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Detonation of Meta-stable Clusters

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ABSTRACT

We consider the energy accumulation in meta-stable clusters. This energy can be much larger than the typical chemical bond energy (~1 ev/atom). For example, polymeric nitrogen can accumulate 4 ev/atom in the N_8 (fcc) structure, while helium can accumulate 9 ev/atom in the excited triplet state He_2^*. They release their energy by cluster fission: $N_8 \rightarrow 4N_2$ and $He_2^* \rightarrow 2He$. We study the locus of states in thermodynamic state space for the detonation of such meta-stable clusters. In particular, the equilibrium isentrope, starting at the *Chapman-Jouguet* state, and expanding down to 1 atmosphere was calculated with the Cheetah code. Large detonation pressures (3 & 16 Mbar), temperatures (12 & 34 kilo-K) and velocities (20 & 43 km/s) are a consequence of the large heats of detonation (6.6 & 50 kilo-cal/g) for nitrogen and helium clusters respectively. If such meta-stable clusters could be synthesized, they offer the potential for large increases in the energy density of materials.

INTRODUCTION

Small meta-stable clusters and molecules are able to accumulate energy that is orders of magnitude larger than the usual exothermic chemical reactions. Energy accumulated in the meta-stable state is released upon transition to the stable equilibrium state with lower energy. Depending on the type of chemical elements of the clusters, the system may transfer into a new stable configuration by either fusion of the clusters into a bulk sample (Type-I clusters), or fission of the large ensemble into small molecules or atoms (Type-II clusters)—analogous to energy release in nuclear matter.

Carbon Clusters

Carbon is a typical representative of the chemical elements that form Type-I clusters. The energy accumulated in carbon clusters increases as the number of atoms in the cluster decreases.

The smallest meta-stable carbon cluster found experimentally is the cage C_{20} discovered by Prinbach [1]. Elesin and co-workers [2,3] have predicted the existence of meta-stable eight-atom carbon cluster C_8: Prismane. They have shown that isolated prismanes accumulate energy of $E_{acc} = 2.3$ ev/atom [2,3]. The lifetime of prismane is macroscopically long at room temperature. Prismanes can form quasi-one-dimensional meta-stable ensembles (see Fig. 1).
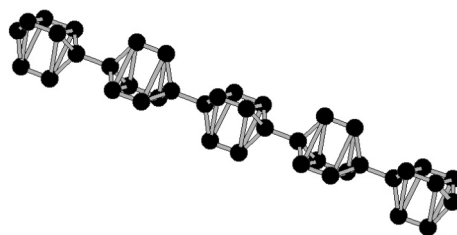

Figure 1. Quasi-one-dimensional ensemble of C_8 Prismane [2,3].

Prismane ensembles accumlate energy of $E_{acc} = 2.1$ ev/atom [3, 4]. However, the energy released upon fusion of prismanes does not exceed 20% of the accumulated energy $E_{rel} = 0.5$ ev/atom [5]. This is due to the transformation of the ensemble into other meta-stable long-lived configurations. This is a common feature of all Type-I clusters.

Nitrogen Clusters

Nitrogen is the typical representative of chemical elements that form Type-II clusters. The most stable form of nitrogen is diatomic molecule N_2. Theoretical calculations by Chen [7, 8] have shown that nitrogen clusters N_4, N_8, N_{20}, etc. are meta-stable and accumulate energy up to $E_{acc} \approx 3$ ev/atom. This energy is released by fission of clusters into isolated N_2 molecules. Isolated nitrogen clusters have not been synthesized yet.

Elesin and co-workers have shown that N_8 boats form meta-stable ensembles while N_8 cubanes do not [6,9]. They have shown that N_8 boat ensembles (Fig. 2) accumulate the energy of $E_{rel} = 2$ ev/atom [6,9]. Their lifetime is macroscopically long at room temperature. The entire

accumulated energy is released upon fission of the boat ensemble into isolated N_2 molecules [6,

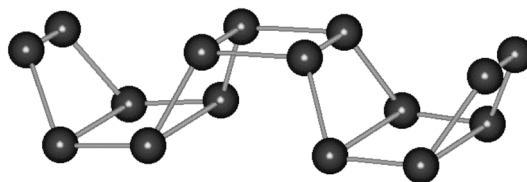9]. This is a common feature of all Type-II clusters.

Figure 2. Meta-stable N_8 boat structure [6,9].

Helium Clusters

Helium atoms in the ground singlet state with spin $S = 0$ are chemically inactive and do

not form even diatomic molecules. The helium atom He^* in the excited triplet state with spin

$S = 1$ is known to be meta-stable with a long lifetime: $\tau \approx 8,000$ seconds [10]. Recently it has

been conclusively demonstrated experimentally by McKinsey et al. [11] that two helium atoms

can form an excited meta-stable molecule: He_2^* with at total spin $S = 1$. Measured lifetime of

He_2^* is $\tau \approx 18$ seconds—in agreement with theoretical predictions ($\tau = 10$ seconds). As shown

both theoretically and experimentally, the energy accumulated in the He_2^* molecule is $E_{acc} = 10$

ev/atom, and is released by electron spin flip. Two meta-stable helium quasi-molecules can form

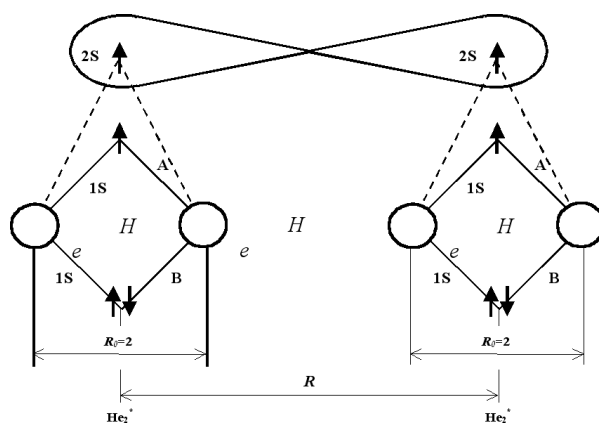the meta-stable cluster He_4^* (Fig. 3) with a total spin of $S = 2$ [6, 12].

Figure 3. Meta-stable He_4^* cluster [6,12].

The energy accumulated in He_4^* cluster is $E_{acc} = 9$ ev/atom. This energy is released upon spin-flip of one of the electrons occupying the excited energy level.

Meta-stable structures of He_n^* clusters based on molecules (quasi-atoms) He_2^* with the number of atoms up to $n=12$ have been found [6, 10]. The energy accumulated in meta-stable clusters of He_n^*, based on molecules (quasi-atoms) He_2^*, is $E_{acc} \approx 9$ ev/atom for $6 \le n \le 12$. It has been shown that such He_n^* clusters are ordered ferro-magnetically, with the total spin of the cluster $S = n/2$. Also, meta-stable structures of fully-spin polarized He_n^{**} clusters have been found [6,10], based on excited triplet atoms of He_1^* with the number of atoms up to $n=3$. The energy accumulated in meta-stable clusters He_n^{**} based on excited triplet atoms He_1^* is calculated to be $E_{acc} \approx 19$ ev/atom for $2 \le n \le 4$. It has been shown that He_n^{**} based on exited triplet atoms He_1^* are ordered ferro-magnetically, the total spin of the cluster being equal to $S = n$. Results of these studies are summarized in Table 1.

Table 1. Energy content of meta-stable systems [6, 10]

Meta-stable Systems	E_{stored} (ev/atom)	$E_{released}$ (%)
Carbon Clusters		—fusion—
C_{20} Cage	**1†**	
C_8 Prismane	2.1	<20%
Nitrogen Clusters		—fission—
N_4 Tetrahedron	1.5—3	
N_8 Cubanes	2—3.5	
N_8 Boats	1.5—2.5	100%
N_8 Boats + H bridges	1.5	100%
N_8 Cubane + C bridges	2—2.5	
N_{20} Cages + C bridges	2—2.5	
Helium Clusters		—fission—
$He_2^* — He_2^*$	**9†**	
He_n^* $(n = 2$-$12)$	9	
He_n^{**} $(n = 2$-$4)$	19	

† confirmed experimentally

THERMODYNAMICS

In this section we explore the thermodynamic properties of the detonation products gases resulting from the explosion of Type-II meta-stable clusters. In particular, we consider the detonation of N_8 clusters and He_2^* clusters.

N_8 Detonation

The internal energy (u)—temperature (T) diagram for the detonation of N_8 clusters is depicted in Fig. 4. It shows the locus of equilibrium states of the detonation products gases, starting at the *Chapman-Jouguet* (*CJ*) point, expanding along the *CJ* isentrope: $S_{CJ} = 1.649$ cal/g, and terminating at room temperature, as calculated by the Cheetah code [13]. Point R denotes the initial state of the *Reactants* (N_8 clusters); the value $u_R = 6,652$ cal/g is based on *ab initio* local-energy-density-functional calculations for the *fcc*-form of polymeric nitrogen, as predicted by Mailhoit et al [14] and synthesized by Eremets et al [15] in a heated diamond anvil. The heat of detonation is $\Delta H_d \equiv u_R(291K) - u_P(291K) = 6,672$ cal/g. A Constant Volume Explosion (CVE) from point R to point P results in a temperature of $T_{CVE} = 6,400$ K.
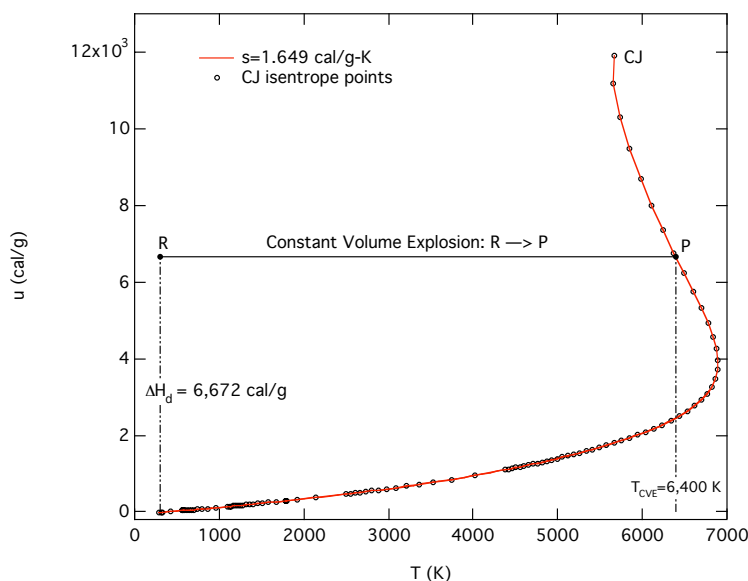

Figure 4. Le Chatelier diagram for the detonation of N_8 (*fcc*) meta-stable clusters.

At temperatures below 6,000 K, the composition of the detonation products consists of diatomic nitrogen (concentration of 35.7 mol/kg). As the energy increases, nitrogen starts to dissociate: at u= 4,000 cal/g the equilibrium composition is 4.87 mol/kg of N and 33.3 mol/kg of N_2. At the *CJ* point, the composition is 66.3 mol/kg of N and 2.6 mol/g of N_2, in other words, the gas is almost fully dissociated. Thus, it is the *change in composition* that causes the non-monotonic behavior of the equilibrium *u-T* curve. Comparison of theoretical calculations of nitrogen in this energy regime prove that it is the equilibrium composition results, not the frozen composition results, that agree with experimental data [16].

The corresponding locus of states of the N_8 detonation products gases in the pressure (p)—volume (v) plane is presented in Fig. 5.
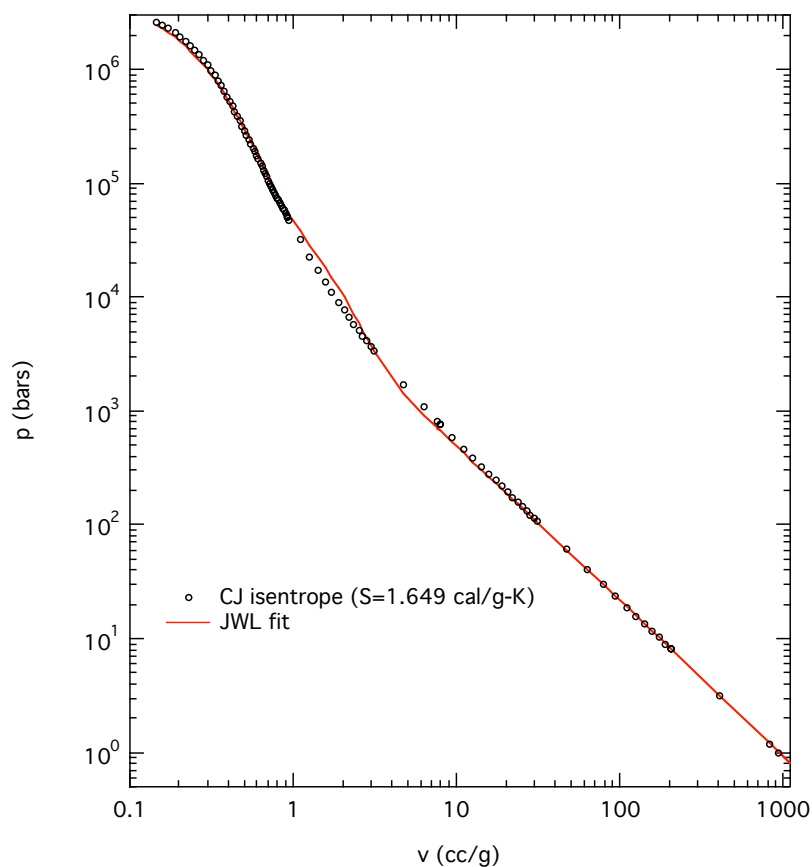

Figure 5. *p-v* diagram for the detonation of N_8 (*fcc*) meta-stable clusters.

The computed points are fit with the JWL function:

$$p_{JWL}(\rho,T) = A\left[1 - \frac{\omega}{R_1 v}\right]\exp(-R_1 v) + B\left[1 - \frac{\omega}{R_1 v}\right]\exp(-R_2 v) + \rho R_{DP} T \qquad (1)$$

The constants are listed in Table 2.

Table 2. JWL constants for the products of meta-stable cluster detonations

Case	A (M-bar)	B (M-bar)	R_1 (—)	R_2 (—)	$\omega = \gamma - 1$ (—)	R_{DP} (bar-cc/g-K)
$N_8(fcc)$	8.04	0.1557	2.2496	0.5	0.1945	2.969
He_2^*	80.06	1.9985	2.5484	0.5	0.2483	20.785

He_2* Detonation

The Le Chatelier diagram for the detonation of He_2^* clusters is depicted in Fig. 6. It shows the locus of equilibrium states of the detonation products gases, starting at the *Chapman-Jouguet* (*CJ*) point, expanding along the *CJ* isentrope: $S_{CJ} = 5.536$ cal/g, and terminating at room temperature, as calculated by the Cheetah code [13]. Point R denotes the initial state of the *Reactants* (He_2^* clusters). The value $u_R = 50,039$ cal/g is based on Elesin's *ab initio* local-energy-density-functional calculations for He_2^*, where the accumulated energy was $E_{acc} = 8.7$ ev/mol [10, 12, 17]. This gives a heat of detonation of $\Delta H_d = 50,039$ cal/g. A constant volume explosion from point R to point P results in a temperature of $T_{CVE} = 27,550$ K. The computed points are well fit by the following cubic function of temperature:

$$u(T) = -824 + 0.767 \cdot T + 5.33 \times 10^{-5} \cdot T^2 - 5.204 \times 10^{-10} \cdot T^3 \qquad (2)$$

The corresponding locus of states of the He_2^* detonation products gases in the pressure (p)—volume (v) plane is presented in Fig. 7. Computed points are fit by the JWL function (1), whose constants for this case are listed in Table 2.
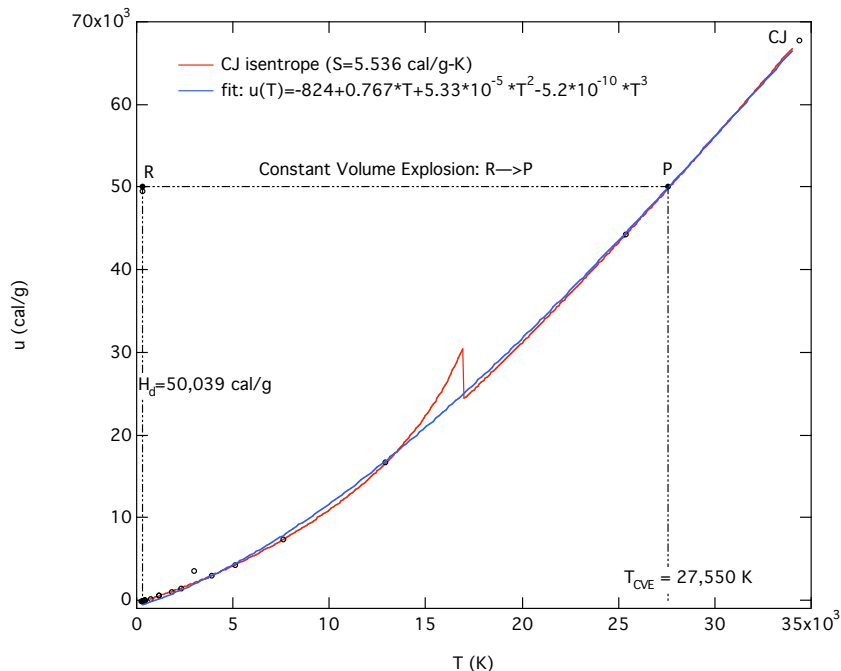
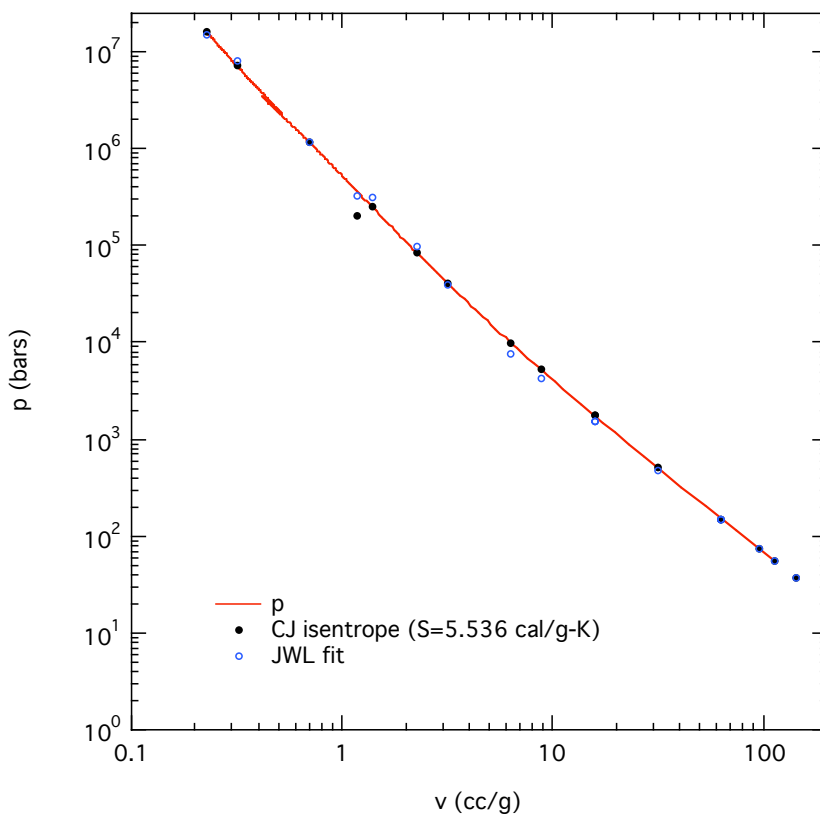Figure 6. Le Chatelier diagram for the detonation products of He_2^* meta-stable clusters.

Figure 7. p-v diagram for the detonation products of He_2^* meta-stable clusters.

Detonation properties of the selected meta-stable clusters are summarized in Table 3. The extraordinarily large detonation pressures (3 & 16 mega-bars), temperatures (12 & 34 thousand K), and wave velocities (20 & 43 kilometers per second) are a consequence of the large energies (and densities) stored in the Reactants state R of the meta-stable clusters of N_8 and He_2^*.

Table 3. Detonation properties of Type-II meta-stable clusters

Property	$N_8(fcc)$	$He*-He*$
ρ_0 (g/cc) *	3.186	3.164
H_d (cal/g)	6,673	50,039
p_{CJ} (M-bars)	3.14	16.3
ρ_{CJ} (g/cc)	4.266	4.423
T_{CJ} (K)	12,061	34,362
W_{CJ} (km/s)	19.7	42.8
U_{CJ} (km/s)	5.0	12.2
a_{CJ} (km/s)	14.7	30.6
Γ_{CJ} (-)	2.948	2.515
p_{CVE} (M-bars)	1.14	8.97
T_{CVE} (K)	10,750	27,550
E_{CVE} (cal/g)	6,673	50,039

* see Appendix for density calculations

EXPLOSION SIMULATIONS

Here we use numerical simulations with our 3-D AMR code [18], to study the explosion environment created by the detonation of 1-g meta-stable clusters in a 6.6-liter chamber (right circular cylinder, d = 20 cm, h = 21 cm) at STP conditions (1 bar and 273 K). The thermodynamic properties of the detonation products (u-T relation, *JWL* function, etc.) from the previous section were used to define the Equation of State (EOS) inputs to the AMR code. To handle the non-convex EOS effects, we used a generalized Godunov scheme of Bell et al [19].

N_8 Cluster Explosion

A 1-g spherical charge of N_8 clusters, with a density of 3.186 g/cc, was located at the center of the chamber filled with N_2 at STP. We assumed an initial value problem where the

energy was released as a constant volume explosion that deposited 6,673 calories instantaneously throughout the charge. With these initial conditions, the AMR code simulated the evolution of the explosion fields in the chamber. Pressure and impulse histories on the chamber lid at $r = 5$ cm are presented in Fig. 8. There they are compared with: (*i*) waveforms from the explosion of 1 gram of Al-SDF charge— releasing 7,400 calories via turbulent combustion with air, and (*ii*) the explosion of 1 gram of TNT charge in nitrogen—releasing 1,148 calories by the detonation wave (no after-burning). These are based on experimental measurements described by Kuhl and Reichenbach [20]. The N_8 blast had a peak value of 89 bars, compared to 23 and 14 bars for the TNT and Al-SDF explosions. The N_8 explosion created 4 times the impulse of the TNT explosion and twice the impulse of the Al-SDF explosion.
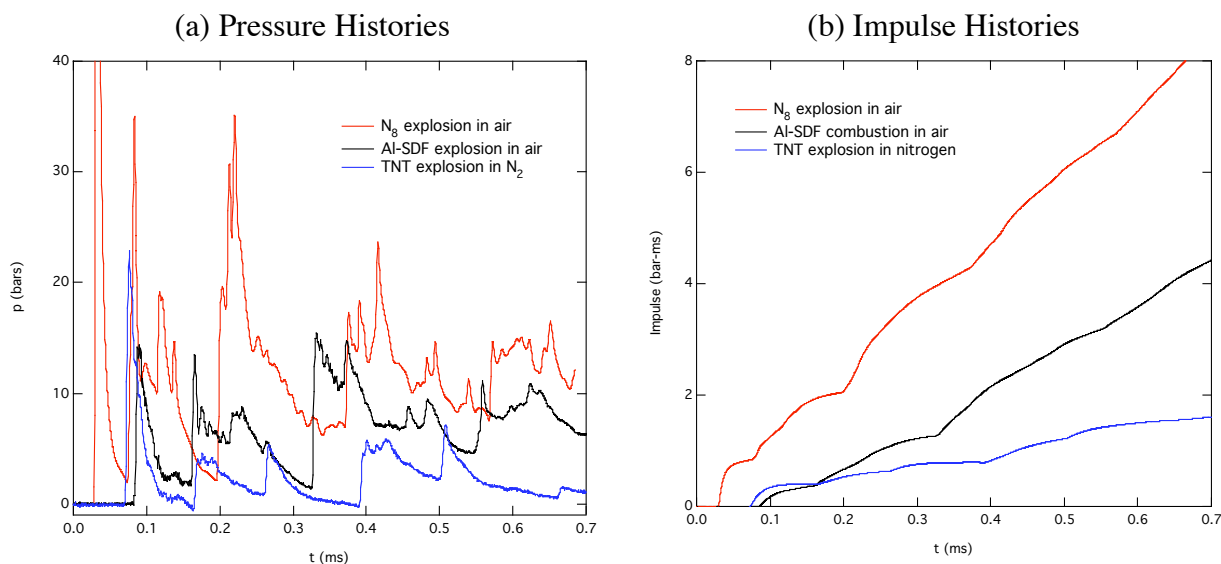

Figure 8. Waveforms created by 1-g explosions in a 6.6-liter chamber. Numerical simulation of a N_8 explosion is compared with data from Al-SDF explosions in air and TNT explosions [20].

He_2* Clusters Explosion

A 1-g spherical charge of He_2^* clusters ($\rho_0 = 3.164$ g/cc) was located at the center of the 6.6-liter chamber filled with *He* at STP. An initial value problem was posed where the energy was released as a constant volume explosion that deposited 50,039 calories instantaneously

throughout the charge. Then, the AMR code simulated the evolution of the explosion in the chamber. Pressure and impulse histories on the chamber lid at $r = 5$ cm are presented in Fig. 9. The He_2^* blast wave had a peak pressure of 743 bars, or more than 8 times the N_8 blast wave.
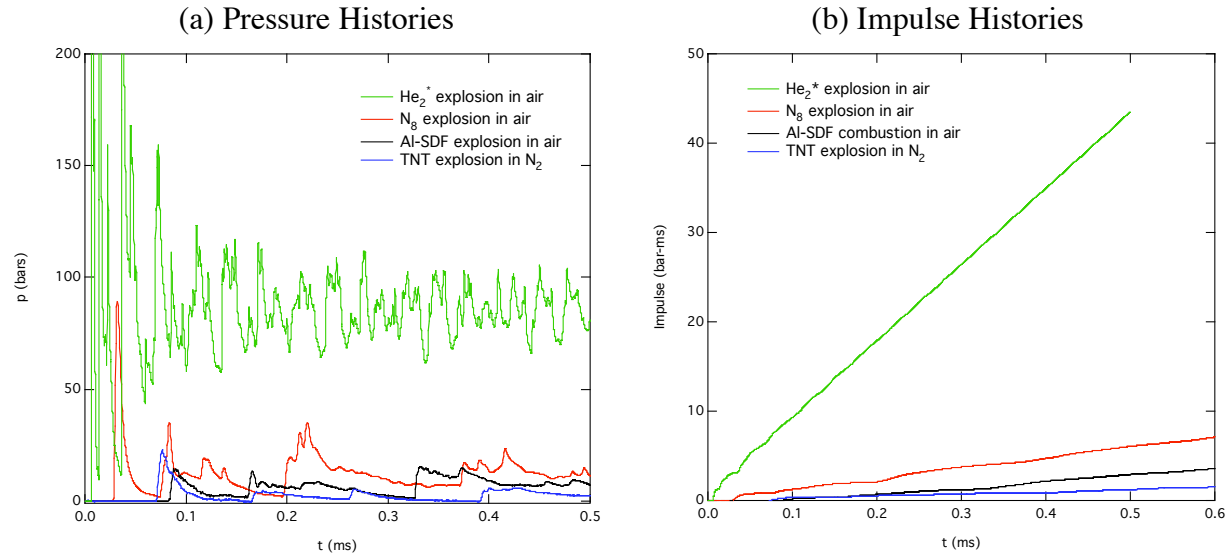

Figure 9. Waveforms created by 1-g explosions in a 6.6-liter chamber. Numerical simulation the explosion of a 1-g He_2^* charge is compared with waveforms from Fig. 8.

Chamber Pressures

The impulse curves of Figs. 8 and 9 were fit with linear functions; their constants are listed in Table 4. The slope of the impulse history represents the mean chamber pressure: $\Delta \bar{p}_c$. The helium cluster explosion created a mean chamber pressure of 86 bars; this is to be compared with 12 bars for the nitrogen cluster explosion in contrast with 8.8 bars and 2.4 bars for the Al-SDF and TNT explosions, respectively.

Table 4. Impulse curve fits: $I_i(t) = a_i + \Delta \bar{p}_{c,i} \cdot t$

Case (i)	a_i (bar-ms)	$\Delta \bar{p}_{c,i}$ (bars)
He_2^* cluster explosion in air	0.496	86.32
$N_8(fcc)$ cluster explosion in air	0.014	11.93
Al-SDF explosion in air	-1.65	8.829
TNT explosion in N_2	0.007	2.357

Flow Field Visualization

Figures 10 and 11 present a cross-section of the temperature field at different times during N_8 and He_2^* cluster explosions, as computed by the AMR code. The Detonation Products (DP) interface is unstable and Taylor cavities (interpenetration of air into the DP), even before the first reflection from the chamber walls. The flow rapidly evolves into an intense mixing layer.

RÉSUMÉ

Theoretically, meta-stable clusters are able to accumulate energy that is much larger than those found in typical exothermic chemical reactions. For example, *ab initio* local-energy-density-functional calculations [10, 12, 14, 17] predict energy accumulation equivalent to heats of detonation of 6,673 cal/g and 50,0039 cal/g for N_8 and He_2^* clusters, respectively. The *Meta-stable Cluster State* (*MCS*) serves as the *Reactants* state for the explosion. Detonation of meta-stable clusters creates *Products* gases such as N_2 molecules and He atoms, respectively. The locus of thermodynamic states of the Products gases in the *u-T* plane and the *p-v* plane have been calculated by use of the thermodynamic code Cheetah [13]. The appropriate assumption for the locus is that the Products are in thermodynamic equilibrium. For nitrogen, this results in a non-monotonic behavior of the $u(T)$ locus—due dissociation of N_2 into atomic nitrogen at large energies [16].

CONCLUSIONS

Meta-stable cluster explosions can produce pressures and impulses that are much larger than TNT detonations and even Al-air combustion systems. Meta-stable clusters of nitrogen and helium have been shown to exist theoretically. If they could be synthesized, then they would offer the potential of much higher energy density media.
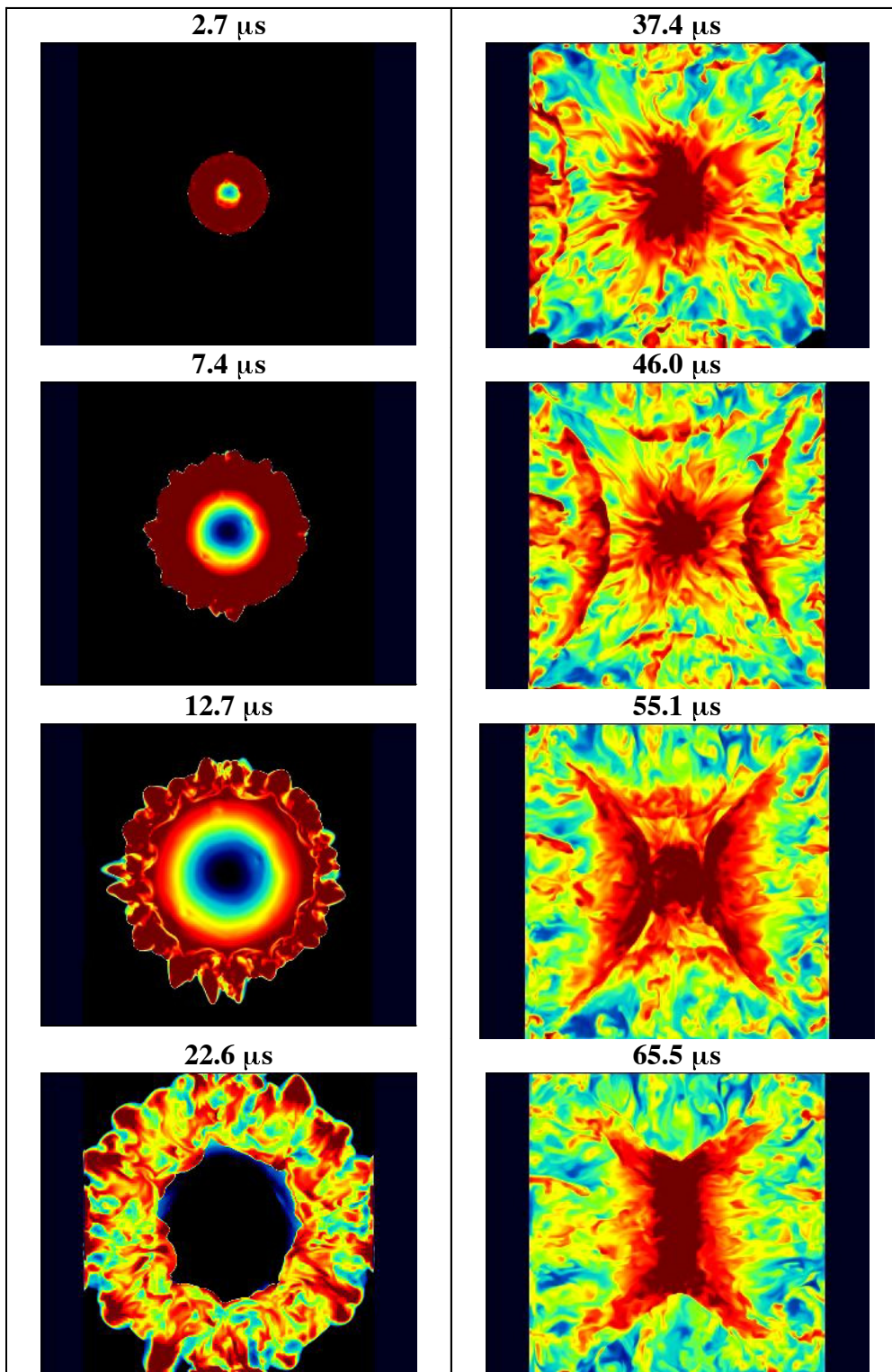
Figure 10. Cross-section of the temperature field at different times during the N_8 cluster explosion in a 6.6-liter chamber (red corresponds to 6,000 K).
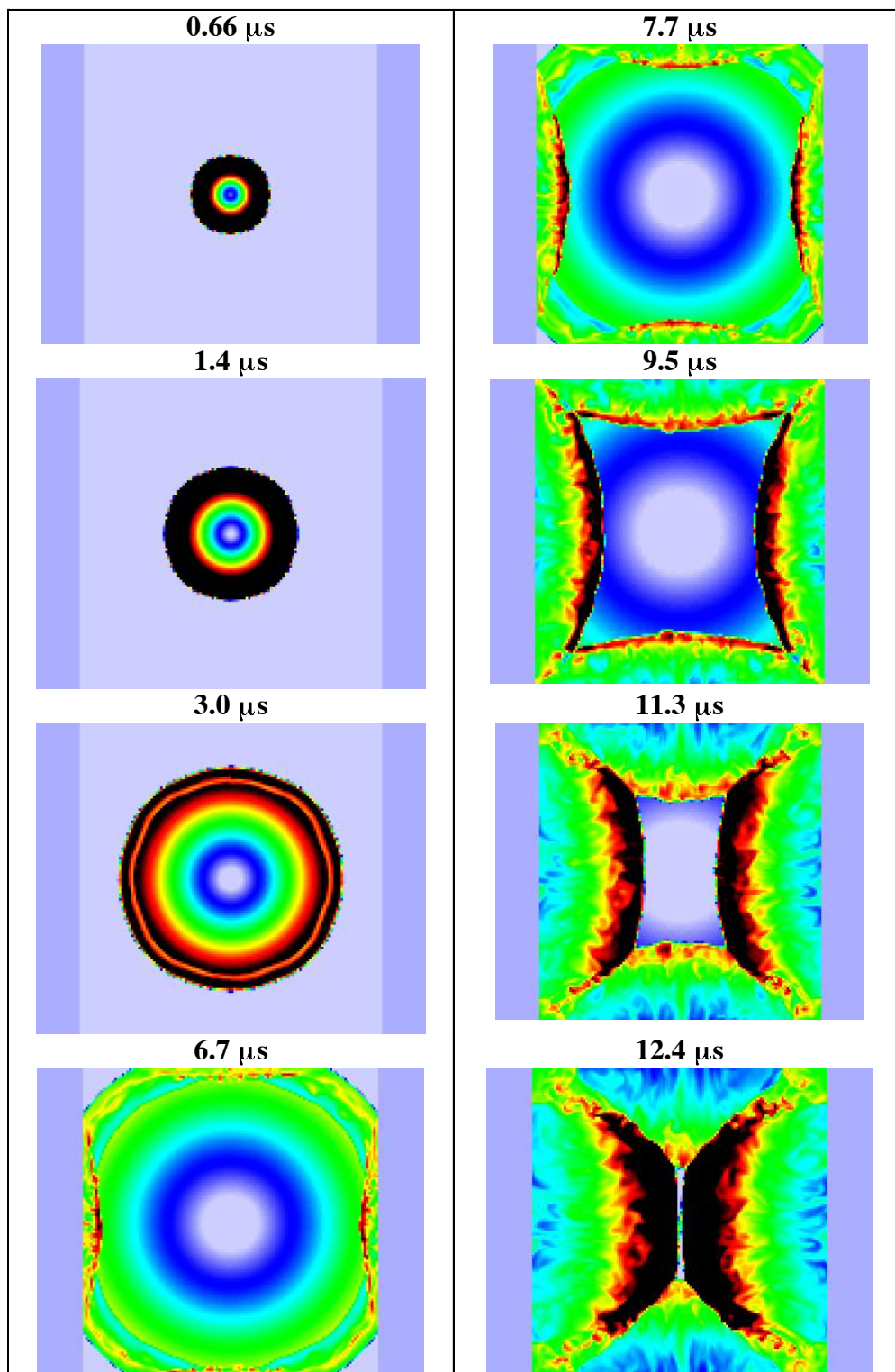
Figure 11. Cross-section of the temperature field at different times during the He_2^* cluster explosion in a 6.6-liter chamber (red corresponds to 27,000 K).

APPENDIX

The initial density of the N_8 (fcc) cluster media was estimated from the relation:

$$\rho_0 = \frac{M}{V_0 \cdot A} = \frac{14 \; g/mol}{7.3 \times 10^{-24} cc \cdot 6.022 \times 10^{23} atoms/mol} = 3.186 \; \text{g/cc}$$

where the volume $V_0 = 7.30(A^0)^3$ was based on Mailhiot's calculations for the fcc-form of polymeric nitrogen [14] and A denotes Avogadro's number. For the $cubic\ gauche$ (cg) form, Mailhiot [14] predicts a volume of $V_0 = 6.67(A^0)^3$ which is close to the value $V_0 = 6.592(A^0)^3$ measured by Eremets [15]—thereby confirming the accuracy of his volume/density predictions for polymeric nitrogen. The initial density for He_2^* was estimated from:

$$\rho_0 = \frac{M}{V_0 \cdot A} = \frac{8 \; g/mol}{4.2 \times 10^{-24} cc \cdot 6.022 \times 10^{23} atoms/mol} = 3.163 \; \text{g/cc}$$

where the volume $V_0 = 4.2(A^0)^3$ is based on an atom-to-atom separation of two angstroms, according to Elesin's calculations for meta-stable He_2^* clusters [10].

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