

TITLE THE THEORY OF DENSE MOLECULAR FLUID EQUATIONS OF STATE WITH  
APPLICATION TO DETONATION PRODUCTS

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THE THEORY OF DENSE MOLECULAR FLUID EQUATIONS OF STATE  
WITH APPLICATION TO DETONATION PRODUCTS

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All current models of the equation of state (EOS) of detonation products are based on spherical potentials. Given a thermodynamic theory, these potentials are usually fit to experimental data using that thermodynamic theory. When one looks at the degree of anisotropy of typical molecules in HE products (the  $N_2-N_2$  potential varies by a factor of 20 with orientation for a fixed internuclear separation and the  $CO_2-CO_2$  potential varies by 3 to 4 orders of magnitude), it is not at all obvious that spherical potentials are adequate. In fitting to Hugoniot data for the individual species, the pressure and energy on the Hugoniot will be correct, but the temperature may not be accurate. When one then calculates the EOS of a mixture, the temperature is important in determining the equilibrium composition. Also, in the mixture the state will not necessarily be near the conditions on the Hugoniots that were fit by the theory. Therefore, the question of how well the EOS extrapolates away from the Hugoniot is important.

Because of the uncertainty in using spherical potentials, we have made a series of benchmark calculations using molecular dynamics (MD) with realistic anisotropic potentials. An EOS calculation using MD involves solving Newton's equation ( $F = ma$ ) for a collection of particles (usually a few hundred) with periodic boundary conditions and a realistic potential. Thermodynamic quantities are then obtained by time averages of appropriate functions. These benchmark values of the EOS enabled us to find approximate methods that gave an accurate representation of that EOS with a very small cost in computer time. Using a perturbation expansion, a spherical reference system was determined that reproduces the thermodynamics of an anisotropic molecular potential with negligible contribution from higher order terms. For a given anisotropic potential, this effective spherical potential gives pres-

tures and energies good to 1.5% for  $N_2$  in the region of  $1.3 \text{ g/cm}^3 \leq \rho \leq 2.3 \text{ g/cm}^3$  and  $500^\circ\text{K} \leq T \leq 12000^\circ\text{K}$  (results for  $CO_2$  agree to about 3%). These results help justify the use of empirical spherical potentials for the equation of state of detonation products.

The above shows that the configurational part of the Helmholtz free energy for an anisotropic molecular system can be obtained by using an equivalent spherical potential. We also found how to obtain that effective potential when the anisotropic potential is known or can be well approximated. We used the Ross<sup>1</sup> procedure to evaluate the configurational free energy,  $A_c$ , for the effective spherical potential because it is both fast and accurate (2% or better in dense fluids). The other contributions to the Helmholtz free energy,  $A$ , for a single species are well approximated by several simple, separable contributions. (Note that the resulting procedure for obtaining  $A$  is essentially that of Ross<sup>2</sup> and Ree<sup>3</sup>. However, the spherical potentials are obtained in a totally different manner.)

We have chosen ideal mixing for our detonation products EOS. More accurate mixing theories require cross potentials, i.e., not only  $\phi_{aa}$  and  $\phi_{bb}$ , but also  $\phi_{ab}$ . For near zero pressure fluid mixtures, a few percent change in the cross potential may lead to a change in sign of excess properties. Also, it is not certain that an accurate mixing theory for spherical potentials is still accurate for effective spherical potentials representing very anisotropic potentials. We intend to look at molecular mixtures with molecular dynamics or Monte Carlo methods, but we will continue with ideal mixing until it is clear what works better for molecular mixtures. The equilibrium composition of the detonation products is determined by minimizing the Gibbs free energy of the mixture. A slightly modified form of the procedure of White et al.<sup>4</sup> was used.

Effective spherical potentials for  $N_2$ ,  $O_2$ ,  $NO$ ,  $CO$ , and  $CO_2$  are obtained by fitting to various experimental and calculate quantities. An equation of state for mixtures of these molecules is determined. Calculations are then compared with Hugoniot data for  $N_2 + O_2$  mixtures and overdriven  $NO$  detonations with excellent agreement. Also, the detonation velocities of  $O_3/O_2$  mixtures,  $NO$ ,  $TNM$ , and  $HNB$  were calculated and were in very good agreement with experiment. Further results

on H<sub>2</sub>O, solid carbon, and mixing will be included as we make progress in these areas.

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