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A SLOW REACTION RATE IN DETONATIONS DUE TO CARBON CLUSTERING*

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Theoretical calculations have been made to estimate the rate of heat release due to the carbon clustering process in detonations where elemental carbon is a reaction product. The process is assumed to be diffusion limited. Diffusion constants are determined using modified Enskog theory and the Stokes-Einstein relation. The carbon cluster energy is treated by a surface correction to the bulk. The amount of energy yet to be released has an asymptotic time dependence of $t^{-1/3}$. For some explosives, this leads to time dependent detonations where the effective CJ pressure is 10–20% above CJ for run distances of the order of centimeters.

1. INTRODUCTION

Solid carbon in detonation products is usually modeled with bulk phases such as diamond, graphite, or amorphous carbon. But, for clusters smaller than roughly $10^8$ atoms, the bulk properties of carbon are significantly perturbed by the surface. In contrast to other products in a typical CHNO explosive, the formation of large clusters of C requires the gathering together of C's from a rather large volume. So, even though the carbon clustering process is very exothermic, the clusters have to diffuse to each other in order to react. It is primarily the time scale for energy release due to diffusion that we are studying here.

We picture the clustering process as carbon clusters executing Brownian motion in a hot, dense background fluid and building up through random collisions. We assume that the particles always stick if they touch. The background fluid keeps the clusters at equilibrium with respect to temperature, carrying off heat when clusters merge and causing the resulting new clusters to anneal.

2. KINETICS OF CLUSTERING

The clustering of particles undergoing Brownian motion is a straightforward diffusion problem that was first studied by Smoluchowski[1] and reviewed in English by Chandrasekhar[2].

For clusters of $i$ carbon atoms with concentrations $\nu_i$ where $i$ is the number of carbon atoms in a cluster, the rate of change of concentration is

$$\frac{d\nu_i}{dt} = 4\pi DR \left( \sum_{j=1}^{\infty} K_{ij} \nu_i \nu_j - 2 \nu_i \sum_{j=1}^{\infty} \nu_j K_{ij} \right).$$

The diffusion coefficient for a cluster of $i$ particles is $D_i$. $D_{ij} = D_i + D_j$, $D = D_i$, $R_i$ is the effective radius of a cluster of $i$ particles, $R = R_i$, $R_j = \frac{1}{3}(R_i + R_j)$, and $K_{ij} = \frac{1}{3}D_i R_i/D_R$. The first summation in the equation is the coalescence of a cluster of $i$ particles and a cluster of $j$ particles. The second summation is due to a cluster of $k$ particles combining with any other cluster. For $R_i \approx R_j$, we have $K_{ij} \approx 1$. The special case $K_{ij} = 1$ for all $i, j$ leads to an analytic solution.

Let $n_i = \nu_i/\nu_0$ and $x = 4\pi D_R t/\nu_0$ with $\nu_0 = \sum_{i=1}^{\infty} \nu_i$ at $t = 0$. For the initial condition $n_1 = 1$ and $n_i = 0$ for $i > 1$, the system of equations (1) has the solution

$$n_i = (1 + x)^{-2} \left( \frac{x}{1 + x} \right)^{k-1}.$$

3. DIFFUSION OF CLUSTERS

We determine $D$, by combining two simple, but qualitatively accurate, methods.

First, we use the Enskog theory which can be found in McQuarrie. The final result for the viscosity $\eta$ is given by

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\[ \eta/\hbar\rho g^0 = Y^{-1} + 0.8 + 0.761 Y = f(Y), \] (3)

where \( \rho \) is the number density, \( Y = \hbar\rho g(\sigma) = (\rho/\rho_kT)^{-1} \), \( \sigma \) is the hard sphere diameter, \( \hbar = 2\pi\sigma^3/3 \), and

\[ \eta^2 = \left( \frac{2\pi\sigma^2}{15} \right) \sqrt{\rho_kT}. \]

The modified Enskog theory is an ad hoc generalization to soft potentials. A real fluid is approximated by a hard sphere fluid for which the pressure is replaced by the "thermal pressure," \( T(\rho p/dT)_\nu \).

Second, we determine \( D_\nu \) using the Stokes-Einstein relation, \( D_\nu = kT/6\pi\eta R_\nu \). A convenient reference is Landau and Lifshitz.

The combined result is

\[ D_\nu = 0.8(kT/\pi m)^{1/3}/(\pi f(Y)\rho_0 R_\nu). \] (4)

4. ENERGY OF CLUSTERS

At the surface of a cluster, not all bonds can be satisfied with the bulk structure because some atoms are missing. As an upper limit one could add the bond strengths of the missing bonds to get the energy difference between the cluster and the bulk, \( \Delta E_n \). The actual cluster will relax the surface atom positions in order to satisfy the bonds at the expense of strain. Alternatively, the dangling bonds might be capped off with CN (cyanide) or H.

For a nearly spherical cluster with non-surface atoms in a bulk-like environment, \( \Delta E_n/n \) is proportional to \( n^{-1/3} \) to leading order. In Fig. 1, we show the available data and calculations of \( \Delta E_n/n \) versus \( n \) on a log-log scale. The line is

\[ \Delta E_n/n = 80n^{-1/3} \text{ kcal/mol (of carbon atoms)} . \] (5)

Except for the special case of \( C_{60} \), the coefficient of 80 kcal/mole appears to give a good lower bound consistent with the available information.

5. RESULTS

We now combine the previous sections to obtain energy release as a function of time. First, we will look at the results as a function of the scaled time variable \( \tau = tD_\nu R/\rho_0 \). Then we will discuss the actual time scale for reasonable choices of the constants involved.

\[ \Delta E_n/n = 80(1 + z)^{-3} \sum_{k=1}^{\infty} \left( \frac{x}{1 + z} \right)^{k-1} k^{1/3} . \] (6)

An accurate evaluation is easily performed on the computer.

On the other hand, the summation can be approximated by an integral for \( z \gg 1 \), where the resulting large \( z \) dependence is

\[ \Delta E/N = 80\tau \left( \frac{5}{3} \right) z^{-1/3} . \] (7)

An ad hoc shift of the origin to agree with the true \( z = 0 \) energy yields

\[ \Delta E/N = 80\tau \left( \frac{5}{3} \right) \left[ x + \frac{5}{3} \right]^{-1/3} . \] (8)

In Fig. 2, we compare the exact solution, Eq. (6), with the approximate expressions, Eqs. (7) and (8). For all \( z \), both Eqs. (7) and Eq. (8) agree very well with Eq. (6). For all \( z \), Eq. (8) is very close to Eq. (6) and is much more convenient to use. Note that the asymptotic time dependence of \( \tau^{-1/3} \) is very slow indeed. For
any given time it takes 8 times as long to release the
next 50% of the carbon energy.

\[ \frac{\Delta E}{N} \text{ (kcal/mol)} \]

\[ \begin{array}{c|c}
X \text{ (Scaled Time)} & \frac{\Delta E}{N} \\
\hline
10^{-2} & 10^0 \\
10^1 & 10^2 \\
10^3 & 10^4 \\
\end{array} \]

**FIGURE 2**
\( \frac{\Delta E}{N} \) versus scaled time, \( x \), for the constant kernel
case. Eq. (6) -- Eq. (7) -- -- Eq. (8).

For the general \( K_{ij} \), we then solved Eq. (1)
numerically by considering only clusters less than a few
thousand atoms. The numerical results for \( \Delta E/N \) are
nearly identical to the \( K_{ij} \) analytic results. More
details of this result and of possible bottleneck effects
may be found in a separate paper.

Now we estimate the value of \( \eta \) for typical
detonation conditions. The principal detonation products
for a typical CHNO explosive are \( H_2O, CO_2, N_2, \) and
solid carbon. In the fluid regime, the effective hard
sphere diameter for a given species is about the radius
at which the potential is equal to \( kT \).

From our previous studies of the EOS of dense
molecular fluids, \( \eta \) s are about 3Å. The value for \( \eta \)
will be taken from the EOS itself through the modified
Enskog prescription, \( \sqrt{\frac{\eta T}{N+1}} = \frac{T}{\langle dp/dT \rangle} \), to give a
value of 4 or higher. Now for an average molecular
weight of about 30 and a typical CJ density of
about 2.4 \( g/cm^3 \), we use Eqs. (3) and (4) to obtain
\( \eta = 0.010 \) \( g/cm^3 \) and \( kT/\eta \approx 2.2 \times 10^{-11} cm^2/s = DR \).

The initial carbon concentration \( f_0 \) is estimated
assuming only \( H_2O, CO_2, N_2, \) and \( C \) are present. Let
\( \Delta H_s \) denote the heat of explosion in kcal/mol of the
explosive, \( M_w \) the molecular weight, \( N_C \) the
number of free carbon atoms in the products per explosive
molecule, and \( \rho_{CJ} \) the CJ density. Then we have
\( f_0 = N_C CO_2 / N_A / M_w \), where \( N_A \) is Avogadro’s number.

Writing \( z = x/t_o \), we have \( t_o = (4\pi DR f_0)^{-1} \). The
fraction of energy remaining to be released due to car-
bon clustering at time \( t \), \( F(t) \), is approximately
\( F(t) = (\Delta E/N)/(\Delta H_s/N_A) = 80 N_{CJ} \left( \frac{z}{t_o} \right)^{-1/2} / \Delta H_s \),
which is proportional to \( N_{CJ}^{3/4} \) if other values are constant.

At \( t = 10^{-7} s \), \( F(t) \) is about 1% for HMX and 3% for
TNT, using conservative values. If instead we take
average values and assume there is some bottleneck
effect, then the energy available for slow release is
more like 2-4% for HMX and 5-10% for TNT. This
energy seems small until we take into account the hy-
drodynamic effects of a slow energy release process
interacting with a fast reaction zone.

Bdzil\(^{6}\) has demonstrated that a slow release of en-
ergy of \( O(\rho^3) \) produces changes in the shock state \( O(t) \)
for times long compared to the slow reaction. This effect
comes primarily from the fact that the Rayleigh
line is tangent to the fully reacted Hugoniot at the
CJ point. (Refer to Fig. 3 for an illustrative exam-
ple using a polytropic gas with \( \gamma = 3.5, p_0 = 0.6a, \rho_0 = 0.04, \)
and \( z = 0.2 \).) The intersection of the partially reacted
Hugoniot with the Rayleigh line is shifted by \( O(t) \).
When the fast, reaction zone is relatively small, the
intersection, denoted \( A \), looks like the von Neumann
spike in the usual ZND theory. For times comparable
to the slow reaction zone and longer, the detonation
runs at the CJ velocity for the fully reacted Hugoniot
rather than for the partially reacted Hugoniot. Until
times much larger than the slow reaction zone, the
states from \( A \) to \( CJ \) along the Rayleigh line appear
to be part of the Taylor wave instead of a separate
negligible reaction zone. So, we are looking at poten-
tial changes in the shock state of 10-20% for time
scales of microseconds and distance scales of centime-
ters. Tung\(^{6}\) has made hydrodynamic calculations that
demonstrate this type of effect for a two rate model of
TA1B.
6. CONCLUSION

We have demonstrated that diffusion limited carbon clustering is inherently a slow reaction mechanism in the detonation regime. The amount of energy released after the fast reactions are complete is sufficient to perturb the flow significantly when coupled with the hydrodynamics.

REFERENCES


