Atomistic Mechanism for Hot Spot Initiation

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We propose a picture of the role of shock-wave interactions with microscopic voids that leads to significant heating, sufficient to thermally initiate chemical reactions in solid explosives, or phase transitions in metals. The key ingredients to this dramatic overshoot in temperature are: (i) a strong enough shock wave to cause vaporization of material into the void; (ii) the stagnation of low-density vapor (for a wide enough gap) at the far side; and (iii) recompression of the gas (pressure-volume work) from low density back to the original shocked density. We explore dependencies on both shock strength and one-dimensional gap width in atomistic simulations of a two-dimensional *unreactive* Lennard-Jones solid, comparing observed thermal overshoot with a straightforward model, to show how hot spots can be generated under shock-wave conditions.

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Detonations in solid explosives are believed to be facilitated by the presence of defects, known as "hot spots," because of enhanced chemical reactivity when a shock wave passes over and possibly interacts strongly with them [1–3]. Using large-scale nonequilibrium molecular-dynamics (NEMD) computer simulations and reactive empirical bond order potentials [4], we have been able to study, at the atomistic level of detail, the influence of a variety of defects upon the threshold impact velocity for detonation, in contrast with the higher threshold for a perfect single crystal[5,6]. If the defects are small and isolated, such as vacancies or free radicals, the shock wave simply passes over them, with no initiation of significant chemistry. More extended defects are therefore required to reduce the detonation threshold. Nevertheless, we found that even planar one-dimensional (1D) gaps have to be of minimum width before reactions begin and grow [5,6]. A similar effect was discovered in the study of shock-wave-induced plasticity [7].

The object of this work is to understand the origin of shock-induced "hot spot" initiation of chemistry, or activation of plasticity, or of phase transitions. Herein we will focus on the 1D gap geometry because it retains many, if not all, of the essential features of the problem, while eliminating the complicating effects of 2D or 3D void shapes. In this geometry, a flyer plate hits a target plate, which has a gap somewhere in its midsection, far enough from the impact plane that a steady bulk shock wave has formed, but has not led to the initiation of chemistry. The dimensions transverse to the shock direction are treated with periodic boundaries, mimicking the laboratory conditions in the central region of the impact of macroscopic plates.

Hot spot initiation at voids is often thought to be caused either by spallation of molecules from the upstream free surface of the void (or gap), or by void collapse [2,3,8]. During void collapse, it might be assumed that the collisions of the spalled molecules with the downstream wall of the void are more energetic because these molecules are traveling at a much higher average velocity than they have in the bulk. This assumption, however, is wrong. The impact velocity of a symmetric flyer plate is $2u_p$; the mean particle velocity behind the resulting shock wave is u_p, also known as the piston velocity. If the particles were elastic beads on a frictionless wire, then the shock front in the bulk solid would be characterized by a particle at rest impacted by its neighbor at $2u_p$. This is exactly the expected spall velocity of ejecta particles at the upstream free surface of the gap, or void. The only difference with the bulk velocity behavior is that the spalled particle is ejected into the void, rather than colliding with its next neighbor in the chain. Thus, the spall velocity is not the cause of subthreshold detonation.

Focusing, or jetting of ejecta due to concave void surfaces, is another possible mechanism for enhanced chemistry at the downstream void wall. Jetting, however, is not really much different from void collapse, insofar as the collapse of a very large void and the closing up of a planar gap are indistinguishable, provided that the speed of closure exceeds some threshold. The principal geometrical difference between a closed void and a planar gap, apart from the slightly higher surface energy of the curved void, is the occurrence of more pronounced jetting, or focusing of the impact at the far side, that occurs for small voids. In other words, as the shock wave is forced to curve around the void, ejecta molecules on either side of the centerline tend to focus their momentum toward the center, thereby forming a jet along the centerline. The enhancement of the impact at the far side due to jetting is obviously diminished for larger voids, which shows that jetting is not the fundamental cause of the minimum void size we observe for subthreshold

initiation. In addition, one would not expect a major reduction in the spall velocity because of increased curvature of the surface of small voids.

It was also possible that the shock wave could race around a closed void, initiating chemical reactions on the far side of the void before it collapsed. In reality, however, the shock front tends to be retarded as it passes a sufficiently large void, and ejecta collide with the far side of the void first.

Movies of our simulations [5] suggested another possible origin for enhanced chemistry as the gap exceeds a critical width for a particular u_p. As molecules fly across the gap, they tend to tumble, and thereby impact the far side of the void with a greater variety of impact orientations than would occur in the bulk molecular crystal. Hence, one could imagine a critical gap width that would facilitate sufficient tumbling during the time of flight, to randomize the impact geometries, and perhaps thereby enhance the probability of chemical reaction. However, simulations of glassy solids with random molecular orientations did not exhibit any significant lowering of the critical impact velocity for detonation. Hence, random impact geometries caused by tumbling do not explain the lowering of the impact velocity for a critical gap width.

By observing the movies more closely, we then noticed that there appeared to be a brief induction period before significant chemistry occurred [5,6]. The initiation also did not appear to occur in the impacted material on the far side of the gap, but rather in the ejecta molecules that were stagnated against the far wall. Stimulated by these results, we began a series of simulations of shocks interacting with different width gaps, but in a *nonreacting* Lennard-Jones (LJ) 2D solid. In this way, we could easily monitor the temperature of the stagnating material with the hope of achieving some quantitative modeling of the gap-collapse thermal history. Also, by doing the simulations in 2D, we could span a wide range of gap widths more economically than in 3D.

The results for the longitudinal temperature maxima (z component, or shock propagation direction, computed from particle z velocities in slab-shaped boxes, with local average velocity subtracted out) are shown in Fig. 1 for five different gap widths ℓ. The temperature profiles at the far wall of the gap exhibit peaks that arrive at the mass-average vapor-ejecta velocity u_ℓ of between u_p and $2u_p$, depending on ℓ. (The very leading edge of this spreading rarefaction wave is faster than the average, by roughly the thermal velocity, or Boltzmann tail, of the first-shocked material; the edge velocity just happens, therefore, to be $\sim 3u_p$.) For small ℓ, u_ℓ equals the particle velocity u_p behind the shock. As ℓ increases, u_ℓ reaches an asymptote of $2u_p$, the spall velocity (equal to the original symmetric-impactor velocity). Between these limits, the vapor-ejecta velocity, as a function of ℓ, appears to behave according to

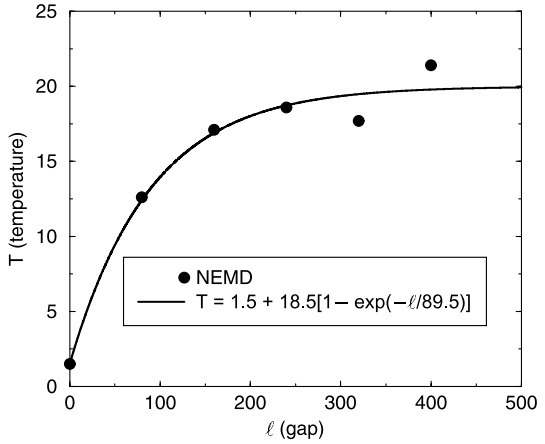

FIG. 1. Temperature maxima at far wall of gap (width = ℓ) in 2D Lennard-Jones solid (LJ units, see text): piston velocity $u_p = 3.0$, shock velocity $u_s = 16.3$, first-shock temperature $T_1 = 1.5$, maximum temperature rise $\Delta T_{\max} = 18.5$, and characteristic length $\ell_0 = 89.5$.

$$u_\ell = u_p(2 - e^{-\ell/\ell_0}), \tag{1}$$

where ℓ_0 is a characteristic phenomenological length scale that depends inversely on u_p. The temperature peak of the ejecta rarefaction wave also appears to fit the analogous form:

$$T = T_1 + \Delta T_{\max}(1 - e^{-\ell/\ell_0}), \tag{2}$$

where T_1 is the first-shock temperature. (See Fig. 1.) This width-dependent temperature rise accounts for the critical gap width required for initiation[5,6]. Next, we shall show how Eq. (2) can arise from the recompression of an expanding spray of ejecta.

Before proceeding, we note that such a temperature buildup occurs only above a critical shock strength, characterized by u_p^*, where the solid melts or vaporizes. We can estimate this threshold by equating the Hugoniot energy jump $\Delta E = \frac{1}{2}m(u_p^*)^2$ to the cohesive energy per particle in the d-dimensional solid $E_{coh} = \frac{1}{2}d(d+1)\epsilon$ to obtain $u_p^* = \sqrt{d(d+1)\epsilon/m}$. In 2D ($d = 2$), $u_p^* \approx 2.4$ (in LJ units: m = atomic mass, r_0 = bond distance, ϵ = bond energy). Below this critical strength, no cloud of vapor ejecta is formed; the solid material in front of the gap then appears to be quite similar to the initial impactor, but at a higher initial temperature T_1 given by the passage of the first shock. Thus, no substantial enhancement of the temperature upon void collapse is seen. If, however, the void is filled with quasi-isentropically expanding (and cooling) ejecta gas, which is thereupon shock recompressed as it stagnates against the far wall of the void, then the temperature of the gas can be increased substantially by the PV work done on it. Mintmire *et al.* observed similar results, noting smooth and symmetrical void closure below the critical shock strength (no ejecta) and "turbulent" collapse above, with higher temperature generated by the jet of ejecta [9].

In Fig. 2, we present a cartoon of the vapor-ejecta formation, showing density as a function of position, at the instant when the leading edge of the vapor cloud (center-of-mass velocity u_ℓ, average density ρ_{00}) has reached the downstream wall of the gap. Meanwhile, the rarefaction wave in the solid has receded from the original upstream gap wall into the shocked material (density ρ) at the sound speed $c(\rho) \approx u_s$ (shock velocity), relative to the incoming shocked material's particle velocity u_p, returning the material to its original solid density ρ_0.

A pressure-volume (P-V) diagram of the subsequent vapor-ejecta recompression is shown in Fig. 3. The area between the release isentrope and the recompression (reshock) Rayleigh line gives the heat-up of the gas temperature ΔT (over and above that of the first shock). We can easily approximate this by the area of the triangle defined by the two Rayleigh lines, which results in an estimate of the overheat that is too large, particularly at lower shock strengths. If we assume that the gas is ideal (dimensionality $d = 2$ or 3), then

$$\begin{aligned}\frac{d}{2}k\Delta T &= \frac{1}{2}P(V_{00} - V_0) \\ &= \frac{1}{2}mu_s u_p\left(\frac{V_{00}}{V_0} - 1\right) \\ \Rightarrow k\Delta T &= \frac{mu_s u_p}{d}\left(\frac{V_{00}}{V_0} - 1\right), \end{aligned} \tag{3}$$

where $P = P_0 + \rho_0 u_s u_p$ is the Hugoniot relation for conservation of momentum across the first shock, starting from an initial low-temperature, low-pressure ($P_0 \approx 0$) solid; $\rho = m/V$; and k is Boltzmann's constant.

We can now obtain the thermal overshoot ΔT in the following way. Assume that the shocked solid sublimes (vaporizes) as the shock emerges from the upstream free surface, at a rate that is determined by the rarefaction wave propagating back into the shocked solid. The mass of the vaporized ejecta can be gotten from the density difference between the shocked solid (density ρ) and the remaining relaxed solid (at approximately the original density ρ_0). (See Fig. 2.) The vapor has an average density ρ_{00} and center-of-mass velocity u_ℓ given by Eq. (1). Dividing by the time of flight to the wall and the cross-sectional area, the mass balance equation is then

$$\begin{aligned}(\rho - \rho_0)(u_s - u_p) &\approx \rho_{00}u_\ell\rho_0 u_p \\ &\approx \rho_{00}u_p(2 - e^{-\ell/\ell_0}) \\ \Rightarrow \rho_0 &\approx \rho_{00}(2 - e^{-\ell/\ell_0}), \end{aligned} \tag{4}$$

where $\rho_0 u_s = \rho(u_s - u_p)$ is the Hugoniot relation for conservation of mass across the first shock. For a sufficiently strong shock that releases adiabatically down an isentrope into the vapor dome of the phase diagram, the volumetric strain u_p/u_s under shock compression is nevertheless small relative to the expansion of the ejecta gas, as shown in Fig. 3. The volumetric expansion strain of the gas is

$$\frac{V_{00}}{V_0} - 1 = \frac{\rho_0}{\rho_{00}} - 1 = 1 - e^{-\ell/\ell_0}, \tag{5}$$

so that the excess heating due to PV work on recompression of the ejecta gas is

$$k\Delta T \approx \frac{mu_s u_p}{d}(1 - e^{-\ell/\ell_0}), \tag{6}$$

in accord with the empirically observed Eq. (2), from which we obtain an estimate of the maximum overheat:

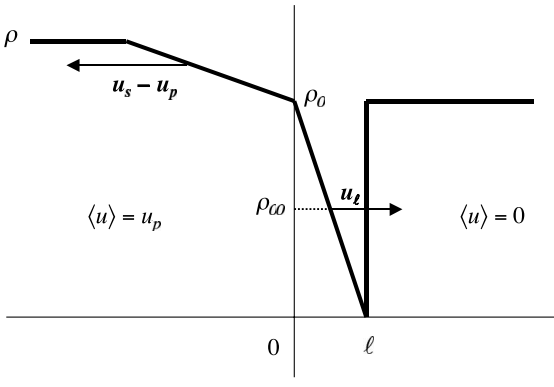

FIG. 2. Idealized density profile in the process of vapor-ejecta generation, after a time required for the leading edge to cross a gap of width ℓ.

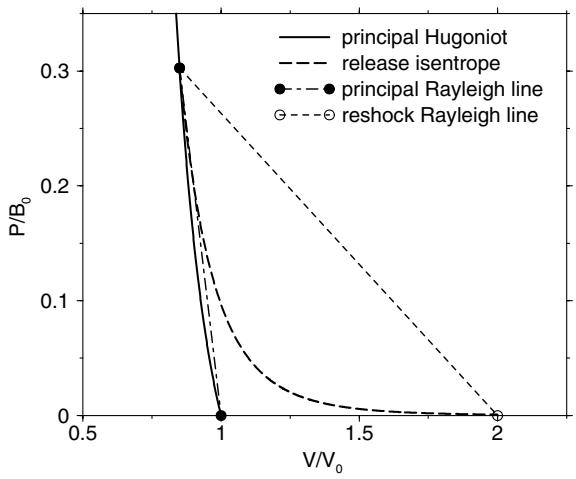

FIG. 3. Idealized pressure-volume (P-V) curves for hot spot generation by recompression of vapor ejecta from a planar gap (initial solid volume V_0, bulk modulus B_0): (1) first-shock Hugoniot in solid (PV area under first-shock Rayleigh line is increase in internal energy for shock pressure P); (2) release isentrope of vapor ejecta; and (3) shock recompression Rayleigh line (area between it and release isentrope is kinetic energy increase in gas). Final vapor-ejecta volume ($2V_0$) is shown for asymptotic gap width ($\ell \gg \ell_0$).

$$k\Delta T_{\max} \approx m u_s u_p / d. \quad (7)$$

In Table I, NEMD values of $\Delta T_{\max}$ for supercritical shock strengths are observed to be a factor of about 2/3 smaller (as anticipated from Fig. 3) than those predicted by Eq. (7) for our "crush-up" model (so called, because of the similarity with the compaction of a low-density foam). The characteristic length scale ℓ_0 for reduction of the maximum asymptotic temperature rise due to finite-width gaps is seen to drop with shock strength.

Thus, we see from this simple crush-up model that hot spots at voids arise from the spallation of ejecta molecules from the upstream side of the void, the expansion of the ejecta gas in a spreading rarefaction wave, and its subsequent recompression upon collision with the far side of the void. The PV work is enough to magnify the temperature far above its first-shock value, so that, if the void is sufficiently wide, the overheat can be enough to facilitate a detonation, even though the impact velocity would not otherwise have caused appreciable reactions in a defect-free crystal. If the void simply collapses at subcritical shock strengths, without forming a gas of ejecta molecules, then no significant overheating can occur — no work is required to compress a vacuum.

Our simple model is consistent with all the evidence we have amassed [5,6]: (i) A critical velocity for detonation exists for a perfect crystal. (ii) The critical velocity can be reduced by shock passage over sufficiently large voids, as long as the shock is strong enough to release into the vapor dome. (iii) The heating by recompression of the spalled (ejecta) gas depends upon the void size and asymptotes to a value considerably above the first-shock temperature. (iv) There is a delay time in the initiation of chemistry, because of the compaction process at the far side of the void. (v) Reactions occur first in the recompressed gas, not in the far wall.

The model confirms the idea that microscopic cracks and voids with dimensions as small as several hundred nanometers can play a key role in enhancing the sensitivity of energetic materials to initiation. This is in contrast to defects such as dislocations and stacking faults, which cannot produce an ejecta gas whose subsequent recompression magnifies the local temperature. Nevertheless, the model also suggests that the material does not have to be free of such cracks and voids to approach the stability of crystalline explosives. What is required is that their characteristic gap width ℓ be kept small compared to ℓ_0, in order to prevent significant local overheating. Finally, our results imply that materials with submicrometer reaction zone lengths can nevertheless require strong shocks to initiate, even if they contain nanometer-wide cracks. Thus, we conjecture that such highly ordered but still imperfect materials might find wide use in tiny devices relying on mesoscale detonations, which necessitate extremely short reaction zone lengths. Moreover, such microexplosives should be easier to synthesize because of their small size.

TABLE I. Temperature rise $\Delta T_{\max}$ in gap closure (asymptotic, as gap width becomes large), as function of shock strength (piston velocity u_p) above threshold for vapor-ejecta production. $\Delta T_{\max}$ is calculated from u_p and shock velocity u_s (first-shock temperature is T_1) and compared to that observed in NEMD simulations for 2D LJ system (table entries in LJ units). Characteristic length $\ell_0 \sim u_p^{-2}$.

u_p	u_s	T_1	$\Delta T_{\max}^{\text{calc}}$	$\Delta T_{\max}^{\text{obs}}$	obs./calc.	ℓ_0
2.5	15.1	1.3	18.9	11.6	0.61	132.0
3.0	16.3	1.5	24.4	18.5	0.76	89.5
4.0	18.6	2.9	37.2	27.9	0.75	39.2

In future work, we will quantify the additional effect of nonplanar gaps, that is, voids of differing shapes (curvature), which can give rise to jetting and focusing. Even so, our crush-up, or recompaction model for vapor ejecta describes an important hot spot mechanism for lowering the detonation threshold. Analogous effects can be expected for other thermally activated, shock-induced phenomena (plasticity, phase transitions, and chemistry).

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