Structure of shock waves in complex molecular liquids

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1 Introduction

The present paper is a continuation of our earlier work on the structure of shock waves in dense media. Simple, monoatomic gas, argon, was considered first [1]. It was found, that the shock thickness in dense argon, when related to the mean distance between the molecules (as suggested by P.W. Bridgman [2]) decreased with increasing density.

In our second paper [3] relatively simple molecular liquids: liquid nitrogen, hydrogen fluoride, hydrogen sulfide and water were considered. We investigated there the influence of the electric charges (dipole and quadrupole moments) of the molecules upon the shock structure. We found, that this influence was visible only when the dipole moments were sufficiently large, as was the case for water and hydrogen fluoride.

Here we investigated more complex molecular liquids: methane (CH_4) and sulfur hexafluoride (SF_6), to see whether and how complexity of the molecules influences the structure of the shock wave. The results were obtained with the standard Molecular Dynamics technique [4]. To illustrate the dependence of the thickness of the shock wave on density of the medium, the results for liquid sulfur hexafluoride were compared with experimental, shock tube results in gas phase at low density.

2 Molecular Dynamics Simulation

The reported simulations were performed with the program MOLDY [5], originally designed for stationary media. Here it was supplemented with additional procedures for calculation of the flow phenomena.

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After the initial equilibration, the medium was set in motion by adding the assumed macroscopic velocity V to the x–component of the thermal velocity of each molecule. At the same time two impermeable, reflecting planes were inserted into the flow at the left and right borders of the calculation domain, thus generating the shock wave moving from the right border to the left and some other disturbance moving from the left border to the right.

The number of molecules taken for each simulation run was equal to 250000. The time step assumed for simulation was equal to 0.001 picosecond, the equilibration period was 6000 time steps long (6 picoseconds). The following actual simulation of the flow was finished after time period sufficiently long to estimate the shock velocity and structure.

As stated in the Introduction, in the present research the flows of methane (CH_4) and sulfur hexafluoride (SF_6) were investigated. The molecule of methane consists of one central carbon atom surrounded by four hydrogen atoms placed at the vertices of a regular tetrahedron. The molecule of sulfur hexafluoride consists of a central atom of sulfur and six atoms of fluorine at the vertices of a regular octahedron. All molecules consisted of atoms rigidly connected (no vibrations were allowed). Each atom interacted with atoms of other molecules through the Lennard – Jones potential.

The assumption of rigidity of the considered molecules was sensible, since relaxation times for the vibrational degrees of freedom were at least an order of magnitude longer than the time, which a molecule needed to pass through the shock wave.

3 Low density experiment

In gaseous sulfur hexafluoride the measurements of the shock wave structure (density) were performed in the low density shock tube at the Institute of Fundamental Technological Research in Warsaw. The tube, was 250 mm in diameter, therefore it was possible to make experiments at initial densities corresponding to mean free paths up to a couple of millimeters.

In the reported experiments the initial pressure of sulfur hexafluoride was about 2.65 Pa, the initial temperature about 300 K, the mean free paths about 0.95 mm and the shock thicknesses about 3 mm. Under such conditions it was possible to measure the density inside the shock with the standard electron beam attenuation technique [6].

4 Results

4.1 Sulfur Hexafluoride

Parameters of the simulated flow in front of the shock wave in liquid sulfur hexafluoride were as follows:

- temperature – $T = 300K$
- mass density – $\rho = 1880kg/m^3$
- number density – $n = 7.7518 * 10^{27}m^{-3}$
- flow velocity – $v = 505.28m/s$
- sound speed [7] – $a = 707.03m/s$

The average distance between neighbouring molecules (according to Bridgman's definition [2]) was equal to:

$\lambda = n^{-3} = 5.0528\mathring{A}$

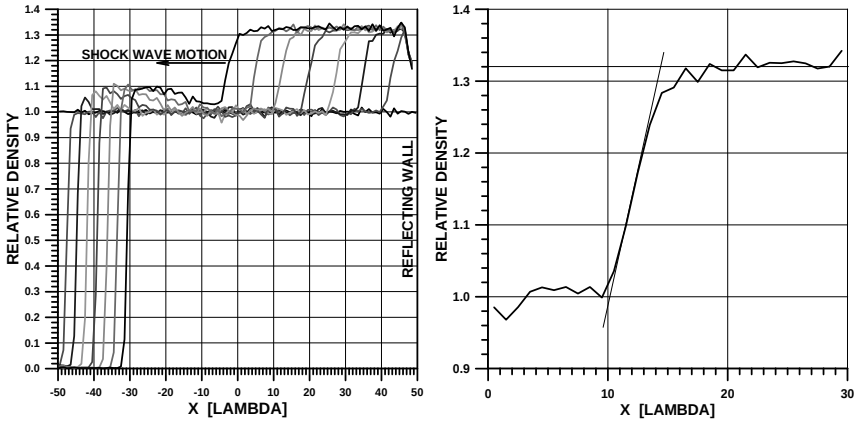

Fig. 1 Liquid sulfur hexafluoride: Left – shock wave moves from the right border to the left; free surface moves from the left border to the right.
Right – density distribution inside the shock wave

Figure 1 – left shows seven diagrams of density distribution along the x-axis as calculated for seven evenly spaced time instants (time elapsed between two neighbouring distributions equal to $\delta t = 2.5ps$). At the right side of the picture the shock wave is moving to the left from the right border of the calculation domain. At the left side the free surface of the liquid is moving to the right. From this picture it is possible to estimate the velocity of the shock with respect to the medium in front of it equal to $Us = 2047.71m/s$ and the Mach number $Ms = 2.896$.

In Figure 2 one of the shock wave density diagrams is shown magnified and extended in time. This makes it possible to estimate the thickness of the shock, which is equal to $L = 4.2\lambda$.

It is interesting to note, that according to our low density experiment, the thickness of the shock wave in gaseous, rarefied SF_6, at initial temperature $T = 300K$, density $\rho = 0.000156kg/m^3$ and shock Mach number $Ms = 2.841$ (comparable to that in liquid SF_6) was equal to $L = 3.3\lambda$ – less than in liquid SF_6. This is different from our earlier result for argon [1], in which shock thickness decreases with increasing density. The reason for this difference may be the influence of the rotational degrees of freedom of the molecules of SF_6. Such molecule has large moment of inertia (the components equal to 185.903, 185.903, 185.903 $amu * Å^2$ respectively) since the six heavy fluorine atoms are placed far from its center of mass. Collisions of the molecules in the gaseous medium possibly induce rotation of the molecules more efficiently than motion of the liquid, in which molecules are in permanent contact.

4.2 Methane

Parameters of the simulated flow in front of the shock wave in liquid methane were:

- temperature – $T = 120K$
- mass density – $\rho = 422.62kg/m^3$
- number density – $n = 1.5864 * 10^{28}m^{-3}$
- flow velocity – $v = 795.96m/s$
- sound speed [8] – $a = 1380.0m/s$

The average distance between neighbouring molecules was this time equal to:
$\lambda = n^{-3} = 3.9798Å$

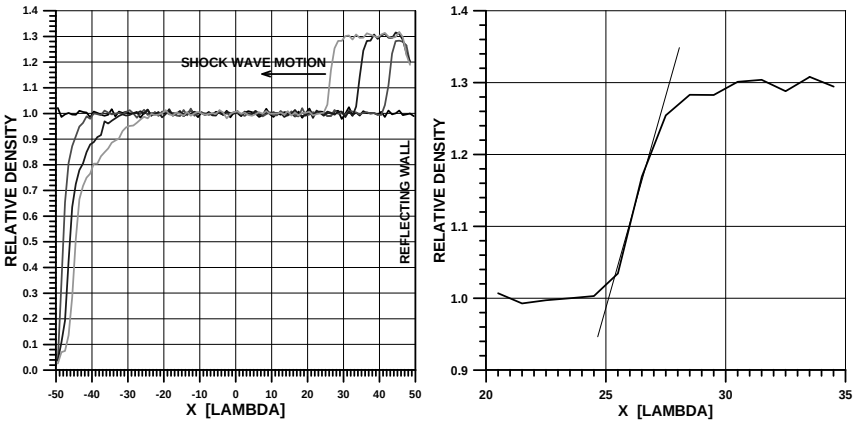

Fig. 2 Liquid methane: Left – shock wave moves from the right border to the left; rarefaction moves from the left border to the right.
Right – density distribution inside the shock wave

Figure 2 – left shows three diagrams of density distribution along the x-axis evenly spaced in time (time between two neighbouring diagrams $\delta t = 1.25ps$). As before it is possible to estimate the velocity of the shock with respect to the medium in front of it, $Us = 3449.71m/s$ and the Mach number $Ms = 2.50$.

Figure 2 – right shows the magnified and extended shock density diagram; shock thickness estimated from it is equal to $L = 2.55\lambda$. This value seems surprising. It is smaller than the value $L = 2.9\lambda$, reported in [1] and [3] for monoatomic gas, argon, at shock Mach number $Ms = 2$ and similar number density - in spite of complex structure of the molecule. However the moment of inertia of the methane molecule is much smaller than that of SF_6 (components 3.15073, 3.15074, 3.15064 $amu * \AA^2$ respectively) since the hydrogen atoms, placed far from the center of mass of the molecule, are much ligter than fluorine atoms in SF_6. It is therefore conceivable, that the methane molecule may behave similarly to the monoatomic molecule of argon.

5 Conclusions

It was demonstrated previously [1], that for monoatomic, noble gas – argon – at high densities the shock thickness related to the mean distance between the molecules decreases when density increases. From the simulations and experiment presented here it follows, that for sulfur hexafluoride, SF_6, whose molecules have large moments of inertia, the shock wave in liquid phase (high density) is thicker than under rarefied gas conditions - contrary to the result for argon. For methane, CH_4, which also has complex molecules, however of small moments of inertia, the situation seems to be similar to monoatomic argon. This might suggest, that rotational degrees of freedom of the molecules are responsible for increasing shock thickness with increasing density of the medium. The rotational degrees of freedom seem to be more easily excited by molecular collisions in rarefied gas than by relative motion of the molecules being in permanent contact with the neighbours, as is the case in liquids. The effect is clearly visible for molecules having large moments of inertia and disappears for molecules with small moments.

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