

STRUCTURE OF SHOCK WAVES IN DENSE GASES AND LIQUIDS - MOLECULAR DYNAMICS SIMULATION

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Abstract: In our earlier paper [3] we reported the investigation of the shock structure in dense, monatomic gas - argon. Here we extend our work to dense molecular gases and to liquids. We investigate, in particular, the influence of the electric charges (electric dipoles, quadrupoles etc.) of the molecules on the shock wave structure.

Key words: Shock structure, Dense media, Molecular Dynamics.

INTRODUCTION

The structure of shock waves in dense media has already been investigated by a number of authors (see e.g. [1] and [2]). The method used most frequently was the Molecular Dynamics simulation. The molecules of the medium were usually modeled as hard spheres, or points interacting with Lennard-Jones potential. The thicknesses of the shock waves were related to the mean free paths, defined as for dilute gases. This in our opinion was incorrect. For dense media such mean free paths tend to zero with increasing density, so the relative shock thicknesses tend to infinity, which is obviously unphysical. As discussed in our earlier paper [3], the proper reference length for dense media is the average distance between the centers of molecules, first suggested by Bridgman [4] – not the mean free path.

In the paper [3] we presented, in addition, the results for a monatomic noble gas – argon, showing that in the whole range of densities the shock thickness decreases smoothly with increasing density when related to the mean free path for a dilute medium and to the mean distance between centers of the molecules for dense, provided that the shock Mach numbers are similar (Fig. 1 – left). As shown there, in dilute argon at the mean free path $\lambda=0.9\text{mm}$ and the shock Mach number $M_s=2.04$ the shock thickness is $L=5\lambda$ (curves 1 and 2 in Fig. 1 – left) while at mass density equal to the density of water (mean distance between centers of the molecules $\lambda=4.048\text{\AA}$) and similar Mach number it is equal to only $L=2.9\lambda$ (curve 5 in Fig. 1 – left).

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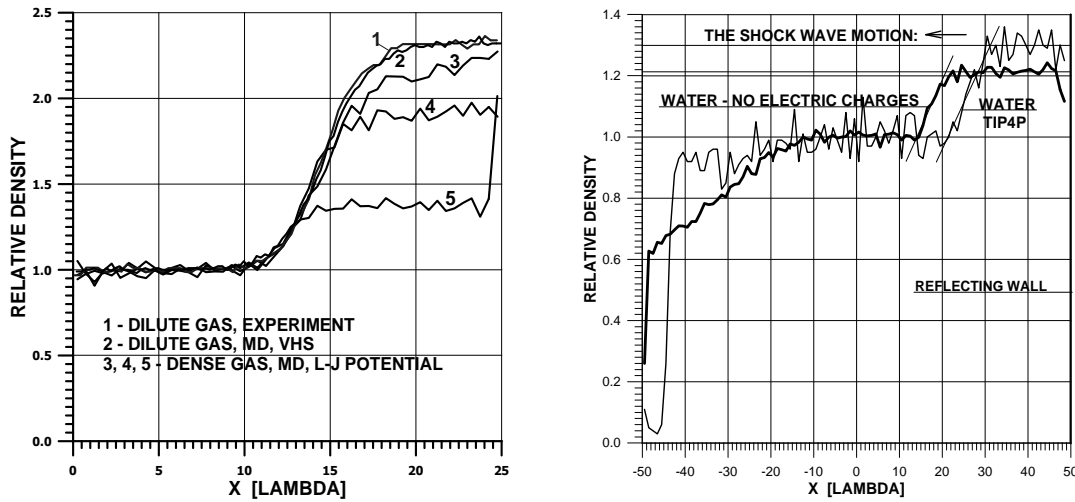


Fig. 1: Shock wave structures in argon (left) and water (right)

In this paper we present the results for more complex substances, obtained with the Molecular Dynamics simulation method with the use of the program MOLDY [5].

SHOCK WAVE IN NITROGEN

We started the present work simulating the shock structures in nitrogen – diatomic gas, with molecular model containing five electric charges symmetrically displaced with respect to the center of the molecule [6]. The results were similar to those for argon: the thickness of the shock in dilute nitrogen for the Mach number $Ms=2.28$ interpolated from experimental results of Linzer and Hornig [7], was equal to $L=3.66\lambda$ (where λ is the mean free path), while the calculated value for dense nitrogen (at mean distance between centers of the molecules $\lambda=4.048\text{\AA}$, similarly to the case of argon) was equal to $L=2.5\lambda$. The presence of electrostatic charges had no visible influence upon the shock structure.

SHOCK WAVES IN MOLECULAR LIQUIDS

At the next step we investigated the shock structure in more complex substances. Water seemed appropriate for the first choice as its molecule was relatively complex and at the same time not too complex to require excessive amount of computing time. Out of large number of models of the water molecule the TIP4P model was selected. It consists of one oxygen atom, two hydrogen atoms, two positive electric charges ($0.52e$, where e - elementary charge) placed at the centers of the hydrogen atoms and one negative charge ($-1.04e$) placed close to the center of the oxygen atom. The molecules interact with each other with the Lennard-Jones potential between the oxygen atoms and with Coulombic forces between the electric charges.

The Molecular Dynamics simulations were performed for two cases: full TIP4P model and the same without electric charges. The shock wave was generated when a mass of water at temperature 300K, moving with velocity $V=620.9\text{m/s}$ collided with a plane,

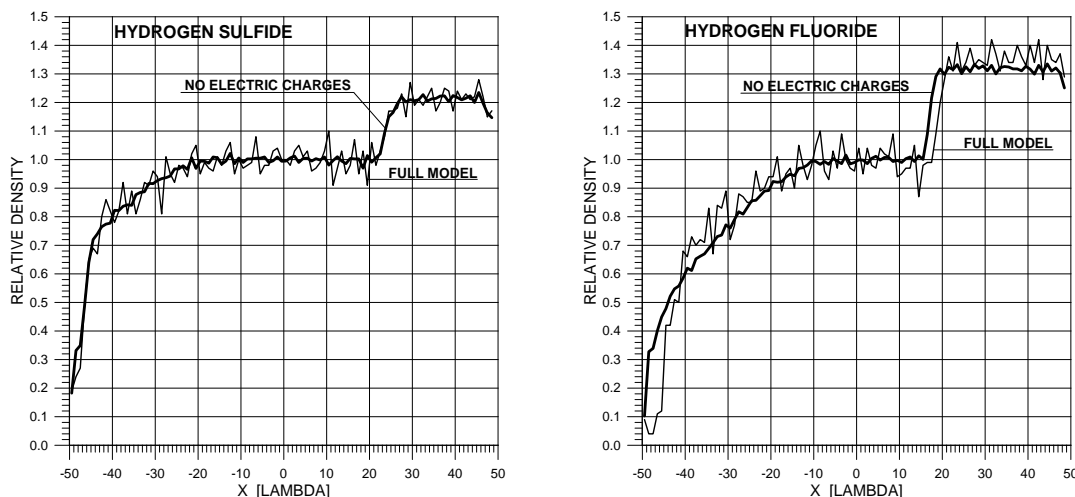


Fig. 2: Shock wave structures in hydrogen sulfide (left) and hydrogen fluoride (right)

perpendicular, impermeable wall. The velocity of the shock with respect to water in front of it was 2700m/s, corresponding to shock Mach number $M_s=1.80$.

Fig. 1 – right shows the density distributions along the axis perpendicular to the reflecting wall for the two simulated cases, for the same time after collision with the wall. It is evident, that lack of the electric charges makes the medium more "rigid" – the density increase across the shock in such "water" is smaller and the shock itself moves faster than in the real case. The density gradients inside the shocks in both cases are comparable, which may suggest, that electric charges do not influence them appreciably.

The next investigated substances were hydrogen sulfide and hydrogen fluoride. They both had nonzero electric dipole moment, similarly to water. Hydrogen sulfide, H_2S , at assumed density $914.9kg/m^3$ and temperature 300K is a liquid. Its molecule is similar to that of water (sulfur atom instead of oxygen) only the electric charges are much smaller: $-0.319e$ at the sulfur atom and $0.1595e$ at hydrogen atoms. It was assumed, that all atoms interact with the Lennard-Jones potentials. As before two cases were simulated – with and without the electric charges. The shock was generated in the same way as before; the initial velocity of the medium was equal to $V=474.6m/s$ and the resulting velocity of the shock with respect to the medium in front of it was 2658m/s.

Fig. 2 – left shows the density distributions for H_2S similar to those in Fig. 1 – right for water. There is practically no difference between the shock structures with and without electric charges – only the curves for the medium without electric charges are smoother since it was then possible to take more molecules for simulation.

Hydrogen fluoride, HF, at density $959kg/m^3$ and temperature 300K is also a liquid. It has a diatomic molecule consisting of atoms of fluorine and hydrogen. Each atom has an electric charge equal to $0.4223e$ – hydrogen positive, fluorine negative. Both atoms interact with the Lennard-Jones potentials. The velocity of the medium before reflection from the wall is this time $V=652m/s$ and the velocity of the shock with respect to the medium is 2484m/s. Simulations with and without electric charges were done.

Fig. 2 – right shows, as before, the density distributions for HF. This time some difference between simulations with and without electric charges is evident, although it is much less pronounced than for water. The density increase across the shock in the medium without electric charges is smaller and the shock speed is higher than otherwise.

CONCLUSIONS

The obtained results seem to indicate that the presence of electric charges (dipoles, quadrupoles etc.) in molecules of the dense medium has generally little influence upon the structure of shock waves. The only exceptions found were water and liquid hydrogen fluoride, which out of all considered substances had the largest electric dipole moments. Comparing thicknesses of the shocks in all considered dense media (2.9λ in argon, 2.5λ in nitrogen, 3.5λ in hydrogen sulfide, 2.6λ in hydrogen fluoride and 10λ in water) one can notice, that the shock wave in water is unexpectedly thick. This suggests, that it might be an artifact, connected with imperfection of the employed water model TIP4P. This might be verified if the thickness of the shock wave in water was measured experimentally, which could be done e.g. with the light reflectivity method of Linzer and Hornig [7].

REFERENCES

- [1] J.M. Montanero, M. Lopez de Haro, A. Santos, V. Garzo, Simple and accurate theory for strong shock waves in a dense hard-sphere fluid. *Phys. Rev. E*, **60**, 7593 (1999)
- [2] S. Schlamp, B.C. Hathorn, Incomplete molecular chaos within dense-fluid shock waves. *Phys. Rev. E*, **76**, 026314 (2007)
- [3] Z.A. Walenta, A.M. Slowicka, Structure of shock waves in dense media. *Shock Waves*, ed. K. Kontis, ISBN:978-3-642-25687-5 (2012)
- [4] P.W. Bridgman, The Thermal Conductivity of Liquids under Pressure. *Proc. Amer. Acad. Arts and Scie*, **59**, 141-169 (1923)
- [5] K. Refson, Moldy: a portable molecular dynamics simulation program for serial and parallel computers. *Comput. Phys. Commun.*, **126**, 3, 309-328 (2010)
- [6] C.S. Murthy, S.F. O’Shea, I.R. McDonald, Electrostatic interactions in molecular crystals. Lattice dynamics of solid nitrogen and carbon dioxide. *Molecular Physics*, **50**, 3, 531-541 (1983)
- [7] M. Linzer, D.F. Hornig, Structure of shock fronts in argon and nitrogen. *Phys. Fluids*, **6**, 12, 1661-1668 (1963)