

Shock Hugoniot calculations and melting in Pb

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Abstract. Shock Hugoniot calculations are carried out for lead (Pb) using both solid and liquid state theories. The Hugoniot in solid and liquid cases are in mutual agreement within the experimental uncertainties. However, the shock temperatures are quite different as computed from solid and liquid state theories. This fact can perhaps be used to detect melting along the shock Hugoniot provided the shock temperatures are accurately measured.

Keywords. Shock; Hugoniot; pseudopotential; temperature.

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1. Introduction

In shock wave physics, there is controversy about the occurrence of melting. This is essentially due to the fact that slope changes due to melting on the shock velocity (U_s) and the particle velocity (U_p) curves are small and most often have alternative interpretation in terms of some electronic changes. The best illustration of this is provided by shock Hugoniot measurements of Gust and Royce (1973) and Carter *et al* (1975) on rare earths. These experiments show the existence of a relatively less compressible high pressure phase (beyond 30 GPa) in all members of the rare earth series. While Gust and Royce (1973) attribute this hardening of the Hugoniot to the onset of repulsive interaction between the noble gas cores, Carter *et al* (1975) identify it with melting. McMahan *et al* (1981) on the other hand have analysed this to be due to completion of $s \rightarrow d$ transfer in La. Theoretically, the location of melting can be done by matching Gibbs-free energies of the two phases as a function of temperature and density. However, very high accuracies are required. Therefore, one of the most challenging problems in the behaviour of materials under shock loading is the location of the melting point.

In recent past activities to detect melting experimentally have increased (Del'puech and Menlin 1983). McQueen *et al* (1983) measured velocity of sound waves behind strong shock waves in aluminium. In these experiments rarefaction waves were produced by impacting a target with a thin plate. An optical technique was used by them to determine where the rarefaction from the back surface of the impactor overtook the shock wave in a step wedge target (shock overtaking technique). Their data indicate that sound speed changes from longitudinal to bulk value at 125 GPa. This change is attributed to melting on the Hugoniot of Al. Also, Moriarty *et al* (1984) carried out detailed theoretical studies of the Al melting curve upto pressures

of 200 GPa. These authors used rigorous generalized pseudopotential theory which involved first principle nonlocal pseudopotential and parametrized local pseudopotential models, the parameters of which had been obtained by fitting to the first-principle band theory and experimental equation-of-state data. These treatments utilized full lattice dynamical calculations of the phonon free energy in the solid, within the harmonic approximation, and fluid variational theory to obtain the free energy of the liquid. With soft sphere reference system (Ross 1979), these workers (Moriarty *et al* 1984) predicted melting on the shock Hugoniot to begin at about 120 GPa and to end at about 155 GPa, in excellent agreement with the measurements of McQueen *et al* (1983) on Al. Again Swenson *et al* (1986) have carried out sound wave overtake measurements on CsI. The results of these experiments were combined by them with the shock wave optical pyrometry data of Radousky *et al* (1985) to confirm that CsI melts along the Hugoniot at a pressure of roughly 30 GPa. Further Brown and McQueen (1986) have determined sound velocities in shock compressed iron upto pressures of 400 GPa. The discontinuity in these measurements at about 245 GPa is believed to indicate the onset of melting.

In the present work we have applied the solid and liquid state theories to investigate the behaviour of shock pressure and shock temperature along the shock Hugoniot of Pb. As in many other materials, the melting temperature in Pb under shock compression is expected to get increased as compared to its normal melting temperature (874 K) and there may be a mixed solid-liquid state region (Bennett *et al* 1978). In Pb, the various estimates of melting pressure on Hugoniot range from 22 to 124 GPa (Duvall and Graham 1977; Carter 1973).

2. Equation of state

2.1 Solid state

We start with the Helmholtz free energy

$$F = E - TS; \quad (1)$$

and obtain the pressures as the volume derivative

$$p = -(\partial F / \partial V)_T. \quad (2)$$

The free energy $F(V, T)$ can be broken into the following parts (for details see Godwal *et al* 1983)

$$F(V, T) = F_c(V) + F_H + F_e. \quad (3)$$

Here F_c is the free energy in the cold-compressed state ($V, T_0 = 0^\circ\text{K}, Z_0$) and is calculated for the valence charge Z_0 . The valence charge is expected to change due to pressure and thermal ionization effects at high compressions along the shock Hugoniot (Godwal *et al* 1983). F_c is equal to the corresponding E_c , the internal energy at 0 K. The zero point energy is neglected. Based on second order pseudopotential theory (Heine and Weaire 1970) this can be written as

$$E_c = Z_0(E_k + E_x + E_c) - \alpha(Z_0^2/r_a) + E_1 + E_2. \quad (4)$$

Here E_k , E_x and E_c represent the kinetic, exchange and correlation energies of the homogeneous electron gas of charge Z_0 . The second term is the electrostatic energy as a function of the atomic radius ($V = 4/3 \pi r_a^3$; $\alpha =$ Madelung constant). E_1 and the last term (E_2) are the first and second order band structure terms. Further, E_2 is given by

$$E_2 = \sum_{\mathbf{g}} \{S[(\mathbf{g})]^2\} * \{v[(\mathbf{g})]^2\} * \chi(\mathbf{g}) * \varepsilon(\mathbf{g}). \quad (5)$$

The various quantities here have the same meaning as given by Heine and Weaire (1970). E_1 is determined from zero pressure condition and E_2 is obtained from numerical integration by knowing the form of electron ion pseudopotential. For the lattice thermal contribution E_{11} , the internal energy is taken as $3k_{\beta} T$ (per atom) and the corresponding pressure term (Zel'dovich and Raizer 1967) is

$$P_{11} = \gamma E_{11}/V \quad (6)$$

and the nuclear Grüneisen parameter values γ are estimated from the phonon frequencies (vs)

$$\gamma(V) = -\langle d \ln \nu / d \ln V \rangle. \quad (7)$$

It has been found that γ is essentially a function of V and does not depend significantly on temperature [Dienes *et al* (1980)].

Finally, the electronic contribution to the free energy F_e (Voropinov *et al* 1970; McMahan *et al* 1977; Godwal 1980)

$$F_e = \sum_k \varepsilon_k [\eta_k(T) - \eta_k(0)] + k_{\beta} T \sum_k [\eta_k \ln \eta_k + (1 - \eta_k) \ln (1 - \eta_k)], \quad (8)$$

where $\varepsilon_k(V)$ are the conduction-electron ground state eigenvalues and $\eta_k(T)$ is the occupancy of any level

$$\eta_k(T) = \{[\exp(\varepsilon_k - \mu)/kT] + 1\}^{-1}, \quad (9)$$

μ is the chemical potential. For small thermal excitations the change in F_e is caused by changes in occupancies of one-electron energy levels and hence

$$P_e = -\sum_k \delta \varepsilon_k(V) / \delta V [\eta_k(T) - \eta_k(0)]. \quad (10)$$

2.2 Liquid state

Many of the terms in the free energy of a liquid metal can be transposed directly from the solid (see equation (4)). It remains, however, to find ways of computing the liquid structure factor and the entropy of the liquid. By analogy with the treatment used in solid state, it is natural to find a variational principle to determine any unknown parameters on which the free energy may depend. All these goals are accomplished with the help of a well-known inequality for the free energy derived from thermodynamic perturbation theory (Mansoori and Canfield 1969; Rasaiah and Stell 1970) and known as the Gibbs-Bogolyubov inequality

$$F \leq F_0 + \langle \Delta U \rangle_0. \quad (11)$$

Here F_0 is the free energy of the reference system and $\langle \Delta U \rangle_0$ is the difference in the potential energy of the real system from the reference system. $\langle \rangle$ denotes the average of ΔU taken over all reference configurations. The collection of hard spheres, soft spheres, corrected rigid spheres (CRIS), and one-component plasma (OCP) have been used as reference systems. We have employed two reference systems in our calculations to judge the variability of results from these different reference systems (Stroud and Ashcroft 1978; Ross 1979; Kerley 1980; Moriarty *et al* 1984—for more details see Godwal *et al* 1983).

3.1 Pseudopotential hard sphere method

If the intermolecular forces are pairwise additive, the first order term in (11) can be calculated from the pair distribution function.

$$F \leq F_{\text{HS}} + N\rho/2 \int_0^\infty g_{\text{HS}}(r, \eta) u(r) d^3r. \quad (12)$$

Here g_{HS} is the pair distribution function of the hard spheres and η is the packing fraction ($\eta = \pi\rho\sigma^3/6$; σ being the hard sphere diameter and ρ the density). g_{HS} can be further expressed in terms of hard sphere structure factor S_{HS} (see Stroud and Ashcroft 1978). Though the hard spheres have attractive features like availability of closed form analytic approximations for g_{HS} , at high density however, the repulsion tends to be too severe.

We now write out the various terms in the approximate liquid free energy

$$F = Z_0(E_k + E_x + E_{co}) + E_M + E_1 + E_2 + E_{\text{kin}} - TS. \quad (13)$$

Using the Percus-Yevick approximation for the hard sphere structure factor, the Madelung energy (E_M) and the entropy (S) terms are known in terms of packing fraction and hard sphere diameter. E_2 is determined from numerical integration using a form for the pseudopotential and hard sphere structure factor. E_{kin} is the ionic kinetic energy ($= 3/2 k_B T$). For specified volume, η is determined by $(\partial F/\partial \sigma)_{V, T} = 0$ and like the solid case, E_1 can also be determined using the condition $(\partial F/\partial V)_T|_{V_0} = 0$.

3.2 CRIS model (corrected rigid spheres)

The CRIS model was developed by Kerley (1980) and has been applied to many systems. This model is based on the perturbation theory of fluids in which explicit knowledge of the interaction potential is not required. Instead, the energy of the fluid molecule in the cage formed by its neighbours is calculated from the zero degree isotherm of the solid, corrected for coordination number in the liquid. This 'cold curve' is usually easier to compute than an effective pair potential. This model is preferred when higher order (three-body) forces are important. In this model, the calculation of the thermodynamic properties proceeds in two steps. Again to first order, the Helmholtz free energy is given by (11). F_0 and the corresponding pressure contribution are fitted to the following expressions

$$[F/(Nk_B T)]_0 = -3 \ln(1 - \eta/\eta_c) + \sum_{k=1}^4 A_k (\eta/\eta_c)^k \quad (14)$$

and

$$[PV/(Nk_{\beta} T)]_0 = 1 + 3\eta/(\eta_c - \eta) + \sum_{k=1}^3 kA_k(\eta/\eta_c)^k. \quad (15)$$

The quantity η ($\eta_c = 0.6452$) is identified as the packing fraction for randomly close-packed spheres. The coefficients A_k have been obtained from virial expansion and have the values viz $A_1 = -0.4194$, $A_2 = 0.5812$, $A_3 = 0.6439$ and $A_4 = 0.4730$.

In order to know $\langle \Delta U \rangle_0$ we note that the CRIS model assumes the nearest neighbours to lie on spherical shells and each molecule is located in a cage formed by these neighbours. The radius of the cage R and the coordination number ν vary from molecule to molecule keeping ν/N fixed. The average value of ΔU over all the configurations of the system assuming the contributions outside the first neighbour cage as negligible can be shown to be

$$\langle \Delta U \rangle_0 = -(\sqrt{2\pi}/3N) \int_0^{R_M} \varphi(R, \nu) g_{s0}(R) R^{-1} dR \quad (16)$$

and

$$\varphi(R, \nu) = (\nu/12) E_c(V_s) = (V_s/V) E_c(V_s), \quad (17)$$

where $V_s = NR^3/\sqrt{2}$. $\varphi(R, \nu)$ is the potential energy of molecule in the fluid and is related with the zero degree isotherm $E_c(V_s)$ of the solid (equation (17)). g_{s0} is the first peak in the radial distribution function (RDF) $g_s(R)$ of the hard sphere fluid. The expression for R_M and the numerically fitted value to analytic function for $g_{s0}(R)$ has been given by Kerley (1980) for hard spheres for $R < \sqrt{2}\sigma$.

4. Application to Pb

The above formalisms have been applied to Pb, using the Krasko-Gurskii electron-ion pseudopotential (Johansson and Rosengren 1974).

$$V_{KG}^{ion}(r) = Z \{ [\exp(-r/r_c) - 1]/r + (a/r_c) \exp(-r/r_c) \}, \quad (18)$$

where a and r_c are model parameters. The Fourier transform of this falls off more rapidly with large q than in the case for the empty core pseudopotential. This property improves the convergence of the sum over the reciprocal lattice vectors contained in the energy expression. Keeping $a = 3.0$ fixed, a value of $r_c = 0.3775$ a.u. gave the best fit of the calculated zero degree isotherm (figure 1) with the shock reduced data of McQueen and Marsh (1960) and with the static pressure data of Vaidya and Kennedy (1970). Further this potential accounted well for the bulk properties like bulk modulus and binding energy. The calculations are made assuming an fcc structure ($V_0 = 203.869$ a.u.) although Pb has been shown to transform from fcc to hcp structure under a static pressure of 13.2 GPa. No such transition has, however, been detected in shock compression experiments. Also, Pb being (sp) metal, the use of local pseudopotential seems to be appropriate. Further, for Pb the relativistic effects are not taken into account. This is perhaps justified as these are not usually discernible in an integral property like equation of state. It may also be noted (figure 1) that the calculated zero degree isotherm is close to that evaluated using a semi-relativistic linear muffin-tin orbital method (LMTO), the details of which are described by Andersen (1973) and

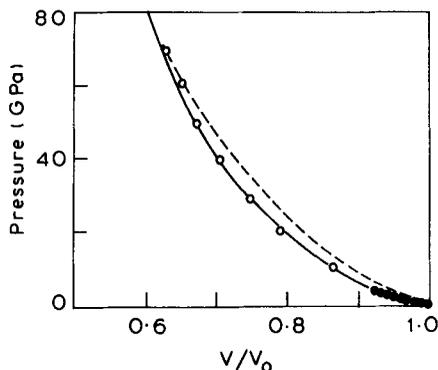


Figure 1. Zero degree isotherm for Pb. The solid curve is calculated using the solid state pseudopotential theory and the dashed curve is obtained using the LMTO program. Open circles are points derived from the experimental shock wave data of McQueen and Marsh (1960) while closed circles are the static pressure data of Vaidya and Kennedy (1970).

Skriver (1984). These self-consistent calculations evaluate the one-electron eigenvalues and wave functions of an ordered solid as a function of the atomic volume and crystal structure, within the general framework of the Kohn-Sham local density formalism (Skriver 1984). Frozen core approximation was employed with s , p , d and f components retained in the angular momentum basis for conduction electrons. In the LMTO pressure calculations, we also included the muffin-tin correction (Glotzel and McMahan 1979) and the contribution due to the core states which under compression are likely to become band states (Sikka and Godwal 1987). However, the contribution to the pressure from bound states was found to be small upto these compressions ($V/V_0 = 0.6$). The calculations for Pb in the liquid phase were carried out using Percus-Yevick and CRIS models. The CRIS model used the zero degree isotherm which was calculated using the solid state theory (figure 1). The shock Hugoniot in solid state was obtained by iterating equations (5) to (10) with Rankine-Hugoniot equation.

$$E - E_0 = 1/2(P + P_0)(V_0 - V). \quad (19)$$

Here E_0 and P_0 are for V_0 . Similarly the liquid state Hugoniot was determined using equations (11) to (18) of liquid state theory. A T^2 electronic excitation contribution was also included in liquid shock Hugoniot calculations at high compressions.

It can be seen from figure 2 that the liquid Hugoniots calculated from Percus-Yevick theory and CRIS models are close to the solid state Hugoniot. The one from CRIS model is in better agreement with experimental data, where Pb is supposed to have melted. In figure 3 we show the shock temperatures for the solid and the liquid Hugoniots (CRIS model) of Pb. It can be seen that the shock temperatures in solid and liquid cases are very much different. The temperatures in the liquid case are much lower. This confirms the observations of Bennett *et al* (1978) for Pb in their studies using an empirical form for the zero degree isotherm. Also a similar trend for shock temperature was observed by us in Al (Godwal *et al* 1983) where we used the pseudopotential hard sphere perturbation method coupled with Percus-Yevick approximation for liquid structure factor.

We obtained an estimate of the melting point of Pb on Hugoniot from the scaling

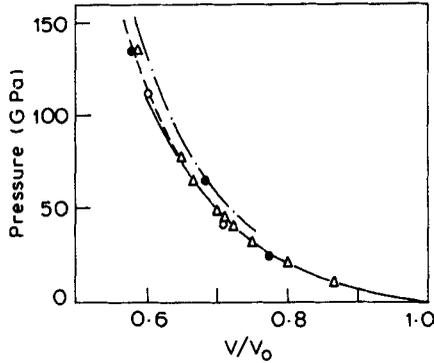


Figure 2. The calculated solid (—) and liquid (---) Hugoniots for Pb. Closed circles are Al'tshuler *et al*'s (1974) experimental points and open circles are the points taken from SESAME library (Bennett *et al* 1978) while Δ are the experimental points of McQueen and Marsh (1960). (— · —) curve is calculated using the Percus Yevick Theory (PY).

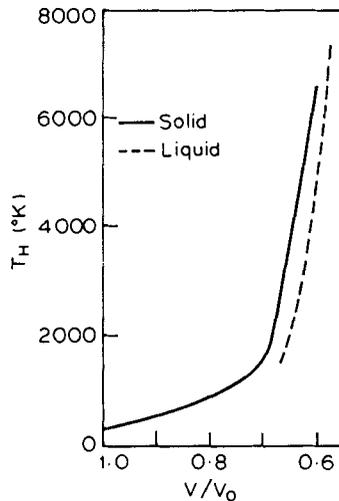


Figure 3. Temperature (T_H) along the shock Hugoniot of Pb versus V/V_0 .

property of the hard sphere reference fluid, where the packing fraction η is nearly constant ($=0.45$) along the melting curve (Ross 1986). This is 6380 K at $V/V_0=0.6$ and $P=118$ GPa. The volume and pressure are close to $V/V_0=0.59$ and the Hugoniot pressure of 129 GPa estimated by Schroeder and McMaster (1972). However, we disagree with Carter (1973), who showed that the calculated melting curve intersects the Rankine-Hugoniot curve close to the point at which a break in the U_s-U_p curve occurs (i.e. 23–25 GPa). Further, Mineev and Savinov (1967) using the viscosity measurements suggested that the melting in Pb behind the shock wave front takes place in the pressure range 41–124 GPa. Our estimate for melting pressure for Pb is, thus, close to their upper limit.

5. Conclusion

The present calculations show that within the current obtainable accuracies in experimental P-V data, the theoretical calculations of shock Hugoniots of Pb are in

mutual agreement when evaluated using solid or liquid state theories. It is also well known that the short range environment in a solid and its liquid is generally very similar and it is this which is dominant in the total energy calculations and perhaps results in very small volume changes on melting at high pressures (Ross 1980). However, the shock temperatures for Pb are very much different in the two cases. It might thus be possible to detect shock melting in Pb by a combination of the measurement of shock temperatures and the theory. Therefore, recent attempts made by Ng *et al* (1985), Radousky *et al* (1986) and Justus *et al* (1986) to directly measure shock temperatures are important steps in this direction. It is expected that the accuracy of these measurements will increase in the near future and direct detection of melting will become possible.

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