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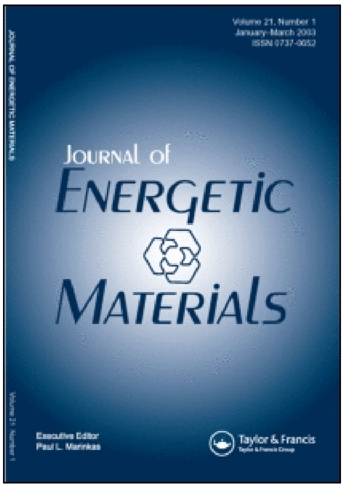

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An Accurate Equation-of-State Model for Thermodynamic Calculations of Chemically Reactive Carbon-Containing Systems

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An Accurate Equation-of-State Model for Thermodynamic Calculations of Chemically Reactive Carbon-Containing Systems

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We present an equation-of-state (EOS) model that allows for reliably computing the thermodynamics and chemical compositions of reactive carbon-containing systems over a wide range of temperatures and densities covering both high pressures up to tens of gigapascals and moderate pressures. The model includes a theoretical EOS of a multicomponent fluid phase and a thermodynamically consistent multiphase EOS of carbon nanoparticles. The results of thermochemical computations based on this model are shown to be in good agreement with a variety of shock wave and static measurements, as well as with detonation experiments that were not used for calibrating the intermolecular potential parameters.

Keywords: intermolecular potential, nanoparticles, perturbation theory, thermochemical code

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Introduction

The knowledge of thermodynamic properties of chemically reactive systems is necessary in solving a variety of practical problems in many fields of science. In particular, high-pressure, high-temperature thermodynamic data on multicomponent systems are needed in fluid science, in geophysics and astrophysics, in the chemistry and physics of shocks and detonations. The development of reliable equation-of-state (EOS) models for such systems is of great theoretical and practical interest.

In this work, we present a new, accurate multiphase EOS model for chemically reactive systems, which was recently incorporated into the thermochemical TDS code [1]. The model is applicable over a wide range of temperatures and densities covering both the high-pressure area (up to tens of gigapascals) and the region of moderate pressures ($P < 1\,\mathrm{GPa}$). The main parts of the model are a theoretical EOS for a multicomponent gaseous (fluid) phase based on an improved version [2] of the KLRR perturbation theory [3,4] and semi-empirical thermodynamically consistent EOSs for the graphite and diamond nanoparticles in the solid and liquid states. Accordingly, thermodynamic computations with the developed model allow one to obtain the data on thermodynamic properties and chemical compositions of reactive carbon-containing systems taking into account the possibility of formation of the carbon nanoparticles in the product mixture and their phase transitions. The examples given in this work show that our model provides accurate description of the thermodynamic states of chemically reactive systems as compared to the data of static, dynamic (shock wave), and detonation experiments. We also present the results of comparisons to the predictions of semi-empirical EOSs and of theoretical (first principles–based) EOS models used in other well-known thermochemical codes [5–8].

Equations of State

It is assumed that molecules i and j of a multicomponent fluid phase interact via a spherically symmetric Exp-6 potential

$$\varphi_{ij}(r) = \frac{\varepsilon_{ij}}{\alpha_{ij} - 6}\left\{6\exp\left[\alpha_{ij}\left(1 - \frac{r}{r_{m,ij}}\right)\right] - \alpha_{ij}\left(\frac{r_{m,ij}}{r}\right)^6\right\}, \tag{1}$$

where r is the intermolecular separation, ε_{ij} is the depth of the attractive well, $r_{m,ij}$ is the position of the potential well minimum, and α_{ij} controls the stiffness of the repulsive part of the potential. This model potential is known to provide a sufficiently realistic description of intermolecular interactions at high pressures and, in particular, under high-pressure, high-temperature conditions relevant to detonation and shock wave problems.

The core of our multicomponent Exp-6 EOS is an accurate theoretical EOS of a single-component Exp-6 fluid. In this work, we use a recently suggested version [2] of the KLRR perturbation theory constructed on the basis of analyzing the assumptions of the well-known Byers-Brown and Horton version [4] of KLRR and carefully investigating how the assumptions may affect the resulting thermodynamic properties being calculated with the theory. In particular, the effects caused by neglecting minor components of the first-order perturbing term of the excess free energy,

$$\Delta F_1 = 2\pi\frac{N^2}{V}\int_0^\infty \varphi_1(r)r^2 g_0(r)dr, \tag{2}$$

were studied. In Eq. (2), g_0 is the radial distribution function of the reference fluid, φ_1 is a long-range perturbing part of the intermolecular potential, N is the number of particles, and V is the volume. It was found that taking some minor terms of ΔF_1 into account allows one to improve the accuracy of the KLRR theory at high densities, especially for stiff potentials ($\alpha > 14$). Computation of these terms is time consuming, and a computational technique, which is based on using Laplace and inverse Laplace transforms and allows for at least several hundred times faster calculations, was developed. The resulting perturbation theory was found to be more accurate in reproducing Monte Carlo (MC) simulation data than its versions [3,4]. Hence, it would be reasonable to build a multicomponent fluid

EOS basing on the improved version of the perturbation theory, and this has been done in the present work.

To calculate the thermodynamic properties of a multicomponent fluid phase, we use an improved van der Waals one-fluid (vdW1f) model, which assumes a mixture of chemical species, interacting via potentials (1), to be a hypothetical one-component fluid with an effective Exp-6 potential. The composition-dependent parameters of the effective potential are given by

$$\alpha = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \alpha_{ij} \varepsilon_{ij} r_{m,ij}^3 / (\varepsilon \cdot r_m^3),$$

$$\varepsilon = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \varepsilon_{ij} r_{m,ij}^3 / (r_m^3),$$

$$r_m = \left[\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j r_{m,ij}^3\right]^{1/3}, \tag{3}$$

where the summation extends over all ij pairs, n is the number of the components, and x_i is the mole fraction of species i. The reliability of vdW1f in predicting the excess thermodynamic parameters of a multicomponent fluid has been shown by Ree [9], who is the author of the α-mixing rule. As seen in Table 1, the multicomponent EOS built in this work provides good agreement with MC data for Exp-6 fluid mixtures over a wide range of pressures and temperatures. The results obtained are more accurate than those of the models based on vdW1f and the Mansoori-Canfield-Rasaiah-Stell-Ross (MCRSR) variational theory or on vdW1f and the Zerah and Hansen's hypernetted-mean spherical approximation (HMSA) integral equations for pair distribution functions. The constructed multicomponent EOS appears to be currently most accurate among existing theoretical EOSs of Exp-6 fluid mixtures.

A multiphase model of nanocarbon used in this work involves semi-empirical EOSs for the solid and liquid nanoparticles of graphite and diamond [10]. The EOSs are based on an accurate

Table 1

Pressures (P) and excess internal energies (ΔU) of H_2-He mixtures computed with the developed EOS model and obtained from Monte Carlo simulations. The relative errors of the EOS (δP, $\delta \Delta U$) are also listed

T (K)	V_M (cm^3/mol)	Mol. ratio H_2-He	P (GPa) (MC)	P (GPa) (EOS)	δP (%)	ΔU (kJ/mol) (MC)	ΔU (kJ/mol) (EOS)	$\delta \Delta U$ (%)
50	20	1:1	0.0473(5)	0.0480	1.47	−0.755(3)	−0.7341	2.77
100	14	1:1	0.338(1)	0.3387	0.22	−0.354(6)	−0.3274	7.53
300	10	1:1	1.856(4)	1.8598	0.20	2.79(2)	2.9076	4.22
300	10	3:1	2.309(7)	2.3271	0.78	3.49(3)	3.6659	5.04
300	10	1:3	1.424(4)	1.4087	1.07	2.08(1)	2.0882	0.39
1000	9	1:1	4.510(7)	4.4214	1.96	8.86(3)	8.8616	0.02
1000	9	3:1	5.255(12)	5.1888	1.26	10.88(5)	10.913	0.30
1000	9	1:3	3.715(8)	3.6335	2.19	6.79(3)	6.6823	1.59
4000	8	1:1	12.43(1)	12.125	2.46	25.12(5)	24.845	1.10
4000	7	1:1	16.33(3)	15.952	2.32	31.4(2)	31.170	0.73
7000	4.5	1:1	54.01(7)	52.759	2.32	84.7(1)	85.548	1.00
7000	4.5	3:1	56.21(7)	56.383	0.31	97.2(2)	99.164	2.02
7000	4.5	1:3	48.83(7)	47.796	2.12	68.0(2)	67.378	0.92
Average relative error, %					1.44			2.12

multiphase model of the bulk carbon and have correction terms that allow for taking into account the effect of the small size of carbon particles on their thermodynamics. The correction terms represent approximate expressions for the surface energy of nanoparticles depending on the material and the size and shape of the particles. The enthalpy and entropy of the nanosize material are calculated by adding the correction terms to the corresponding quantities of the same bulk material. The present model shifts the solid nanographite–solid nanodiamond phase equilibrium line upward in pressure relative to the bulk graphite–diamond equilibrium line, so that in a limited region of temperatures and pressures between those two lines, the graphite nanoparticles remain thermodynamically stable, whereas the bulk graphite is unstable under the same conditions. The model also shifts the nanocarbon melting line downward in temperature. The determined absolute values of the heat of formation of the graphite and diamond nanoparticles are consistent with the available measurements for the heat of formation of carbon particles recovered from detonation calorimetry experiments.

Results and Comparisons with Experiments and with Predictions of Other Models

For practical applications of the obtained multicomponent EOS, one should determine the intermolecular potential parameters for species that are considered as possible gaseous (fluid) products in the chemical system being investigated. In this work, we assume the gaseous phase to consist of molecules N_2, N, CO_2, CO, NO, NO_2, N_2O, O_2, and O that are the major products in reactive systems (including energetic materials) composed of C, N, and O atoms. It is appropriate to mention here that molecules of energetic materials may also include the atoms of hydrogen, which typically leads to the formation of such additional product species as H_2O, NH_3, CH_4, and so on. Although the developed EOS model can be applied to hydrogen-containing reactive systems as well, they will be considered in our separate work. The present article deals with hydrogen-free systems taking into account the primary goals of this study. One of them is to show that the obtained model allows one to predict the properties of real reactive systems more reliably, in better agreement with the results of measurements compared to those EOS models that describe molecular simulations less accurately. In this sense, reactive systems composed of C, N, and O atoms provide us with better examples than one could obtain from examining hydrogen-containing systems. The reason is that a realistic description of intermolecular forces in fluids containing polar molecules (such as H_2O, NH_3) requires temperature-dependent modifications of the Exp-6 potential [5–7,11] or some special approaches [8]. In either case, this leads to introducing additional parameters to the model, and possible errors in those parameters may affect the final results of thermochemical computations, making difficulties for determining the true source of deviations. Thus, reactive systems composed of C, N, and O atoms are more suitable for the purposes of this work. Furthermore, this choice of elemental composition is also motivated by practical importance of having a reliable EOS model, which could be applied to thermodynamic modeling of new, recently synthesized hydrogen-free energetic materials [12].

The potential parameters have been determined mostly by matching experimental Hugoniot data and available results of static experiments for the region of moderate pressures and temperatures. The unlike-pair Exp-6 parameters are additive for all pairs except for CO_2-O, for which we found the best-fitting value of $k_{CO_2\text{-}O} = 0.91$, where k_{ij} is the factor determining the deviation from the Lorentz-Berthelot combination rule for $r_{m,ij}$. The obtained values of the potential parameters are listed in Table 2.

Using the TDS code with the developed EOS model, we have computed the thermodynamic properties of a number of chemical systems over a wide range of pressures and temperatures. The results are in good agreement with a variety of experimental shock wave data (up to high temperatures and high pressures of about tens of gigapascal) and static measurements (at moderate temperatures and pressures $P < 1\,\text{GPa}$). Some examples are given in Figs. 1–3. To check the reliability of our EOS model

Table 2
The like-pair Exp-6 potential parameters

Species	$\varepsilon_{0,ii}/k_B$ (K)	$r_{m,ii}$ (m^{-10})	α_{ii}	Species	$\varepsilon_{0,ii}/k_B$ (K)	$r_{m,ii}$ (m^{-10})	α_{ii}
N_2	100.6	4.25	12.3	NO_2	326.2	4.27	13.8
N	120.0	2.65	10.4	N_2O	234.3	4.27	13.8
O_2	96.2	3.79	14.7	CO_2	230.2	4.22	13.8
O	277.0	2.57	11.5	CO	103.5	4.12	14.0
NO	140.2	3.70	13.9				

in reproducing the experimental data on more complicated chemical systems, we have computed the detonation parameters of a few liquid and solid energetic materials. The detonation

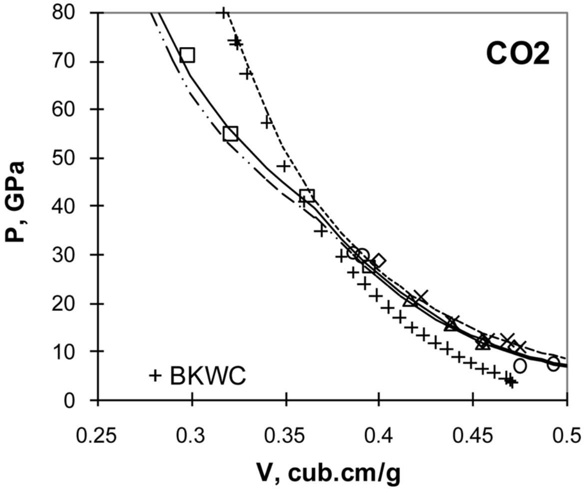


Figure 1. Shock Hugoniot of initially liquid CO_2. Symbols (except for +) are the measured values. Symbol + represent the results computed with semi-empirical BKWC EOS [13]. Lines are our computations with different theoretical EOS models. Dotted and dashed-dotted lines correspond to the models in Charlet et al. [7] and Fried [8], respectively. Solid line represents computations based on the model developed in this work.

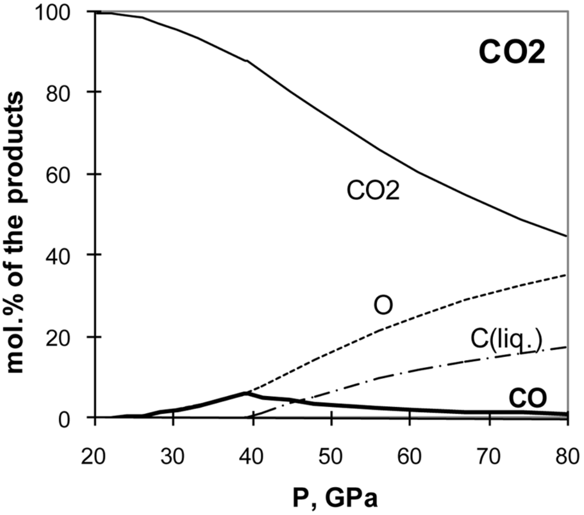
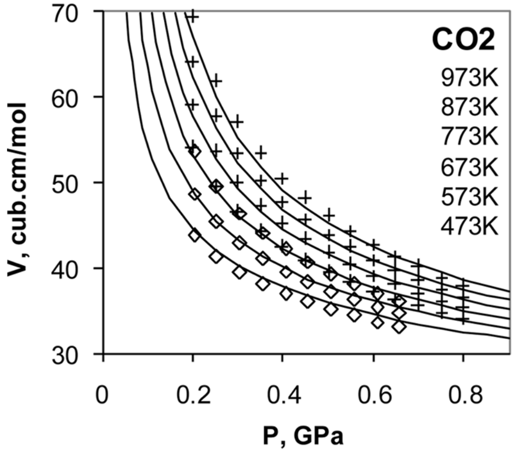
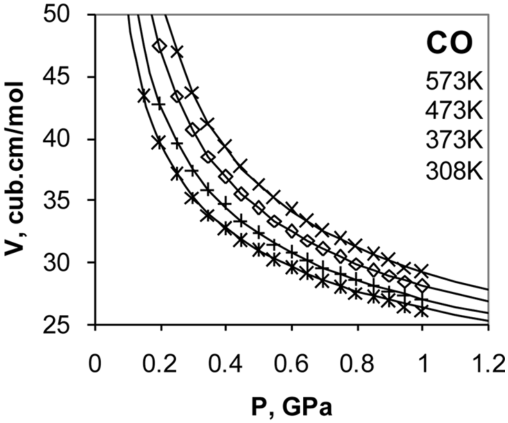


Figure 2. Chemical composition of the products along shock Hugoniot of initially liquid CO_2 computed with the model developed in this work. The formation of liquid carbon nanoparticles at $P > 40$ GPa is responsible for the change of the P vs. V slope in this range of pressures (see Fig. 1).

products are hot reactive mixtures consisting of a number of fluid components and, for some explosives, also of one or more condensed phases. That is why thermodynamic modeling of detonations makes a good test for EOS models. The results of TDS detonation computations are listed in Table 3 and demonstrate very good agreement with measurements. Figure 4 gives an example of isentrope calculations and allows one to see how the parameters and chemical composition of the product mixture vary as the products expand from the Chapman-Jouguet (CJ) state. It is important to mention here that detonation experiments were not used for calibrating the potential parameters of the model. Thus, good agreement with the measured detonation characteristics confirms reliability of the developed EOS model. TDS code detonation computations have also been done for the same energetic materials with semi-empirical



(a)



(b)

Figure 3. The isotherms of CO_2 (a) and CO (b). Symbols are the measured values. Lines are our computations with the model developed in this work.

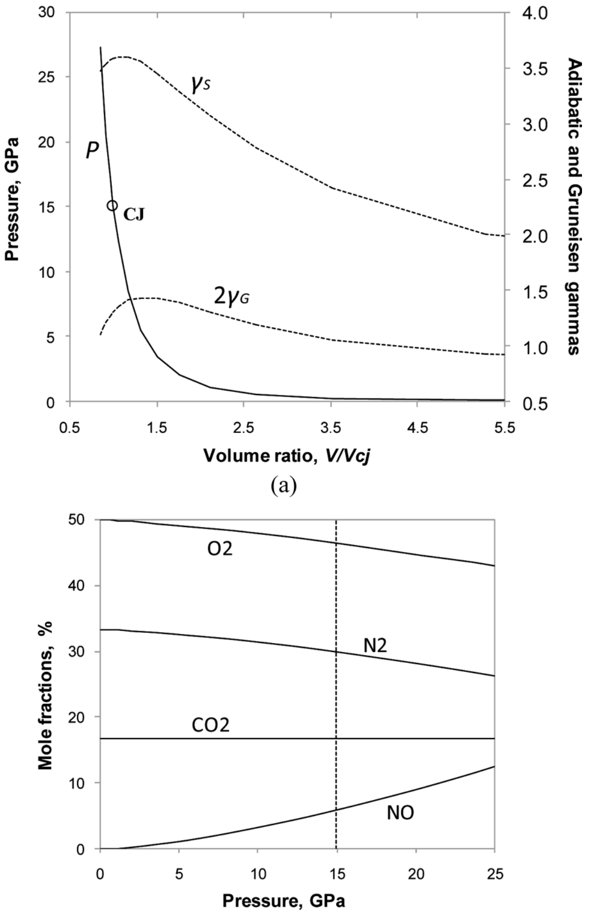
Becker-Kistiakowsky-Wilson EOS using its well-known parameterizations of Finger et al. (BKWR) [17] and of Fried and Souers (BKWC) [13], with theoretical (first principles–based) EOS models [5–8]. The resulting statistics are given in Table 4. The results obtained with the presented EOS model are shown to

Table 3

The experimental (D_{exp}, $P_{CJ,\mathrm{exp}}$) and computed (D, P_{CJ}, T_{CJ}) detonation parameters of different liquid and solid energetic materials. Also listed are the measured values of initial density ρ_0 and enthalpy H_0 and the computed values of isochoric heat capacity C_V, adiabatic gamma $\gamma_S = -(\partial \ln P / \partial \ln V)_S$, and Gruneisen gamma $\gamma_G = V(\partial P / \partial E)_V$. Computations are performed with the TDS code and the EOS model developed in this work

Energetic material[a]	ρ_0 (g/cm^3)	H_0 (kcal/mol)	D_{exp} (km/s)	D (km/s)	$P_{CJ,\mathrm{exp}}$ (GPa)	P_{CJ} (GPa)	T_{CJ} (K)	C_{V} (J/[g $*$ K])	γ_S	γ_G
NO [14,15]	1.30	19.0	5.62 ± 0.07	5.55	10 ± 1	9.52	2,858	1.500	3.201	0.553
C_3N_{12} [16]	1.15	218.6	5.60	5.65		8.87	3,954	1.398	3.145	0.532
CN_4O_8 [16]	1.65	8.8	6.45	6.46	15.5	15.0	2,231	1.524	3.582	0.654
$C_2N_6O_{12}$ [16]	1.86	28.6	7.58	7.58		23.8	2,527	1.621	3.487	0.561
$C_6N_6O_{12}$ [13]	1.973	10.0	9.33	9.34		39.0	4,896	2.061	3.418	0.517
$C_6N_{12}O_6$ [16]	1.74	270.4	8.58	8.60		31.3	4,472	1.733	3.103	0.799
$C_4N_8O_8$ [12]	1.77	159.6	9.00 ± 0.10	8.94		33.3	5,541	2.173	3.246	0.512

[a] References given after the chemical formulas correspond to papers from which the experimental data are taken.



(a)

(b)

Figure 4. The expansion isentrope from the CJ state for CN_4O_8: pressure, adiabatic gamma, and Gruneisen gamma versus volume ratio V/V_{CJ} (a) and concentrations of the major product species versus pressure (b). The CJ state is denoted by a circle (a) and by a vertical dotted line (b).

be much more reliable compared to the results of calculations with semi-empirical EOSs of dense gaseous mixtures and more accurate, to a greater or lesser extent, than the computations

Table 4
Statistics of comparisons of the measured detonation parameters to the results of our thermochemical computations with the model presented in this work, with theoretical models [5–8], and with semi-empirical BKWR [17] and BKWC [13] EOSs[a]

Energetic material	This work	Reference [8]	[7]	[6]	[5]	BKWR	BKWC
NO	+	+/−	+	+	−	+	+/−
C_3N_{12}	+	+/−	−	+/−	+	−	−
CN_4O_8	+	+	+	+	−	−	−
$C_2N_6O_{12}$	+	+/−	+	+	−	−	+
$C_6N_6O_{12}$	+	+	+/−	−	−	−	−
$C_6N_{12}O_6$	+	+	+	+	−	−	+/−
$C_4N_8O_8$	+	+/−	−	−	−	−	+

[a] Symbols +, +/−, and − mean good (within the experimental uncertainties), satisfactory, and poor agreement with experiments, respectively.

based on the examined theoretical EOSs from other thermochemical codes. The success of the EOS model developed in this work can be explained by (a) using an accurate statistical–mechanical theory, (b) carefully determining the potential parameters from a variety of experimental data including those at moderate pressures and temperatures, and (c) taking into account the effect of nanosizes of carbon particles and correct determination of their phase state.

Conclusions

We have developed an EOS model that allows for reliably computing the thermodynamic properties and chemical compositions of reactive multicomponent and multiphase carbon-containing systems over a wide range of temperatures and densities covering both the high-pressure area up to tens of gigapascals and the region of moderate pressures. The model includes a theoretical EOS of multicomponent gaseous phases, which appears to be currently most accurate among existing theoretical EOSs of Exp-6 fluid mixtures and a semi-empirical thermodynamically consistent multiphase EOS of carbon nanoparticles. High predictive abilities of the presented EOS model allow one to apply it to solving a variety of practical and theoretical tasks in geophysics and astrophysics and in the chemistry and physics of shock waves and detonations. In particular, the model can be used for predicting the detonation properties of new energetic materials and for studying, in the framework of recently suggested technique [5], a complex multifront structure of detonation wave for explosives whose detonation products undergo nanocarbon phase transitions.

References

[1] Victorov, S. B. 2002. The effect of Al_2O_3 phase transitions on detonation properties of aluminized explosives. In *Proceedings of the 12th International Detonation Symposium*, ed. J. Short. Arlington, VA: Office of Naval Research.

[2] Victorov, S. B. and S. A. Gubin. 2006. A new accurate equation of state for fluid detonation products based on an improved version of the KLRR perturbation theory. In *Proceedings of the 13th International Detonation Symposium*, ed. S. M. Peiris. Norfolk, VA: Office of Naval Research.

[3] Kang, H. S., C. S. Lee, T. Ree, and F. H. Ree. 1985. A perturbation theory of classical equilibrium fluids. *Journal of Chemical Physics*, 82(1): 414–423.

[4] Byers-Brown, W. and T. V. Horton. 1988. Hard-sphere perturbation theory for classical fluids to high densities. *Molecular Physics*, 63(1): 125–138.

[5] Ree, F. H. 1986. Supercritical fluid phase separation: Implication for detonation properties of condensed explosives. *Journal of Chemical Physics*, 84(10): 5845–5856.

[6] Jones, H. D. and F. J. Zerilli. 1991. Theoretical equation of state for aluminized nitromethane. *Journal of Applied Physics*, 69(7): 3893–3900.

[7] Charlet, F., M.-L. Turkel, J.-F. Danel, and L. Kazandjian. 1998. Evaluation of various theoretical equations of state used in calculation of detonation properties. *Journal of Applied Physics*, 84: 4227–4238.

[8] Fried, L. E., W. M. Howard, and P. C. Souers. 2002. Exp-6: A new equation of state library for high pressure thermochemistry. In *Proceedings of the 12th International Detonation Symposium*, ed. J. Short. Arlington, VA: Office of Naval Research.

[9] Ree, F. H. 1983. Simple mixing rule for mixtures with Exp-6 interactions. *Journal of Chemical Physics*, 78(1): 409–415.

[10] Victorov, S. B., S. A. Gubin, I. V. Maklashova, and V. I. Pepekin. 2005. Predicting the detonation characteristics of hydrogen-free explosives. *Khimicheskaya Fizika*, 24(12): 22–45.

[11] Victorov, S. B. and S. A. Gubin. 2006. A double-front structure of detonation wave as the result of phase transitions. *Shock Waves*, 15(2): 113–128.

[12] Akimova, L. N., G. T. Afanas'ev, V. G. Schetinin, and V. I. Pepekin. 2002. Explosive properties of 4,4-dinitro-3,3-diazenoforoxan. *Khimicheskaya Fizika*, 21(3): 93.

[13] Fried, L. E. and P. C. Souers. 1996. BKWC: An empirical BKW parameterization based on cylinder test data. *Propellants, Explosives, Pyrotechnics*, 21: 215.

[14] Ramsay, J. B. and W. C. Chiles. 1976. In *Proceedings of the 6th Symposium (International) on Detonation*, ed. D. J. Edwards. Arlington, VA: Office of Naval Research.

[15] Schott, G. L., M. S. Shaw, and J. D. Johnson. 1985. Shocked states from initially liquid oxygen-nitrogen systems. *Journal of Chemical Physics*, 82(9): 4264–4275.

[16] Gubin, S. A., V. V. Odintsov, and V. I. Pepekin. 1986. *Thermodynamic Calculations of Condensed Explosive Detonations*. Chernogolovka, Russia: IChPh USSR Academy of Sciences. Preprint.

[17] Finger, M. E., E. Lee, F. H. Helm, B. Hayes, H. Hornig, R. McGuire, M. Kahara, and M. Guidry. 1976. The Effect of Elemental Composition on the Detonation Behavior of Explosives. In *Proceedings of the 6th Symposium (International) on Detonation*, ed. D. J. Edwards, p. 710, Arlington, VA: Office of Naval Research.