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Structure of a Shock-Wave Front in a Liquid

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Solutions of the Navier-Stokes equations for strong shock waves in a dense fluid agree well with recent atomistic simulations using nonequilibrium molecular dynamics.

In the last few years nonequilibrium molecular dynamics has been applied to the simulation of transport processes in dense fluids, where transport is dominated by interparticle forces. A significant advance in nonequilibrium molecular dynamics has just been published by Klimenko and Dremin.[1] Their novel simulations now make it possible for us to assess the usefulness of the Navier-Stokes description of strong shock waves in liquid argon. These two cases correspond to shock waves traveling at 1.8 and 2.6 km/sec. (The velocity estimate of 2.0 km/sec quoted in Ref. 1 for the weaker shock is inconsistent with the profiles published in that paper.) They used the Lennard-Jones potential

$$\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] \qquad (1)$$

with $\epsilon/k = 120$ K and $\sigma = 0.3405$ nm. For both calculations the initial molar volume was 36 cm^3 and the temperature 131 K. The resulting data are of great interest because they represent the first detailed simulations of a realistic dense shocked fluid, far from equilibrium, in which the equations of motion are solved without approximation. Previous work on shock waves has been primarily devoted to the ideal-gas case[2-4] although Niki and Ono have studied an imperfect gas of hard spheres at densities up to about one-third the freezing density.[5] Tsai[6] and Holian and Straub[6] have also carried out dense-fluid shock simulations. Holian and Straub have obtained preliminary results very similar to those of Ref. 1.

A hydrodynamic understanding of the atomistic shock structure requires a complete description of the constitutive behavior of the Lennard-Jones fluid. This information is now available. Ree[7] has developed analytic expressions for the pressure and energy as functions of volume and temperature. Although similar to the Levesque-Verlet[8] equation of state, Ree's is specifically designed to handle the high-temperature, high-density region in which equations based on the collision-diameter approach fail. Transport coefficients for the Lennard-Jones fluid are available over a wide range of density and temperature. Ashurst[9] has suggested analytic forms describing the variation of the thermal conductivity and shear viscosity with density and temperature. The comprehensive work on hard spheres[10] has shown that the bulk and shear viscosities are nearly equal at dense-fluid densities up to about 85% of the freezing density. In the present work the excess, relative to the low-density limit, shear viscosity is used as an estimate for the bulk viscosity. The hard-sphere work suggests that this bulk-viscosity approximation could be in error perhaps by 10%.

I have used the equilibrium and transport data to solve the Navier-Stokes equations for the same shock waves simulated in Ref. 1. The equations can be solved for the density as a function of temperature through the shock-wave front, and this solution can then be used to find profiles of thermodynamic and hydrodynamic variables through the shock. It is convenient to begin the numerical integration[11] from the high-temperature, high-density state.

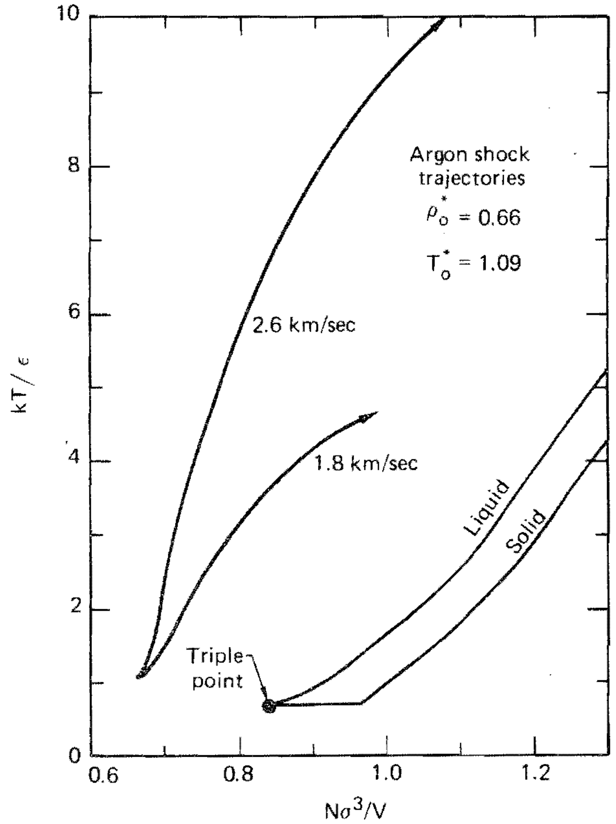

FIG. 1. Thermodynamic density-temperature states in the Lennard-Jones shock waves as calculated from the Navier-Stokes equations. The triple point and the phase boundaries separating the liquid and solid phases from the two-phase region are shown.

In Fig. 1, I indicate the thermodynamic states through which the two shocks travel. In Figs. 2 and 3 we compare our calculated profiles with those taken from Ref. 1. To make the temperature comparison I have used the average of T_x, T_y, and T_z from Ref. 1. Because the shock widths indicated are all of order 1 nm, the procedure used in Ref. 1—averaging over an 0.3-nm zone—seems valid. The Navier-Stokes profiles calculated here agree well with those found in the microscopic simulation. Note that in every case

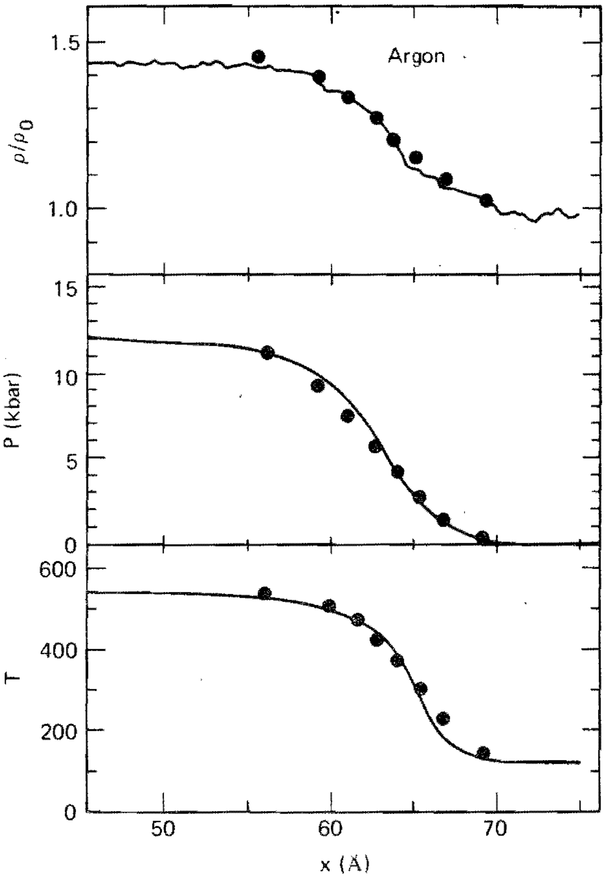

FIG. 2. Density, pressure, and temperature profiles taken from Ref. 1. The full curves are the results from atomistic molecular dynamics. The dots are the present calculations, the solution of the Navier-Stokes equations. Density relative to the initial density, pressure in kilobars, and temperatures in kelvins are given as functions of distance (angstroms). The pressure dots represent the local-thermodynamic-equilibrium pressure. The full curves include, from the Navier-Stokes viewpoint, the bulk-viscosity contribution to the mean pressure. The data shown correspond to a shock velocity of 1.8 km/sec.

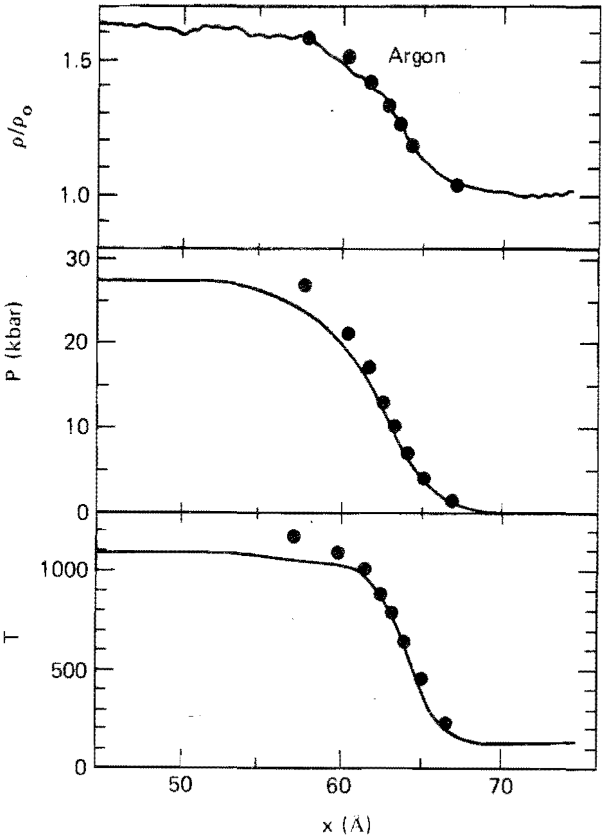

FIG. 3. Same as Fig. 2 except that the shock velocity is 2.6 km/sec. The poorer agreement of pressure and temperature at smaller x is probably due to small errors in the dynamical equation of state of Ref. 1.

the temperature gradient maximum leads the density-gradient maximum. Both gradients rise more steeply than they fall. These same features have been noted in a systematic study of Navier-Stokes dense-fluid shock structure carried out on the purely repulsive inverse-power soft-sphere potential.[12]

The shock structures found are qualitatively different from those based on solutions of the Boltzmann equation. If the low-density Boltzmann-equation transport coefficients are used, then the shock width is unrealistically small, less than the interparticle spacing. The order-of-magnitude increase in shock width over the Boltzmann-equation prediction is a consequence of the enhanced transport from interparticle forces.

It is apparent from Figs. 2 and 3 that the Navier-Stokes equations estimate the increase very well. The results are insensitive to variations in the thermal conductivity. If the conductivity is reduced by a factor of 2, the shock width is reduced by only 10%. Viscosity is more important. Both linear and nonlinear effects can be considered in modifying the Navier-Stokes equations. First, from the standpoint of generalized linear hydrodynamics,[13] the wavelength- and frequency-dependent transport coefficients could be used. A conservative estimate of the wavelength and frequency effects can be made by fitting a sine curve to the steepest portion of the shock profile. The resulting estimates for wavelength and frequency would give rise to shock-width reductions of at least 10%. A more significant modification would be the inclusion of nonlinear viscosity. The nonequilibrium molecular-dynamics calculations show that the shear stress required to sustain a finite strain rate increases less rapidly with strain rate than the linear Newtonian prediction.[14] The Ree-Eyring theory of non-Newtonian flow fits the nonequilibrium molecular-dynamics results well:

$$\eta/\eta_0 = [\sinh^{-1}(\omega\tau)]/\omega\tau. \qquad (2)$$

In Eq. (2) η_0 is the Newtonian viscosity, ω is the strain rate, and τ is a relaxation time.

The maximum strain rates found in the shock profiles lie well outside the range which can be treated with the steady-shear nonequilibrium methods of Ref. 14. Using a relaxation time of $9(m\sigma^2/\epsilon)^{1/2}$ to estimate the viscosity reduction in the shock from Eq. (2), we find a decrease exceeding a factor of 2, considerably larger than the frequency and wavelength effects predicted by generalized linear hydrodynamics. This extrapolated nonlinear decrease in viscosity is inconsistent with the dynamical profiles shown in Figs. 2 and 3. I conclude that the unmodified Navier-Stokes equations do provide a semiquantitative picture of the shock transition in a dense liquid, useful enough for most assessments of shock phenomena.

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