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EFFECTIVE SPHERICAL POTENTIALS FOR DETONATION PRODUCTS EOS

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Using a perturbation expansion, a spherical reference system is found 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 pressures and energies good to 1.5% for N_2 in the region of 1.3 g/cm^3 $\leq \rho \leq$ 2.3 g/cm^3 and 500°K $\leq T \leq$ 12000°K. Preliminary 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.

All current models[1] 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. For example, the temperature is two-thirds of the average kinetic energy per atom in a monatomic system. For a sufficiently large number of particles, boundary effects and number dependence are negligible. The only remaining error is the statistical fluctuation of the time-averaged functions. For a typical run

length, these errors are about 0.5% but the computer time required is 5 to 10 minutes on the Cray-1 for a single EOS value.

Given the benchmark values of the EOS, we began to look for approximate methods that gave an accurate representation of that EOS with a very small cost in computer time. For spherical potentials, there are a number of methods[2] based on hard-sphere perturbation theory that are both accurate and fast. We chose to use the Mansouri-Canfield-Ross[2] method to try out various spherical potentials. Two spherical averaging procedures were tried without success. The arithmetic mean, $\bar{\phi} = \int\int \phi(r,\Omega)d\Omega$, corresponds to a freely rotating molecule. This gave a potential too high by 35% for N_2 and by about 1000% for CO_2. The average used by Perram and White,[3] $\langle\phi\rangle = -\beta^{-1}\,\ell n\,(\int\int e^{-\beta\phi(r,\Omega)}d\Omega)$, is exact at low density and corresponds to the assumption that the orientation of each pair of molecules is independent of the orientation of any other neighboring molecules. At high densities this gives pressures and energies that are typically 20% too low for N_2. Finally we fit a potential to the pressure, energy, and temperature, along the MD-generated Hugoniot. We then compared the EOS along isotherms using the same potential. The agreement was excellent, as can be seen in Fig. 1. Preliminary results for CO_2 were nearly as good.

We then had a procedure for obtaining an effective spherical potential from an anisotropic one, but this required making many MD runs to generate a Hugoniot. One could still empirically fit to Hugoniot data, but this can leave a great deal of uncertainty in the temperature. We then looked for and found a perturbation theory approach that gave an essentially identical spherical potential directly from the anisotropic potential. The rest of the paper deals with the derivation of that potential and the results obtained with it.

Thermodynamic perturbation series can be formulated in a fairly general form as shown by Smith.[3] The configurational part of the Helmholtz free energy, A, for a given pair potential $u(r,\Omega)$ can be expanded in a Taylor series about a reference point A_0 given by a pair potential $u_0(r,\Omega)$. This is done by defining a potential $u_\gamma(r,\Omega)$ subject to the constraints $u_{\gamma=1}(r,\Omega) = u(r,\Omega)$ and $u_{\gamma=0}(r,\Omega) = u_0(r,\Omega)$. Then we can write

$$A = A_{\gamma=1} = A_{\gamma=0} + \left(\frac{\partial A_\gamma}{\partial\gamma}\right)_{\gamma=0} + \frac{1}{2}\left(\frac{\partial^2 A_\gamma}{\partial\gamma^2}\right)_{\gamma=0} + \cdots \quad , \tag{1}$$

the usual Taylor series in the variable γ. The values of the derivatives can be obtained from the definition of A.

$$A_\gamma = -\frac{1}{\beta}\,\ell n\, Q_\gamma$$

$$= -\frac{1}{\beta}\,\ell n\left[\frac{1}{V^n}\int \exp\left(-\beta\,\frac{1}{2}\sum_{i=1}^{N}\sum_{i\neq j}^{N} u_\gamma(r_{ij},\Omega_{ij})\right)d^3r_1\cdots d^3r_N d\hat{\omega}_1\cdots d\hat{\omega}_N\right] \quad . \qquad (2)$$

where Q_γ is the excess part of the partition function, $r_{ij} = |\vec{r}_i - \vec{r}_j|$, Ω_{ij} is shorthand for $\hat{\omega}_i,\hat{\omega}_j$ and $\hat{\omega}_0$ is shorthand for polar coordinates of the orientation of molecules i; θ_i,ϕ_i. If we let R_i stand for $\vec{r}_{ij}\hat{\omega}_i$ and $U_\gamma = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} u_\gamma(r_{ij},\Omega_{ij})$ be the total potential energy, then

$$A_\gamma = -\frac{1}{\beta}\left[\ell n\ \frac{1}{V^N}\int \exp\,(-\beta U_\gamma)d\vec{R}^N\right] \quad . \qquad (3)$$

Evaluating the first two derivatives, we have

$$\frac{\partial A_\gamma}{\partial \gamma} = \frac{1}{Q_\gamma V^N}\int \frac{\partial U_\gamma}{\partial \gamma}\exp\,(-\beta U_\gamma)d\vec{R}^N \qquad (4)$$

and

$$\frac{\partial^2 A_\gamma}{\partial \gamma^2} = \frac{1}{\beta}\left(\frac{\partial A_\gamma}{\partial \gamma}\right)^2 + \frac{1}{Q_\gamma V^N}\int\left[\frac{\partial^2 U_\gamma}{\partial \gamma^2} - \beta\left(\frac{\partial U_\gamma}{\partial \gamma}\right)^2\right]\exp\,(-\beta U_\gamma)d\vec{R}^N \quad . \qquad (5)$$

The derivatives of the total potential are easily written as

$$\frac{\partial^n U_\gamma}{\partial \gamma^n} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{\partial^n u_\gamma(r_{ij},\Omega_{ij})}{\partial \gamma^n} \quad . \qquad (6)$$

Now note that the radial distribution function, $g_\gamma(r_{12},\Omega_{12})$, has the definition

$$g_\gamma(r_{12},\Omega_{12}) = \frac{V^2}{Q_\gamma V^N} \int \exp(-\beta U_\gamma) d\vec{R}_3 \cdots d\vec{R}_N \quad . \tag{7}$$

This is the probability that given a molecule at $\vec{r}_1$ with orientation $\hat{\omega}_1$ there is a molecule at $\vec{r}_2$ with orientation $\hat{\omega}_2$.

Each term in Eq. (6) can be integrated separately in Eq. (4) and by a change of variables each term in the summation is identical, giving the result:

$$\frac{\partial A_\gamma}{\partial \gamma} = \frac{1}{2} \frac{N^2}{V^2} \iint g_\gamma(r_{12},\Omega_{12}) \frac{\partial u_\gamma(r_{12},\Omega_{12})}{\partial \gamma} d^3r_1 d^3r_2 d\Omega_{12} \quad . \tag{8}$$

For the choice u_0 spherical, then g_0 is also spherical and we can write

$$\left.\frac{\partial A_\gamma}{\partial \gamma}\right)_{\gamma=0} = \frac{\rho^2}{2} \int g_0(r_{12}) d^3r_1 d^3r_2 \int \left.\frac{\partial u_\gamma(r_{12},\Omega_{12})}{\partial \gamma}\right)_{\gamma=0} d\Omega_{12} \quad . \tag{9}$$

The second derivative is more complicated because the $(\partial U_\gamma/\partial\gamma)^2$ term requires up to four particle distribution functions and care must be taken with certain limits. The full expression is given in Smith.[3] For our purpose, it is sufficient to recognize that each term in the higher derivatives of A_γ has integrands proportional to products of derivatives of u_γ.

We now need a convenient form for $u_\gamma(r,\Omega)$. Smith[3] gave a very general form,

$$S(u_\gamma) = S(u_0) + \gamma[S(u_1) - S(u_0)] \quad , \tag{10}$$

where S is an arbitrary invertible function. One can see by inspection that this form has the proper values at $\gamma = 0$ and $\gamma = 1$. For the choice $S(x) = x$, one obtains the usual λ expansion. We specialize S to the form $S(x) = R(B(x - u_0))$ where R is an odd invertible function with no singularities near the real axis and B is a parameter.[4] Then from Eq. (10),

$$R(B(u_\gamma - u_0)) = \gamma R(B(u_1 - u_0)) \quad . \tag{11}$$

With the notation $u_0^{(n)} \equiv \left.\frac{\partial^n u_\gamma}{\partial \gamma^n}\right)_{\gamma=0}$ we have

$$u_0^{(n)} = B^{-1} R_I^{(n)} [R(B(u_1 - u_0))]^n \tag{12}$$

where $R_I^{(n)} \equiv d^n R^{-1}(x)/dx^n|_{x=0}$. Note that $u_0^{(2n)} = 0$ for all values of n because $R^{-1}(x)$ is also odd. This sets a large fraction of the terms in the perturbation series to zero. From Eq. (9), we see that a sufficient condition for $\left.\frac{\partial A_r}{\partial \gamma}\right)_{\gamma=0} = 0$ is that

$$\iint R(B(u_1 - u_0))d\Omega = 0 \quad . \tag{13}$$

We then choose $u_0(r)$ such that Eq. (13) is satisfied for all values of r.

We still have to choose a functional form for R. Note that if $R_I^{(n)}$ is bounded and R(x) behaves, at worst, like $(\ell n\ x)^k$ as $x \to \infty$, then $u_0^{(n)}$ will be small for large values of B. We have used $R(x) = \sinh^{-1}(x)$. This leads to simple values for $R_I^{(n)}$;, i.e.,

$$R_I^{(n)} = \begin{cases} 0 \text{ if n even} \\ 1 \text{ if n odd} \end{cases} \tag{14}$$

Equation (12) then becomes

$$u_0^{(2n+1)} = B^{-1}[\sinh^{-1}(B(u_1 - u_0))]^{2n+1} \tag{15}$$

(For large x, $\sinh^{-1}(x) \to \ell n(2x)$. For small x, $\sinh^{-1}(x) \to x$.) Equation (13) then becomes

$$\iint \sinh^{-1}(B(u_1 - u_0))d\Omega = 0 \quad . \tag{16}$$

Figure 2 shows the dependence of u_0 on B for a fixed value of r. At small values of B, one gets the usual λ-expansion which yields the arithmetic mean.

As B increases, u_0 rapidly approaches a constant value. In the limit of $B \to \infty$ this is just the median of the potential. One does not expect the perturbation series to converge in the $B \to \infty$ limit, but for intermediate values of B the series can converge and the u_0 obtained is almost identical to that for the $B \to \infty$ limit. Therefore, in practice we use the median as our choice of an effective spherical potential.

With a transformation of variables, one can obtain perturbation theories that give nearly the same results even in the small B limit where the convergence properties of the series are better. One special case we will call radial averaging. For a $u_1(r,\Omega)$ that is invertible, we can construct a radial function $r_1(u,\Omega)$ which is its inverse. The effective spherical potential is $r_0(u)$, which can be inverted to obtain $u_0(r)$. With the definition of r_γ given by

$$R(B(r_\gamma - r_0)) = \gamma R(B(r_1 - r_0)) \quad , \tag{17}$$

we obtain

$$r_0^{(2n+1)} = \left.\frac{\partial^{(2n+1)} r_\gamma}{\partial \gamma^{(2n+1)}}\right|_{\gamma=0} = B^{-1}\, R_I^{(2n+1)} [R(B(r_1 - r_0))]^{2n+1} \quad . \tag{18}$$

and

$$r_0^{(2n)} = 0 \quad , \qquad n \text{ a non-negative integer.}$$

We can then transform back to obtain the $u_0^{(n)}$ that are used in the perturbation series. In particular,

$$u_0^{(1)} = -\frac{du_0}{dr}\, r_0^{(1)} \quad , \tag{19}$$

which implies

$$\int\int R(B(r_1 - r_0))d\Omega = 0 \tag{20}$$

is the transformed form of Eq. (13). Figure 2 also shows the B dependence of this potential. Note that even at $B \to 0$, the potential is within a few percent of th large B value. By changing variables, the anisotropy has been

reduced from a factor of 20 to about 30%. Of course the radius needs to be known more accurately to get the same accuracy in the potential, but the perturbation series converges faster because the anisotropy is smaller.

The repulsive part of the potential can be treated in this manner but the attractive part is not invertible. However, we can write a general transformation of coordinates and choose a form that is similar to radial averaging but preserves invertibility for the entire potential. Let $F(u,r)$ be an invertible function of potential and radius. Also let $u_\gamma(F,\Omega)$ depend on $F(u,r)$ instead of r. One then has

$$\left.\frac{\partial u_\gamma(\gamma=0)}{\partial\gamma}\right|_{F,\Omega} = \frac{1}{B}\, R_I^{(1)}[R(B(u_1 - u_0))] \quad , \tag{21}$$

which differs from Eq. (12) in that the derivative is evaluated at constant F,Ω instead of r,Ω. We must then transform back to $\left.\frac{\partial u_\gamma(\gamma=0)}{\partial\gamma}\right)_{r,\Omega}$. From the chain rule,

$$\left.\frac{\partial u}{\partial\gamma}\right)_{r,\Omega} = \left.\frac{\partial u}{\partial\gamma}\right)_{F,\Omega} + \left.\frac{\partial u}{\partial F}\right)_{\gamma,\Omega} \left.\frac{\partial F}{\partial\gamma}\right)_{r,\Omega} \quad , \tag{22}$$

$$\left.\frac{\partial F}{\partial u}\right)_{\gamma,\Omega} = \left.\frac{\partial F}{\partial u}\right)_{r} + \left.\frac{\partial F}{\partial r}\right)_{u} \left.\frac{\partial r}{\partial u}\right)_{\gamma,\Omega} \quad , \tag{23}$$

and

$$\left.\frac{\partial F}{\partial\gamma}\right)_{r,\Omega} = \left.\frac{\partial F}{\partial u}\right)_{r} \left.\frac{\partial u}{\partial\gamma}\right)_{r,\Omega} \quad . \tag{24}$$

Note that for $\gamma = 0$, $\left.\frac{\partial u}{\partial r}\right)_{\gamma,\Omega} = \frac{du_0}{dr}$. Substituting Eqs. (23) and (24) in Eq. (22) and solving for $\left.\frac{\partial u}{\partial\gamma}\right)_{r,\Omega}$, we have

$$\left.\frac{\partial u}{\partial\gamma}\right)_{r,\Omega} = \left.\frac{\partial u}{\partial\gamma}\right)_{F,\Omega} \left(\frac{\left.\frac{\partial F}{\partial u}\right)_r}{\left.\frac{\partial F}{\partial r}\right)_u \frac{dr}{du_0}} + 1 \right) \quad . \tag{25}$$

The term in parentheses is independent of Ω, so we have in analogy to Eq. (13),

$$\iint R(B(u_1(F,\Omega) - u_0(F)))d\Omega = 0 \quad , \tag{26}$$

for the determination of $u_0(F)$. As a special case, we have chosen $F = u + sr$, where s is a constant. For a proper choice of s, lines of constant F will be steeper than the slope of the potential for all values of r,Ω. This leads to an invertible transformation and a well defined value of u_0. For a choice of $s = -100°K/Å$, the results are nearly the same as for the radial averaging but are also defined for the attractive region.

Using the median as the effective spherical potential, the results for N_2 are good to 1.5% or better in the region of $1.3\ g/cm^3 < \rho < 2.3\ g/cm^3$ and $500°K < T < 12000°K$. Preliminary results for CO_2 indicate an accuracy of about 3%. So we have demonstrated the existence of an accurate effective spherical potential for molecules commonly found in detonation products and have shown how to find these potentials where the anisotropic potentials are known. These results make reasonable the procedure of fitting spherical potentials to data. They imply an even better empirical method. That is, to fit the data with an anisotropic potential where the thermodynamics is evaluated using the effective spherical potential.

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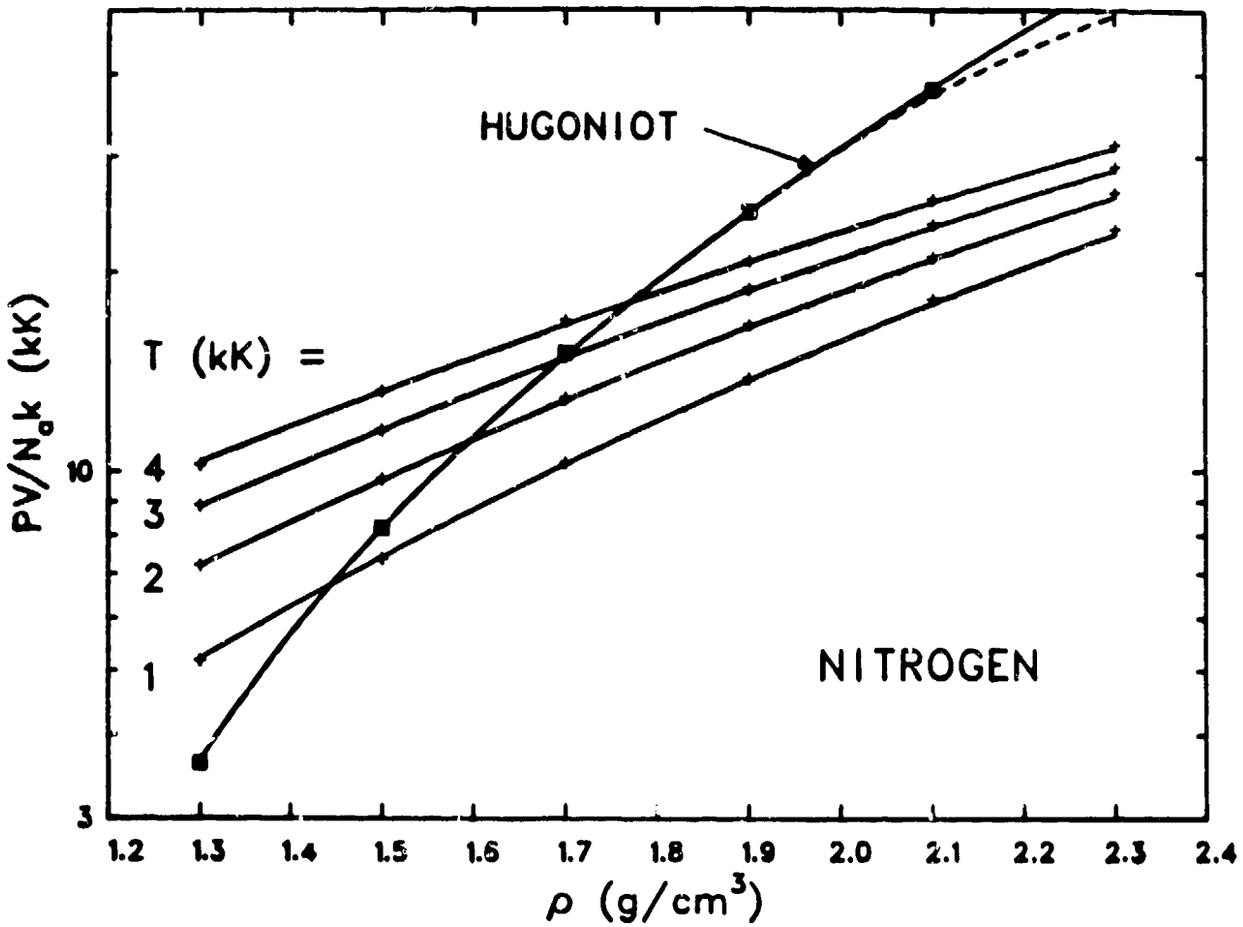

Fig. 1.
Isotherms and Hugoniot for N_2 from MD (+ = isotherm, ⊠ = Hugoniot) and an effective spherical potential (line) fit to pressure, energy, and temperature on the MD Hugoniot. (kK = 10^3 Kelvin.)

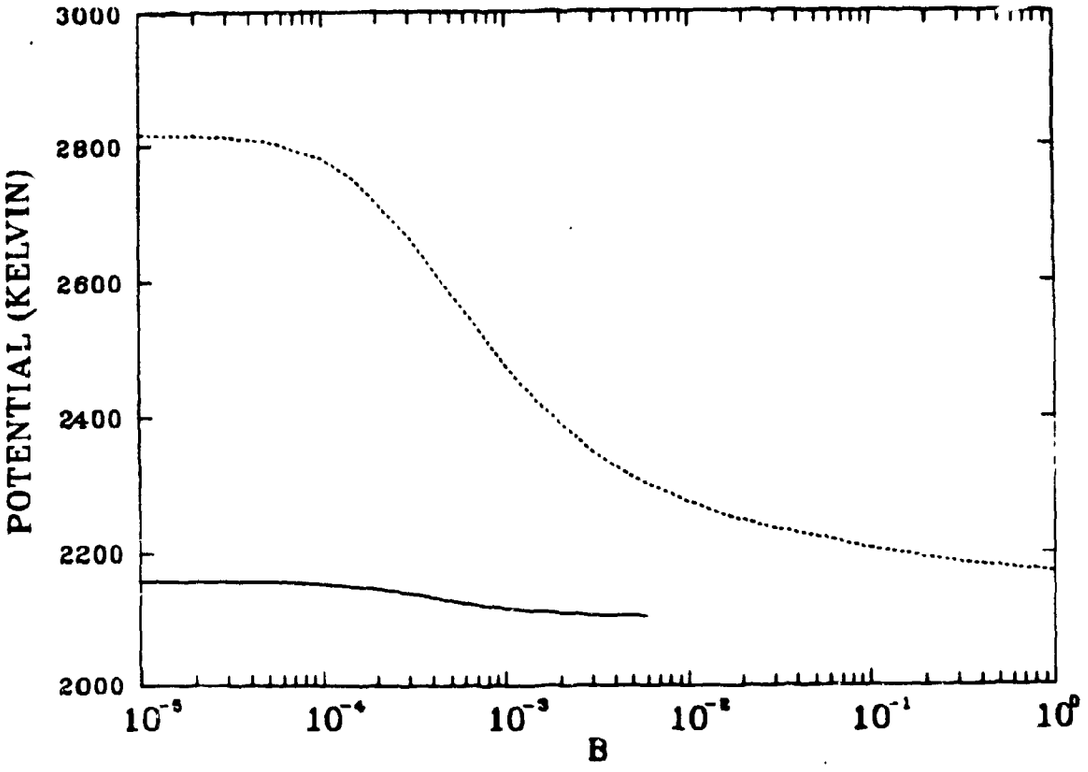

Fig. 2.
Spherical potential at r = 3.0 Å for potential averaging (dashed line, Eq. (13)) and radial averaging (solid line, Eq. (20)) as a function of the parameter B. The radial averaging is plotted vs 10^{-4} B since 10^{4} BΔr roughly correlates with BΔu.