Theoretical solid and liquid state shock Hugoniots of Al, Ta, Mo and W

Theoretical solid and liquid state shock Hugoniots of Al, Ta, Mo and W

A K Verma, R S Rao and B K Godwal

High Pressure Physics Division, Bhabha Atomic Research Centre, Mumbai-400 085, India

Abstract
We present the Hugoniots of Al, Ta, Mo and W in their solid as well as
liquid phases. The liquid phase calculations are carried out on the basis
of the corrected rigid spheres (CRIS) model. The 0 K isotherm of the
solid phases, which are the necessary inputs for our computations, have been
obtained by full potential first principles electronic structure calculations with
generalized gradient approximation (GGA) for the exchange–correlation terms.
The melting curve as a function of pressure was obtained according to the
recently published model based on dislocation mediated melting, and also
compared with that using Lindemann criterion. Though the adiabatic pressure–
volume curve is affected little by melting, the pressure–temperature curve shows
substantial change.

1. Introduction

The equation of state (EOS) (i.e., the relation between P, V, T) of a substance is very important
in basic and applied sciences. It provides a test for theoretical models of cohesion, which can
a priori predict the onset of phase transitions. An accurate EOS is necessary for interpreting
static as well as dynamic high pressure experiments, for pressure calibration to convert the
measured pressure variation of physical quantities to volume variations and vice versa, etc.
The EOS is also used as vital input for hydrodynamical calculations in controlled fission–
fusion research. Hence considerable efforts have been made, both experimentally for data
collection, and theoretically for predictive capabilities, in EOS studies (Ross and Young 1993,
Godwal 1995). Regarding the predictive part, proper account of thermal excitations of atoms
and electrons has to be taken, except for the 0 K isotherm, in the theoretical models used for
the predictions. As is well known, though high accuracy can be achieved in predicting the
0 K EOS by density functional theory (DFT) (Hohenberg and Kohn 1964) based calculations,
which can also account for core delocalization effects under compression by considering the
relevant states in the valence electron panel, estimating the temperature effects on the EOS is
still a daunting task. Recently some refined works have been carried out for Cu (Narasimhan

and Gironcoli 2002) and Ta (Cohen and Gülseren 2001) using *ab initio* methods. Earlier Wang *et al* (2000) constructed a mean field potential in terms of 0 K total energies obtained by *ab initio* electronic structure calculations, and reported shock Hugoniots of Al, Cu, Ta, Mo and W up to 1 TPa. However, in their studies of the adiabatic EOS, the shock melting effect has been neglected. As is well known, irreversible shock heating leads to temperatures which could be much higher than the melting temperature of the material, and thus it is necessary to estimate the resulting effect of induced disorder on the shock Hugoniots. Currently very little work on liquid Hugoniots exists, and thus the influence of melting on them is not very well understood. Note that incorporating the thermal effects in the EOS simulations, on the same footing as in the 0 K EOS, is prohibitively cumbersome in most of the cases. Besides, unlike in a solid crystal in which the lattice periodicity can be exploited to a considerable extent, the first principles calculations for liquids are much more troublesome. Hence, we have carried out the Hugoniot calculations in the liquid phase of Al, Mo, Ta, and W based on the corrected rigid spheres (CRIS) model (Kerley 1980a) to estimate the melting effects on them. Our Hugoniot studies on Cu have been reported elsewhere (Shukla *et al* 2003).

The approach of the CRIS model to the study of thermodynamic properties of liquids and dense gases is by the perturbation method. The thermodynamic properties are calculated from an expansion about a hard sphere fluid reference system, in which the hard sphere diameter is chosen by a variational principle. The model also incorporates corrections to first order perturbation theory. The energy of a fluid molecule is defined to depend upon the local configuration of its neighbours, and all terms in the expansion are given by the averages of this quantity. The corrections to first order theory are approximated by using the concepts of macroscopic fluctuation theory. The theory is developed in terms of a general set of variables and the corresponding distribution functions, which describe the short range structure of fluids. Three main assumptions have been made. The first assumption is that in any configuration of the liquid, each molecule sits at the centre of the spherical shell formed by its nearest neighbours. Let R be the radius of the shell and ν be the coordination number. It is clear that the shell radius R and coordination number ν will vary from molecule to molecule throughout the liquid. The probability of a particular shell size is related to the pair distribution function of the hard spheres system. The second assumption is that the coordination number ν varies along with the radius R in such a way that the volume per molecule is constant and equal to the macroscopic value. The average coordination number will be proportional to the ratio of shell volume and macroscopic volume per molecule. The third assumption is that the potential energy of a molecule in the fields of its neighbours depends only on the nearest neighbour distance and the coordination number. The potential is taken to be central, pair-wise additive, and extending to only nearest neighbours. Using these assumptions the energy of a liquid molecule can be calculated from the zero-temperature isotherm of the solid at the same nearest neighbour distance by taking properly the correction due to change in the coordination number. The reader is referred to Kerley (1980a, 1980b) for a detailed mathematical treatment of the model.

It may be noted that shock Hugoniot simulations are much more lengthy as compared to those of isotherms, as various temperatures will have to be tried iteratively in getting the solutions to the Rankine–Hugoniot equation. Thus the first principles calculations of melting effects on Hugoniots are currently not easy, but some useful estimates can be obtained by adopting simple models like the one employed in the present work, the details of which are given below.

2. Details of calculations

The details of the methods used to estimate the thermal effects in the isotherm and Hugoniot are well-documented in the literature for solids and liquids (Godwal *et al* 1983, Godwal and

Jeanloz 1989, Kerley 1980a), and we summarize below only the key aspects of the formulation. Briefly, we have evaluated the internal energy at various volumes as a sum of three terms,

$$E = E_c + E_{lt} + E_{ee}, \tag{1}$$

where E_c represents the 0 K total energy, E_{lt} the vibrational energy of the ions, and E_{ee} the energy due to thermal excitation of electrons. We have used the full potential (FP) linear augmented plane wave (LAPW) method (Blaha *et al* 1990, 2001) with generalized gradient approximation (GGA) (Perdew *et al* 1996) for the exchange–correlation energy to calculate E_c. The FP-LAPW calculations were carried out with constant muffin-tin radii (1.8 au for Al, 2.0 au for Ta, 2.0 au for Mo and 2.0 au for W) with $RK_{max} = 9$. E_c per atom was evaluated with a tolerance of 10^{-5} Ryd with 5000 **k**-points for Brillouin zone summation.

E_{lt} and E_{ee} were evaluated by using the relations shown below (Godwal *et al* 1983, Godwal and Jeanloz 1989):

$$E_{ee} = 0.5\beta T^2 \tag{2}$$
$$E_{lt} = 3k_B T \mathcal{D}(\theta_D/T), \tag{3}$$

where β represents the electronic specific heat, $\mathcal{D}(\theta_D/T)$ is the Debye function, and θ_D is the Debye temperature. We have also accounted for E_{ee} by *ab initio* electronic band structure calculations at non-zero temperatures, which enable us to compute $[E_c + E_{ee}]$, in place of E_c of the 0 K calculations (see Godwal *et al* 2003 for details; Mermin 1965). However, as these *ab initio* computations are quite exhaustive within the iterative scheme for the Hugoniot estimate, they are mainly used to verify that the model formulations employed here for E_{ee} are adequate, so that the bulk of the necessary estimates are carried out with this model. The lattice vibrational energy was estimated by the Debye–Mie Grüneisen model, which is based on the assumption that the vibrational energy levels of ions are the same as those of harmonic oscillators (Zel'dovich and Raizer 1976). The electronic thermal excitation energy was estimated by the free electron formula using the density of states at the Fermi level obtained by our FP-LAPW calculations. The corresponding equation for pressure is given by Hixson and Fritz (1992), Godwal *et al* (1983)

$$P = -\Delta E_c/\Delta V + \gamma_{lt} E_{lt}/V + \gamma_e E_{ee}/V, \tag{4}$$

where

$$P_{ee} = \gamma_e E_{ee}/V \tag{5}$$
$$P_{lt} = \gamma_{lt} E_{lt}/V, \tag{6}$$

γ_e and γ_{lt} being the electronic and lattice Grüneisen parameters. $\gamma_{lt}(P)$ under pressure (P) at density (ρ) was obtained by

$$\gamma_{lt}(P) = \gamma_{lt}(0)\rho_0/\rho + 2/3(1 - \rho_0/\rho). \tag{7}$$

The solid and liquid Hugoniots (a Hugoniot is the locus of all possible states that can be reached by using a single shock from a given initial state) are obtained by using the following equation:

$$E - E_0 = (P + P_0)(V_0 - V)/2, \tag{8}$$

where E, P, V refer to the shocked material, and E_0, P_0, V_0 refer to the unshocked material. Clearly, the liquid Hugoniot below the melting point does not have any physical interpretation, especially as some of the assumptions made in the CRIS model may not hold valid in that region. Similarly the solid Hugoniot above the melting point should also not correspond to any physical state of the system, though it can be used, by comparing with the liquid state Hugoniot, to estimate the energy used in creating various disorder effects in the liquid state.

The melting curves under pressure were obtained by two methods.

Table 1. Estimated equilibrium properties from the first principles electronic structure calculations. The quantities in parentheses are from the experimental data.

Element	Calculated equilibrium volume as a fraction of ambient pressure experimental volume (V_{exp}) i.e., V/V_{exp}	Bulk modulus (GPa)	Calculated density (g cm^{-3})
Al	0.9999	81 (76)	2.7003 (2.700)
Ta	1.011	204 (200)	16.4688 (16.65)
Mo	1.028	236.8 (230)	9.9416 (10.22)
W	1.029	327 (310)	18.7075 (19.25)

2.1. Lindemann law

The Lindemann rule is based on the hypothesis that all elements melt when the amplitude of atomic vibration is a fixed fraction, $\cong 1/8$, of the nearest interatomic distance (Lindemann 1910). The melting temperature $T_m(P)$ at pressure P is given by

$$T_m(P) = T_m(0)(V/V_0)^{2/3} \exp[2\gamma_{lt}(1 - V/V_0)], \tag{9}$$

where $T_m(0)$ is the ambient pressure melting temperature.

2.2. Dislocation-mediated melting

This effective theory of melting (Burakovsky *et al* 2000) treats dislocations as perfectly screened and non-interacting, which is quite an adequate approximation when the dislocation density is very high. A dislocation in the dense ensemble of other dislocations is assumed to be a random loop, i.e., the possible configurations of a dislocation loop are closed random walks, and short-range steric interactions are neglected. With further techniques of statistical mechanics, the solid to liquid transition is modelled as a transition from a translationally symmetric to a disordered system, and the order–disorder transition temperature, at which the dislocations are copiously produced, is taken as the melting temperature. As per this model, the melting temperature at pressure P is given by

$$T_m(P) = T_m(0)(1 + PB'/B)^{-(1/B')}[1 + PG'/G(1 + PB'/B)^{-(1/3B')}], \tag{10}$$

where B, G are ambient condition bulk and shear moduli, respectively, and the B', G' are the first pressure derivatives of the respective quantities at ambient pressure. Comprehensive comparison with experimental data on over half of the elements in the periodic table shows that the melting relation obtained by the model is accurate to 17% (Burakovsky *et al* 2000).

3. Results and discussion

Table 1 summarizes the ambient condition estimates of some of the physical properties obtained by our first principles calculations, which show good agreement with the experimental data (Pearson 1967, www.webelements.com). Briefly, the equilibrium lattice constant for Al, evaluated by estimating the minimum of the total energy versus volume curve, obtained by the first principles calculations, shows excellent agreement with the experimental data. However, our calculations overestimate the equilibrium volumes (and hence underestimate the densities) of Ta by 1% and of Mo and W by about 3%. These marginal expansions of the theoretically predicted equilibrium volumes are consistent with the fact that GGA often underestimates the cohesive energy, and thus overestimates the lattice constants (Narasimhan and Gironcoli 2002). Moreover, all the equilibrium volumes (densities) listed in table 1 are within the

accepted tolerance of about 6%, generally occurring in many first principles electronic structure calculations. Also the bulk moduli, obtained by finding the derivatives of the pressure versus volume curves, show good agreements with the experimental data. Our estimate of 81 GPa for the bulk modulus of Al shows about 6% deviation from the experimental value of 76 GPa. For Ta, our calculations (204 GPa) agree within 2% of the experimental value of 200 GPa. In Mo, our estimated bulk modulus (236.8 GPa) is within about 3% of the experimental value (230 GPa), whereas in W it (327 GPa) differs from the available data (310 GPa) by about 5%. Thus the agreements between our calculated values of bulk moduli and the experimental data are quite satisfactory, especially as the errors get compounded in evaluating the derivatives. In view of these good agreements displayed in table 1, other quantities predicted by using the results of the present calculations should be reliable. It might be possible to obtain better equilibrium properties by judicious choice of the exchange–correlation terms, as has been found in some metals and intermetallics (Godwal *et al* 2002); but the experimental errors in the data currently available for comparison with the Hugoniot calculations are larger than the refinements obtained by such an exercise.

Figure 1(a) shows the 300 K isotherm of Al and figure 1(b) shows its solid and liquid phase Hugoniots. Both the curves show very good agreement with the experimental data (Nellis *et al* 1988, Mitchell *et al* 1981, 1991). We have also tested the effect of second order correction to the first order perturbation terms in the CRIS model and found that the change due to this correction is less than 8%. This result is in agreement with the observations made by Kerley (1980b) in the original study of this model that the second order correction has little effect. The shock melting based on the dislocation mediated model takes place at about 130 GPa pressure, as per our estimate, above which the liquid Hugoniot is relevant rather than the solid one. Though the adiabatic P–V curve is affected little by melting and is within the tolerance of agreement with available experimental data, the P–T curve shows substantial change due to melting. Thus it is important to consider the effects of melting in these shock Hugoniot related studies. It may be noted that similar mismatch of solid and liquid P–T Hugoniots as compared to the thermal P–V curve have been obtained from more elaborate first principles based calculations for iron (Alfe *et al* 2002). They used the thermodynamic integration to evaluate the change in free energy in going from a simple reference system to the *ab initio* system. They used the inverse power potential for the reference system, and obtained the required thermal averages by *ab initio* molecular dynamics. Experimental data from shock temperature measurements (for example, by the pyrometric method (Yoo *et al* 1993)) are desired to resolve the disagreement.

It may be noteworthy that though the models used in the current work to estimate the thermal effects are simple and do not demand heavy computations, the agreement with the experimental data is remarkable, especially in view of the large errors involved in the shock measurement data.

Figures 2–4 show the results for Ta, Mo and W. The P–V curves (both isothermal and Hugoniot) show very good agreement with experimental data (Cynn and Yoo 1999, Mitchell *et al* 1981, 1991, Hixson and Fritz 1992) and also show little effect of melting. Among the melting curves, the Lindemann rule gives much slower rise with pressure as compared to that of dislocation mediated melting in all the cases studied. It is worth comparing these results with experimental melting curves or those obtained by first principles simulations. Neither data are currently available on these metals. It may be noted that neither of the two employed models on melting accounts for the high pressure structural transition of the assumed solid phase (the ambient phase physical quantities like bulk modulus, its pressure derivatives, etc, are used), and thus *a priori* knowledge of any structural transition under pressure is needed to rectify the predicted curves. It is well known that anomalies in the melting curve exist due to
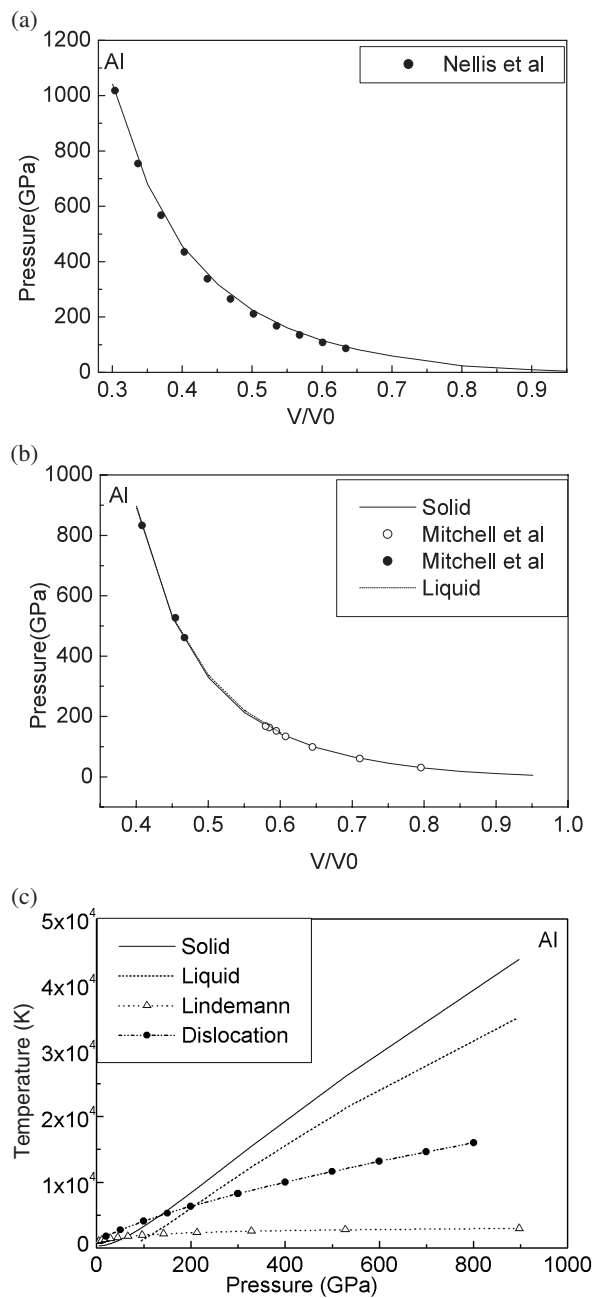
Figure 1. (a) 300 K isotherm with experimental data (filled diamonds) from Nellis *et al* (1988) for Al. (b) Theoretical solid and liquid Hugoniots with experimental data (open and filled diamonds) from (Mitchell *et al* 1991, 1981) for Al. (c) *P*–*T* Hugoniot for Al, and the melting curves under pressure based on the Lindemann rule and dislocation model. Triangles (Lindemann rule) and circles (dislocation model) are used to contrast the melting curves from the Hugoniots (and unlike in parts (a) and (b), these symbols do not represent any experimental data).

structural transition in the solid phase under compression (Errandonea *et al* 2002), which calls for improved formulations based on these models.
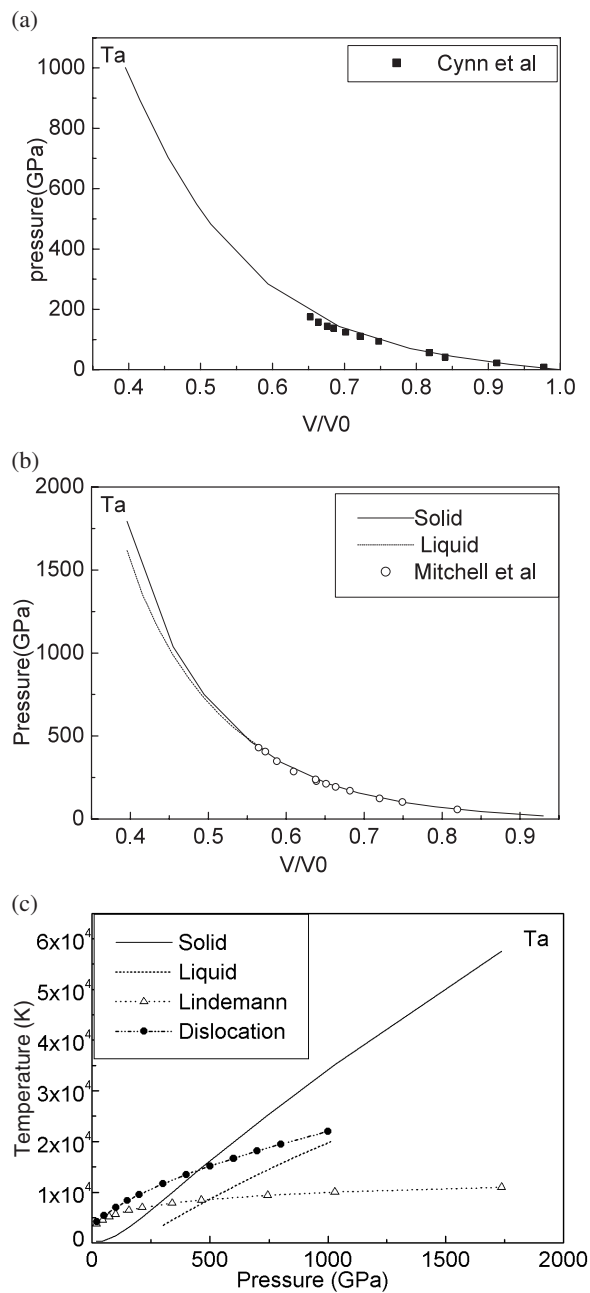
Figure 2. (a) 293 K isotherm with experimental data (filled squares) from Cynn and Yoo (1999) for Ta. (b) Theoretical solid and liquid Hugoniots with experimental data (diamonds) from Mitchell *et al* (1981) for Ta. (c) *P–T* Hugoniot and melting curves for Ta. Notations are like those of figure 1(c).

We have used the results of the first principles electronic structure calculations to obtain the EOS, including thermal effects based on simple models. The same method can be employed
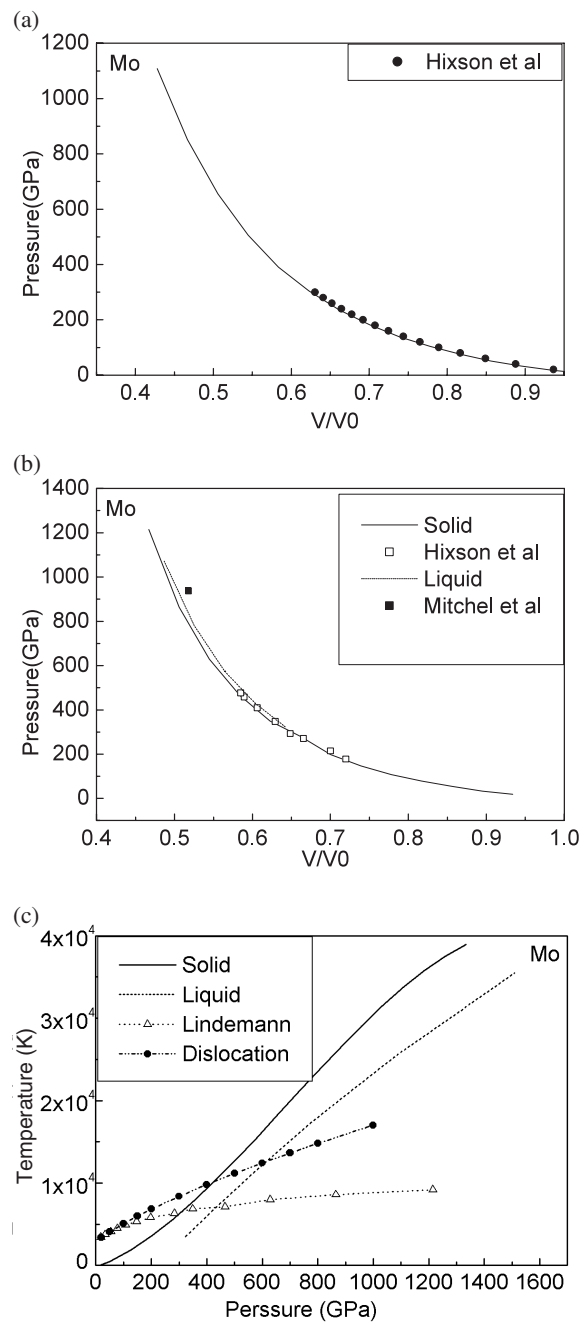
Figure 3. (a) 293 K isotherm with experimental data (filled diamonds) from Hixson and Fritz (1992) for Mo. (b) Theoretical solid and liquid Hugoniots with experimental data from Mitchell *et al* (1981) (filled squares) and Hixson and Fritz (1992) (open squares) for Mo. (c) *P–T* Hugoniot and melting curves for Mo. Notations are like those of figure 1(c).

in the difficult *intermediate pressure region* (1–10 TPa) (Godwal *et al* 1983). The estimated shock Hugoniots for Al, Ta, Mo, and W are compared with the data available in the literature.
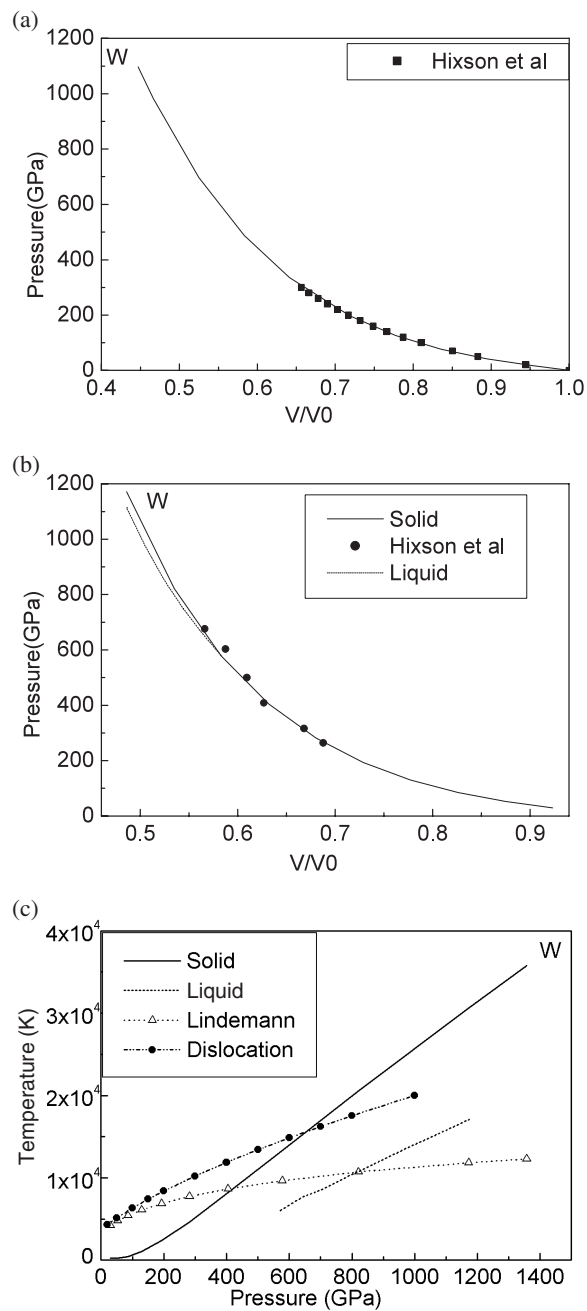
Figure 4. (a) 293 K isotherm with experimental data (filled squares) from Hixson and Fritz (1992) for W. (b) Theoretical solid and liquid Hugoniots with experimental data (filled diamonds) from Hixson and Fritz (1992) for W. (c) $P-T$ Hugoniot and melting curves for W. Notations are like those of figure 1(c).

The agreement with the experimental data, depicted in figures 1–4, of our simulations using simplified models to evaluate the ionic and electronic thermal excitation effects, within the

currently achievable experimental accuracies, emphasizes the usefulness of the procedure. Our method is especially useful for predictions at the multimegabar pressure range—which may not yet be easily achievable, and also off the shock Hugoniots. Note that, in principle, non-zero temperature band structure calculations, discussed earlier (Mermin 1965, Godwal *et al* 2003), and first principles evaluation of ionic thermal effects by Car and Parrinello (1985) or by using embedded atom type potentials (Ercolessi and Adams 1994) in a high temperature molecular dynamics simulations can be employed to obtain the shock Hugoniots. But note that in solving the Rankine–Hugoniot condition (equation (8)) at a fixed volume V, one has to try a range of temperatures and evaluate the energy E on the left-hand side of equation (8), and pressure P on the right-hand side for each temperature, and look for satisfying the equation by iteration. Generally it takes very many iterations, which increase with compression, to reach a reasonable tolerance of satisfying equation (8). Note that a further iteration on the packing fraction is needed for a fixed volume in a liquid, and for each packing fraction the temperature trails are needed. Moreover, the temperatures involved can be of the order of 10^5 K or so at high compression (see figure 2(c)). Thus repeated first principles calculations to get the Hugoniot iteratively are extremely tedious even with the most powerful computers available to date. Note that in the Car–Parrinello-type simulations of shock Hugoniots, the thermal excitations of electronic states would necessitate a prohibitively large number of electronic states to be included in the calculations, as the thermal energy (kT) involved at the temperatures of Hugoniot calculations are comparable to the Fermi energy.

Our method of calculation can take into account the core-delocalization effects under static pressure, as the core states begin to overlap, and possibly move above the Fermi level. But the ionization effects due to shock impacts cannot be easily incorporated in this framework, though those due to electronic thermal excitations can be included via finite temperature band structure calculations; but they will have to be evaluated at many temperatures repeatedly while looking for Rankine–Hugoniot equations iteratively. These and other factors, like the temperature dependence of exchange–correlation terms, can be considered when the experimental accuracies improve and provide a more stringent testing ground to the theoretical models, especially those which can simulate the interesting anomalies in the EOS due to ionization effects.

Thus it is worth noting that it is not essential to go through elaborate first principles calculations for thermal effects to obtain reliable Hugoniots, especially when the relevant experimental accuracies are limited, and when the required data on essential physical parameters like the Grüneisen parameter, Debye temperature, etc, are available or estimated using the results of *ab initio* calculations. No doubt a complete first principles procedure will have the merit of possessing independent predictive powers, especially for novel materials; but with their colossal computational demands to predict Hugoniots, they may be used only when the data required for simplified model studies are unavailable.

References

Alfe D, Price G D and Gillan M J 2002 *Phys. Rev.* B **65** 165118
Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *An Augmented Plane Wave + Local Orbital Program for Calculating Crystal Properties* (Austria: Techn. Universität Wien) ISBN-3-9501031-1-2
Blaha P *et al* 1990 *Comput. Phys. Commun.* **59** 399
Burakovsky L, Preston D L and Siblar R R 2000 *Phys. Rev.* B **61** 15011
Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471
Cohen R E and Gülseren O 2001 *Phys. Rev.* B **63** 4101
Cynn H and Yoo C S 1999 *Phys. Rev.* B **59** 8256
Ercolessi F and Adams J B 1994 *Eur. Phys. Lett.* **26** 583

Errandonea D, Boehler R and Ross M 2002 *Phys. Rev.* B **65** 012108

Godwal B K 1995 *Advances in High pressure Science and Technology* ed A K Singh (New Delhi: Tata McGraw-Hill) p 23

Godwal B K and Jeanloz R 1989 *Phys. Rev.* B **40** 7501

Godwal B K, Meenakshi S, Modak P, Rao R S, Sikka S K, Vijayakumar V, Bussetto E and Lausi A 2002 *Phys. Rev.* B **65** 140101

Godwal B K, Modak P and Rao R S 2003 *Solid State Commun.* **125** 401

Godwal B K, Sikka S K and Chidambaram R 1983 *Phys. Rep.* **102** 121

Hixson R S and Fritz J N 1992 *J. Appl. Phys.* **71** 1721

Hohenberg P C and Kohn W 1964 *Phys. Rev.* B **136** 864

Kerley G I 1980a *J. Chem. Phys.* **73** 469

Kerley G I 1980b *J. Chem. Phys.* **73** 478

Lindemann F A 1910 *Z. Phys.* **11** 609

Mermin N D 1965 *Phys. Rev.* A **137** 1441

Mitchell A C *et al* 1981 *J. Appl. Phys.* **52** 3363

Mitchell A C *et al* 1991 *J. Appl. Phys.* **69** 2891

Narasimhan S and Gironcoli S 2002 *Phys. Rev.* B **65** 064302

Nellis W J *et al* 1988 *Phys. Rev. Lett.* **60** 1414

Pearson W B 1967 *A Handbook of Lattice Spacings and Structures of Metals and Alloys* vol 2 (Oxford: Pergamon) see also www.webelements.com

Perdew J P, Burke K and Ernzerhoh M 1996 *Phys. Rev. Lett.* **77** 3866

Ross M and Young D A 1993 *Annu. Rev. Phys. Chem.* **44** 61

Shukla M, Pant H C, Senecha V K, Rai V N, Khare P, Verma A K, Rao R S, Gupta N K and Godwal B K 2003 *Curr. Sci.* **85** 802

Wang Y, Chen D and Zhang X 2000 *Phys. Rev. Lett.* **84** 3220

Yoo C S, Holmes N C, Ross M, Webb D J and Pike C 1993 *Phys. Rev. Lett.* **70** 3931

Zel'dovich Ya B and Raizer Yu P 1976 *Physics of Shock waves and High Temperature Hydrodynamics Phenomena* vol 1 and 2 (New York: Academic)