A Double Front Structure of Detonation Wave as the Effect of Phase Transitions

Sergey B. Victorov, Sergey A. Gubin

Moscow Engineering Physics Institute (State University)

31 Kashirskoe chaussee, Moscow 115409, Russia

E-mail: sb_victorov@mtu-net.ru

We show that phase transitions, if they occur in the detonation products, can strongly affect the detonation parameters and may cause an unusual regime of the steady detonation that we called an anomalous mode of detonation. This detonation regime has a variety of inherent features, e.g., the failure of the Chapman–Jouguet condition, an unusual behavior of the dependencies of D and P on initial charge density, and so on. The most interesting peculiarity appears to be the presence of the sonic plane within a rarefaction wave. The latter feature makes it possible to explain, e.g., contradictory experimental data on the CJ pressure and the length of the reaction zone for TNT. Our calculations predict that the anomalous regime of detonation occurs for many carbon-rich explosives due to the graphite-to-diamond transition. Most of the conclusions seem to be also correct for the anomalous detonations caused by distinctly different phase transitions. We believe that the anomalous detonation is a popular phenomenon and may occur due to phase transitions of various species.

Key words: double-front detonation, thermodynamic modeling, intermolecular potentials, phase transition

Detonation products are complex multicomponent mixtures that may exhibit various chemical transformations including phase transitions. Using our thermochemical TDS code, in this work we show that the phase transitions can strongly affect both the detonation parameters and the structure of a detonation wave, and may cause an unusual regime of the steady detonation that we called an anomalous mode of detonation.

Thermodynamic properties of the fluid detonation products are computed from a theoretical equation of state (EOS) based on Exp-6 intermolecular potentials and the HMSA integral equations for pair distribution functions of Zerah and Hansen [1] that accurately reproduce Monte Carlo and molecular dynamics simulations. The graphite and diamond nanoparticles are treated with our semi-empirical model [2] that takes into account the effect of the small size of carbon particles on their thermodynamics.

If phase transitions occur in the detonation products behind the detonation front, the entropy along the reactive Hugoniot may have multiple local minima, and the CJ condition $D–u=c$ may become illegal because of a possible break in the sound velocity caused by the phase transitions. To determine the global minimum of entropy, it is necessary to locate and compute all the local minima that lie on the Hugoniot. Thermochemical codes that employ the Newton–Raphson or similar techniques usually fail in solving such a problem due to both the multiple minima and a break in some thermodynamic derivatives because of phase transitions. For this reason, we have developed and incorporated into the TDS code a special numerical solver for detonation problems. This solver guarantees that all local minima of the entropy along the reactive Hugoniot will be found so that the global entropy minimum will be correctly determined.

Such a situation with several minima of entropy along the reactive Hugoniot is typical, e.g., for carbon-rich HE whose detonation produces the nanoparticles of the condensed carbon that may change their phase state behind the detonation front. So, our calculations show that many carbon-rich explosives have a range of their initial densities, ρ_0, where the entropy of detonation products, S, has a double minimum along the reactive Hugoniot because of the graphite-to-diamond transition.

A good example is TNT, whose reactive Hugoniot at initial density $\rho_0 = 1.62$ g/cm^3 is plotted in Fig. 1. Figure 1(a) represents a S-vs-ρ plot, where ρ is density of the products. The Mach number $M=(D–u)/c$ is shown in Fig. 1(b) as a M-vs-ρ plot. At densities $\rho < \rho_B$, i.e. to the left of the point "B", the condensed products are the graphite nanoparticles only. The graphite-to-diamond transition is started at the point “B” and, at densities $\rho_B < \rho < \rho_C$, i.e. within the region between the points “B” and “C”, both phases of the condensed carbon are present in the products. The phase transition is completed at the point “C” and, at densities $\rho > \rho_C$, the condensed products consist of the diamond nanoparticles only. It is seen that there are two minima of entropy, the points “A” and “C” in Fig. 1(a). The point “A” is a usual “smooth” local minimum and all the three conditions of the steady detonation, namely, S=min, D=min, and $D–u=c$ are satisfied at this point. Since the second local minimum of entropy, i.e. the point “C”, corresponds to the end of the phase transition, at this point there is a break in some thermodynamic derivatives including the sound velocity. The latter is considerably lower within the transition region when both phases of carbon coexist. As a consequence, the Mach number is greater than 1 to the left of the point “C” and $M < 1$ to the right of this point as seen in Fig. 1(b). Thus, the CJ condition $D–u=c$ is not satisfied at the point “C”.

At initial TNT densities $\rho_0 < 1.55$ g/cm^3, the point “A” is the global minimum of entropy along the reactive Hugoniot because $S_A < S_C$. Hence, the point “A” is the CJ point for TNT at $\rho_0 < 1.55$ g/cm^3 and detonation occurs classically in the CJ mode, and the graphite nanoparticles are produced at the CJ point. At initial densities $\rho_0 > 1.55$ g/cm^3, however, the global minimum of entropy moves from the point “A” to the point “C”, i.e. now S_C becomes lower than S_A as shown in Fig. 1(a) for $\rho_0 = 1.62$ g/cm^3. The CJ condition $D–u=c$ is not satisfied at the point “C” as discussed above and shown in Fig. 1(b). Nevertheless, within the framework of an ideal detonation theory that assumes the S=min condition to be the criterion of the steady detonation, this point should be considered as a pseudo-CJ point. It determines all the detonation parameters behind the detonation front including the detonation velocity. Thus, point “C” is the CJ point for TNT detonations at $\rho_0 > 1.55$ g/cm^3, the condensed detonation products consist of the diamond nanoparticles at the CJ state and the diamond-to-graphite transition is started immediately behind the CJ plane as the products expand. We called this pseudo-steady detonation mode, which is caused by phase transitions and has a number of unusual special features, including the failure of the CJ condition $D–u=c$, an anomalous mode of detonation [5].

The calculated detonation velocities of TNT are in excellent agreement with the experimental data over a wide range of initial TNT densities as seen in Fig. 2(a). Both the computed and measured D-vs-ρ_0 curves have a break in slope at $\rho_0 = 1.55$ g/cm^3, when the CJ mode, as theoretically predicted, is replaced with the anomalous regime. Furthermore, the shape of the computed curve at $\rho_0 > 1.55$ g/cm^3 accurately reproduces the shape of the experimental D-vs-ρ_0 dependence that was approximated by Urisar as quadratic in ρ_0.

Figure 2(b) represents the computed and measured detonation pressures of TNT versus the initial density. The theoretical pressures are in good agreement with the experimental data at $\rho_0 < 1.55$ g/cm^3 when the calculations predict the classical CJ detonation. Furthermore, at $\rho_0 = 1.64$ g/cm^3 the calculated pressure of the anomalous detonation $P_{CJ} = 22.3$ GPa is practically equal to the value of 22 GPa measured by Schefield et al. [6]. At $\rho_0 = 1.55$ g/cm^3 the computed P_{CJ}-vs-ρ_0 dependence has a break and then, within the region of the anomalous detonation, the theoretical P_{CJ} exhibits an unusual behavior, the pressure decreases with increasing ρ_0 [see the solid line in Fig. 2(b)]. However, such a behavior of the theoretical P_{CJ}-vs-ρ_0 plot is contrary to the experimental data of Dremin et al. [7], who report that, as it usually is, the pressure grows almost linearly with increasing ρ_0 over entire range of initial densities including the region $\rho_0 > 1.55$ g/cm^3. The computed pressures lie well above the values of Dremin et al. at $\rho_0 > 1.55$ g/cm^3 as seen in Fig. 2(b). This qualitative and quantitative disagreement in the theoretical and experimental P_{CJ}-vs-ρ_0 dependencies, however, should not be considered as poor predictive ability of the anomalous detonation model. That will be seen below where we describe one more interesting feature of the anomalous detonation, namely, an unusual structure of a rarefaction wave. It will be shown there that the model of the anomalous detonation yields theoretical pressures that agree with both experimental results [6] and [7].

Our calculations show that the graphite-to-diamond transition causes the anomalous mode of detonation for a number of carbon-rich HE. For some of these explosives there are experimental detonation velocities that confirm the presence of a break in the D-vs-ρ_0 slope. The TDS code, using the model of the anomalous detonation and the EOS described above, generally predicts the detonation parameters in good agreement with the experimental data including the location of a break in the D-vs-ρ_0 slope in the ρ_0–axis. As an example, Fig. 3(a) represents the computed and measured D-vs-ρ_0 plots for HNS. The anomalous detonation is predicted to occur at initial HNS densities $\rho_0 > 1.60$ g/cm^3. The graphite-to-diamond transition may also cause the anomalous detonation for carbon-poor explosives. However, since their detonations can produce just small amounts of the condensed carbon in the products, the anomalous mode takes place in a narrow range of initial densities and the corresponding break in the D-vs-ρ_0 slope is almost indistinguishable. An example is given in Fig. 3(b) for RDX. Its detonations are predicted to be anomalous just at initial densities $1.50 < \rho_0 < 1.56$ g/cm^3.

Among the special features of the anomalous detonation, e.g., the failure of the CJ condition, a break in the D-vs-ρ_0 slope, a decrease of P_{CJ} with increasing ρ_0, and so on, there is one more interesting peculiarity concerning a rarefaction wave. In the classical case that no phase transitions occur in the detonation products, the Mach number exhibits a monotonous increasing from the value of 1 at the CJ point as the products expand. The reason is that, on the one hand, the mass velocity grows and, on the other hand, the sound velocity decreases with reducing the pressure. In the case of the anomalous detonation, the phase transition, which is started immediately behind the CJ plane, strongly affects the sound velocity and, hence, M. As discussed above, the Mach number has a break at the CJ point, it is lower than 1 at the CJ state and greater than unity immediately behind the CJ plane. The condition $M > 1$ is satisfied over entire region of the phase transition, the Mach number grows here with expanding the detonation products. However, there is a break in the sound velocity and in M at the end of the phase transition. The sound velocity considerably increases at this point, the Mach number respectively decreases and its value may become less than 1. As the products continue their expansion from the state at the end of the phase transition, the Mach number monotonously grows due to the usual reasons. Hence, as the products expand, there will be a point of the rarefaction wave where M=1. Then the Mach number continues to grow and is greater than unity as it usually is behind the CJ plane in the classical case. In this work we describe a thermodynamic method of searching the location of the second sonic plane. The method is as accurate as hydrodynamic simulations usually used to compute the parameters of rarefaction waves.

We find that the described behavior of the Mach number behind the CJ plane takes place for the anomalous detonations caused by the graphite-to-diamond transition. Thus, all the investigated carbon-containing HE, whose detonation occurs in the anomalous mode, have the sonic plane within the rarefaction wave, i.e. the plane where the Mach number is equal to unity. This may also be the case for aluminized explosives due to the Al_2O_3 melting [4]. The presence of the sonic plane within the rarefaction wave appears to be a common special feature of the anomalous detonations.

Our hydrodynamic simulation [3] of the structure of the rarefaction wave for TNT detonation products shows that the profiles of the mass velocity and pressure have an inherent bend at the location of the sonic plane. The shape of this bend is similar to that of a profile bend generally corresponding to the CJ point of the classical detonation. That is why such a bend in the experimental mass velocity profile may be easily recognized as the CJ point, though the true CJ state of the anomalous detonation lies at a higher pressure as discussed above. It would be interesting to know whether a theoretical mass velocity profile obtained from hydrodynamic simulations has a bend at the true non-sonic CJ point and how the bend shape looks like. It is our preliminary opinion that this bend may be distinguishable to a lesser extent than the clearly visible second bend corresponding to the sonic plane within the rarefaction wave. Further theoretical investigations are to be done to exactly solve whether or not the whole complex including the CJ plane and the sonic one is stationary. The simulations [3] show that the parameters at the sonic plane are constant in time and the distance between the CJ plane and the sonic one varies with time only slightly. We currently consider the complex as pseudo-stationary and are working on the mentioned problems.

We believe that the experimental data [7] on P_{CJ} for TNT at $\rho_0 > 1.55$ g/cm^3 give the pressure at the sonic plane rather than the pressure at the true non-sonic CJ point. To check out this assumption, we have computed the corresponding P_{S}-vs-ρ_0 dependence, where P_{S} is the pressure at the sonic plane within the rarefaction wave. The obtained P_{S}-vs-ρ_0 plot is shown in Fig. 2(b) as a dashed line. The results agree with the measured pressures both qualitatively and quantitatively. The calculated P_{S}

grows with increasing the initial density in contrast to the behavior of theoretical P_{CJ}. The values of P_{S} are about 20–35% less than the calculated P_{CJ} and lie well within the experimental uncertainties. Thus, the pressures measured in [7] are very likely to be the P_{S} rather than the true P_{CJ}. The experimental pressure of Schefield et al. [6] shown as a filled rectangle in Fig. 2(b) is in excellent agreement with the computed P_{CJ} and may probably be the true CJ pressure.

There is one more experimental result obtained in [6] and [7], which strengthens the case for the assumption that the pressures [7] correspond to the sonic plane within the rarefaction wave. That is the length of the reaction zone. The value of Schefield et al. is 0.55 mm (80 ns) at $\rho_0 = 1.64$ g/cm^3. The result of Dremin et al. is significantly higher, 1.27 mm (260 ns), at rather close initial density of 1.62 g/cm^3. The latter result may be the total length of the reaction zone and the region between the CJ plane and the sonic one. Dremin et al. have also given a dependence of the reaction zone length on the initial density. At densities $0.8 < \rho_0 < 1.59$ g/cm^3 this dependence exhibits the general tendency for a decrease of the reaction zone length with increasing ρ_0. However, the result at 1.62 g/cm^3 suddenly becomes about 30% higher than the value of 0.97 mm (200 ns) measured at $\rho_0 = 1.59$ g/cm^3. This appears to confirm that the high-density data [7] correspond to the predicted sonic plane located within the rarefaction wave rather than to the true CJ plane. Thus, we conclude that though the data on the CJ pressure and the length of the reaction zone obtained by Schefield et al. and by Dremin et al. differ from each other considerably, both the experimental results agree well with the model of the anomalous detonation.

It is appropriate to mention here that in our earlier papers on the anomalous detonation (see, e.g. [5]) we employed distinctly different EOS, e.g. the semi-empirical BKW EOS for fluids and very simple EOS for the graphite and diamond. In this work we use much more sophisticated EOS for both fluids and solids and it comes as no surprise that now there is much better quantitative agreement with the experimental data. However, the basic features of the anomalous detonation are qualitatively the same as previously. Thus, the qualitative special features of the anomalous detonation seem to be invariant with EOS. All the examples in this work are given for the case of the graphite-to-diamond transition, which is predicted to occur in the detonation products of many carbon-rich HE. However, the carbon should not be considered as the only species whose phase transitions cause the anomalous mode of detonation. For example, the recent work [4] assumes that this regime might be the case for aluminized explosives due to the Al_2O_3 melting. We believe that the anomalous detonation with all its special features is "the rule rather than the exception" and may be caused by phase transitions of various species.

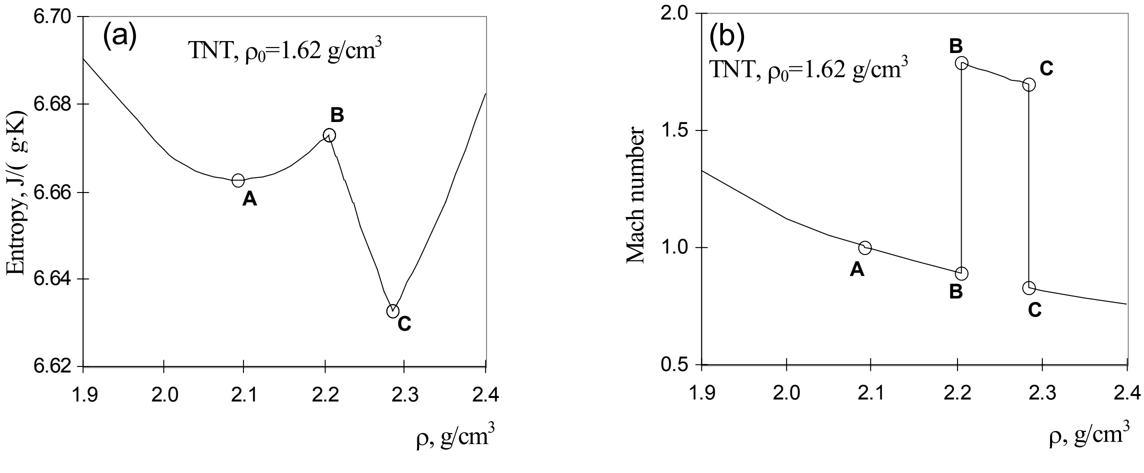

Fig. 1. Entropy of products [(1a)] and the Mach number, $(D–u)/c$, [(1b)] along the reactive Hugoniot of TNT at $\rho_0 = 1.62$ g/cm^3. The points "A" and "C" are two minima of entropy. The points "B" and "C" correspond to the beginning and the end of the graphite-to-diamond transition, respectively. The CJ condition $D–u=c$ is satisfied at the point "A" only.

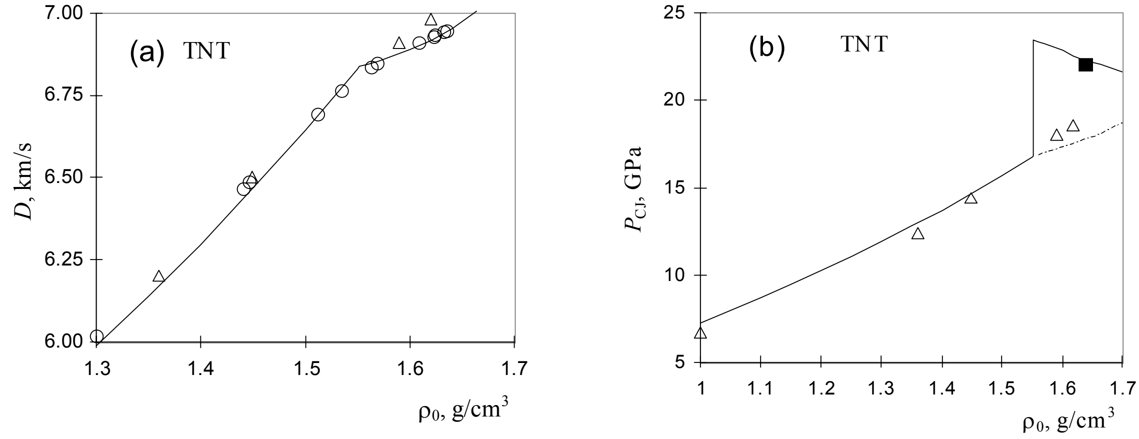

Fig. 2. Detonation velocity [(2a)] and the CJ pressure [(2b)] of TNT. The lines are our calculations, the symbols are the measured values. The dashed line in [(2b)] shows the calculated pressures at the sonic plane within a rarefaction wave (see the text).

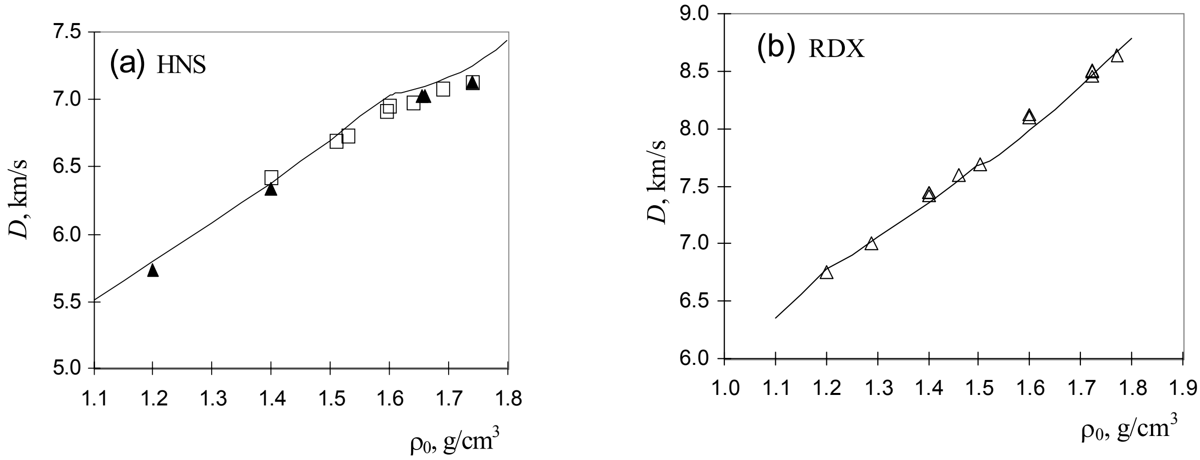

Fig. 3. Detonation velocity of HNS [3(a)] and RDX [3(b)]. The lines are our calculations, the symbols are the measured values. The anomalous mode of detonation is predicted to occur at initial densities $\rho_0 > 1.60$ g/cm^3 for HNS and at $1.50 < \rho_0 < 1.56$ g/cm^3 for RDX.

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