TRANSPORT PROPERTIES OF FLUID MIXTURES AT HIGH PRESSURES AND TEMPERATURES. APPLICATION TO THE DETONATION PRODUCTS OF HMX

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The detonation of modern high explosives (HE) leaves behind a mixture of fluid and dispersed solid phases at high pressures and temperatures. The last decades have witnessed tremendous progress in the equation of state modeling of fluid mixtures and mixed phases, that has been already successfully applied to the prediction of HE detonation properties [1]. The calculation of transport properties on the other hand, e.g. viscosity and thermal conductivity, has advanced at a much slower pace due to inherent theoretical and computational difficulties. We show here, with the help of molecular dynamics simulations, that the Enskog transport theory can be successfully used to predict the viscosity and thermal conductivity of realistically modeled hot, dense fluid mixtures, such as those obtained after the detonation of HMX ($C_4H_8N_8O_8$). We also analyze the effect of the resulting carbon clusters on the transport properties of the post-detonation multiphase system, and find that their contribution is very significant.

INTRODUCTION

The detonation of condensed CHNO explosives, i.e. those containing mostly C, H, N and O, results in a mixture of many chemical species in one or more fluid phases and a condensed carbon phase usually in the form of small, dispersed clusters. The temperature and pressure dependent composition of the detonation mixture can be reliably determined in a statistical mechanics framework by minimizing the Gibbs free energy - $G(P, T, \{n_i\})$ - of the multi-component, multiphase system over the space of all possible species concentrations $\{n_i\}$, consistent with the stoichiometric constraints [1]. This approach

has been proved to yield reliable equations of state (EOS) and detonation properties, e.g. detonation velocity D, for many frequently used explosives [1]. The EOS is a crucial ingredient in the hydrodynamic performance study of high explosive, but the transport coefficients, e.g. thermal conductivity and viscosity, also play a very important role in the complete hydrodynamic modeling, in particular in the high temperature and high pressure regions.

The most important chemical species present after detonation in the fluid phases are typically N_2, H_2O, CO_2, CO, with others like H_2, NH_3 etc. usually present in much smaller concentrations. Once reliable interaction potentials between these

molecular products are determined using experimental data and theoretical approaches [1-3], generally in *exp-6* form,

$$V(r) = \frac{\varepsilon}{\alpha - 6}\left\{6\exp[\alpha(1 - r/r_0)] - \alpha(r_0/r)^6\right\}$$

the thermodynamic properties of the fluid phases can be accurately predicted [1-6]. Although purely isotropic, these potentials are good representations of the effective molecular interactions at high temperatures and pressures [7,8]. Here we test the use of realistic *exp-6* intermolecular potentials in an adapted, effective hard sphere diameter Enskog mixture theory to also predict the thermal conductivity and viscosity of hot, dense mixed fluids.

The determination of the equation of state of detonation products is generally complicated by the slow release of energy due to the coagulation and phase transformation kinetics of the excess carbon, [9-13], in particular for carbon-rich explosives such as TNT and TATB. In the present work we focus on HMX ($C_4H_8N_8O_8$), which is a widely used, relatively ideal explosive with a fairly low carbon content. While we do not discuss here the kinetic effects, we analyze the effect of the carbon clusters on the transport properties of the post-detonated multiphase system.

MOLECULAR DYNAMICS SIMU-LATIONS

The composition of the HMX detonation products is calculated using a statistical mechanics theory embodied in the chemical equilibrium code *CHEQ* [1] along the Chapman-Jouguet (CJ) isentrope and the *T=4000K* isotherm. We show for example in Fig. 1 the resulting detonation products on the CJ adiabat as a function of pressure (the temperatures vary between 2300K to

4200K). The major chemical species present in the fluid mixture are N_2, CO_2, CO, H_2O, H_2 and NH_3, which at higher pressures are separated into nitrogen-rich and water-rich fluid phases [6]. Using the calculated compositions we perform extensive molecular dynamics (MD) simulations with the same *exp-6* potentials as those used in the chemical equilibrium calculation and at the calculated thermodynamic conditions. They allow us to determine the appropriate time-correlation functions of the Green-Kubo theory, that we use to evaluate the shear viscosity and thermal conductivity of the two fluid phases.
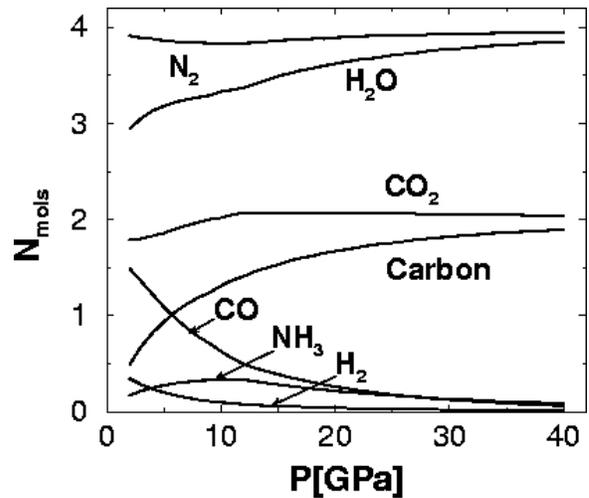

FIGURE 1. DETONATION PRODUCTS OF HMX ALONG THE CJ ISENTROPE

To be specific, we calculate the microscopic stress tensor σ and energy current J^E,

$$\sigma_{xz}(t) = \sum_i [m_i v_{ix}(t)v_{iz}(t) + z_i(t)F_{ix}(t)]$$

$$J_z^E(t) = \sum_i v_{iz}(t)\left\{\frac{1}{2}m_i \mathbf{v}_i^2(t) + \frac{1}{2}\sum_{j \neq i} V_{ij}[r_{ij}(t)]\right\}$$

$$+ \frac{1}{2}\sum_i \sum_{j \neq i}[z_i(t) - z_j(t)]\mathbf{v}_i(t) \cdot \mathbf{F}_{ij}(t)$$

which yield the shear viscosity η and thermal conductivity λ through the Green-Kubo formalism [14]:

$$\eta = \lim_{t \to \infty} \eta(t)$$

$$\eta(t) = \frac{1}{V k_B T} \int_0^t \langle \sigma_{xz}(0) \sigma_{xz}(\tau) \rangle d\tau$$

$$\lambda = \lim_{t \to \infty} \lambda(t)$$

$$\lambda(t) = \frac{1}{V k_B T^2} \int_0^t \langle J_z^E(0) J_z^E(\tau) \rangle d\tau$$
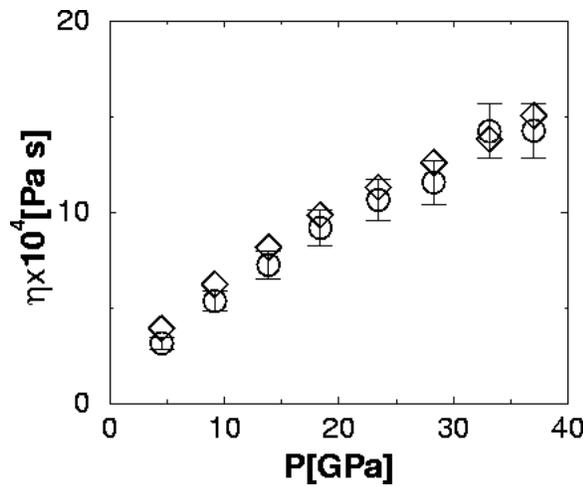

FIGURE 2. VISCOSITY OF THE H₂O-RICH PHASE ALONG THE CJ ISENTROPE: MD SIMULATIONS (CIRCLES) AND EFFECTIVE DIAMETER ENSKOG THEORY (DIAMONDS).

The MD simulations were performed in the microcanonical (NVE) ensemble with the total linear momentum set to zero, with systems of 500 to 864 molecules. The typical running times were very long, of the order of 10 million time steps, which is generally necessary for the accurate determination of transport coefficients using the equilibrium time correlation functions approach [14-16].
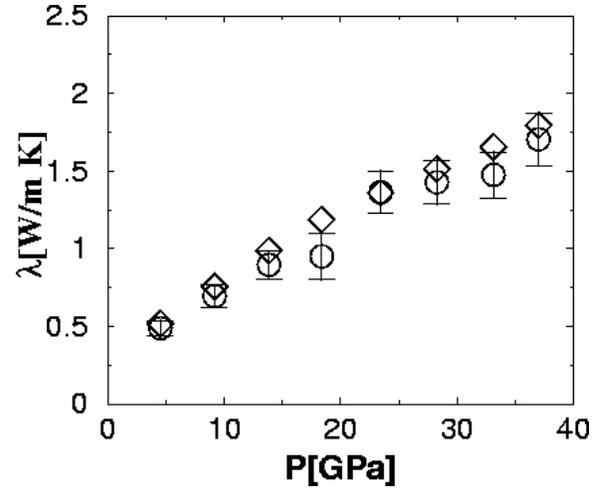

FIGURE 3. THERMAL CONDUC-TIVITY OF THE H₂O-RICH PHASE ALONG THE CJ ISENTROPE: MD SIMULATIONS (CIRCLES) AND EFFECTIVE DIAMETER ENSKOG THEORY (DIAMONDS).

We show in Fig. 1 and Fig. 2 the viscosity and thermal conductivity of the H2O-rich phase and in Fig. 3 and Fig. 4 the results for the N2-rich phase as a function of pressure.
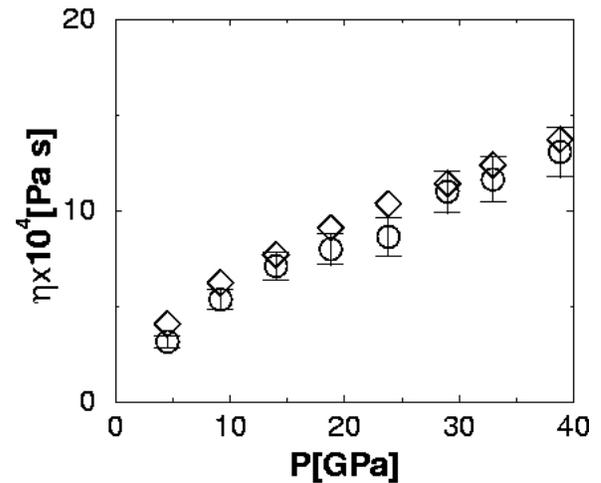

FIGURE 4. VISCOSITY OF THE N₂-RICH PHASE ALONG THE CJ ISENTROPE: MD SIMULATIONS (CIRCLES) AND EFFECTIVE DIAMETER ENSKOG THEORY (DIAMONDS).
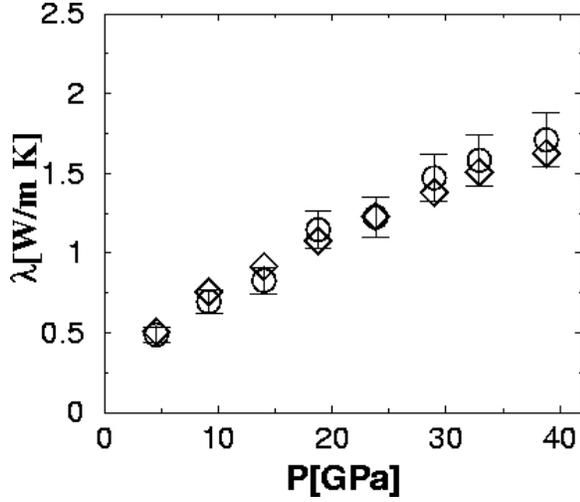
FIGURE 5. THERMAL CONDUC-TIVITY OF THE N$_2$-RICH PHASE ALONG THE CJ ISENTROPE: MD SIMULATIONS (CIRCLES) AND EFFECTIVE DIAMETER ENSKOG THEORY (DIAMONDS).

We note that no long time corrections to the time correlation functions have been included in the transport coefficients calculation. While possible for hard sphere mixtures [14], this would be difficult to do in a reasonable, reliable way for the complicated system that we are studying. We estimate however that the errors in the determined transport coefficients are approximately 10%.

EFFECTIVE DIAMETER ENSKOG THEORY

The hydrodynamics of hard sphere mixtures, and by extension that of fluid mixtures at high densities, is well described by the Enskog theory [17]. The Enskog treatment has a sound physical basis, has been carefully tested by MD simulations [14-16], and the domain of its validity and its limitations are now well understood. In the following we use therefore the predictions of the Enskog formalism to determine the shear viscosity and thermal conductivity of the fluid mixtures and compare with the MD simulation results. We believe that this method holds better promise than the numerous empirical approaches that are currently available and being used in engineering applications [18,19].

Because the fluid mixtures that we are interested in consist of molecules interacting through realistic, *exp-6* potentials, and not hard cores, the original Enskog theory needs to be adapted to account for these soft interactions. The usual modifications fall under the heading of modified Enskog theories (MET) [20], and are essentially based on identifying the "thermal pressure" of the real system, $T\left(\dfrac{\partial p}{\partial T}\right)_\rho$, with that of a hard sphere fluid. These modifications have been successfully tested for pure fluids and mixtures close to normal conditions of pressure and temperature [20,21]. However, as pointed out by Karkheck and Stell [22,23], MET is plagued by physical consistency problems, and cannot be expected to work at high densities. They proposed instead the use of effective hard sphere diameters in the original Enskog theory. These effective diameters can be determined in either perturbative or variational statistical mechanics treatments of fluids [22-24], with the variational approach being in general the more promising one.

We quote the results of the Enskog theory for the viscosity and thermal conductivity of a mixture of hard spheres [14,17]:

$$\eta = \frac{k_B T}{2}\sum_i \frac{K_i' n_i}{n} b_0^{(i)} +$$
$$\frac{4}{15}\sum_i\sum_j\left(\frac{2\pi k_B T m_i m_j}{m_i+m_j}\right)^{1/2} n_i n_j d_{ij}^4 \chi_{ij}^c \qquad (1)$$

$$\lambda = \frac{5k_B}{4}\sum_i \frac{K_i n_i}{n}\left[a_1^{(i)} - \frac{5}{2}\sum_j \frac{K_j'' n_j}{n} d_{i,1}^{(j)}\right]$$

$$+ \frac{4k_B}{3}\sum_i \sum_j \left(\frac{2\pi k_B T m_i m_j}{m_i + m_j}\right)^{1/2} \frac{n_i n_j d_{ij}^4 \chi_{ij}^c}{m_i + m_j} \quad (2)$$

$$+ \frac{25k_B}{8}\sum_i \frac{K_i'' n_i}{n}\sum_j \frac{n_j}{n}\left[K_j'' d_{j,0}^{(i)} - K_j d_{j,1}^{(i)}\right]$$

$$K_i = 1 + \frac{12}{5}\sum_j b_{ij} \frac{m_i m_j}{(m_i + m_j)^2}\chi_{ij}^c$$

$$K_i' = 1 + \frac{4}{5}\sum_j b_{ij} \frac{m_j}{m_i + m_j}\chi_{ij}^c$$

$$K_i'' = 1 + \frac{4}{5}\sum_j b_{ij} \frac{m_i}{m_i + m_j}\chi_{ij}^c$$

$$b_{ij} = \frac{2\pi n_j d_{ij}^3}{3}$$

In the above n_i are the number densities of the molecular components, n is the total number density, d_{ij} are the hard sphere diameters for the interaction between the i and j molecules, χ_{ij}^c are the corresponding contact values of the pair correlations functions and a, b, and d are Sonine polynomials coefficients [17]. These relations will be adapted as described below to predict the viscosity and thermal conductivity of the system that we are studying [25].

Due to the high complexity of the mixtures resulting after detonation a Van der Waals one-fluid treatment has been adopted in [1] and has proved to be successful in predicting the fluid thermodynamics. In this approach a mixture is represented by a pure fluid with all molecules interacting through an effective *exp-6* potential that depends on interactions between all components and also concentrations [5]. The molecular masses are irrelevant for the thermodynamics (in the classical regime relevant here), but they do however enter the prediction of transport coefficients.
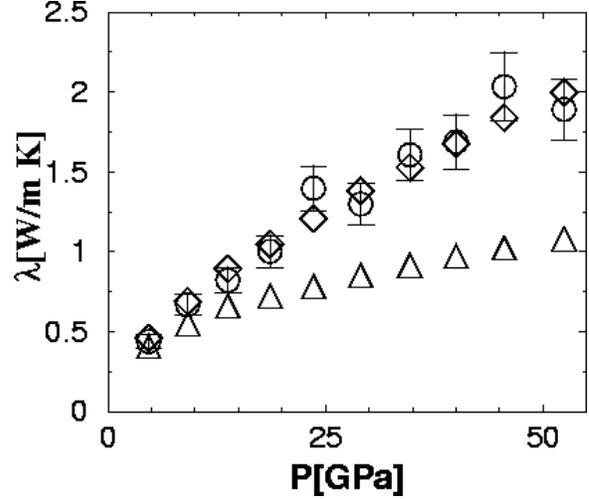

FIGURE 6. THERMAL CONDUC-TIVITY OF THE N2-RICH PHASE ALONG THE 4000K ISOTHERM: MD SIMULATIONS (CIRCLES), EFFEC-TIVE DIAMETER ENSKOG THEORY (DIAMONDS), MODIFIED ENSKOG THEORY (TRIANGLES).

We apply therefore the Enskog mixture theory, relations (1) and (2), in the same one-fluid context as far as the interactions are concerned, but keep the full mass description for all molecular components. This is consistent with and takes advantage of the simplicity of the equilibrium thermodynamic theory, which yields a single effective hard sphere diameter d for a fluid mixture through the use of the Ross variational theory [1,4,5]. Our prescription for the shear viscosity and thermal conductivity involves therefore the replacement of all d_{ij} with d and χ_{ij}^c with χ^c in (1) and (2), where

$$\chi^c = \frac{1}{\frac{2\pi}{3}nd^3}\left(\frac{p_{HS}}{nk_B T} - 1\right)$$

and p_{HS} is the pressure of a system of hard spheres with diameter d at number density n

and temperature T, in the Carnahan-Starling approximation [26].

The theoretical results so obtained are shown in Fig. 2 to 5. We note that the agreement with the MD results is very good over the entire range of pressures and temperatures studied [27]. We find that less satisfactory agreement is obtained if, for example, the Barker-Henderson perturbative definition of the effective hard-core [22] is used for the one-fluid system. We also calculated the transport coefficients in the usual MET approach [20] and found large disagreements with the MD results, particularly at high pressures, see Fig. 6.

Once the individual transport coefficients of the two fluid phases are calculated using the described formalism, we turn to the properties of the two-phase fluid system. Because the mixed system is unstable with respect to phase segregation in the two-phase region of the phase diagram, the kinetics of phase separation is generally important. However, it should be noted that this kinetics is typically rather slow, and it will probably not be relevant on the time–scale of detonation problems that we are interested in. The domains of the two-phases should be small compared with the length scale important for hydrodynamic modeling of detonation. Therefore we can estimate the transport coefficients of the two-phase fluid as

$$\frac{v_1 + v_2}{\eta} = \frac{v_1}{\eta_1} + \frac{v_2}{\eta_2}$$

$$\frac{v_1 + v_2}{\lambda} = \frac{v_1}{\lambda_1} + \frac{v_2}{\lambda_2} \tag{3}$$

where v_1 and v_2 are the volume fractions of the two fluid phases.

CARBON CLUSTERS EFFECTS

The volume fraction of post-detonation condensed carbon v_c is of the order 5% even for a relatively low carbon content high explosive such as HMX, see Fig. 7. (The kink in the pressure dependence of v_c is due to the graphite-diamond transition [9].) The condensed carbon is found in nano and micro-sized particles undergoing Brownian diffusion in the hot, dense, generally two-phase fluid system.
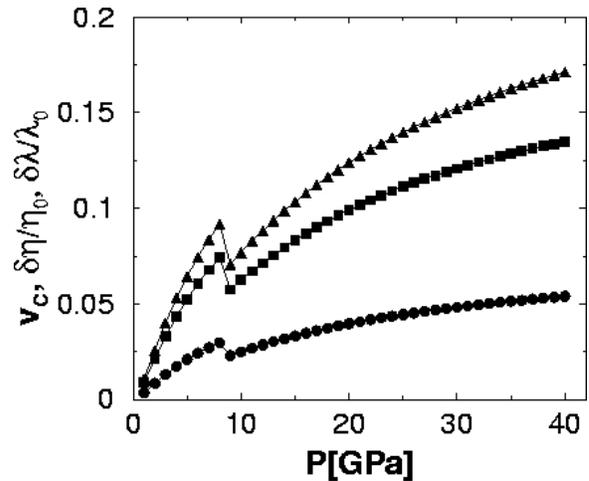

FIGURE 7. VOLUME FRACTION OF CONDENSED CARBON ALONG THE CJ ISENTROPE (CIRCLES) AND THE INDUCED VISCOSITY (SQUARES) AND THERMAL CONDUCTIVITY (TRIANGLES) ENHANCEMENTS.

The study of the effect of Brownian particles on the viscosity of a fluid matrix has a long history [28]. The presence of dispersed solid clusters leads to an enhancement of the viscosity dependent on the volume fraction of the solid inclusions. There are numerous subtle effects associated with the case of large volume fractions [29], the microscopic particle roughness [30], and the effect of particle coagulation [31]. While such effects may be expected to be important, we use here only the first order result,

$$\eta_{eff} = \eta\left(1 + \frac{5v_c}{2}\right) \qquad (4)$$

This indicates that the viscosity enhancement due to dispersed carbon particles can be close to 15% along the CJ isentrope, see Fig. 7. Fig. 8 shows the full shear viscosity, η_{eff}, of the detonation products along the CJ isentrope calculated using relations (1)-(5).
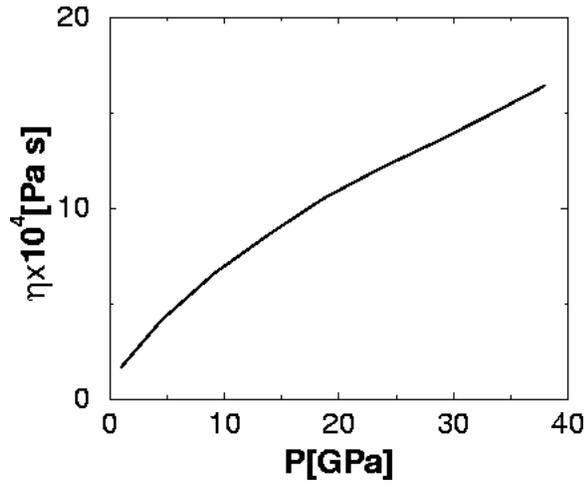

FIGURE 8. TOTAL VISCOSITY OF HMX DETONATION PRODUCTS ALONG THE CJ ISENTROPE.

The influence of small solid inclusions on the thermal conductivity of a fluid has an equally long history [32], and is generally treated, as is the viscosity case, in the effective medium framework [33,34]. If the solid particles have a larger thermal conductivity than the fluid they lead to a thermal conductivity enhancement, dependent again on their volume fraction. The effective thermal conductivity can be written as [33]:

$$\lambda_{eff} = \lambda\left[\frac{\lambda_C + (f-1)\lambda - (f-1)v_C(\lambda - \lambda_C)}{\lambda_C + (f-1)\lambda + v_C(\lambda - \lambda_C)}\right]$$

where λ_C is the thermal conductivity of carbon clusters and f is a shape factor. Under the assumption that the carbon clusters are spherical, $f = 3$, and that the thermal conductivity of carbon at these pressures and temperatures is much higher than that of the surrounding fluid, $\lambda_C \gg \lambda$, which should be very well satisfied, the total thermal conductivity of the system is well approximated by:

$$\lambda_{eff} = \lambda\left(\frac{1 + 2v_c}{1 - v_c}\right) \qquad (5)$$

We see in Fig. 7 that the thermal conductivity enhancements are even larger than those for the viscosity. Fig. 9 shows the total calculated thermal conductivity, λ_{eff}, of the detonation products along the CJ isentrope.
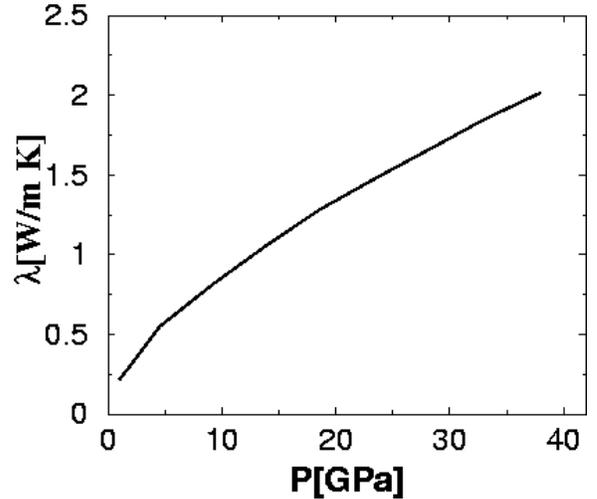

FIGURE 9. THERMAL CONDUCTIVITY OF THE HMX DETONATION PRODUCTS ALONG THE CJ ISENTROPE.

In conclusion, formulas (1)-(5) are our recommended prescription for the shear viscosity and thermal conductivity of detonation products, in the equilibrium thermodynamics [1] and Enskog kinetic

theory framework [14,17,35] that we discussed. Finally, regarding the effect of dispersed carbon particles on the transport properties, we note that issues such as the anomalously large effect of solid nanoclusters on the thermal conductivity at very small volume fractions [36], large volume fraction corrections, as well as kinetic effects are certainly deserving of further study in the context of detonation problems, particularly for carbon-rich explosives. We believe however that the present framework provides a very promising step in accurately predicting the transport coefficients of multi-phase high explosive detonation products.

ACKNOWLEDGEMENTS

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