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RICHARD GROVER

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METALLIC HIGH PRESSURE EQUATION-OF-STATE DERIVED FROM
EXPERIMENTAL DATA*

Richard Grover

University of California
Lawrence Livermore Laboratory
Livermore, California

INTRODUCTION

I would like to describe a program of making 'global' fits to the large amount of experimental equation-of-state (EOS) data on monatomic metals that has become available in recent years. The fits are made within the framework of a phenomenological scaling theory for metallic liquids which incorporates recently discovered general theoretical properties of the EOS of liquids. The theory is expected to be applicable to monatomic metals up to high temperatures ($\sim 10 - 100 \times$ the melting temperature, T_m) and at all densities, so long as the metallic bonding does not change character - as for instance might be caused by electronic phase transitions or sufficiently large thermal electron excitations. The goal of the present fitting studies is to obtain consistent tabular representations of the EOS of metals over a wide range of densities ($.5 \leq \frac{\rho}{\rho_0} \leq 2$) and temperatures (up to several eV) which are reliable enough both to be used in applied work (errors $< 5\%$) and to serve as a guide to future theoretical and experimental studies of metals. Fits to experimental data for examples of three different types of metals - N_a , Pb, and Ta - will be discussed.

A lack of a reliable theoretical model for the EOS of metals has frequently led to the need to fit high-temperature, high-pressure experimental data. These fits have been made for the most part with models of limited applicability (e.g. Gruneisen ^[1]

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or to limited ranges of T , P data with special mathematical forms thought to be suitable for extrapolation to more extreme conditions [2]. The wide range of data now available however makes such limited fits inappropriate. Figure 1 for example shows various thermodynamic paths for Po , extending over a wide range of p , T space in all phases along which two or more EOS quantities can now be measured. On some paths having a long excursion from normal conditions, such as the principle Hugoniot compression curve H_0 , only a few quantities are currently measurable — $P(p)$ and $E(p)$ — while along some shorter paths, such as T_0 , much more data is available. Since the data generally becomes less accurate away from normal conditions it is desirable to fit experimental data, as directly as possible. For this reason the fits to be described were obtained with the use of an interactive, display computer code which permits such comparisons of model predictions with experimentally measured quantities.

LIQUID SCALING MODEL

The most serious deficiency in previous EOS fitting efforts on metals has been the lack of a realistic model for the liquid phase. The EOS scaling model used in this study is a modification of an earlier version [3] based mainly on general EOS properties observed in more recent computer simulations of high density liquids with a variety of pairwise repulsive interparticle forces. In the computer calculation for these many particle systems it can be recognized [4] that the melting transition and the thermal EOS are determined up to very high temperature ($10-100 T_M$) by some average force constant (or second derivative) derived essentially from the repulsive part of the pair interaction. Such a picture correlates in a simple way the three main computer results [4]: the systematics of the entropy and volume

changes at melting, the Lindemann law behavior of the melting temperature and the universal form for the temperature dependence of the thermal EOS in the liquid phase. Strong effective pair repulsions arise naturally in the pseudo-potential theory of metals from the shielding and polarization properties of the conduction-band, electron gas. It is not surprising that liquid metals have experimental properties in the vicinity of T_m similar to those of the computer model fluids, including a universal temperature dependence for the specific heat [3].

More specifically the model is based on the following assumed properties of liquid metals

1. The thermal EOS can be written as a sum of independent contributions from atomic motions and electron excitations.
2. The atomic component has a melting transition with a constant entropy of fusion ($\Delta_m S \approx R$) which satisfies the compression form of the Lindemann law

$$\lambda \equiv \frac{d \ln T_m}{d \ln \rho} = 2\gamma_G - 2/3 \quad (1)$$

γ_G is the usual Gruneisen coefficient $V(\frac{d\theta}{dV})$ which in the Gruneisen model for a solid is related to the density dependence of the characteristic Gruneisen temperature which determines the high temperature free energy of the solid [5]

$$\gamma_G \equiv - \frac{d \ln \theta}{d \ln \rho} G \quad (2)$$

3. At higher temperatures in the liquid phase the non-ideal atomic part of the thermal EOS is assumed to scale with the melting temperature. The specific form can be derived from the specific heat (C_V) dependence

on temperature suggested by Eq. (5):

$$C_V = \frac{3}{2} kT + \frac{1}{1 + \alpha T/T_M} kT, \quad \alpha T/T_M \quad (3)$$

This modification of the original linear specific heat form [3] has been found to fit all computer simulation data adequately. The comparison is shown in Fig. 2 where the non-ideal part of the thermal energy is plotted against τ . The line derived from Eq. (3) for $\alpha = .1$ is a good average representation of all the calculations including those made for the 'Coulombic' system of positive ions in a neutralizing uniform negative background.

4. The electronic excitations are treated in a low temperature approximation in which the electronic specific heat is linear in the temperature. However the coefficient of proportionality, g_e , is that appropriate to $T > T_G$ and will in general be density dependent. Thus the electronic gamma, $\gamma_e = + d \ln g_e / d \ln V$ is non-zero.

These assumptions restrict the range of application of the model to be less than both $\sim 100 T_M$ and $\sim$ one fifth the electron Fermi temperature of the metal. Most of the experimental data however was well within these limits.

It is then possible to represent the metallic EOS in the liquid phase simply as an additive correction to the usual solid EOS of the Gruneisen form. From the specific heat form (3) simple expressions for the entropy, internal energy or pressure of a liquid can be derived

$$S_l = S_s + \lambda S - \frac{3}{2} \ln(1 + \lambda)$$

$$E_l = U_s + RT \ln \left(\frac{S}{S_s} - \frac{3}{4} + \frac{3}{2} R \ln \left(\frac{1 + \lambda}{1 + \lambda_s} \right) - 1 \right) \quad (4)$$

$$VP_l = VP_s + \lambda(E_s - E_s)$$

This form of liquid EOS shares another property with the Gruneisen EOS which considerably simplifies the process of fitting experimental data. Like the solid EOS, the liquid EOS is completely determined by the zero degree isotherm, $P_0(V)$, and density dependence of γ_0 and γ_e . In addition this simplification permits compact representation of the complete EOS by tables of these quantities [4].

THREE EXAMPLES OF EOS FITS

In order to test the generality of our fitting model, examples of three different types of metals were chosen — Na, Ta and Pb — for which a substantial amount of data was available. The fitting is done by trial and error adjustments of parameters in functions representing $\gamma_0(\rho)$, $\gamma_e(\rho)$ and the Hugoniot. Separate fits are made for the expanded states where $\rho < \rho_0$ and compressed states where $\rho > \rho_0$ in such a way that all functions are continuously and smoothly joined at ρ_0 . The process of finding a fit in this manner, although slower than an automated least squares search, provides some experience for judging the uniqueness of the fits.

A number of fits to experimental data on Pb, Na and Ta are shown in Fig. 3-6. Figure 3 illustrates the wide range of dynamic compression data (up to 2.5-fold-compression) that is reproduced by the EOS fits. The comparably wide density range of EOS data now available from isobaric expansion experiments must also be

produced as shown in Fig. 4. Because of the central role of the Lindemann law in the EOS model it is not surprising to find that the pressure dependence of the melting temperature when the experimental data covers a significant volume range, as it does in the case of Na shown in Fig. 5. While these fits appear to be satisfactory on a 'global' scale, they are often not accurate enough to represent the fine structure claimed for the data by the experimentalists. This is particularly true for derivative quantities such as the specific heat and thermal expansion data in the vicinity of melting. When however direct measurements of EOS derivative quantities such as the sound velocity shown in Fig. 6 are available over a significant range of conditions, it is necessary to obtain good fits

the basic EOS functions for Pb, Na and Ta shown in Fig. 7 and 8 from which these fits derive have a number of interesting properties which will be discussed below. In evaluating such fitting results one should first however take into consideration the reliability and uniqueness of the fit in view of the limitations of the experimental data and the fitting procedure. For instance shock compression data (Fig. 3) is not adequate to determine $P_0(\rho)$ and $\gamma_G(\rho)$ uniquely at high density. The different types of measurements possible in isobaric expansion experiments make on the other hand determination of $\gamma_G(\rho)$, $\gamma_E(\rho)$ and $P_0(\rho)$ more reliable in expansion. Compression values of these functions were then primarily determined by a smooth extrapolation the expansion values in such a manner that $P_0(\rho)$ appeared well behaved. In the case of Ta and Pb it was found that fits were obtained most simply when g_0 was close to its unrenormalized value as estimated theoretically from cryogenic specific heat data. [9] The behavior of $\gamma_E(\rho)$ for both Pb and Ta seemed then to be at least qualitatively fixed by the data fit.

Experience has shown however that these fits should not be considered absolutely unique. It is probably possible to find other combinations of ρ_0 , γ_0 , γ_e , ρ_{00} which will fit the limited available data within the expected uncertainties of the data and model.

COMPARISON WITH METALLIC SOLID STATE THEORY

The functions $P_0(\rho)$, $\gamma_G(\rho)$, and $\gamma_e(\rho)$ obtained from these fits represent properties of the low-temperature solid phase of the metal. Their predicted behavior over a wide range of densities is summarized in Fig. 7 and 8, and will be compared with what is theoretically known about these metals.

The zero temperature compression curves $P_0(V/V_0)$ in the form shown in Fig. 7 have been scaled by the normal bulk modulus of the metal to permit a clear comparison in one figure. The expected minima of P_0 in expansion can be seen to be located over a wide range of relative volumes, from 1.2 to 1.5 reflecting perhaps characteristic of the different type of metallic bonding in these metals. Electron band theory calculations of equation-of-state have not been carried out over a wide range of densities for these metals although they appear to be feasible, if lengthy. For a free electron-like metals such as Na pseudo-potential calculations are reliable and are in good agreement with the static compression data [15] and our fits up to 25% compression. The interestingly different behavior of Ta and Pb in expansion however is unexplained. The differences in the behavior of the curves at high compression is less pronounced but also less reliable as mentioned above. Dynamic or static high compression experiments to check these derived curves would be very desirable.

The behavior of $\gamma_0(V/V_0)$ shown in Fig. 3 is similar for all these metals, exhibiting an overall change in level by an effective volume α at normal density and a leveling-off at large expansion. No reliable theoretical methods apparently exist at present for calculating metallic γ_0 's [13]. Qualitatively the shapes of these curves are reasonable however. At large V volumes a constant γ_0 is consistent with the finite size of the ions. Most scaling theories of γ_0 such as the Slater-Landau formula [7] predict γ_0 will decrease rapidly with compression in agreement with our fitting results. Again the values of γ_0 at small volumes are less reliable. For instance in the case of Pb they can be anywhere below 1.3.

In the case of Pb and Ta a careful adjustment of g_{20} led to 1.3, 1 and 2.2 $\times 10^{-3}$ J/gm at respectively for Pb, Na and Ta respectively. These values are close to the cryogenic values when corrected for phonon renormalization [19]. For Pb the decreasing line for γ_0 in Fig. 3 helped fit the porous Hugoniot data in Fig. 3 and the $U-V$ data in Fig. 4 at large V . The small average value of $\gamma_0^{(2/3)}$ is consistent with the free-electron nature of the electron Fermi surface in Pb. No band theory calculations for either Pb or Ta are available however to make a more detailed comparison. Larger values of γ_0 were necessary in Ta with its large electronic specific heat in order to fit isobaric expansion data. Such a large value is not surprising in narrow band transition metals and is similar to values that have been calculated for Fe from band theory at normal density [19].

In conclusion the solid state properties derived from our fits on three distinct types of metals seem at least theoretically consistent with, if not confirmed by, theory. The resulting EOS thus appears to be a reliable guide to material properties suitable for technical applications as well as research.

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Notations

- B_S - isentropic bulk modulus
- C_B - bulk sound speed
- C_V - specific heat at constant volume
- E - internal energy per gm atom
- F - Helmholtz free energy
- g_{eo} - electronic specific heat coefficient at $T=0$
- H - enthalpy
- P - pressure
- P_m - melting pressure
- R - gas constant
- S - entropy
- T - temperature
- T_M - melting temperature
- U_p - particle velocity
- U_s - shock velocity
- α - liquid EOS scaling parameter
- γ_e, γ_G - electronic and lattice Gruneisen coefficients
- λ - melting temperature exponent
- ρ - density
- τ - scaled temperature T/T_M
- θ_G - Gruneisen characteristic temperature

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Figure 1: Diagram showing the Hugoniot curve and its shifts along which experiments are attempted. Arrows indicate ranges within data is now available.

T_0 - 300 K isobar	T_m - melting line
H_1, H_{10} - .3 and 1 GPa isobar	H_1 - porous Hugoniot from $P_0 = 6.79$
H_0 - principle Hugoniot	H_r - reflected Hugoniot from 35 GPa
S_r - release isentrope	

Figure 2: Comparison of model internal potential energy with Monte Carlo computer calculations for r^{-12} interaction potentials. The bars indicate the increase of computer results [7] with n in the range $4 \leq n \leq 12$. The circles are computer results for the Coulombic system [8]. The thin line represents the interpolation model of Kormer et al [2].

Figure 3: Comparison of experimental shock velocity and particle velocity data with model calculations for Ta and Pb [9].

Figure 4: Comparison of experimental isobaric enthalpy volume data with model calculations for Ta [10] and Pb [11].

Figure 5: Comparison of experimental bulk sound velocity temperature data with model calculations for Na [12] and Pb [13].

- Figure 6 Comparison of experimental melting temperature-pressure data with model calculations for Pb [14] and Na [11,15].
- Figure 7 Zero-degree pressure, scaled by the normal bulk modulus, B_0 as a function of relative volume from fits to experimental data on Pb, Na and Ta. The B_0 used for these metals are 44.77, 6.69 and 194.1 GPa respectively.
- Figure 8 Relative volume dependence of Gruneisen γ_G and electronic γ_e from fits to experimental data for Pb, Na and Ta.

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