

Crack propagation induced heating in crystalline energetic materials

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A model is presented for time and spatial dependences of the heating of molecular vibrations and the possible initiation of chemical reaction from heat dissipated in the vicinity of a propagating crack in a molecular crystal. In the model, energy from a moving crack tip is released as phonons in proximity to the crack. Initially the phonons and the molecular vibrations are not in thermal equilibrium. Subsequently, there is a competition between excitation of molecular vibrations by multiphonon up-pumping and diffusion of phonons from the crack region. If the coupling between the locally hot phonon bath and the molecular vibrations is sufficiently large, a transitory high vibrational temperature will be achieved prior to eventual thermal equilibration with the bulk of the crystal. It is found that the peak vibrational temperature can be sufficiently high for a significant time period for chemical reactions to occur. The model calculates the local time-dependent vibrational temperature using reasonable values of the physical input parameters. For a crack tip moving near the speed of sound, the calculations show that vibrational temperatures can reach ~ 800 K in 55 ps and exceed 550 K for ~ 1 ns after the initial heating. This temperature change is sufficient to produce chemical reaction in a secondary explosive such as HMX, but given the duration and size of the heated region, a single crack should not result in self-sustaining chemical reaction. The role that cracks may play in shock sensitivity is discussed. © 1999 American Institute of Physics. [S0021-9606(99)01007-7]

I. INTRODUCTION

In this paper a model is presented for crack propagation induced molecular heating and chemical reaction. Usually mechanical disturbances that produce chemical reactions involve shock waves. Shock-initiated molecular reactions occur through the transfer of mechanical energy from a shock front to internal molecular vibrational states. In energetic materials used in explosives, strong shocks lead to the initiation of substantial chemistry and detonation. A specific motivation for the work presented below is the problem of energetic material sensitivity. Sensitivity refers to explosions caused by perturbations which are ordinarily insufficient to produce a detonation. Anomalous sensitivity leads to unwanted detonations.

A model has been developed that describes the initial steps of shock induced chemistry in terms of multiphonon up-pumping.¹ A shock wave produces a bath of highly excited phonons, which flow into the lowest vibrational modes (doorway modes) of the molecules that make up a crystal. Continued flow of energy from the hot phonon bath into the doorway modes leads to higher and higher levels of vibrational excitation. The internal vibrational molecular modes equilibrate very rapidly, and the internal temperature of the molecule rises. If the initial phonon temperature is sufficiently high, multiphonon vibrational up-pumping will heat the molecules to temperatures at which chemical bonds break. Using reasonable parameters to characterize molecular crystals, for moderate shock pressures, up-pumping times of a few tens of ps were calculated with the model. Subse-

quently, Dlott and co-workers measured that up-pumping in liquid nitromethane requires 100 ps.² Molecular dynamics simulations of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)³ and triaminotrinitrobenzene (TATB)⁴ yield up-pumping times of 10 ps. The increase in up-pumping rates compared to nitromethane has been attributed to more doorway modes in complex molecules like HMX.⁵

In the following, a model is developed and used to investigate the possible role of crystalline cracking and crack propagation in the initiation of chemistry in molecular crystals. The model is related to the shock induced multiphonon up-pumping model. Cracks can be produced by small mechanical perturbations that are insufficient to produce the strong shocks that are required for detonation of explosives. The results of the calculations presented below show that local heating from stored elastic energy dissipated as heat in the vicinity of a propagating crack can cause significant increases in internal molecular temperatures, and may be sufficient to produce some chemical reactions in a molecular crystal of an energetic material such as HMX. Optical calorimetric experiments on metals,⁶ quartz,⁷ and plastics⁸ have shown that temperatures as high as 4000 K can occur in the vicinity of cracks. These temperatures are high enough to break bonds and initiate reactions. Measurements on carbonates, CaCO_3 , MgCO_3 , and PbCO_3 , and azide materials PbN_3 and NaN_3 , have shown that chemical reactions are induced by the formation of cracks, and from the extent of chemical reaction, temperatures in proximity to cracks have been estimated.⁹

While observations have been made of crack induced heating and chemical reactions, there is no molecular level model that describes the dynamical processes that give rise

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to the chemical reactions. Molecular crystals composed of complex molecules (naphthalene or HMX) have larger heat capacities than the species, such as CaCO_3 , that have shown crack induced chemistry. The larger heat capacities of complex molecular crystals arise from a vibrational structure with many more modes per molecule than CaCO_3 . Because of the higher heat capacities of complex molecular crystals, the ultimate temperature reached following cracking will be lower than in crystals such as carbonates, if the same amount of initial energy is released by cracking.

In the following, a model is presented that describes the competition between thermal diffusion into the bulk solid and vibrational heating of molecules in the small volume directly heated by a propagating crack. If the anharmonic phonon-vibrational interactions that cause energy to flow into the internal vibrational degrees of freedom of a molecule are sufficiently strong, the internal molecular temperature will rise substantially before heat can diffuse out of the small region in which energy is released by the propagating crack. The model considers both a rapidly propagating crack (moving near the velocity of sound) and a slowly propagating crack (crack velocity slow on a characteristic time scale for thermal diffusion). The theory developed to describe shock induced multiphonon up-pumping¹ is adapted to the problem considered here. This permits the rate of up-pumping to be calculated from a time-dependent phonon temperature and a variety of physical parameters. Because the necessary input parameters are not all known for a single material, they are drawn from values obtained from a number of systems. Thus the picture that emerges from numerical calculations is a composite that, nonetheless, should be accurate enough to provide insights into the role of cracking in the initiation of chemistry, and, in energetic material sensitivity. For reasonable choices of parameters, the results indicate that phonon heating followed by multiphonon up-pumping arising from crystal cracking can result in chemical reactions in a material like HMX. Based on detailed modeling of chemical reactions and heat release in HMX by Tarver *et al.*,¹⁰ the results indicate that a single crack is insufficient to result in detonation. However, cracks may play an indirect role in shock sensitivity.

II. MODEL OF CRACK INDUCED VIBRATIONAL HEATING

Cracks originate from strain fields extending over several unit cells.⁷ The strain is released when elastic energy exceeds the binding energy of the crystal. The crack starts at a point and propagates across the material. At the crack tip, the crystal strain is so high that the crystalline bonds between unit cells are broken and crystal planes move relative to one another. Two limits of the crack propagation are considered: fast and slow cracks. The heat flow away from the crack for these two cases is illustrated schematically in Fig. 1. For fast cracks, the crack tip travels much faster than heat can diffuse away from the crack. There is initially a hot planar slab, and the heat from the initial plane, which is several unit cells thick, spreads into the bulk crystal. The initial conditions for thermal diffusion in this limit are taken along a slab of the crack, hence, the heat flow away from the crack slab is de-

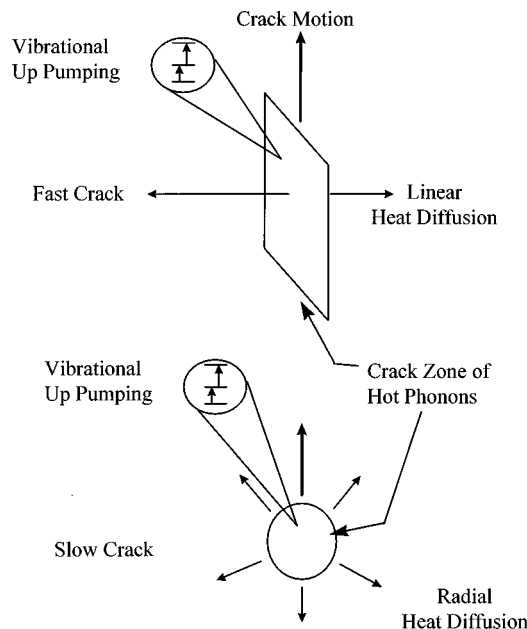


FIG. 1. The upper diagram illustrates a fast crack (crack velocity fast on the time scale of thermal diffusion). The crack zone is a planar region of hot phonons. Vibrational up-pumping and linear heat diffusion compete. The lower diagram illustrates a slow crack (crack velocity slow on the time scale of thermal diffusion). Vibrational up-pumping and radial heat diffusion compete.

scribed by a linear heat flow equation. For slow cracks, the heat diffuses away from the crack tip faster than the crack travels. The heat is generated along the crack line as it moves forward, and the heat diffuses out radially with cylindrical symmetry around the crack line faster than the crack moves forward. The initial conditions in this case are taken to be a cylinder, and the heat flow away from the crack tip is described by the heat flow equation in a cylindrical geometry.

For cracks which propagate near the speed of sound, more than half the elastic energy is converted into heat. The remaining energy results in plastic deformation near the crack.^{6,7,9} The initial strain field extends over a number of unit cells. When the strain is released, the energy is initially deposited into some distribution of acoustic and optical phonons. Because the phonon-phonon interactions are strong compared to phonon-vibrational interactions, the phonons will equilibrate rapidly on the time scale of vibrational up-pumping¹ or thermal diffusion. Thus the initial condition in the region adjacent to the crack is a locally equilibrated hot phonon distribution that is at a phonon quasitemperature. The phonon temperature is a quasitemperature because the phonons and vibrations are not yet in thermal equilibrium. The phonons are hot while the vibrations are still at ambient temperature. The phonon quasitemperature at any time is T_{ph} . Initially, prior to thermal diffusion or vibrational up-pumping, the phonon quasitemperature is a maximum, which is labeled T_{ph}^m .

The region heated by the propagating crack is called the crack zone. Estimates of the width of the crack zone, δ , are on the order of a few unit cells. The initial phonon quasitemperature, T_{ph}^m , can be obtained from

$$Q = \int_{T_0}^{T_{\text{ph}}^m} dT \delta^2 C_p^{\text{ph}}(T), \quad (1)$$

where T_0 is the ambient temperature, C_p^{ph} is the specific heat of the phonons at constant pressure in J/K cm^3 , and Q is a heat per unit length at the crack tip. For fast cracks, T_{ph}^m is the phonon temperature in a slab of thickness 2δ . For slow cracks, T_{ph}^m is the phonon temperature in a cylinder of radius δ .

There are two paths for T_{ph} in the crack zone to decrease, vibrational up-pumping and diffusion of phonons out of the crack zone. The first path, vibrational up-pumping, has been discussed in detail in the context in which a shock wave initially excites phonons.¹ Using numerical simulations, it was found that the rate limiting step for transfer of heat from the phonons to the vibrations is the initial step involving transfer into the lowest frequency vibrational modes, called doorway modes.^{1,11} Once heat has been transferred to the doorway modes (or mode), the vibrational energy redistributes to all vibrational modes of the molecule rapidly compared to the rate of energy flow through the doorway modes into the molecule.¹¹ Furthermore, the diffusion of heat through vibrations is negligible compared to diffusion via phonons.¹² Therefore, the vibrations are described using a vibrational quasitemperature, T_{vib} . At the high temperatures involved in multiphonon up-pumping (above room temperature), the coupling to a doorway mode can be modeled as $\xi(T_{\text{ph}} - T_{\text{vib}})$, where ξ is proportional to the square of the anharmonic coupling matrix element and the phonon-doorway mode joint density of states.¹ ξ can be obtained experimentally.¹

The time dependence of T_{vib} is given by

$$C_p^{\text{vib}} \frac{dT_{\text{vib}}}{dt} = \xi(T_{\text{ph}} - T_{\text{vib}}), \quad (2)$$

where the vibrational heat capacity is

$$C_p^{\text{vib}} = k_B \sum_{i=1}^N \frac{\left(\frac{\phi_i}{T}\right)^2 \exp\left(\frac{\phi_i}{T}\right)}{\left(1 - \exp\left(\frac{\phi_i}{T}\right)\right)^2}. \quad (3)$$

ϕ_i is the characteristic temperature of the i th molecular vibration, and k_B is Boltzmann's constant.

The second path that decreases T_{ph} is diffusive flow of the acoustic phonons away from the crack region. The time and position dependence of T_{ph} are calculated using the diffusion equation

$$C_p^{\text{ph}} \frac{dT_{\text{ph}}}{dt} = -\xi(T_{\text{ph}} - T_{\text{vib}}) + \nabla \cdot [\kappa(T_{\text{ph}}) \nabla T_{\text{ph}}], \quad (4)$$

where $\kappa(T_{\text{ph}})$ is the thermal conductivity.

There are two regimes which can be considered without any simplification of Eqs. (2) and (4): the weak and strong coupling regimes. In the weak coupling regime, the heat diffuses so rapidly that none is transferred to the molecular vibrations. The heat flow of the phonons is simple diffusion. In the strong coupling regime, ξ is very large. The initial excitation of phonons transfers essentially simultaneously to

vibrations, so $T_{\text{ph}} \approx T_{\text{vib}}$. Equation (4) is modified by substituting $C_p^{\text{tot}} = C_p^{\text{ph}} + C_p^{\text{vib}}$ for C_p^{ph} . The value of T_{ph}^m is found by using C_p^{tot} in Eq. (1). This value of T_{ph}^m , in the strong coupling regime, is the maximum temperature attainable for the vibrations for a given initial phonon temperature. The vibrations reach thermal equilibrium with the phonons prior to thermal diffusion out of the crack zone. The heat diffusion in the strong coupling limit is identical to that for weak coupling except with the larger C_p^{tot} .

III. NUMERICAL CALCULATIONS

In the intermediate regime, the phonon and vibrational temperatures are calculated as a function of time using a fourth-order Runge Kutta numerical integration of the coupled Eqs. (2) and (4). The equations were solved for both the linear (fast crack) and radial (slow crack) heat flow geometries. The numerical integration program was verified by checking its agreement with the analytical solutions for simple diffusion from a delta function source at $t=0$ in both the linear and the radial heat flow geometries.¹³ In addition, the multiphonon up-pumping results of Ref. 1 in the absence of phonon diffusion were reproduced.

The calculations illustrate the range of behaviors in the intermediate regime. Various values of T_{ph}^m were used. For the fast crack (linear heat flow), the crack zone is a slab of width 2δ . For radial heat flow, the crack zone is a cylinder of radius δ . For all calculations, a value of $\delta = 3a$, where a is the unit cell dimension, was employed. The values of the phonon-vibration coupling used for the calculations are normalized to a unit thermal conductivity. The length scale is normalized to a unit cell dimension, a . The time scale is normalized to the thermal diffusion time across one unit cell which has the value $\tau_d = a^2 C_p^{\text{ph}} / \kappa$.

The values of C_p^{ph} , C_p^{vib} , and κ for energetic materials, which are necessary for the calculations, are not available. Since energetic materials form molecular crystals, the properties of a well-studied molecular crystal, naphthalene, are used. For the situations under consideration, the phonon temperatures are very high ($T > 1000$ K). The melting point of naphthalene is ≈ 360 K so the measured values of C_p^{ph} and κ for crystalline naphthalene cannot be used directly in this regime. At high temperatures, $T \gg \Theta_D$, where $\Theta_D \approx 180$ K is the Debye temperature of naphthalene crystals,¹⁴ the phonons behave classically. In addition to acoustic phonons, molecular crystals such as naphthalene or C_{60} crystals¹⁵ have optical phonons. Based on the properties of such molecular crystals, a reasonable value of C_p^{ph} is $C_p^{\text{ph}} = 6k_B / V_c \approx 0.36 \text{ J/K cm}^3$, where the prefactor of 6 accounts for the translational and librational degrees of freedom, and $V_c = 2.32 \times 10^{-22} \text{ cm}^3$ is the unit cell volume.¹⁴ The sum of C_p^{ph} estimated above and the naphthalene vibrational heat capacity at 360 K, calculated using Eq. (3), and published vibrational frequencies,¹¹ agree with the measured naphthalene total heat capacity.¹⁶

The thermal conductivity is calculated using the gas kinetic formula $\kappa = c_p v_s \ell / 3$, for each traveling mode, where v_s is the appropriate average speed of sound and ℓ is the phonon mean free path. The value of v_s for the acoustic

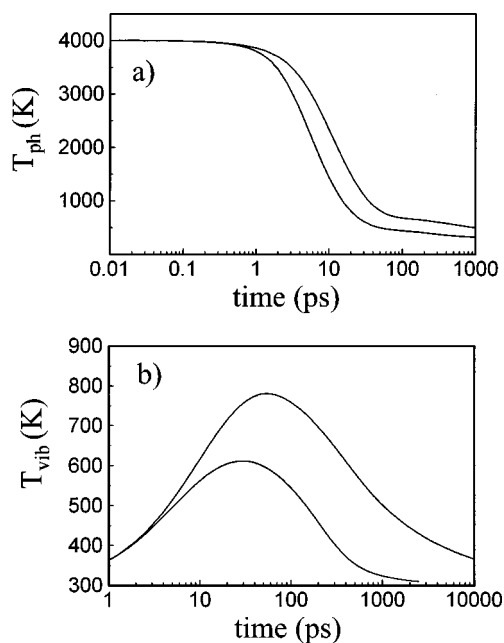


FIG. 2. In each panel the upper curve is for a fast crack and the lower curve is for a slow crack. (a) Phonon quasitemperature, T_{ph} , in the crack zone for an initial phonon quasitemperature of 4000 K. T_{ph} decays because of multiphonon up-pumping and thermal diffusion out of the crack zone. (b) Vibrational quasitemperature, T_{vib} , in the crack zone for an initial phonon quasitemperature of 4000 K. T_{vib} first increases because of multiphonon up-pumping and then decays due to thermal diffusion out of the crack zone. Note the logarithmic time scale.

phonons in naphthalene is taken to be $v_s \approx 2 \times 10^5$ cm/s and for optical modes is $v_s/2 \approx 1 \times 10^5$ cm/s.¹⁴ The phonon mean free path is likely limited by scattering between the acoustic and optical phonons. This gives $\ell \approx a$ where $a \approx 8$ Å is the average lattice constant for naphthalene. Using the above, a value for $\kappa \approx 1.5$ mW/cm-K is obtained.

Using the estimated values of C_p^{ph} and κ , the diffusion time across one unit cell in naphthalene, with an average unit cell length of $a \approx 8$ Å, is $\tau_d \approx 9a/v_s \approx 2.5$ ps. The thermal diffusivity, $D = \kappa/C_p^{ph}$, calculated from the various estimates, gives $D \approx 3 \times 10^{-3}$ cm²/s, which agrees with the measured value.¹⁷ Using constant C_p^{ph} and κ is an assumption in several models of heating near cracks.⁶⁻⁸

Figure 2 displays the phonon (a) and vibrational (b) quasitemperatures at the center of the crack zone as a function of time with $T_{ph}^m = 4000$ K for both fast and slow cracks. (Estimates of T_{ph}^m based on the very limited available experimental data are discussed below. 4000 K is a physically reasonable value.) The vibrational heat capacity and the phonon-vibration coupling ($\xi = 2.7$ J/K-ps-mol) used for these calculations are the values for naphthalene.¹ T_{ph} falls to half its initial value in ~ 20 ps for a fast crack and in ~ 8 ps for a slow crack. The temperature of the phonons relaxes more quickly for a slow crack than for a fast crack. The explanation for this is illustrated in Fig. 1. For the slow crack, the heat diffuses in all directions, since all neighboring regions around the crack zone are at a lower temperature. While in the fast crack, regions parallel to the surface of the crack zone are at high temperature, so the heat diffuses only in a line perpendicular to the plane of the crack zone. It follows

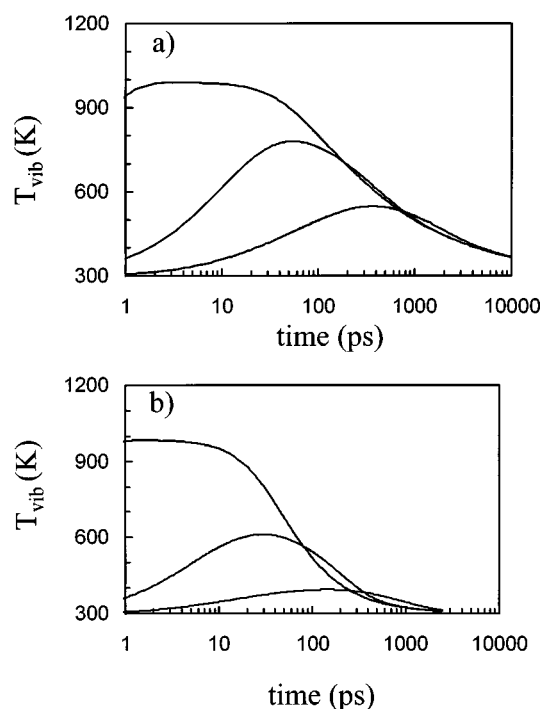


FIG. 3. Vibrational quasitemperature, T_{vib} , in the crack zone for an initial phonon quasitemperature of 4000 K. (a) fast crack, and (b) slow crack. The calculations are for three values of ξ , the phonon-vibration coupling parameter. From top to bottom in each panel: $\xi = 13.5$, 2.7, and 0.27. $\xi = 2.7$ corresponds to the experimentally determined value for naphthalene. For the largest coupling, the phonons and vibrations come into thermal equilibrium prior to significant thermal diffusion, giving rise to the flat region at short times. Note the logarithmic time scale.

that the vibrations in the crack zone for a fast crack reach a higher temperature than for the slow crack [see panel (b)]. The analysis for a fast crack is self consistent, since the time for the crack tip to travel one unit cell, $\tau_{crack} = (1/v_s)a \approx 0.3$ ps, is much less than the phonon relaxation time (20 ps) and the vibrational up-pumping time (50 ps). The crack tip travels ~ 60 unit cells in the time required for the phonon temperature to decrease by half. The vibrational temperature reaches a maximum value of ~ 780 K. This is much lower than the initial phonon temperature, both because the vibrational heat capacity is much larger than the phonon heat capacity, and because thermal diffusion is removing heat from the crack zone. For the fast crack, the vibrational temperature remains high, > 550 K, for a time period ~ 1 ns. The fast crack description should apply when the crack velocity is high enough that the crack propagates many unit cells on the time scale of significant cooling of the crack zone by thermal diffusion. For a crack tip velocity as low as $1/3 V_s$, which may apply to molecular crystals, the fast crack calculation is still applicable. The fast crack and the slow crack are the limiting cases, and the calculations are upper and lower bounds, respectively. In these calculations, the amount of energy released in the crack zone is related to the initial phonon temperature, T_{ph}^m , which is held constant independent of the crack velocity.

The vibrational temperature at the center of the crack zone is shown for three values of ξ in Fig. 3 [fast crack (a) and slow crack (b)]. The middle curves in each panel are

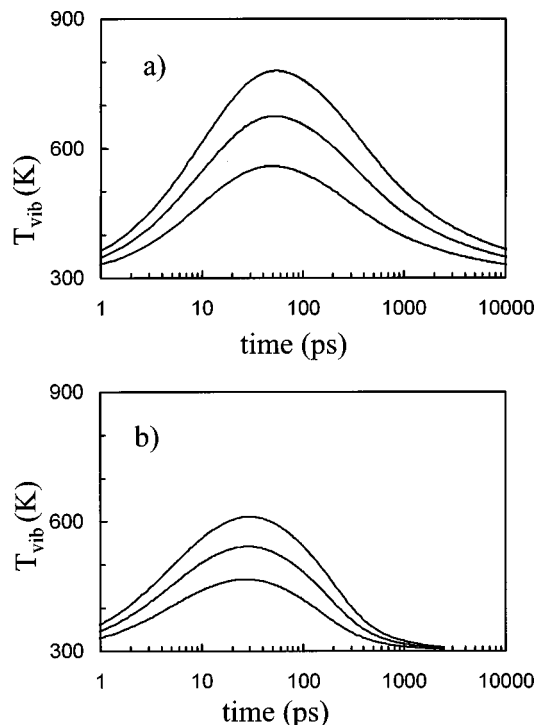


FIG. 4. Vibrational quasitemperature, T_{vib} , in the crack zone for initial phonon quasitemperatures of 4000, 3000, and 2000 K from top to bottom of each panel. (a) fast crack, and (b) slow crack. Note the logarithmic time scale.

calculated with the value of ξ for naphthalene. The upper curves in both panels are the vibrational temperatures for a value of ξ that is five times that of naphthalene. Note that the vibrational temperature reaches a plateau temperature of ~ 980 K very rapidly. This is the equilibrium temperature of the phonons and vibrations calculated for the strong coupling limit. For larger values of ξ , the phonons and vibrations will reach equilibrium even more quickly; however, the maximum temperature remains the same for a given T_{ph}^m . The maximum temperature is determined by T_{ph}^m , and the ratio of C_p^{ph} to C_p^{tot} . Equilibrium is reached prior to significant thermal diffusion out of the crack zone. The temperature then decays at a rate determined by linear thermal diffusion (a) and radial thermal diffusion (b). The lower curves in both panels of Fig. 3 are the vibrational temperatures for a value of ξ a factor of 10 smaller than that for naphthalene. Thermal diffusion is relatively fast compared to the rate of vibrational up-pumping, and the maximum temperature is decreased. Even so, the maximum vibrational temperature for the fast crack, ~ 550 K, is still significantly above the ambient temperature of 300 K and persists for several ns.

Figure 4 shows the vibrational temperature within the crack zone for values of T_{ph}^m ranging from 2000 to 4000 K [fast crack (a); slow crack (b)]. The ξ value for naphthalene is used. As expected, the vibrational temperatures decrease with decreasing initial phonon temperature. The maxima of the vibrational temperatures in the crack zone for fast cracks are always larger than those for slow cracks. For a fast crack there is a significant increase in the vibrational temperature even for a $T_{\text{ph}}^m = 2000$ K.

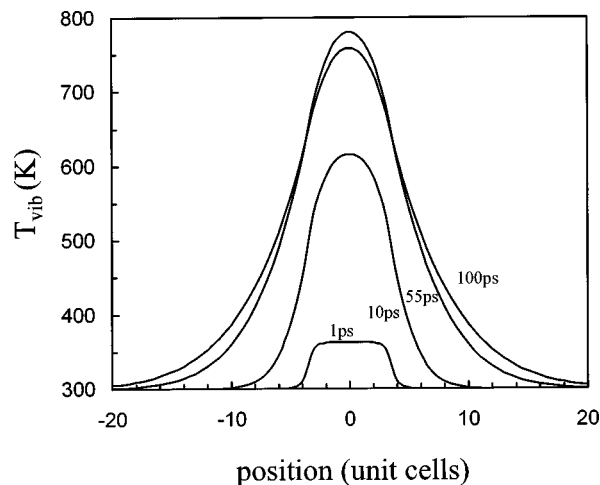


FIG. 5. The vibrational temperature as a function of position about the center of the crack zone at times 1, 10, 55, and 100 ps for an initial phonon quasitemperature of 4000 K and $\xi = 2.7$.

The vibrational temperatures evolve from the initial step function form to a Gaussian form at later times. Figures 5 and 6 display information on the spatial dependence of the T_{vib} as a function of time. In Fig. 5, the spatial distribution of the vibrational quasitemperature is shown at several discrete times ($T_{\text{ph}}^m = 4000$ K; $\xi = 2.7$, the naphthalene coupling parameter; fast crack). The full time dependence of T_{vib} at three positions with respect to the center of the crack is shown in

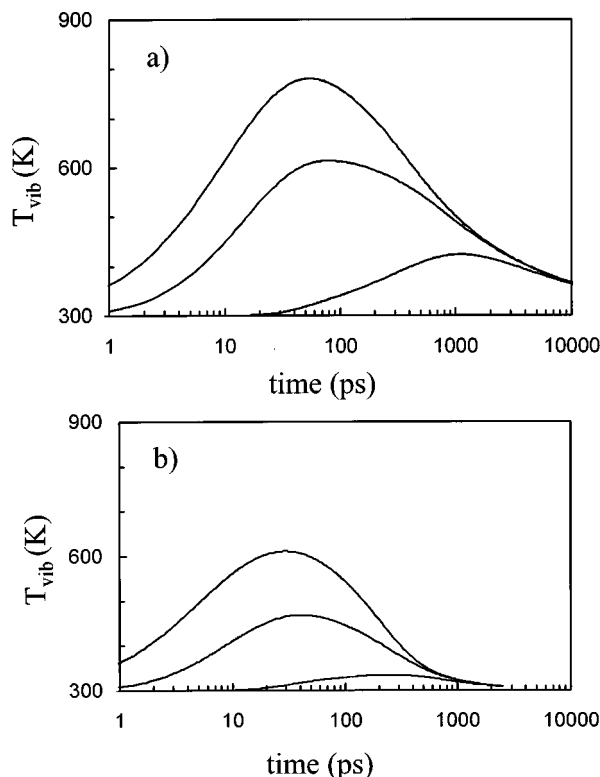


FIG. 6. The vibrational quasitemperature for three positions about the center of the crack zone. From top to bottom in each panel, center of crack zone (0 nm), one unit cell outside of crack zone (3.2 nm), and ten unit cells from center of crack zone (8 nm). The crack zone is three unit cells (2.4 nm) wide. (a) fast crack, and (b) slow crack. Note the logarithmic time scale.

Fig. 6 ($T_{\text{ph}}^m = 4000$ K, $\xi = 2.7$, the naphthalene coupling parameter) for a fast crack in (a) and a slow crack in (b). The curves are shown for the center of the crack zone (top curve), one unit cell past the edge of the crack zone (middle curve), and ten unit cells from the center of the crack zone (bottom curve). As the distance increases from the crack zone, the vibrational temperature reaches a lower maximum value and the maximum is shifted out in time. Up-pumping cannot occur in a region outside of the crack zone until heat has diffused into it, delaying the vibrational temperature rise. Since the heat has expanded into a larger volume and been decreased by vibrational up-pumping in the crack zone, the maximum is reduced.

Initial phonon temperatures are not known for molecular crystals. As discussed above, there have been measurements on several systems. The best estimates of these initial conditions are found by applying the model developed in this paper to the measurements made on carbonates.⁹ From the measured release of CO_2 and measured kinetics of the $\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$, the crack zone temperature was deduced.⁹ Fox *et al.* estimated crack zone temperatures range from 850 K for PbCO_3 (cerrusite), 1250 K for CaCO_3 (calcite), and 15 000 K for MgCO_3 (magnesite).⁹ Since this method measures the production of CO_2 , the deduced temperature is for a situation in which phonon–vibration equilibrium has been achieved.

For the calculations presented here, T_{ph}^m , the initial maximum phonon temperature, is needed. Using the model, the phonon temperature for calcite can be estimated. The vibrational heat capacity was calculated using the vibrational spectrum¹⁸ and Eq. (3). In the strong phonon–vibration coupling limit (no thermal diffusion prior to phonon–vibration equilibration), T_{ph}^m is calculated to be >2200 K. This is a lower bound on the phonon temperature, since the phonons and vibrations equilibrate before any diffuses away from the crack zone. This represents the extreme situation. In the more likely case, in which the vibrational equilibration requires a few tens of ps, thermal diffusion reduces the maximum internal molecular temperature (see Fig. 3). These considerations lead to an estimate of $T_{\text{ph}}^m = 4000$ K. Clearly, experimental measurements on molecular crystals are necessary to determine crack tip temperatures.

IV. CRACK INDUCED REACTIVITY IN ENERGETIC MATERIALS

The results presented above show that a propagating crack can produce a substantial increase in the internal temperature of molecules in and near the crack zone, and that the temperature increase will remain for some time. The question arises as to whether the conditions predicted by the model have implications for the low impact sensitivity of crystals of energetic materials. For crack induced heating to be responsible for energetic material sensitivity, the temperatures, durations, and material volumes that emerge from the calculations must result in a substantial amount of chemical reaction. To determine whether any chemical decomposition of HMX will occur, the analysis of Tokmakoff *et al.*¹ is used along with the chemical kinetic data for HMX. The

TABLE I. The reaction probability, N , within the crack zone for fast and slow cracks for various initial phonon temperatures. HMX reaction rate parameters and the value of ξ , the phonon–vibration coupling parameter for naphthalene, were used in the calculations.

Initial phonon temperature	4000 K	3000 K	2000 K
Fast crack	$N = 0.92$	$N = 0.011$	$N = 2.6 \times 10^{-6}$
Slow crack	$N = 8.6 \times 10^{-4}$	$N = 3 \times 10^{-6}$	$N = 9.4 \times 10^{-10}$

temperature-dependent reaction rate of decomposition of the energetic molecule is described using Arrhenius kinetics,

$$k(T) = \frac{k_B T}{h} \exp[\Delta S^*(0)/R] \exp[-\Delta H^*(0)/RT], \quad (5)$$

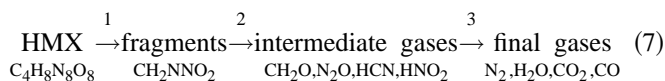
where $\Delta S^*(0)$ is the activation entropy, and $\Delta H^*(0)$ is the enthalpy of activation. For HMX, $\Delta S^*(0) = 128$ J/mol-K and $\Delta H^*(0) = 218$ kJ/mol.¹⁹ The pressure dependence of these quantities is important for pressure changes of the order of several GPa. The effective pressure increases in the crack zone are estimated to be ~ 1 MPa. Therefore, the pressure dependence is not considered. The vibrational temperature, $T_{\text{vib}}(t)$, which is the relevant internal molecular temperature, is large only for a finite duration. Thus, it is necessary to integrate the reaction rate over the time interval, Δt , for which T_{vib} deviates from ambient temperature to determine, N , the reaction probability,

$$N = 1 - \exp\left(-\int_{\Delta t} \frac{k_b T_{\text{vib}}}{h} \exp[\Delta S^*(0)/R] \times \exp[-\Delta H^*(0)/RT_{\text{vib}}] dt\right). \quad (6)$$

$T_{\text{vib}}(t)$ is calculated using Eqs. (2) and (4), which give results such as those shown in Fig. 2(b).

N was calculated for the fast and slow cracks with the ξ for naphthalene and the three initial phonon temperatures used in Fig. 4. The results are summarized in Table I. Given the choice of parameters, the slow crack results in negligible reaction probability. However, for the fast crack, above a $T_{\text{ph}}^m = 3000$ K, the reaction probability becomes significant. For $T_{\text{ph}}^m = 4000$ K, the reaction probability is 92%.

The results in Table I indicate that under the right circumstances, the conditions produced by a propagating crack can be sufficient to cause chemical decomposition of HMX. However, this reaction is endothermic and does not lead directly to heat release that can sustain further chemistry. Tarver *et al.*¹⁰ have used the following three-stage reaction scheme to do detailed modeling of the conditions under which self-sustaining chemistry will occur.



Using this reaction scheme and performing chemical kinetics calculations that included such details as the activation energies, thermal conductivities, and heat capacities, etc., for the various species, Tarver *et al.* were able to reproduce temperature-dependent thermal explosion data for HMX.¹⁰ Their model was also used to calculate critical hot spot

temperatures–size relationships for planar, cylindrical, and spherical shapes.¹⁰ For each geometry, the calculations determine, for a given temperature, the size of the hot spot necessary to produce an explosion. The planar geometry, as is generated by a fast crack, requires slightly lower temperature for a given size for an explosion to occur. However, the calculations of Tarver *et al.* show that for the best case listed in Table I, i.e., a fast crack with a 4000 K initial phonon temperature (~ 800 K peak vibrational temperature), the crack zone is orders of magnitude too narrow and the duration of the temperature rise is too short for an explosion to occur.

V. CONCLUDING REMARKS

The model and results presented above provide insights into the nature of local heating generated by cracking of crystals. Small impacts inducing cracks or even spontaneous cracking can lead to sufficient heat release to produce chemical reactions. In primary explosives, such cracking may be sufficient to cause detonation. However, the results presented above demonstrate that a single crack in an otherwise perfect crystal of a secondary explosive, such as HMX, will not generate a hot spot that is large enough or sufficiently high in temperature to produce an explosion.

Nonetheless, it is possible that cracking can play a role in the sensitivity of secondary energetic materials. First, if a large number of closely spaced cracks are simultaneously produced, then the situation will be somewhat different. Rather than thermal diffusion taking heat from a crack zone into a cold bulk material, the surrounding region will be at a high temperature because of heat flow from other cracks. The result will be a larger region that remains hot for a longer period of time than in the case of a single crack. A high density of cracks might be produced if a crystal is crushed. However, unless the initial phonon temperatures are much higher than those estimated above, the maximum temperatures reached are unchanged even with multiple cracks.

Perhaps a more significant role for cracks in generating sensitivity is the production of chemical decomposition products. As discussed in Sec. IV, the temperatures and durations of elevated temperature generated by a single crack can be sufficient to produce some chemical decomposition of HMX. Thus cracking may seed an energetic material with chemical decomposition products as in step 1 of Eq. (7). In the region around the crack, there may be a significant concentration of molecular fragments. Reaction of the fragments has a smaller ΔH than HMX, is weakly exothermic, and leads to products with highly exothermic reactions.¹⁰ Thus cracking may leave behind a chemical environment that is primed to exaggerate the effect of a subsequent shock that otherwise might be of insufficient magnitude to produce extensive exothermic chemistry. In addition, the decomposition fragments will disrupt the lattice, producing a large number of defects. It has been proposed that such local defects can influence the anharmonic coupling between phonons and vibrations, and generate hot spots under mild shock conditions.¹

If the production of decomposition fragments by cracking does enhance sensitivity, the model presented above may also provide a way to explain differences in sensitivity for

seemingly very similar materials. In the treatment of shock induced multiphonon up-pumping applied to a perfect crystal,¹ the phonon-vibration coupling parameter, ξ , determines the rate of up-pumping for given initial conditions. A larger value of ξ leads to faster up-pumping. The time scale for up-pumping for moderate shocks was found to be ~ 30 ps, and following the up-pumping, the shocked region stays hot for a long time period. Faster up-pumping does not necessarily lead to a greater probability of shock induced chemistry and detonation since the relevant chemistry occurs on much longer time scales than the up-pumping. Within the context of the multiphonon up-pumping model of Ref. 1, the magnitudes of the phonon–vibration anharmonic coupling matrix elements and the joint density of states do not determine reaction probability. The final temperature obtained once the vibrations and the phonons have equilibrated, and the density, determine the reaction probability, not differences of a few tens of ps in the time required to reach equilibrium.

However, the situation is quite different for crack induced up-pumping. Since the heat is released in the narrow crack zone, there is a competition between up-pumping and thermal diffusion out of the zone. If ξ is large, up-pumping occurs before local cooling by thermal diffusion, and high internal molecular temperatures are reached. If ξ is small, up-pumping is slow compared to thermal diffusion, and the increase in molecular temperatures is not significant. This is illustrated in Fig. 3. Thus, the competition between up-pumping and diffusion will determine the extent to which a crack produces chemical decomposition, which may enhance sensitivity. In addition, the nature of the crystals a compound forms, or the manner in which a material is processed, could influence its tendency to crack and the nature of the cracks, and, therefore, influence sensitivity.

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