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Implications of Many-Body Forces for Equations of State at High Pressure [and Discussion]

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Implications of many-body forces for equations of state at high pressure

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In this paper we review our recent work concerned with assessing the significance of many-body forces for short-range interactions of closed shell atoms and molecules. *Ab initio* molecular orbital calculations (of the supermolecule type) have been carried out to determine three-body potentials for the following species: He, Ne, H_2, N_2, CO and CO_2. For He, Ne, H_2 and N_2 we have also carried out calculations of the four-body potential for a limited number of orientations. These studies show that, for all these species, there are significant deviations from pair-wise additivity at short separations. The effect of these many-body interactions on the equation of state for dense fluids (such as detonation products) is being investigated by Monte Carlo simulation, and recent results for high-pressure helium are described.

1. Introduction

The purpose of this paper is to review recent work on many-body forces in dense fluids, and to assess the likely significance of these to detonation processes.

The products formed by a detonating explosive are important in two respects. First, they support the shock front, and therefore are necessary for the continued propagation of the detonation. Secondly, they are responsible for the external work performed by the explosive. For these reasons an understanding of the properties of the detonation products is essential for both predicting detonation performance (as in ideal detonation codes such as TIGER), and for modelling the effect of explosives on external systems (as in hydrocode simulations).

The final products of detonation from most common explosives are mainly small gaseous molecules (e.g. N_2, oxides of nitrogen, oxides of carbon and H_2O) and some solid carbon. These products are formed at high pressure and temperature (*ca.* 30 GPa and 3000 K) and consequently exhibit highly non-ideal behaviour. The first step in obtaining a fundamental model of this behaviour is to clearly understand the intermolecular forces operating. There are other aspects to the problem, not directly linked to the intermolecular forces, which ultimately need consideration. Chief amongst these are; carbon cluster formation, molecular dissociation and the effect of transient/unstable species. However, in this paper we shall concentrate entirely on the fundamental problem of obtaining an accurate description of the intermolecular forces, and in particular at the breakdown of the pair-wise additivity assumption. We shall additionally restrict our discussion to the repulsive (i.e. short-range) part of the potential.

2. Many-body forces

A number of recent studies (Ree & Bender 1974; Haskins & Cook 1988; Cook & Haskins 1990) have highlighted the large deviations from pairwise additivity which

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can arise at short intermolecular separations. For closed shell species these deviations are in the main due to non-additivity of the first-order exchange interaction, although in polar molecules it is possible that the non-additivity of induction or exchange-induction energies could be significant, and possibly even dominate the many-body effect (Cook & Haskins 1990). In this paper we will concentrate on helium to illustrate the discussion, as studies have reached a more advanced stage with this simple element (Haskins & Cook 1988, 1990, 1992), but the relevance to detonation products will be clearly indicated.

Most calculations of many-body, and indeed pair, potentials have been carried out using the supermolecule approach. This method entails computing the total energy of the interacting molecules, considered as a complex, and the individual molecules. The interaction energies are then simply obtained by taking the appropriate differences:

$$E^2(R) = E_2(R)-2E_1, \quad E^3(R) = E_3(R)-3\{E_2(R)-E_1\}, \text{ etc.},$$

where the E^i represent the ith-body potentials, and the E_j represent the total energy of the complex containing j atoms or molecules.

The energy calculations are most commonly carried out using a molecular orbital method. The approximations used in the molecular orbital treatment, and their effect on the accuracy of the potential, are discussed by Haskins & Cook (1990).

It is well known that in the repulsive region, pair potentials between closed shell species increase approximately exponentially as the separation is decreased. This arises from the dependence of the potential on overlap, and it is consequently not surprising that an exponential dependence appears to dominate the many-body interactions that have been studied to date. However, the behaviour of the many-body terms is rather more complex due to a strong dependence on geometric arrangement. Some three-body energies for helium are illustrated in figure 1, and are typical of other non-polar closed shell systems. Figure 1 shows the results of fourth-order Moller–Plesset calculations using a 6-311G** basis set. Six potential curves are shown, each representing a different geometric arrangement of the atoms. The atoms were placed at the corners of an isosceles triangle and six values of the included angle θ (between the equal sides) were considered.

From figure 1 it can be seen that for $\theta < 120°$ the three-body energy is always negative (i.e. it softens the potential). The three-body energy increases approximately exponentially in magnitude as the separation is reduced. However, for $\theta = 150°$ and 180° a different pattern of behaviour is observed. The three-body contribution to the potential is now repulsive for separations down to *ca.* 0.7 Å†, below which the curves turn over sharply, and the three-body term rapidly becomes an attractive contribution, as observed for smaller values of θ. This behaviour is consistent with the constraint that at zero separation, where all geometries are equivalent, the three-body energies must be the same for all orientations. Indeed simple application of united atom perturbation theory at zero order shows that at $R = 0$, the three-body energy, $E^3(0)$, will be given by:

$$E^3(0) = E_{\mathrm{C}}-3\{E_{\mathrm{Be}}-E_{\mathrm{He}}\},$$

where E_{C}, E_{Be} and E_{He} are the electronic energies of carbon, beryllium and helium

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† $1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

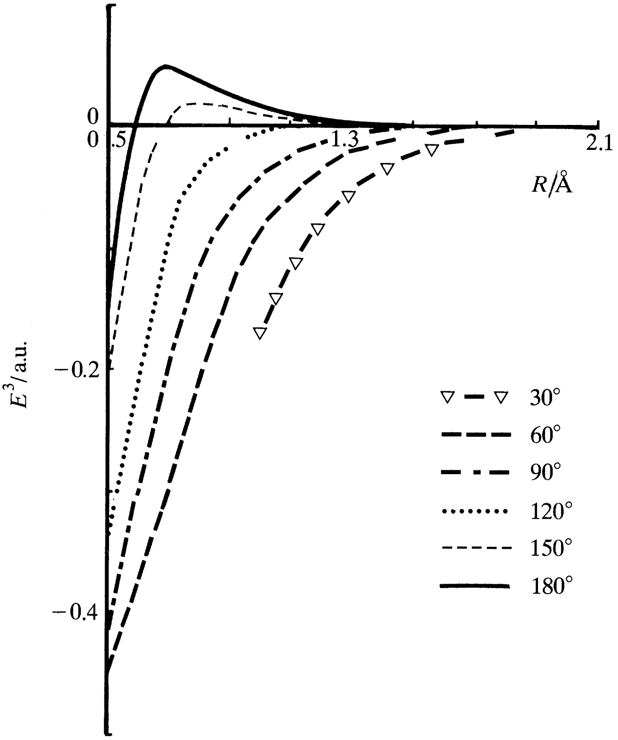

Figure 1. The three-body energies for helium in a range of isosceles triangle geometries. The angle quoted refers to that between the equal sides.

respectively. The above expression yields $E^3(0) = -2.56$ a.u.†, showing that for helium all three-body orientations will yield a negative three-body potential for sufficiently small R. Extension of this argument to four-bodies yields $E^4(0) \approx -0.08$ a.u. Considered alongside the electronic pair interaction energy at zero separation (i.e. excluding the infinite nuclear–nuclear repulsion), which has a value of -8.87 a.u., these calculations suggest that the many body series may converge quite rapidly at very short distances. However, great care must be taken in deciding where to truncate such a series, because in bulk matter there are in general more $(n+1)$-body clusters than there are n-body clusters, and the density and packing arrangement will effect the convergence. For He, Ne, H_2 and N_2 we have carried out some calculations of four-body potentials for a limited number of configurations. The general features shown by the results of these calculations are the following.

1. A repulsive interaction for all geometries considered (tetrahedral, square and linear). This means that for linear geometries the four-body energy has the same sign as the three-body, whereas for the other configurations they oppose each other. This may lead to significant cancellations, particularly in solid lattices.
2. The four-body potential is always smaller than the three-body.
3. An approximately exponential increase in magnitude of the four-body term with decreasing separation. At very short distances the four-body energies calculated for helium show signs of turning over to become negative as predicted by united atom arguments.

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† 1 a.u. $\approx 1.11265 \times 10^{-10}\,\mathrm{C^2\,m^{-1}\,J^{-1}}$.

Although the significance of four-body and more-body terms will clearly increase with increase in pressure and packing density, at the present time studies of these forces are not sufficiently well advanced to make any general statements concerning their importance.

The magnitude of three-body energies (such as those displayed in figure 1) can be best appreciated by expressing them as a percentage of the total pair interaction for the three-body cluster. These percentage deviations from pair-wise additivity initially increase as the separation is reduced, but at very short distances they reach a maximum and eventually decrease in significance as the interaction becomes dominated by the nuclear–nuclear repulsion. The equilateral triangle arrangement yields the largest three-body effect, and for helium in this configuration a maximum deviation of 20.6% is obtained at a separation of 0.9 Å. When compared at equal points on the potential curve very similar deviations from additivity are obtained for the isoelectronic hydrogen molecule (Haskins & Cook 1986), but slightly smaller effects have been found for heavier atoms/molecules (Haskins & Cook 1986, 1988; Cook & Haskins 1990). Although the deviations for first row atom and molecules are a little smaller they are still highly significant, and for N_2 (in D_{3h} symmetry) range from 2–11% over the range 2.8–1.6 Å. Similar significant deviations have been found in other common detonation products. Hay *et al.* (1984) computed a highly accurate pair potential for N_2 and compared a theoretical Hugoniot based on this potential with experimental data. They found that the theoretical potential was too stiff to give good agreement and concluded that for hot dense N_2 many-body effects were probably responsible for the discrepancy. The calculations of three-body energies in N_2 would appear to support this conclusion.

3. Monte Carlo simulation

The calculations discussed in the last section clearly indicate that many-body effects can be expected to have a pronounced effect on the equation of state for hot dense fluids such as detonation products. However, to fully understand the importance of these terms it is necessary to calculate the thermodynamics of a system both with and without consideration of many-body effects. To illustrate this approach we review, in this section, our recent Monte Carlo simulations of dense helium.

In our calculations on helium (Haskins & Cook 1992) we have adopted a pair potential based on the HFDHE2 potential of Aziz *et al.* (1979) for separations greater than 1.04 Å. At shorter distances our potential is based on the work of Pathak & Thakkar (1987), which uses an interpolation function to link the HFDHE2 potential to the united atom perturbation theory results for very short (less than 0.26 Å) separations. This approach gives an improved representation of the pair interaction at short distances with the correct limiting behaviour as $R \rightarrow 0$. For simplicity we will call this combined pair potential HF2, and in figure 2 it is shown plotted together with the pair potential obtained from MP4/6-31G** calculations. The reasonable agreement between these potentials (over the range 0.5–2.0 Å) enables us to adopt three-body potentials computed at the MP4 level as corrections to the HF2 potential. A curve fit has been obtained for the three-body energies (shown in figure 1), and the HF2 potential supplemented with this three-body term will be referred to as the HF3 potential.

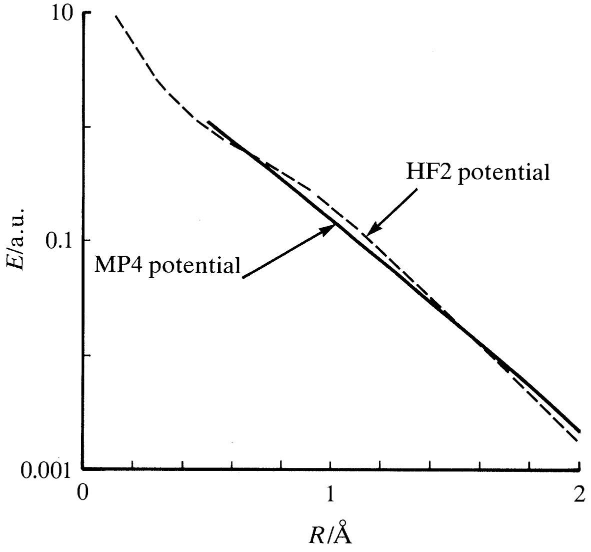

Figure 2. Pair potentials for helium.

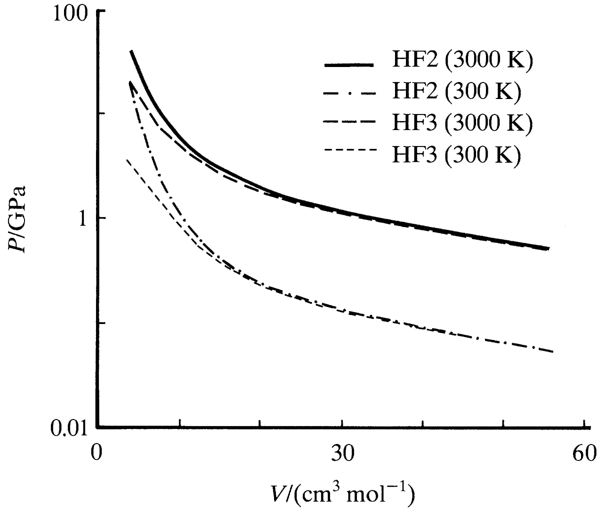

Figure 3. Isotherms (300 K and 3000 K) for helium computed using the HF2 and HF3 potentials.

We have used both the HF2 and HF3 potentials in Monte Carlo simulations of dense helium. The Monte Carlo code used was essentially a standard implementation of the Metropolis method with generalizations to handle explicit dependence on three-body potentials. Two isotherms (300 K and 3000 K) have been computed covering a volume range 3.9–55 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$. The calculations were carried out using a central cell of 864 atoms, which for these conditions results in no significant errors from neglect of long-range interactions. The pressures computed are shown in figure 3.

Examination of figure 3 clearly shows that the effect of including three-body interactions is to produce an effective softening of the potential. Significant deviations from pair-wise additivity become apparent at volumes less than *ca.* 11 $\text{cm}^3\ \text{mol}^{-1}$ for both isotherms. For a temperature of 3000 K and pressures of 10 GPa and above (i.e. typical detonation conditions) the three-body term leads to large corrections, indicating that, despite the smaller three-body energies of most detonation products, there will probably be an important many-body contribution to the detonation product equation of state.

In addition to the isotherms we have computed theoretical Hugoniots based on the HF2 and HF3 potentials. To enable comparison with experimental data to be made we have used the initial conditions used in the shock experiments of Nellis *et al.* (1984), namely $T = 4.3$ K, $v = 32\ \text{cm}^3\ \text{mol}^{-1}$, and $P = 0.1$ GPa. The computed Hugoniots and the shock data are shown in figure 4.

It is clear from figure 4 that the HF3 potential gives a Hugoniot in excellent agreement with the shock data, whereas the HF2 potential is too stiff at the higher pressures. Nellis *et al.* (1984) found that the HFDHE2 and other pair potentials were too stiff to give good agreement with their experimental data and concluded that many-body effects were important. The excellent fit obtained with the HF3 potential confirms this assertion, and shows that at pressures up to 16 GPa an accurate description of helium can be obtained with a theoretically based three-body potential.

Some preliminary calculations at higher compressions have shown that at volumes below *ca.* 3 $\text{cm}^3\ \text{mol}^{-1}$ the three-body corrections lead to an excessive lowering of the energy (eventually leading to unphysical negative values for the excess internal energy). This suggests that at very high pressures four-body forces are important and need to be included to compensate for the excessive softening effect of the three-body terms. Similar conclusions have been reached in studies of solid molecular hydrogen (Ree & Bender 1974).

4. Conclusions

In this paper we have reviewed recent studies of many-body forces. Molecular orbital calculations clearly show that at small intermolecular separations significant deviations from pairwise additivity occur for many light elements and small molecules. Although the importance of these forces to detonation processes is yet to be confirmed there is considerable evidence to suggest that they do make a significant contribution. In particular, the Monte Carlo studies of helium show the very important contribution of three-body forces, for this element, under detonation-like conditions.

The problem of where the many-body series can be terminated with negligible error is not easily answered. Clearly it is influenced by the atomic/molecular species and the pressure and temperature being considered. However, from the work on helium, which can be expected to have more pronounced many-body contributions than detonation products, it looks probable that consideration of three-body effects will suffice to describe the detonation fume equation of state.

In the near future we hope to carry out Monte Carlo simulations, similar to those on helium, for a number of common detonation product species. Because of the computational difficulty in handling many-body potentials in treatments of bulk matter we intend initially to use these studies to obtain theoretically based ‘effective pair potentials’ (i.e. pair potentials which incorporate an averaged many-body effect) which can be used in modelling applications. Looking into the more distant future it may, with the advent of massively parallel computer systems, ultimately

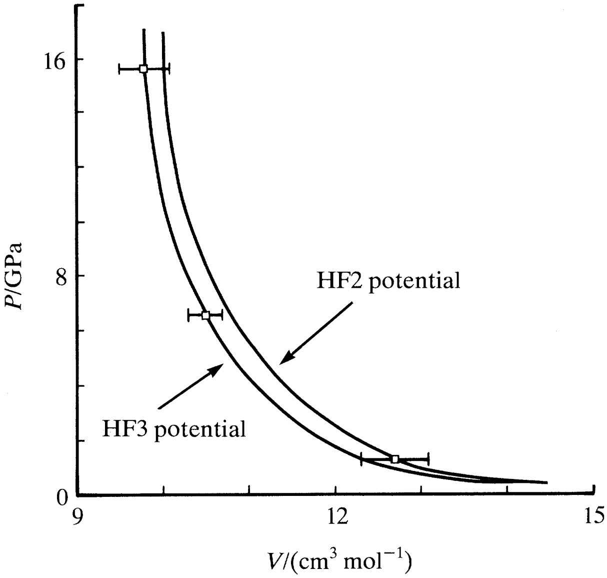

Figure 4. Hugoniots for helium computed using the HF2 and HF3 potentials. The experimental shock data (with error bars) is also shown for comparison.

become feasible to treat such many-body effects explicitly in real modelling applications.

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Discussion

F. Volk (*Fraunhofer Institute, F.R.G.*). By detonating in helium will there be a change in the products when the much higher heat of conduction of helium is taken into account?

P. J. Haskins. Our work has not really addressed the effects of inert atmospheres on detonation processes, but it is possible that changes in the properties of the atmosphere could alter the final freezing-out of reaction products. However, I would expect the effects to be small unless very high pressures were used.