motion exclusively. This observation is consistent with the use of the Smoluchowski model in the forthcoming kinetic study. Accordingly, no collisional velocity was applied in the subsequent simulations.

2. Pressure effect

A set of symmetric and asymmetric simulations were run at 3000 K both in vacuum and under 30 GPa pressure. Some of the final structures are presented in Fig. 1 and show that

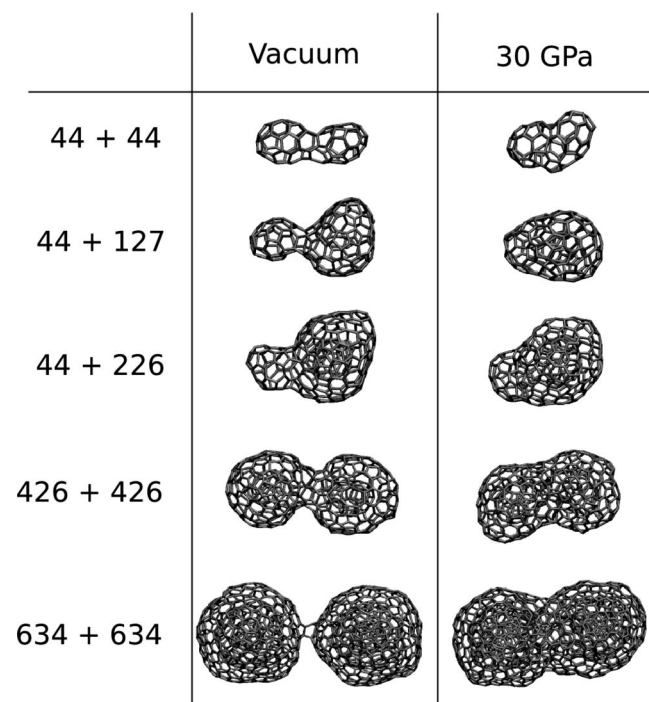


FIG. 1. Final configurations of a selection of coalescence simulations with or without applied pressure (30 GPa). Pressure improves the coalescence substantially, yielding higher merge of the clusters. Simulations in vacuum were not 100% efficient with a certain probability of rebound of the interacting clusters. Simulations under pressure yielded 100% coalescence.

pressure enhances the coalescence yield, with more spherical final structures due to a more efficient merge of the two clusters. We did not obtain sphericity for large clusters on the time scale of the simulations, showing such processes are beyond the capability of conventional molecular dynamics methods. However, all the simulations under pressure yielded coalescence, implying a 100% efficiency: this result is consistent with the Smoluchowski model and rules out the need for an estimate of reaction probabilities with respect to cluster size or mass mismatch. In comparison, we obtained a non-negligible probability of rebound for the simulations in vacuum, using a statistical estimate of the coalescence efficiency averaged over relative cluster orientation. For example the 44 + 44 and 44 + 226 cases in vacuum yielded coalescence probabilities of 41% and 29%, respectively: this decrease is probably related to the lower curvature of the surface of large clusters, resulting in lower surface energy and reactivity.

3. Temperature effect

The full set of symmetric and asymmetric cases were simulated under 30 GPa pressure and temperatures ranging from 3000 K to 6000 K, a range of thermodynamic conditions that is compatible with local fluctuations at the CJ point for carbon-rich explosives such as TATB.

As an example, the coalescence mechanism of the 127 + 127 case is detailed in Fig. 2. At 3000 K, the coalescence process consists in the merge of the equivalent layers of the

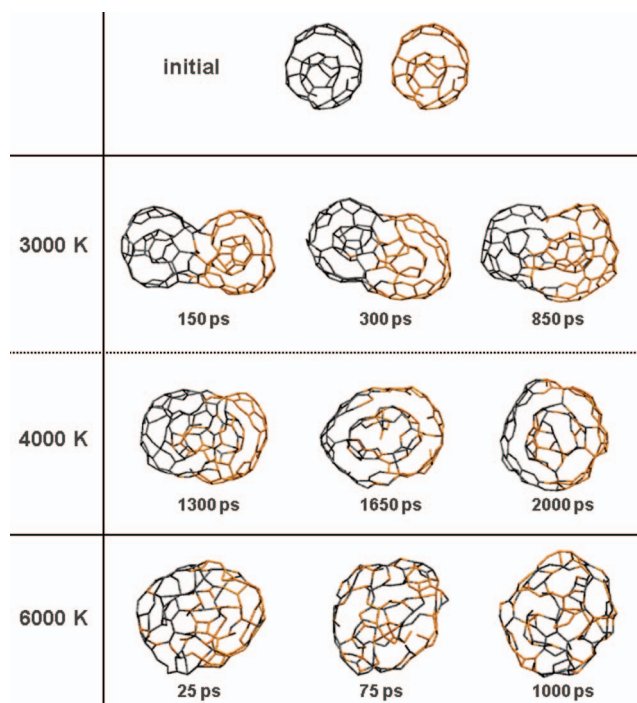


FIG. 2. Slices of 6 Å of the coalescence process of two 226-atom clusters from molecular dynamics simulations under 30 GPa pressure and 3000 K, 4000 K, and 6000 K temperatures. A first simulation was run for 1 ns at 3000 K, starting from nano-onion clusters, then the temperature was increased to 4000 K for another 1 ns. A second simulation was run independently at 6000 K starting from liquid nanocarbons. The color code is a guide to distinguish the carbon atoms from each initial cluster.

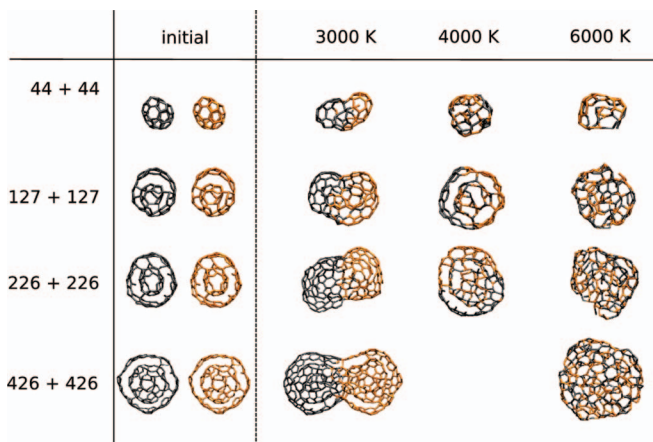


FIG. 3. Initial and final internal structures for the full set of coalescence simulations at 30 GPa and with increasing temperature, for initial clusters of the same size (symmetric case). No simulation was run for the 426 + 426 case at 4000 K.

two clusters, that is first the external layers then the internal ones merge, resulting in a peanut-like structure. Mixing remains incomplete after up to 1 ns of simulation with a clear spatial separation evidenced by the distinct colors used for the initial left and right clusters. The final cluster remains solid, as shown by the absence of sphericity and the preservation of the layered structure throughout the coalescence process. Heating up to 4000 K leads to a spherical cluster consisting in a solid (fullerene-like) external layer and a liquid core (the internal atoms of both initial clusters are mixed, which is characteristic of a diffusive, i.e., liquid-like, behavior). The existence of this “quasi-liquid” cluster was predicted previously¹⁴ and interpreted in terms of location of the structural defects (the highly curved inner layers of the nano-onion clusters), where melting is more likely to nucleate. At 6000 K the coalescence process results in a perfectly spherical liquid cluster within a few ten picoseconds.

All the final structures are presented in Figs. 3 and 4 (symmetric and asymmetric case, respectively). The trends correspond to those observed for the 127 + 127 case excepting for the mono-layer 44 + 44 case which yields a liquid

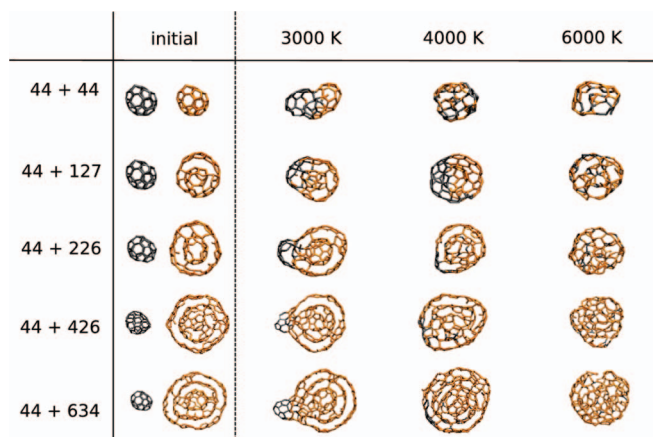


FIG. 4. Same as Fig. 3 for clusters of different sizes (asymmetric case). Smaller system snapshots are magnified for better visualization, which results in unrespected spatial scale.

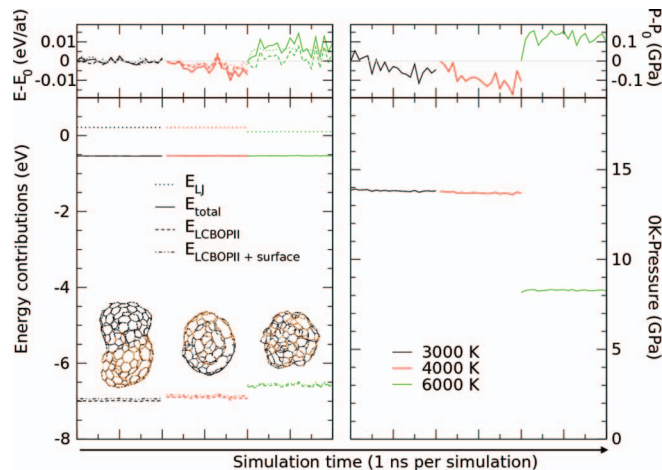


FIG. 5. Energy and pressure of the minimized structures along the 226 + 226 coalescence simulations at 3000 K, 4000 K, and 6000 K (black-red-green curves, respectively). The total (full), LJ (dotted), LCBOPII (dashed), and LCBOPII + surface (dotted-dashed) energy contributions are presented (LCBOPII + surface contains the LCBOPII and interfacial C/Ar LJ energies). Note that the LCBOPII contributions are given “per carbon atom” contrary to the total and LJ energies which are given “per atom”. The lower plots give absolute values, while the upper plots give relative evolutions with respect to the beginning of each simulation. The snapshots represent slices of the final 0 K-structures and show little structural rearrangements occurred along the minimization process.

cluster as soon as 4000 K due to the high surface curvature of the unique shell. For the asymmetric cases with high mass mismatch (Fig. 4) low temperatures lead to merging of the small cluster with the external layer of the large cluster, while at high temperatures diffusion of the small cluster atoms is observed throughout the final cluster.

For the 226 + 226 case, we performed an energy minimization of the full system every 50 ps using a steepest descent algorithm, yielding 20 optimized structures for each temperature.

The time evolution of the 0 K energy and pressure are presented in Fig. 5. They show that (i) at 3000 K and 4000 K the coalescence process results in a decrease of all the components of the potential energy and (ii) increasing the temperature from 3000 K to 4000 K leads to higher energy structures as shown by the increase in total/LCBOPII/LCBOPII + surface energies (although the energy/pressure contributions are not fully converged after 1 ns, we believe our final structures are reasonably close to fully equilibrated ones). This latter result is unexpected and suggests the existence of an energy barrier along the coalescence reaction coordinate, resulting in a temperature-dependent coalescence rate. Therefore, we suggest that fully coalesced spherical clusters cannot be obtained below a threshold temperature, which cannot be evaluated directly from our simulations.

In the mean time, the 0 K pressure tends to decrease (i) in the course of individual simulations (fixed T , except at 6000 K for which the equilibrium is reached very fast, resulting in fluctuations around a constant 8 GPa value) and (ii) with increasing temperature. This can be explained by the decrease in volume of the carbon cluster during coalescence, resulting in the expansion of the argon bath (the total volume is constant). For NPT simulations we would expect a similar effect

with presumably enhanced coalescence due to the extra-work of non-decreasing pressure forces.

We conclude that the driving force for carbon cluster coalescence is the external pressure imposed by the LJ bath, with possibly some additional entropic contribution due to the increase of the LJ volume (although counter-balanced by the assumed entropy decrease associated to cluster coalescence). Note that the pressure jump observed between 4000 K and 6000 K may be mainly attributed to the lower argon density used at 6000 K to obtain a 30 GPa pressure, while minor contributions may come from the decrease in cluster volume due to a higher coalescence rate combined with the solid/liquid transition.

C. Discussion

These results validate the use of the Smoluchowski model for the subsequent kinetic studies of the full-scale clustering process since (i) they illustrate the Brownian behavior of the carbon clusters (viscosity dissipates any initial cluster velocity on very short time scales) and (ii) they show coalescence occurs as soon as the two carbon clusters come within interaction distance, provided sufficient external pressure is applied.

Besides, these simulations give some interesting details on the clustering mechanism and driving forces at play during the detonation of carbon rich explosives, showing that depending on the local thermodynamic properties of the detonation gas, a variety of final structures may be formed, over time scales that are not always compatible with the MD capabilities.

We should stress that during the course of our simulations (up to 1 ns), we did not observe the evaporation of surface atoms or groups of atoms, which confirms some observations made, but not reported, in previous MD simulations of the nucleation/growth of carbon clusters in detonation products conditions.¹³ This comment is important in view to determine the surface processes relevant to extend the Smoluchowski model.

III. KINETIC STUDY

A. The Smoluchowski model

We used the Smoluchowski model^{9,10} in order to simulate the clustering kinetics of carbon clusters in thermodynamic conditions relevant for detonation products. The basic model is based on the following assumptions: (i) the solvent particles are all similar with same spherical size, (ii) the solute particle concentration is uniform throughout the solution, and (iii) the solute particles undergo Brownian motion so long as no other solute particle comes within their sphere of influence. In our case, the carbon clusters and the detonation gas molecules are defined as the solute and solvent particles, respectively. The sphere of influence of a solute particle i is defined as the distance R_i below which this particle coalesces with another solute particle. Then the new “double” particle undergoes Brownian motion at a reduced rate due to its increased size. The model is thus defined by a set of differential

equations giving the production rate dC_k/dt of solute particles of size k

$$\frac{dC_k}{dt} = 4\pi \sum_{\substack{i+j=k \\ j>i}} C_i C_j D_{ij} R_{ij} \left(1 + \frac{R_{ij}}{(\pi D_{ij} t)^{1/2}}\right) - 4\pi(1 + \delta_{j,k}) C_k \sum_{j=1}^{\infty} C_j D_{kj} R_{kj} \left(1 + \frac{R_{kj}}{(\pi D_{kj} t)^{1/2}}\right), \quad (1)$$

with

$$\delta_{j,k} = \begin{cases} 0 & \text{if } j \neq k, \\ 1 & \text{if } j = k, \end{cases}$$

where the Kronecker delta is added to correct for the single occurrence of the kk consumption case when all other kj cases (with $j \neq k$) occur twice in the algorithm (kj and jk). The first sum in Eq. (1) corresponds to the formation of clusters of size k by coalescence of $i + j$ and the second sum corresponds to the consumption of k due to coalescence with clusters j . C_i is the concentration of clusters i , D_{ij} is the relative diffusion constant of i with respect to j , and R_{ij} is the coalescence distance for an ij pair, with $D_{ij} = D_i + D_j$ and $R_{ij} = (R_i + R_j)/2$. The diffusion constant is obtained with the Stokes-Einstein relation

$$D_i = \frac{k_B T}{6\pi R_i \eta}, \quad (2)$$

where η is the viscosity and can be calculated for a dense fluid of hard spheres using the Enskog theory

$$\eta = \eta_0 b_0 \rho \left(\frac{1}{Y} + 0.800 + 0.761 Y \right), \quad (3)$$

with

$$\eta_0 = \frac{5}{16\sqrt{\pi}} \left(\frac{\sqrt{MRT}}{N_a \sigma^2} \right), \quad (4)$$

$$b_0 = \frac{2}{3} \pi \sigma^3, \quad (5)$$

$$Y = \frac{P}{\rho k_B T} - 1, \quad (6)$$

where σ is the diameter of the hard sphere, M the molar mass, R , k_B , and N_a the Rydberg, Boltzmann, and Avogadro constants, respectively, and (ρ, P, T) the thermodynamic properties of the system. Applied to the CJ properties of TATB ($\rho = 2.41 \text{ g/cm}^3$, $x_{\text{H}_2\text{O}} = 0.3959$, $x_{\text{CO}_2} = 0.2027$, $x_{\text{N}_2} = 0.4014$), with the excluded molecular volumes $\sigma_{\text{H}_2\text{O}} = 2.4 \text{ \AA}$, $\sigma_{\text{N}_2} = 2.9 \text{ \AA}$, $\sigma_{\text{CO}_2} = 3.2 \text{ \AA}$, the Enskog theory yields a viscosity value of $2.447 \text{ g m}^{-1} \text{ s}^{-1}$ in qualitative agreement with Shaw⁵ ($\eta = 1 \text{ g m}^{-1} \text{ s}^{-1}$) but smaller by two orders of magnitude than the value proposed by Mal'kov ($\eta = 100 \text{ g m}^{-1} \text{ s}^{-1}$).⁶

In previous studies, the Smoluchowski equation was used in forms that neglect the influence of cluster size on the diffusion/coagulation rate constants,^{4,5} based on the neglect of the first-order correction $R_{ij}/(\pi D_{ij} t)^{1/2}$ in the

original Smoluchowski rate constant $k_{ij}dt = 4\pi C_i C_j D_{ij} R_{ij} (1 + R_{ij}/(\pi D_{ij}t)^{1/2})dt$. However, neglecting this first-order correction may be unsafe since the radii of detonation carbon clusters range from fractions of up to several nanometers, the diffusion constants are of the order of $10^{-10} \text{ m}^2 \text{ s}^{-1}$, and the coalescence times range up to 10^{-6} s , yielding first-order corrections between 0.05 and 10^4 , that is potentially $\gg 1$. Besides a constant viscosity was used for the detonation gas which does not account for the evolution of the thermodynamic properties in the release wave beyond the CJ point (the time scale of the coalescence process is not negligible with respect to the full release to ambient conditions).

Therefore we decided to use a complete formulation of the Smoluchowski equation, including first-order corrections to the diffusion rates and introducing time-dependent thermodynamic properties (ρ , P , T) consistent with a high explosive release wave. The resulting dependence of the diffusion rates on R_i and R_j called for a realistic model for cluster size. We did not include any correction due to clustering efficiency since MD simulations under pressure yielded 100% coalescence.

1. Size model for carbon clusters

The cluster size is defined by the number of atoms composing the cluster, although the Smoluchowski model requires the knowledge of the cluster radius. Previous direct molecular dynamics simulations of the nucleation/growth mechanism of carbon clusters in nitromethane detonation products yielded mono-layer fullerene structures of up to 140 atoms,¹³ although typical cluster sizes involved in the full process range up to a few ten thousands (experiments give indications on the formation times of 1000 and 10 000 atom clusters approximately). Therefore direct simulations do not cover the full range of sizes that are desirable for the full aggregation process and an approximate model is necessary for $N > 140$. For $N < 140$, we used the MD simulations of Ref. 13 to get a reasonable statistical distribution of cluster shapes and we derived the $R = f(N)$ relationship based on an estimated effective radius R_{eff} for each cluster

$$R(N) = R_{vdW} + \frac{1}{n} \sum_{i=1}^n R_{eff}(N),$$

with

$$R_{eff}(N) = \left(\frac{1}{N} \sum_{i=1}^N r_i^2 \right)^{1/2}, \quad (7)$$

with r_i the distance between the atom i and the center of mass of the cluster, N the number of atoms in the cluster, and n the number of clusters of size N . R_{vdW} is defined as the van der Waals exclusion radius of a single carbon atom (set to 1.75 \AA in Ref. 25). Including all the encountered cluster types allowed to account for the existence of non-fullerene shapes such as chains, rings, or flakes. This approach makes the rather harmless assumption that shape and size distributions only weakly depend on the explosive excess in carbon.

For $N > 140$ we used the thermodynamic equilibrium results from Ref. 14 which showed that clusters of up to a few

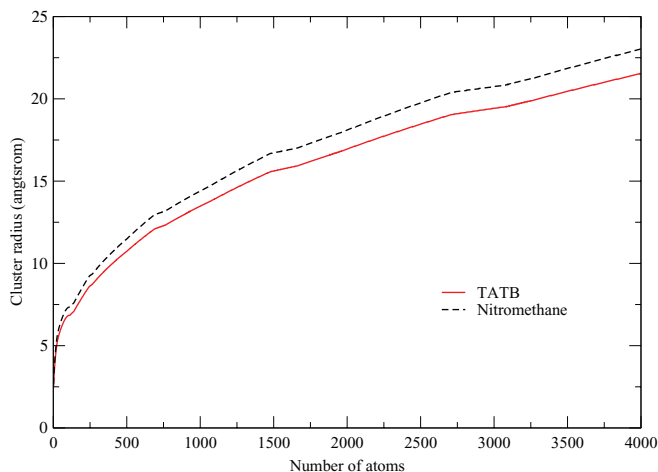


FIG. 6. Average cluster radius as a function of the number of atoms. For $N < 140$, the radius is obtained from a statistical average over structures extracted from previous molecular dynamics simulations.¹³ For $N > 140$, a phenomenological model is used.²⁶ The changes of slope are caused by the discrete increase of the number of nano-onion shells when N reaches critical values. Size models for the detonation products of TATB and nitromethane are plotted.

thousand atoms are more likely to adopt a nano-onion structure. We used a size model designed for these nano-onions based on their russian-doll structure²⁶ yielding a typical layer by layer increase of the cluster radius with increasing N

$$R_0 = R_i + (n_s - 1) \times \Delta r + R_{vdW}, \quad (8)$$

with R_i the radius of the inner shell, n_s the number of shells, Δr the inter-shell distance, and R_{vdW} the previously defined van der Waals radius. Pressure and temperature were included in the model through a thermal expansion and compressibility coefficient.²⁷ The subsequent $R = f(N)$ relationship is plotted in Fig. 6 for nitromethane and TATB, showing larger cluster sizes for nitromethane due to lower pressure and larger temperature at the CJ point.²⁸

2. Time dependence of the thermodynamic properties in the release wave

In order to evaluate the time evolution of the thermodynamic properties in a high explosive release wave, we performed Direct Numerical Simulations of a detonation wave propagating in TATB using the HESIONE hydrocode developed at CEA. We first performed 1D Lagrangian calculations in plane geometry, corresponding to the assumptions of the ZND model for a 1D detonation wave. For the sake of comparison, we have also performed 2D Lagrangian and Eulerian calculations in both plane and axisymmetric geometries, in order to study the influence of dimensions and boundary conditions on the late time dependence of the hydrodynamics. In all calculations, the dimensions of the explosive sample were chosen large enough to ensure the formation of a stationary sustained detonation wave. Moreover, we used a constant mesh size of $5 \mu\text{m}$ ensuring convergence in all our configurations. For all these calculations, we used the classical Empirical Hot Spot (or JTF) reactive burn model^{29,30} coupled with a Cochran-Chan EOS (Ref. 31) for the unreacted

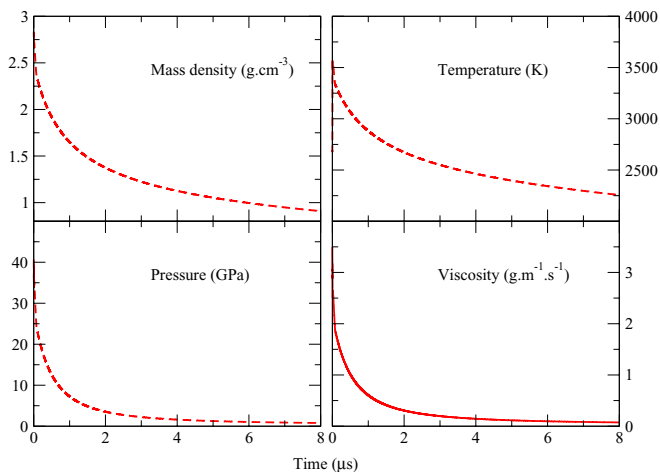
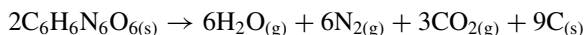


FIG. 7. Time evolution of the density, temperature, pressure, and resulting viscosity of the detonation products of TATB calculated from the hydrodynamic simulation of the propagation of a planar detonation wave. The viscosity is calculated with the Enskog theory (Eqs. (3) and (6)) using the computed thermodynamic properties. $t = 0$ corresponds to the ZND peak.

TATB and a JWL EOS (Ref. 32) for the reaction products. We stored the evolution of density, temperature, and pressure of the detonation products at the rear face of the sample as a function of time, starting from the ZND peak. Using the Enskog theory (Eqs. (3) and (6)) we could then estimate the resulting time dependence of the viscosity of the detonation gas. The only difference between our 1D and 2D calculations lies in the fact that in 2D geometry release waves coming from the different boundaries are going to induce a faster release of the detonation wave compared to 1D, resulting in discrepancies for late times only (typically several microseconds for reasonably large samples). However, the aggregation process is assumed to be completed at these times, therefore these differences can be neglected in the kinetic study. The results for the 1D plane simulations, corresponding to the ideal 1D detonation wave of the ZND theory, are plotted in Fig 7. Besides, we use the time dependent mass density to compute the volume expansion coefficient ($\rho_{(t+\Delta t)}/\rho_{(t)}$) of the system and account for a realistic decrease of the cluster concentrations by $C_i = C_i \times \rho_{(t+\Delta t)}/\rho_{(t)}$.

B. Results

We computed the time evolution of the size distribution of carbon clusters by solving the system of differential equations (1) with a time step of 1 fs, allowing good balance between computational efficiency and numerical stability. The maximal cluster size was set to 20.000 atoms, about twice the size of the nanodiamonds observed in experiments. The initial excess carbon concentration C_0 can be obtained using the dissociation reaction of TATB



which shows that $C_0 = (9/2)C_{TATB}$. At the ZND peak, the density of TATB is 2.835 g/cm^3 corresponding to $C_{TATB} = 0.011 \text{ mol/cm}^3$ (the molar mass of TATB is 258 g/cm^3),

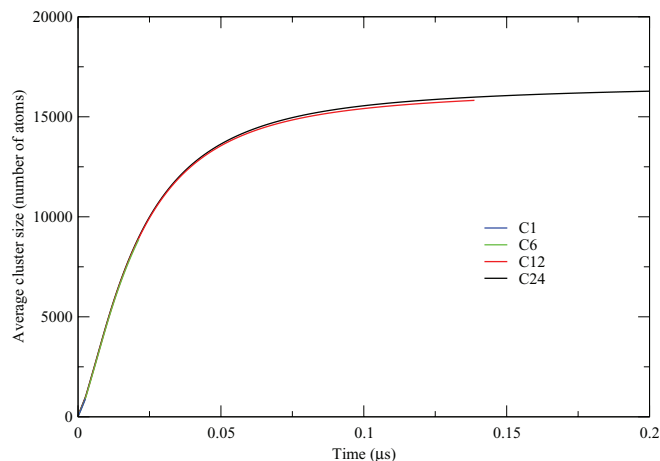


FIG. 8. Time evolution of the average size of carbon clusters depending on the initial size distribution. Initial sizes of 1, 6, 12, and 24 atoms are shown.

and therefore to a total excess carbon concentration $C_0 = 0.0495 \text{ mol/cm}^3$.

1. Influence of the initial distribution

In a first set of simulations we investigated the influence of the initial size distribution of the carbon clusters. In four separate calculations, we successively assigned the excess carbon concentration C_0 to the cluster types C_1 , C_6 , C_{12} , and C_{24} . We preferentially used C_{6*n} species assuming a coalescence process based on the six-membered ring of TATB, as suggested by the dimerization/polymerization processes observed in Ref. 11. The time evolution of the mean size of the carbon clusters plotted in Fig. 8 shows very fast clustering kinetics with 1000 atom average sizes reached over a few nanoseconds, to be compared to the experimental estimate of 100 ns, that is nearly two orders of magnitude faster. Accordingly, 10 000 atom sizes are reached over $\sim 25 \text{ ns}$,³³ against an experimental order of magnitude of 1 μs .

The initial distribution does not seem to influence the kinetics since all the curves are superimposed and barely distinguishable. Two practical consequences of this result are that (i) we can leave the initial distribution issue which is irrelevant here and (ii) all subsequent calculations will be run starting from C_{24} distributions for the sake of computational efficiency.

2. Influence of the parameters

We analyzed the influence of the main parameters and approximations applied to the Smoluchowski equation, namely the cluster size model, the total excess carbon concentration C_0 , the time-dependent thermodynamic properties, and the viscosity model. A new set of simulations were run, each of which had one parameter modified with respect to the reference simulation set: respectively, we increased all cluster radii arbitrarily by 25%, we changed the total carbon density to match that of nitromethane (an explosive less carbon-rich than TATB with $C_0 = 0.0072 \text{ mol cm}^{-3}$), we disconnected the time-dependent thermodynamic properties, and we used the

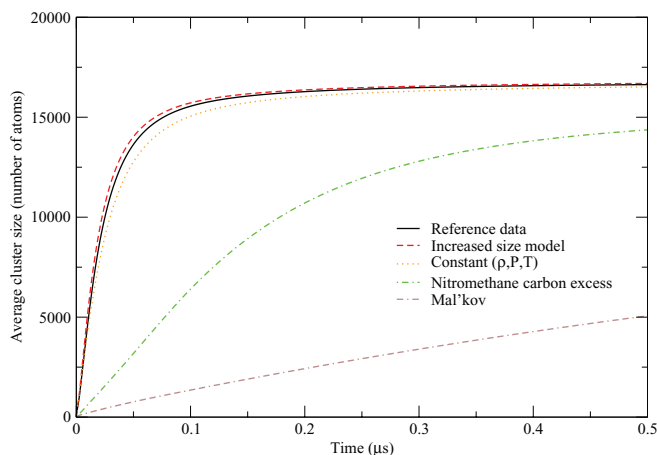


FIG. 9. Influence of the model parameters and approximations on the time dependence of the average cluster size for initial C_{24} cluster distributions. The reference curve of Fig. 8 is in black. Increased cluster size model in red, disconnected hydrodynamic parameters in orange, nitromethane carbon concentration in green, and Mal'kov viscosity in brown.

constant viscosity parameter of Mal'kov.⁶ Accordingly with the previous observation, we used the C_{24} initial distribution to speed up the calculations. The resulting time dependence of the average cluster size is presented in Fig. 9, with comparison to the reference data of Fig. 8.

We found that most modifications yielded negligible differences with the reference data, except for the total excess carbon concentration C_0 and the viscosity model. When using the carbon excess concentration of nitromethane the kinetics is decreased by a factor of five approximately, yielding cluster sizes of about 6.400 atoms after 100 ns (~ 15.000 for TATB), and converging towards 15.000 atoms after half a microsecond, about 15% lower than TATB.

Although these values are still too large with respect to experiment, the initial concentration seems to play an important role on kinetics, yielding clustering rate differences that may be evidenced in future experiments. However, C_0 is an intrinsic property that depends on the stoichiometry of the $C_wH_xO_yN_z$ explosive and on the efficiency of the burning process, which in turn depends on the experimental setup (geometry and dimensions of the explosive, external constraints, etc.). Therefore, it cannot be considered a parameter of the model contrary to the viscosity model which appears to have a strong influence: when applying the constant value proposed by Mal'kov, the clustering kinetics is dramatically reduced and yields a profile consistent with the experimental estimates. However, the viscosity of Mal'kov is 50 times larger than the one obtained through the Enskog theory, which is consistent with the value proposed by Shaw and Johnson.⁵ In the absence of clear justification for this choice of viscosity, we can only assume that it has actually been adjusted to match the experimental data. The absence of influence of parameters such as the cluster size model, or the time-dependence of the thermodynamic properties show that further investigations or improvements in those directions are clearly a dead-end. Although the thermodynamic properties are strongly varying in the release wave of the detonation product, we found that the decrease of the corresponding viscosity is compensated

by the concomitant temperature decrease in the calculation of the diffusion constant D_i (Eq. (2)).

Last, we did not test numerically the assumption that all cluster collisions yield coalescence, implying a reaction probability of one which may be questioned for large clusters whose surface reactivity should be lower due to their high curvature radius. Moreover, we showed that the efficiency of the clustering mechanism is sensitive to external pressure, which decreases along the release process. However, after one microsecond of release, the external pressure computed from hydrodynamic simulations is still superior to 7 GPa (Fig. 7) and MD simulations show that clustering is still 100% efficient for clusters up to more than 400 atoms. Therefore, we assume this approximation is reasonably safe for all cluster sizes along the relevant clustering time scale.

C. Surface reactivity effects

Carbon clusters under high temperatures in a chemically complex environment may be subjected to many surface processes such as atom/cluster evaporation, surface reactivity, and so on. For example, endothermic surface reactions such as $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$ occur spontaneously at high temperatures and may compete with the clustering process to yield an equilibrium cluster size.

Viecelli *et al.*⁴ suggested fragmentation mechanisms could provide such a counter-balancing effect and added an "evaporation" term to the Smoluchowski model. Although we never observed any evaporation in our MD simulations under detonation product conditions, we applied a similar approach in view of surface reactivity. We expect surface reactivity to be a very complex process involving a large number of chemical reactions with variable rate constants. However, a global approach including a limited number of simple contributions may be sufficient to correct the behavior of the clustering kinetics, such as

$$\begin{aligned} \frac{dC_k}{dt} = & 4\pi \sum_{\substack{i+j=k \\ j>i}} C_i C_j D_{ij} R_{ij} \left(1 + \frac{R_{ij}}{(\pi D_{ij} t)^{1/2}} \right) \\ & - 4\pi (1 + \delta_{j,k}) C_k \sum_{j=1}^{\infty} C_j D_{kj} R_{kj} \left(1 + \frac{R_{ij}}{(\pi D_{ij} t)^{1/2}} \right) \\ & + \sum_{1 \leq n < N} \lambda_n (C_{k+n} - C_k) + \lambda_n \delta_{k,n} \sum_{l=n+1}^{\infty} C_l, \end{aligned} \quad (9)$$

where the third and fourth terms include surface reactions involving up to N carbon atoms with λ_n an average rate constant for n -atom processes. For each cluster size we expect the reaction rates to be proportional to the surface area, so the rate constants are defined as $\lambda_n = \lambda_n^0 N_{at}^{2/3} s^{-1}$, where λ_n^0 is a constant and N_{at} is the number of atoms of the clusters.³⁴

We computed the time evolution of the size distribution of carbon clusters by solving the system of differential equations (9). For viscosity we kept the physically based Enskog model, rather than the estimate of Mal'kov, assuming that the discrepancy between our previous calculations and the experimental data is due to the absence of any surface reaction

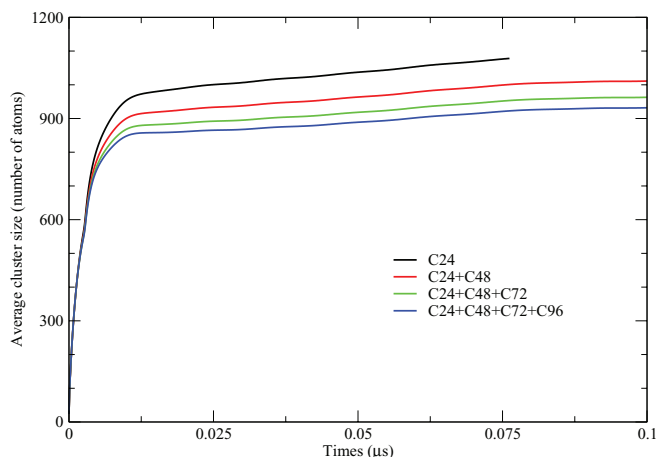


FIG. 10. Dependence of the average cluster size on the model of surface reaction processes. Surface reactions involving 24/48/72/96 atom clusters are considered. The rate constant λ^0 is adjusted to $5 \times 10^6 \text{ s}^{-1}$ to approach the first experimental estimate of 1000 atoms at 100 ns.

process. As for the aggregation process, the basic block for surface reactivity is a 24-atom cluster. We optimized the λ^0 constant to approach the first experimental criteria of 1000 atom clusters after ~ 100 ns, yielding a value of $5 \times 10^6 \text{ s}^{-1}$. Figure 10 summarizes the results obtained for four cases consisting in surface reactions involving 24, $24 \rightarrow 48$, $24 \rightarrow 72$, and $24 \rightarrow 96$ atom clusters. The results show consistent convergence of the average cluster size after 100 ns for all the calculated cases, with a clear but limited decrease of clustering kinetics when surface reactivity involves particles of increasing size. However, with this optimized value of λ^0 , the time required to reach 10 000 atom sizes tends to infinity suggesting the second experimental estimate (10 000 atoms after 1 μs) cannot be met simultaneously. The subsequent yield of the surface reactions was estimated to a few tens of atoms per nanosecond, a time scale compatible with our MD simulations: the absence of surface evaporation in these simulations suggests that surface reactivity with the external detonation gas is a more appropriate counter-balancing process.

We conclude that a simple surface reaction model slows down substantially the clustering kinetics yielded by the purely aggregational Smoluchowski model, although we were unsuccessful with its adjustment to all the available experimental estimates, i.e., 1000 atoms at 100 ns and 10 000 at 1 μs . This empirical fit is not satisfactory; however, the extensive treatment of the surface reactions involved, and the estimate of the corresponding rate constants, is clearly a very difficult task.

IV. CONCLUSION

In this study, we performed a combined molecular dynamics and kinetic study of the carbon clustering process in thermodynamic conditions relevant for the detonation products of carbon-rich explosives.

The molecular dynamics simulations confirm that under gigapascal pressure the clusters undergo Brownian motion and that cluster-cluster encounters yield 100% coalescence probabilities, which partially validates the use of a Smolu-

chowski model for the subsequent kinetic studies. Besides, we found that the coalescence process under high temperature and pressure is spontaneous and temperature-dependent, yielding clusters that can be (i) solid at 3000 K, adopting peanut-like structure, (ii) “quasi-liquid” and spherical at 4000 K (consisting of a liquid core surrounded by a solid surface), or (iii) liquid and spherical at 6000 K.

The subsequent kinetic study was based on an improved Smoluchowski model with realistic physical properties specific of the detonation gas conditions. We found purely aggregational Smoluchowski models yield too fast kinetics, with 10 000 atom clusters formed within 10 ns when the experimental estimates point towards an order of magnitude of a microsecond. Including adjustable surface reactivity allows to slow down the kinetics so that one experimental criterion can be met at a time (1000 atoms in 0.1 μs or 10 000 atoms in 1 μs), but not both. Apart from the surface reactivity for which we expect the modeling to be a tedious task, further improvements to the kinetic model may come from a more accurate description of the nature of the reactive systems and physical and chemical processes at play, such as including the influence of the non-negligible fraction of heteroatoms in the coalescing clusters, or using a two-step kinetics to model more accurately the first part of the reactive process, when the detonation mixture is essentially composed of small fractions of gaseous molecules embedded in a polymeric CHNO matrix (therefore very far from the Smoluchowski approximations). We expect the latter modification will strongly decrease the initial rates of formation of clusters, thus hopefully allowing for a better match with the 1000 atom/0.1 μs criterion.

ACKNOWLEDGMENTS

Nicolas Pineau wishes to thank Laurent Soulard and Emeric Bourasseau for fruitful discussions.

- ¹E. Bourasseau, V. Dubois, N. Desbiens, and J.-B. Maillet, *J. Chem. Phys.* **127**, 084513 (2007).
- ²K. A. Ten, V. M. Aulchenko, L. A. Lukjanchikov, E. R. Prueel, L. I. Shekhtman, B. P. Tolochko, I. L. Zhogin, and V. V. Zhulanov, *Nucl. Instrum. Methods A* **603**, 102 (2009).
- ³S. A. Sheffield, D. D. Bloomquist, and C. M. Tarver, *J. Chem. Phys.* **80**, 3831 (1984).
- ⁴J. A. Viecelli and J. N. Glosli, *J. Chem. Phys.* **117**, 11352 (2002).
- ⁵M. S. Shaw and J. D. Johnson, *J. Appl. Phys.* **62**, 2080 (1987).
- ⁶I. Y. Mal'kov, *Combust., Explos. Shock Waves* **30**, 720 (1994).
- ⁷F. H. Ree, J. A. Viecelli, and J. N. Glosli, *J. Comput.-Aided Mater. Des.* **5**, 265 (1998).
- ⁸J. A. Viecelli and F. H. Ree, *J. Appl. Phys.* **86**, 237 (1999).
- ⁹M. V. Smoluchowski, *Phys. Z.* **17**, 585 (1916).
- ¹⁰S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).
- ¹¹L. Zhang, S. V. Zybin, A. C. T. van Duin, S. Dasgupta, and W. A. Goddard III, *J. Phys. Chem. A* **113**, 10619 (2009).
- ¹²M. R. Manaa, E. J. Reed, L. E. Fried, and N. Goldman, *J. Am. Chem. Soc.* **131**, 5483 (2009).
- ¹³N. Pineau, L. Soulard, J. Los, and A. Fasolino, *J. Chem. Phys.* **129**, 024708 (2008).
- ¹⁴G. Chevrot, E. Bourasseau, J.-B. Maillet, and N. Pineau, *Carbon* **47**, 3392 (2009).
- ¹⁵J. H. Los, L. M. Ghiringhelli, E. J. Meijer, and A. Fasolino, *Phys. Rev. B* **72**, 214102 (2005).
- ¹⁶L. M. Ghiringhelli, J. H. Los, A. Fasolino, and E. J. Meijer, *Phys. Rev. B* **72**, 214103 (2005).

- ¹⁷J. H. Los, N. Pineau, G. Chevrot, G. Vignoles, and J. M. Leyssale, *Phys. Rev. B* **80**, 155420 (2009).
- ¹⁸A. L. Kupershtokh, A. P. Ershov, and D. A. Medvedev, *Combust. Explos. Shock Waves* **34**, 460 (1998).
- ¹⁹P. Chen, *Carbon* **41**, 2093 (2003).
- ²⁰V. V. Danilenko, *Combust. Explos. Shock Waves* **41**, 460 (2005).
- ²¹D. Pantea, S. Brochu, S. Thiboutot, G. Ampleman, and G. Schloz, *Chemosphere* **65**, 821 (2006).
- ²²C. C. Yang and S. Li, *J. Phys. Chem. C* **112**, 1423 (2008).
- ²³A. C. T. van Duin, S. Dasgupta, F. Lorient, and W. A. Goddard, *J. Phys. Chem. A* **105**, 9396 (2001).
- ²⁴A. G. Shashkov, A. F. Zolotukhina, T. N. Abramenko, B. P. Mathur, and S. C. Saxena, *J. Phys. B* **12**, 3619 (1979).
- ²⁵R. S. Rowland and R. Taylor, *J. Phys. Chem.* **100**, 7384 (1996).
- ²⁶J.-B. Maillet, private communication (2010).
- ²⁷Based on our MD simulations of nano-onion aggregates,¹⁴ we observed that the cluster volume increases linearly with temperature. We were then able to determine a thermal expansion coefficient ($\alpha_V = 1.58 \times 10^{-4} \text{ \AA}^3/\text{at/K}$) yielding the cluster volume as a function of T and N : $V = V_0 + \alpha_V \times N \times T$ with N the number of atoms and T the temperature. V_0 , the volume at 0 K, depends on the potential pressure P_{0K} and its value can be obtained by solving numerically the pressure relationship derived from the universal binding energy³⁵:
- $$P_{0K} = \exp\left(-\alpha\left(\left(\frac{V_0}{V_{00}}\right)^{1/3} - 1\right)\right) \times \frac{\alpha^2 V_0^{-2/3}}{3V_{00}^{-1/3}} E_0 \left(\left(\frac{V_0}{V_{00}}\right)^{1/3} - 1\right)$$
- where V_{00} the zero-pressure volume, E_0 the potential energy and α are derived from the MD simulations.
- ²⁸Estimated by thermochemical calculations around 12 GPa vs. 25 GPa, and 3500 K vs. 2700 K for nitromethane and TATB, respectively.
- ²⁹J. N. Johnson, P. K. Tang, and C. A. Forest, *J. Appl. Phys.* **57**, 4323 (1985).
- ³⁰P. K. Tang, J. N. Johnson, and C. A. Forest, in *Proceedings of the 8th International Detonation Symposium, Albuquerque, NM, July 1985* (Office of Naval Research, Arlington, VA, 1985), pp. 52–61.
- ³¹S. G. Cochran and J. Chan, Lawrence Livermore Laboratory Report UCID-18024, 1979.
- ³²J. W. Kury, H. C. Hornig, E. L. Lee, J. L. McDonnel, D. L. Ornellas, M. Finger, F. M. Strange, and M. L. Wilkins, in *Proceedings of the 4th International Detonation Symposium, Silver Spring, MD, October 1965* (Office of Naval Research, Arlington, VA, 1965), pp. 3–13.
- ³³These 25 ns may be over-estimated due to the maximal cluster size used in the calculation which was set to 20 000, thus limiting the “reactivity” of the larger clusters. However, this does not impact on the conclusion that pure Smoluchowski kinetics are too fast with respect to experimental estimates since increasing the maximal cluster size can only yield even faster kinetics.
- ³⁴For the sake of simplicity we assumed all clusters are perfectly spherical and did not account for the temperature-dependent topologies observed in the MD simulations. More realistic accounting of the cluster topologies would only be useful if combined with a surface reactivity model based on accurate estimates of the rate constants.
- ³⁵A. Banerjea and J. R. Smith, *Phys. Rev. B* **37**, 6632 (1988).