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THEORETICAL PHYSICS

HIGH PRESSURE STRUCTURAL PHASE TRANSITION IN Na, Mg AND Al

John A. Moriarty and A. K. McMahan

- We predict new, as yet undetected, structural phase transitions in Na, Mg and Al under compression. These transitions arise from the effect of the downward motion of the initially empty 3d band. While this investigation was carried out up to ten-fold compression, a number of these transitions occur in the Mbar region and below, and should be observable by existing experimental techniques.

The ability to calculate the extremely small energy differences between different structures of a material, by first principles electron band theory, appears to be now within grasp. Successful comparisons between predictions of the linear-muffin-tin-orbital (LMTO) method and the ab initio pseudopotential method used at Berkeley have already been reported for the case of Si.¹ Here we report a much more extensive comparison between the LMTO method and the generalized pseudopotential theory² (GPT) of the present first author for the case of Mg and Al up to ten-fold compression. Not only is there excellent qualitative agreement, but the major cause of quantitative differences is understood, and can be remedied. Furthermore, these successful comparisons serve to verify the atom-atom pair potentials generated by the GPT method in the present cases, suggesting that further calculations of the phonon spectra and lattice Grüneisen parameters from these potentials will be reliable.

The present calculations also predict a series of phase transitions in compressed Na, Mg and Al, of considerable interest in their own right. Figs. 1 and 2 show the results of total energy calculations for the bcc, hcp and fcc phases of these three materials as a function of relative volume, Ω/Ω_0 . The total energies in each case are given relative to that for the fcc structure. Figs. 1(a) and 1(b) show our GPT results for Na and Mg, respectively, while Figs. 2(a) and 2(b) give a direct comparison of our LMTO and GPT results for Al. As can be seen in Fig. 2, the qualitative agreement between GPT and LMTO predictions about phase stability in Al is excellent: both show large regions of fcc stability near normal volume and bcc stability at high compression separated by a small island of hcp stability. The

qualitative agreement for Mg is comparable. No LMTO calculations on Na were attempted due to the tiny energy differences (typically < 0.1 mRy) in that metal.

On the basis of these calculations, we suggest the possible sequence of structures hcp $\rightarrow$ bcc $\rightarrow$ hcp in Na, hcp $\rightarrow$ bcc $\rightarrow$ fcc in Mg, and fcc $\rightarrow$ hcp $\rightarrow$ bcc in Al under increasing pressure. We estimate the initial hcp $\rightarrow$ bcc transitions in Na and Mg, and fcc $\rightarrow$ hcp transition in Al, to occur at pressures of about 10, 570 and 1300 kbar at zero temperature, corresponding to $\Omega/\Omega_0 = 0.86, 0.56$ and 0.58 respectively. These numbers reflect the addition of small zero-point energy contributions to the static lattice energy differences shown in the figures.

The structural energy differences in Mg and Al are profoundly influenced at small volumes by the presence of d electrons. Under compression, the initially empty 3d band moves downward toward the Fermi level E_F , narrowing relative to the sp bands in the process. In Al, the LMTO X_3 level (approximately the bottom of the 3d band) moves below E_F at $\Omega/\Omega_0 = 0.15$, at which point each Wigner-Seitz cell contains about one d electron. We have directly assessed the effect of this d charge by repeating the LMTO calculations with d components removed from the angular momentum basis. The effect is striking, as shown in Fig. 3 for Al. The resultant bcc-fcc and hcp-fcc total energy differences now remain positive throughout the whole volume range considered. Analogous behavior is found for Mg. Thus without d electrons Mg and Al would remain hcp and fcc, respectively, down to at least $\Omega/\Omega_0 = 0.1$. Moreover, the addition of f components to the basis changes the results in Figs. 2(a) and 3 only slightly.

The increasing quantitative discrepancies between GPT and LMTO results with decreasing volume, as seen in Fig. 3, are probably due to differing treatments of d states. While the LMTO method is presumably treating the d states accurately regardless of their spatial character (i.e., either nearly-free-electron or tight-binding like), the GPT, as applied here in the simple-metal limit, is treating the d states accurately only to the extent that they remain nearly-free-electron like. Indeed, the purely p-like X_4 , and L_2 , levels are calculated to within a few percent of each other by the

two techniques at all volumes. The sd hybrid X_1 level, on the other hand, shows close agreement only near normal volume, with the LMTO value moving progressively lower than the GPT value upon compression. This lowering is exactly the type of hybridization effect one expects from a narrowed d band centered above E_F and suggests that the 3d band in Al is slowly developing some tight-binding-like character under pressure, which the present simple-metal form of GPT is not picking up. The natural remedy to this situation is to treat Al as an empty-d-band metal in the manner of the heavy alkali and alkaline-earth metals. This possibility is currently under study.

THERMAL AND COMPRESSIBILITY PROPERTIES OF THE ALKALI METALS

R. Grover

- Static and dynamic compression data have been analyzed together to obtain an improved representation of alkali metal compression properties. By combining both types of data, one obtains information on both the thermal and compressibility equation-of-state of the alkali metals over a large range of temperatures and densities which is of interest to nuclear reactor technology. This work is being prepared for the Handbook on Thermodynamic and Transport Properties of the Alkali Metals (IUPAC, edited by R. W. Ohse).

Introduction

Dynamic shock compression data extends the range of available experimental data on the alkali metals from compressions η ($\equiv \rho/\rho_0$) ~ 1.4 to ~ 3 and up to temperatures $\sim 30 T_M$ (the melting temperature). Model equations-of-state must be used to interpret this data since by itself the data is neither sufficiently accurate nor extensive to completely characterize the EOS. The model EOS must include the liquid phase since the shock compression data is almost completely in the liquid phase.

Although a simpler form of corresponding states theory can be used for alkali metal EOS at normal and lower densities,³ it is known that at higher densities, systematic variations with atomic number will occur due to influence of electronic core and d-band states. The phenomenological model EOS which we have used is based on three assumptions which appear reasonable in these circumstances:

1) The effective ion-ion forces are the same in both the solid and liquid metallic phases, relating the liquid EOS to a solid one, at the same ρ and T , in a simple way.

2) The changes in the thermal ion-ion forces (and therefore in Grüneisen coefficient γ_G) are directly related to the changes in the compressibility of the metal which are caused by electron band anomalies.

3) Electron excitations make relatively small contributions to the "thermal" EOS of the alkali metals which can be represented by a quasi-free-electron approximation since all electron bands should be relatively wide.

Assumption (2) is conventionally used in the form of a modified Slater equation for γ_G , to reduce the shock compression data on metals. In addition it has been successfully applied, together with detailed band theory calculations, to the metals Cs and La where d-band crossings occur.⁴

Method and Results

Previous work on alkali metal compression data consisted for the most part in separate analyses of the static and dynamic data.⁵ In this work we have extended careful fits to normal compression data into the density range of shock data in order to obtain more reliable estimates of the EOS systematics of the alkali metals at high density.

In more detail, the present study differs from previous work in two ways. First, the zero-degree isotherm pressure, which is used in a Grüneisen EOS model, is represented by an extended Birch equation

$$P(\eta) = \frac{3}{2} B_0 \eta^{5/3} x \frac{[1 + \frac{3}{4} (B'_0 - 4)x + S_2 x^3]}{1 + S_4 x^5} \quad (1)$$

$$x \equiv \eta^{2/3} - 1$$

in terms of the normal density ρ_0 , bulk modulus B_0 and its pressure derivative B'_0 . The additional coefficients S_2 and S_4 are used to make additions or subtractions to the first two, conventional terms and the exponents S_3 and S_5 to adjust the compression ranges of these modifications. The conventional Birch expansion is known to be the best systematic expansion for fitting normal compression data up to $\eta \approx 1.4$. Secondly, the Grüneisen coefficient γ_G in the thermal EOS is related to the zero degree isotherm, Eq. (1), by a generalized Slater equation

$$\gamma_G = V \left(\frac{\partial P}{\partial E} \right)_{V, \text{solid}} = m - \frac{1}{6} + \frac{1}{2} (B' - 2n/3) / (1 - \frac{2nP}{3B}) \quad (2)$$

In addition to the usual n parameter, which selects the theories of Slater, free volume, etc., Eq. (2) contains the parameter m to allow γ_G and its derivative $\epsilon \equiv d\ln\gamma_G/d\ln V$ at normal density to be simply fitted to

experimental data where available. Equation (2) retains the strong dependence of γ_G on $B' \equiv dB/dP|_{T=0}$ which is indicated by both theory and experimental data. Otherwise the liquid EOS model, the Lindemann law and the free electron excitation model are the same as in previous work.⁵

Finally these models are accurately normalized to the experimental shock data⁶ by adjusting the parameters remaining in Eqs. (1) and (2) after fitting the normal compression data, B_0 , B'_0 and ϵ .

The results for Li, Na, K, and Rb are summarized in the figures where both γ_G and $\ln B$ (on the zero degree isotherm) are plotted against relative volume. Bulk modulus plots provide a sensitive method of comparing different types of experimental compression data with each other and our EOS model representation. It can be seen in Fig. 4 that normal density compressibility data is quite consistent and that for the worst case, Na, our model still represents the experimental data within the range of two recent sets of static data up to 30% compression.^{3,7}

In addition the $\ln B$ and γ_G plots show with increasing sensitivity the systematic variation of the high pressure EOS with atomic number. The high pressure stiffening of the zero degree isotherm seen in the $\ln B$ plot, Fig. 1, becomes stronger through sequence Li $\rightarrow$ K, as is expected from the lowering of the electron d-bands and the larger cores of closed shell electrons. In the $\gamma(V/V_0)$ plot, Fig. 5, there is a rapid increase in the amount of lowering between Na and the heavier metals which may reflect the importance of d-band hybridization in the valence band. Moreover the rapid increase in γ for Rb at the highest compressions may be an indication of the long expected electronic phase transition corresponding to the well known, 42 kb transition in Cs. Unfortunately the available shock data for Rb does not extend to the high pressure achieved in the other alkali metals. The inflection point in the $\gamma(V/V_0)$ for Li may be an artifact of the experimental data or the fitting procedure. In this connection it should also be noted that the Li EOS is based on a fit to shock data from two laboratories which are unusually inconsistent. Current experimental shock work on Li at this laboratory is being carried out to resolve this discrepancy.

ELECTRICAL CONDUCTIVITY OF HYDROGEN PLASMAS

David B. Boercker

- The electrical conductivity of hydrogen plasmas is calculated using a recent result which relates the conductivity to the equilibrium structure of the plasma. A simple, analytic expression for the conductivity, designed to be accurate in the weak coupling limit gives good agreement with experimental results. A more elaborate calculation in more strongly coupled plasmas gives generally good agreement with molecular dynamics simulations at high density.

The electrical conductivity, σ , of a plasma can be related to the electron-ion collision frequency, ν , through,⁹

$$\sigma = \lambda \frac{ne^2}{m\nu} \quad (1)$$

where n , m , and e are the electron number density, mass, and charge, respectively. The effects of electron-electron collisions are contained in the factor, λ . For weakly coupled plasmas, λ is well-approximated by 1.93.¹⁰ However, for strongly-coupled plasmas, λ can be significantly less than this value.¹¹

The evaluation of the collision frequency has been discussed in detail elsewhere,¹ and the principal result is that if λ is selected to be 1.93, and the conductivity is scaled to the electron plasma frequency, $\omega_p = (4\pi ne^2/m)^{1/2}$, one obtains

$$\sigma^* \equiv \frac{\sigma}{\omega_p} = \frac{1.93 (3\pi/2)^{1/2}}{4\pi \Gamma^{3/2} \Lambda} = \frac{0.3334}{\Gamma^{3/2} \Lambda} \quad (2)$$

where $\Gamma = \beta e^2 (4\pi n/3)^{1/3}$ is the plasma coupling parameter, and Λ is a generalization of the Coulomb logarithm defined by,

$$\Lambda \equiv \frac{1}{4\pi\beta e^2} \int_0^\infty dk k e^{-\beta \hbar^2 k^2 / 8m} \frac{c_{ei}(k)}{(\epsilon_e(k))^2} S_{ii}(k) \quad (3)$$

In the above, β is the inverse temperature and $\hbar$ is Planck's constant over 2π . The functions $S_{ii}(k)$ and $c_{ei}(k)$ are the ion-ion structure factor

and the electron-ion direct correlation function, respectively. The screening factor, ϵ_e , is related to the electron-electron direct correlation function through,

$$\epsilon_e(k) = 1 - n c_{ee}(k) . \quad (4)$$

In the Debye-Hückel limit the integral in Eq. (3) may be done analytically with the result

$$\Lambda_{DH} = e^{1/\alpha} E_1\left(\frac{1}{\alpha}\right) - \frac{1}{2} e^{1/2\alpha} E_1\left(\frac{1}{2\alpha}\right) \\ \sim \frac{1}{2} (\ln \alpha - 1.27) \quad (5)$$

in which $\alpha = (m/\pi\beta^2 h^2 n e^2)$ and E_1 is the exponential integral.¹² The second line in Eq. (5) applies when $\alpha \gg 1$. Table I shows experimentally measured conductivities¹³ in hydrogen and compares them to the results calculated from Eqs. (2) and (5) and from the Spitzer theory.¹⁴ In general, the present theory agrees with the experiment to within about 15% and is somewhat better than the Spitzer theory.

Of course, this would not be of much significance if it were not for the fact that Eq. (3), as well as Eq. (5), can be used in regions where Spitzer fails. In Table II the conductivity found from molecular dynamics simulation of a hydrogen plasma¹⁵ is compared to calculations using Eq. (2) with both Eq. (5) and the direct numerical evaluation of Eq. (3). The rather large disagreement at the largest Γ value can be attributed to two sources. First is the failure of the approximation, $\lambda = 1.93$, and second is the difference in the way quantum mechanics is treated in this theory and in the molecular dynamics. Work directed at correcting the former shortcoming is progressing rapidly.

In summary, an expression for the electrical conductivity has been presented which can be applied to weak and moderately coupled plasmas ($\Gamma \leq 2$). In the weak coupling limit, it agrees with available experimental data to within about 15% and is an improvement over the standard Spitzer expression. For stronger coupling it is in general agreement with molecular dynamics

simulations. It is hoped that in the near future the more elaborate pseudopotentials of Rogers¹⁶ can be used to study the conductivity of more complicated and interesting plasmas.

Table I. Comparison of theoretical and experimental values of σ^* .

T(°K)	Γ	σ^*	$\sigma_{\text{Spitzer}}^*$	σ_{exp}^*
15,400	0.165	1.34	1.57	1.16
18,750	0.161	1.41	1.61	1.32
21,500	0.144	1.62	1.81	1.55

Table II. Comparison with molecular dynamics results ($r_s = (4\pi n/3)^{-1/3}/a_0$,
 a_0 = Bohr radius).

Γ	r_s	σ^*	σ_{DH}^*	σ_{MD}^*
0.5	0.4	4.00	3.55	3.6
0.5	1.0	1.93	1.87	2.15
2.0	1.0	2.39	3.11	1.1

PLASMA PSEUDOPOTENTIALS

F. J. Rogers, D. B. Boercker, and H. E. DeWitt

- Numerical calculations of plasma pseudopotentials that preclude strong bound states have been carried out. Application to the hypernetted chain integral equation are discussed.

The thermodynamic properties of classical models of dense fluids and plasmas can be obtained from Monte Carlo, molecular dynamics, and integral equation methods. However, realistic models of electron-ion plasmas require a quantum-mechanical treatment. It is very difficult to apply the standard methods in this case. An approximate procedure for doing this is to introduce a pseudopotential that has quantum effects built-in at short-distances, but which goes over to the Coulomb potential at distances large compared to the deBroglie wavelength. This removes the short-ranged divergence in the electron-ion distribution function, g_{ei} , which is present in the classical problem. At low temperature, due to the formation of composite particles, numerical difficulties still exist.

The low temperature numerical difficulties can be circumvented by separating the Slater sum into a bound state part, due to low lying bound states, and an interaction part due to continuum states and high lying bound states. Larkin¹⁷ has shown the proper way to carry out this separation in the partition function. Essentially the partition function is separated into a convergent part and a non-convergent part. The resulting convergent bound state part is referred to as the Planck-Larkin partition function.

The corresponding separation in the Slater sum is

$$S_{ei} = S_{ei}^{BS} + S_{ei}^I \quad (1)$$

where

$$S_{ei}^{BS} = \left(\frac{2\pi\beta h^2}{\mu_{ei}} \right)^{3/2} \sum_{nl} (2l+1) \psi_{nl}^*(r) (e^{-\beta E_{nl}} - 1 + \beta E_{nl}) \psi_{nl}(r)$$

$$S_{ei}^I = \left(\frac{2\pi\beta\hbar^2}{\mu_{ei}} \right)^{3/2} \sum_{\ell} (2\ell+1) \int_0^{\infty} \psi_{\ell}^*(r,p) e^{-\beta p^2/\mu_{ei}} \psi_{\ell}(r,p) dp$$

$$- \sum_{n\ell} (2\ell+1) \psi_{n\ell}^*(r) (1 - \beta E_{n\ell}) \psi_{n\ell}(r)$$

where the symbols have their usual meaning. Barker¹⁸ obtained pseudopotentials according to

$$\beta u_{ei}(r, \beta) = - \ln S_{ei} \quad (2)$$

In the present work we will define a pseudopotential which precludes strong bound states according to

$$\beta u_{ei}(r, \beta) = - \ln S_{ei}^I \quad (3)$$

We will refer to this as the Planck-Larkin pseudopotential.

The wavefunctions required to evaluate Eq. (1) were obtained numerically. Previous work on this problem has been analytic and limited to hydrogen. The interest here is more general. We are interested ultimately in obtaining the equation of state and transport properties of dense partially ionized plasmas. We will treat composite particles by utilizing the electron-ion effective potentials, V_{ei} presented in Ref. 19.

Numerical calculations are difficult for a potential having a Coulomb tail. This presents no particular difficulty since quantum effects are only important for $r < \lambda_{ij}$, the deBroglie wavelength. The procedure is to carry out the calculations for screened potentials having a tail of the form $(e^{-r/\alpha_{ij}})/r$ where $\alpha_{ij} \gg \lambda_{ij}$. Small deviations from the isolated atom limit ($\alpha_{ij} \rightarrow \infty$) are easily removed by extrapolation. In the current work hydrogen is used to illustrate the method.

Figure 6 compares the Barker and Planck-Larkin electron-proton pseudopotentials for $kT = 2$ eV, $\rho = 0.0166$ g/cm³ and $\alpha_{ep} = 80 \alpha_0$. The

pseudopotential given by Deutsch²⁰ and used by Hansen and McDonald²¹ in molecular dynamics simulations of an electron-proton plasma is also shown in Fig. 6. For a potential with a screened tail it has the form

$$u_{ij} = \frac{z_i z_j e^2}{r} (e^{-r/\alpha_{ij}} - e^{-Cr}) \quad , \quad (4)$$

where $C = 1/\lambda_{ij}$. The constant C was chosen to match $g_{ij}(0)$ for $kT > 1$ Ryd. The Deutsch pseudopotential is only approximate and is used in applications because of its analytic simplicity.

At high temperature ($kT > 1$ Ryd) the Deutsch pseudopotential is rather close to the Planck-Larkin pseudopotential. As the temperature is reduced below a Rydberg due to partial inclusion of strong bound states, the Deutsch pseudopotential moves lower than the Planck-Larkin pseudopotential (see Figs. 6 and 7). This has important implications in some hypernetted chain calculations with the Deutsch pseudopotential for a three component $e - p - Fe^{24+}$ plasma we have been studying. In this work it was noted that the large peaks in $g_{eFe^{24+}}$ near $r = 0$ caused the integral equation iteration procedure to become unstable. Since the Planck-Larkin pseudopotential is weaker it gives electron-ion distribution functions which are less strongly peaked. This should aid in stabilizing the hypernetted-chain iteration procedure.

Figure 8 compares the electron-proton hypernetted chain distribution functions given by the Deutsch and Planck-Larkin pseudopotentials for $kT = 2$ eV and $\alpha_{ep} = \infty$. Since the electron-electron and proton-proton interactions do not produce bound states the Deutsch pseudopotential was used for these interactions. Hypernetted chain calculations for both pseudopotentials are stable in this example, but $g_{ep}(0)$ for the Deutsch pseudopotential is 2 1/2 times larger than the Planck-Larkin pseudopotential. At lower temperatures and/or lower densities the hypernetted chain calculations for the Deutsch pseudopotential become unstable, while calculations with the Planck-Larkin pseudopotential are stable.

THEORY OF THERMONUCLEAR REACTION RATES IN STRONGLY COUPLED PLASMAS

Hugh E. DeWitt

- The DeWitt, Graboske, Cooper theory of enhancement of thermonuclear reaction rates in stellar interiors is modified by use of Monte Carlo results for strongly coupled plasma mixtures. A mixing formula proposed by Rosenfeld is shown to be valid in the weak and strong coupling limits and leads to a reaction rate enhancement valid for most LLNL applications. The result may be used for calculating the reaction rate of DT in the presence of high Z impurities.

The thermonuclear reaction rate of charged particles in high temperature dense plasmas is enhanced by a lowering of the Coulomb barrier due to correlational effects of the plasma in the vicinity of a reacting pair of charges. A detailed theory of this enhancement effect was given by DeWitt, Graboske, and Cooper (DGC) in 1973 for intermediate and strong coupling.²² The DGC formulae were largely based on the Monte Carlo study of the one component plasma (OCP) of Brush, Sahlin, and Teller,²³ and consequently were most dependable for reacting pairs of charges in a plasma of one ionic charge, for example, DT reactions in laser fusion experiments. The theory of 1973 was not accurate enough to handle reactions of pairs with very different charges nor situations involving DT reactions in the presence of high Z impurities. Due to recent theoretical and numerical simulation work on strongly coupled plasma mixtures, it is now possible to markedly improve the DGC theory of the screening enhancement of the reaction rate.

We consider a plasma of several different ionic species with charge number, Z_1, Z_2, Z_v , and with chemical compositions, $x_i = N_i/N$ ($N = N_1 + N_2 + \dots + N_v$). The reacting pair, (Z_1, Z_2) results in a composite particle of charge $(Z_1 + Z_2)$. The reacting charges are part of a thermal distribution, $\beta = 1/kT$, and can react if they surmount the repulsive potential barrier defined by the potential of mean force, $w_{12}(r)$, and obtained from the equilibrium pair distribution:

$$g_{12}(r) = \exp(-\beta w_{12}(r)) = \exp\{-\beta Z_1 Z_2 e^2/r + H_{12}(r)\} \quad (1)$$

$H_{12}(r)$ is the screening function that reduces the repulsive Coulomb potential, $z_1 z_2 e^2/r$, and at a zero particle separation gives the reaction rate enhancement as:

$$\langle \sigma v \rangle_{12, \text{ plasma}} \cong e^{-H_{12}(0)} \langle \sigma v \rangle_{12, \text{ vacuum}} \quad (2)$$

The complete calculation of the reaction rate is also influenced by the r dependence of $H_{12}(r)$ as the charges move into the potential barrier^{24,25} but here only the lowering of the barrier by $H_{12}(0)$ will be discussed. The Coulombic effects that enhance the reaction rate are dominated in intermediate and strong coupling by the interactions among the various ions; the electrons at sufficiently high density form a degenerate neutralizing background which, for the present discussion, will be considered as a rigid background. Realistic electron screening can be incorporated at a later stage. With the assumption of classical ions moving in a rigid neutralizing background the interaction Helmholtz free energy may be written as:

$$\beta F/N = f_v(\Gamma_o \bar{z}^{1/3}, x_1, z_1, x_2, z_2, \dots, x_v, z_v) \quad (3)$$

with

$$\Gamma_o = \beta e^2/a, \quad a = \left(\frac{4\pi}{3} \frac{N}{V}\right)^{-1/3}$$

$$\bar{z} = x_1 z_1 + x_2 z_2 + \dots + x_v z_v$$

The interaction internal energy as obtained from the Helmholtz free energy is:

$$\beta U/N = \beta \frac{\partial (\beta F/N)}{\partial \Gamma} = \Gamma_o \frac{\partial f}{\partial \Gamma_o} \quad (4)$$

In practice the definitive data for the internal energy are obtained by Monte Carlo simulation of the classical plasma mixtures and the free energy function is constructed by integrating Eq. 4.

DGC showed that the Coulomb barrier lowering, $H_{12}(0)$, was also a thermodynamic function, namely the difference of the free energies before and after the reaction, $z_1 + z_2 \rightarrow (z_1 + z_2)^1$.

$$H_{12}(0) = -(N-1)f_v + 1(\Gamma_o \bar{z}^{-1/3}, \frac{N_1 - 1}{N - 1}, z_1, \frac{N_2 - 1}{N - 1}, z_2, \dots, \frac{N_v}{N - 1}, \frac{1}{N - 1}, (z_1 + z_2)) + Nf_v(\Gamma_o \bar{z}^{-1/3}, \frac{N_1}{N}, z_1, \frac{N_2}{N}, z_2, \dots, \frac{N_v}{N}, z_v) \quad (5)$$

In 1973 this relation provided the structure of the DGC theory but because of lack of information about strongly coupled plasma mixtures it could not be used directly. Instead DGC had to construct the $H_{12}(0)$ published at that time by using the limited OCP data for $g(r)$ and extrapolating $H(r)$ to $r = 0$. Now with an abundance of very accurate OCP and binary ionic mixture Monte Carlo data it is possible to use Eq. 5 directly. The calculation requires two things:

- i) exact OCP energy data from which the OCP Helmholtz free energy function, $f_1(\Gamma)$, can be constructed.
- ii) an accurate mixture rule from which v component free energy f_v can be obtained from $f_1(\Gamma)$.

The OCP energy results are known from solution of the hyper-netted chain equation (HNC) ($0 < \Gamma < .8$), and from long Monte Carlo simulations (collaboration with W. Slattery and G. Doolen at LANL).^{26,27}

The mixture problem is awkward because two limits must be satisfied. For weak coupling the Debye-Hückel theory gives an exact result:

$$\beta F_v / N = f_v = - \frac{(\sqrt{3}\Gamma_o^{3/2})^{-3/2}}{3} z^{-3/2}, \quad \Gamma_o \ll 1 \quad (6)$$

while in strong coupling the mixture is dominated by the ion-sphere result:

$$\beta F_{\nu}/N \approx -\frac{9}{10} \Gamma_0 \bar{z}^{1/3} \bar{z}^{5/3}, \quad \Gamma_0 \ll 1 \quad (7)$$

Hansen, Torrie, and Vieillefosse²⁸ proposed a 'linear' mixture formula which satisfied their binary mixture solutions of coupled HNC equations and a small amount of binary mixture Monte Carlo data:

$$f_{\nu, \text{linear}} = \sum_{i=1}^V x_i f_{i1} (\Gamma_0 \bar{z}^{1/3} z_i^{5/3}) \quad (8)$$

This empirical result was checked with more extensive mixture MC and HNC calculations at LLNL²⁹ and found to be in good agreement with the numerical data. The Hansen, *et al.* 'linear' law clearly gives the expected ion-sphere result for strong coupling, but leads to an incorrect result for weak coupling. Consequently, efforts to calculate $H_{12}(0)$ for intermediate and even strong coupling using the 'linear' law would be suspect. Recently Rosenfeld³⁰ studied the mixture problem by using known exact lower bounds for Helmholtz free energy³¹ for weak and strong coupling. By minimizing the free energy with respect to both lower bounds he was able to derive an approximate, but highly accurate mixing rule:

$$f_{\nu, R} = \left(\frac{\bar{z}}{z^2} \right) \sum_{i=1}^V x_i z_i f_{i1} (\Gamma_0 \bar{z}^{1/3} z_i^{2/3} \bar{z}^2 / \bar{z}) \quad (9)$$

This expression for the plasma free energy mixture recovers both known limits, Eqs. 6 and 7, and consequently it can be used for intermediate coupling. When applied to the LLNL Monte Carlo mixture data²⁹ the agreement is slightly less good than the agreement with the linear formula, Eq. 8, but the difference is near the limit of the accuracy of the Monte Carlo simulation.

In applying the Rosenfeld mixture formula to the evaluation of $H_{12}(0)$ using Eq. 5 some care must be maintained to pick up contributions of order $1/N_1$ and $1/N$. The result is:

$$H_{12}(0) = -\left(\frac{\bar{z}}{z^2}\right) \{ (z_1 + z_2) f_1(\Gamma_{12}) - z_1 f_1(\Gamma_1) - z_2 f_1(\Gamma_2) \} \quad (10)$$

$$+ \frac{2z_1 z_2 \bar{z}}{(z^2)^2} \sum_{i=1}^v x_i z_i (f_1(\Gamma_i) - \Gamma_i \frac{df_1}{d\Gamma_i})$$

where

$$\Gamma_i = \Gamma_o \bar{z}^{1/3} z_i^{2/3} \bar{z} / z$$

The derivative term in this expression is essential to give the weak coupling limit:

$$H_{12}(0) = - z_1 z_2 \bar{z}^{-1/2} (\sqrt{3} \Gamma_o)^{3/2} \quad (11)$$

The OCP free energy function vs. Γ is shown in Fig. 9. For strong coupling the OCP free energy function has the form:

$$f_1(\Gamma) = - A\Gamma + 4B\Gamma^{1/4} - C \ln \Gamma - D - 4E/\Gamma^{1/4} \dots \quad (12)$$

for $\Gamma > .8$. Note that the Madelung term of the strong coupling free energy, $- A\Gamma$, in Eq. 11 gives the expected ion-sphere result:

$$H_{12}(0) \cong A\Gamma_o \bar{z}^{1/3} \{ (z_1 + z_2)^{5/3} - z_1^{5/3} - z_2^{5/3} \} \quad (13)$$

with $A = .8979$

Equation 10 is the desired expression for the lowering of the Coulomb barrier, and should be used in place of Eq. 53 in the 1973 paper of DGC. Precise limits on the validity of these results have not been established yet, but it is expected that they will be adequate for nuclear reaction rate calculations for DT reactions in the presence of one or more high Z impurities.

Future work on the reaction rate problem will focus on proper incorporation of the electrons allowing for polarization of the electrons by linear response theory, and a direct calculation of H_{12} from coupled HNC equations modified to include bridge graph corrections.

APPLICATIONS PHYSICS

THERMODYNAMIC CONSISTENCY IN BQL INTERPOLANTS

Doug Daniel

- We examine the mathematical limitations to thermodynamic consistency imposed by BQL pressure and energy interpolants used for EOS representations. The answer impacts directly on how well an energy-transport hydrocode can adhere to the first law of thermodynamics.

There is some concern within the user community about thermodynamic consistency of equations of state (EOS) represented by bi-quadratic-Lagrange (BQL) interpolants. To solve the problem we applied the appropriate Maxwell relation to the interpolants and examined the resultant functional forms. We choose to derive the energy interpolant from a BQL pressure surface. We then compare the consistent energy functional with a BQL energy interpolant.

The interpolants used in BQL representations are:

$$P(\rho, T) = \sum_{i=0}^2 \sum_{j=0}^2 b_{ij} \rho^i T^j \quad (1)$$

$$E(\rho, T) = \sum_{i=0}^2 \sum_{j=0}^2 a_{ij} \rho^i T^j \quad (3)$$

The Maxwell relation with ρ, T independent variable is easily derived from the first law of thermodynamics

$$dE = TdS + \frac{P}{\rho^2} d\rho$$

and the definition of Helmholtz free energy

$$F = E - TS.$$

Hence

$$T \left(\frac{\partial P}{\partial T} \right)_{\rho} + \rho^2 \left(\frac{\partial E}{\partial \rho} \right)_T = P$$

is the Maxwell relation in ρ, T space.

By integration, we have

$$E - E_0(T) = \int [P - T \left(\frac{\partial P}{\partial T} \right)_{\rho}] \frac{1}{\rho^2} d\rho$$

We obtain the consistent energy interpolant by imposing the above integration on the BQL pressure function (1)

$$E - E_0(T) = \sum_{j=0}^2 T^j (1-j) \left[\frac{-b_{0j}}{P} + b_{1j} \ln \rho + b_{2j} \rho \right] \quad (3)$$

One can determine by comparing (2) and (3) that BQL pressure and energies cannot be rigorously consistent. Clearly, the degree of inconsistency is determined by the ρ, T mesh and the order of approximation of (3) to (2). A Taylor's expansion of eq. (3) minus eq. (1) shows the approximation to be quite good in T but first order in ρ only for small $\Delta\rho$ or large density.

One can conclude that for the best case (when the primary data base is thermodynamically consistent and the fit reproduces the data exactly) that a BQL energy surface can intersect a consistent energy surface only at the mesh points and be rigorously consistent at no more than nine points.

CONTINUUM MECHANICS

NONEQUILIBRIUM MOLECULAR DYNAMICS OF PLASTIC FLOW

William G. Hoover

- Computer simulations of high strain-rate plastic flow, in two-dimensional solids, reveal the dependence of energy and stress on density, strain-rate, temperature, and the scale of flow.

Nonequilibrium molecular dynamics is being developed to simulate constrained flow processes. This technique is now being applied to steady flows in two-dimensional periodic solids in order to relate high-strain-rate deformation to microscopic models of plasticity. The original nonequilibrium molecular dynamics work³² established that periodic rescaling of atomic momenta (relative to the local hydrodynamic velocity) could be used to impose constant velocity and constant temperature boundary conditions. These could then be used to simulate viscous heat conducting flows.

More recently a periodic scaling of space has been introduced directly into Hamilton's equations of motion. This technique can be used to maintain either a constant strain rate³³ or a constant stress³⁴ on a fluid or solid system. Our current work combines these two ideas.³⁵ The adiabatic Hamiltonian equations of motion (two dimensions) for a particle undergoing steady shear, with $du_x/dy = \epsilon$ are

$$\dot{x} = (p_x/m) + \epsilon y; \dot{y} = (p_y/m); \dot{p}_x = F_x; \dot{p}_y = F_y - \epsilon p_x.$$

The velocity dependent force $-\epsilon p_x$ can be thought of as a Coriolis force arising from the rotational nature of simple shear flow. If to these adiabatic equations of motion are added "frictional" contributions, chosen to maintain the kinetic temperature constant, $(d/dt)\Sigma p_x^2 = (d/dt)\Sigma p_y^2 = 0$, then the friction constants ζ_x and ζ_y can be evaluated, as functions of time:

$$\begin{aligned}\dot{p}_x &= F_x - \zeta_x p_x & ; & & \zeta_x &= \Sigma p_x F_x / \Sigma p_x^2 & ; \\ \dot{p}_y &= F_y - \zeta_y p_y - \dot{e} p_x & ; & & \zeta_y &= \Sigma (p_y F_y - \dot{e} p_x p_y) / \Sigma p_y^2 .\end{aligned}$$

These deforming isothermal equations have been implemented on the CRAY and 7600 computers. Tests with zero strain rate show that the equations of motion are stable and correctly reproduce the thermodynamic properties of quasiharmonic crystals. Tests with nonzero strain rates on periodic crystals containing a few hundred particles are also stable and allow us to measure the energy and the stress tensor as functions of thermodynamic state (including strain rate and system size). These simulations, when complete, will be related to ongoing theoretical studies³⁶ of the properties of edge dislocations in atomistic crystals. The latter work has established the core energy of these dislocations as well as the functional relationships between dislocation velocity and stress.³⁷

CONSTITUTIVE MODELS IN THE LLNL HYDRODYNAMIC CODES

W. Moss and L. Glenn

- A program to review critically the constitutive models that are being used in our hydrodynamic codes was initiated in October 1981. We are examining the validity of the fundamental assumptions, self consistency, previously neglected physics, and uniqueness (unambiguous determination of parameters) of the models. The elastic-plastic constitutive model, which consists of a von Mises yield criterion, Prandtl-Reuss flow rule, and a pressure dependent yield strength is being studied currently. A pressure dependent yield strength, with a consistent (associated) flow rule causes plastic dilatation, which increases the pressure in the material. Concurrent with our elastic-plastic constitutive model development, we have modified an existing computer code (AFTON), so that any constitutive model we develop can be easily tested.

Our elastic-plastic constitutive model is based on the von Mises theory of the plastic potential.³⁸ A convex (closed) yield surface is postulated to exist:

$$f = 0 \quad (1)$$

For isotropic materials, f must be a function of stress invariants. Stress states inside the yield surface, $f < 0$, represent elastic states, whereas, stress states on the yield surface, $f = 0$ represent plastic states. Stress states outside the yield surface, $f > 0$, are not allowed. The flow rule obtained from plastic potential theory is:

$$de_{ij}^p = \lambda \frac{\partial f}{\partial \sigma_{ij}} ; \lambda > 0 \quad (2)$$

where de_{ij}^p is the incremental plastic strain, σ_{ij} is the stress, and λ is a positive constant. Equation (2) is equivalent to requiring that plastic flow is normal to the yield surface. Equation (2) is called an associated flow rule, because the plastic strain increments are associated with the yield function.

For our elastic-plastic constitutive model, we choose f to be identical to the form used in the hydrodynamic code model, which is a von Mises yield criterion:

$$f = J_2' - \frac{1}{3} Y^2 ; J_2' = \frac{1}{2} S_{ij} S_{ij} \quad (3)$$

where J_2' is the second invariant of the stress deviator tensor, and is a measure of the mean square shear stress. Y is a function of pressure, temperature, and equivalent plastic strain.

We obtain flow rules from Eq. (2), by considering two cases: (i) Y is pressure independent, and (ii) Y is pressure dependent.

When $Y = Y(P)$, Eq. (2) yields

$$de_{ij}^P = \lambda S_{ij} \quad (4a)$$

Equation (4a) is the Prandtl-Reuss flow rule. We note that the incremental plastic dilatation, which is the trace of the incremental plastic strain tensor, is zero:

$$de_{ii}^P = \lambda S_{ii} = 0 \quad (4b)$$

When $Y = Y(P)$, Eq. (2) yields

$$de_{ij}^P = \lambda \left[S_{ij} - \frac{2}{3} Y \frac{\partial Y}{\partial \sigma_{ij}} \right] \quad (5a)$$

$$de_{ii}^P = - \frac{2}{3} \lambda Y \frac{\partial Y}{\partial \sigma_{ii}} = \frac{2}{3} \lambda Y \frac{\partial Y}{\partial P} \quad (5b)$$

Equation (5a) is the Prandtl-Reuss flow rule, with an additional term that is due to the stress dependence of Y . Equation (5b) shows that the plastic dilatation is nonzero, if the yield strength is a function of pressure.

The hydrodynamic code model consists of Eqs. (1), (3), and (4a). Our model would be identical to the former, if the yield strength was pressure independent. However, Eq. (5) must replace Eq. (4), in order to have a self-consistent theory.

We note that the von Mises theory of the plastic potential is one of many elastic-plastic theories. More complicated yield functions can be postulated and nonassociated flow rules may be used. We are investigating the plastic potential theory because it is similar to our present code model, but adds the potentially important effects of plastic dilatation.

The physical significance of Eq. (5) is that plastic dilatation increases the pressure in the material. Figure 10 shows how this occurs. In the figure, $\sqrt{J_2}'$ is plotted, as a function of P . We assume that at time $n-1$, the material is elastic ($f < 0$), therefore, the point $(P_{n-1}, \sqrt{J_2}')_{n-1}$ is inside the yield surface $f = 0$, which is a function of pressure. A trial compression produces a change in pressure dP^T . In some codes, the trial compression is calculated from Newton's Laws. If the resulting $\sqrt{J_2}',^T$ (calculated by assuming the trial compression is totally elastic), which corresponds to $P^T = P_{n-1} + dP^T$, is inside the yield surface, then the stress state is elastic and the calculation is finished. However, if $(P^T, \sqrt{J_2}',^T)$ corresponds to a virtual state outside the yield surface, then a flow rule is needed to determine the path back to the yield surface. The Prandtl-Reuss flow rule allows no plastic dilatation; therefore, the path to the yield surface occurs at constant pressure, P^T . Plastic potential theory requires that plastic flow is normal to the yield surface, therefore, the pressure increases by dP^P , as shown in the figure. The total change in pressure is $dP = dP^T + dP^P$. We note that the flow rule (5) can couple the elastic-plastic constitutive model to the equation of state, thus changing the effective bulk modulus of the material. Future work will consist of testing this elastic-plastic model by examining the effects of plastic dilatation on wave profiles.

TURBULENCE INTERACTION WITH THERMOCHEMICALLY INERT SOLID PARTICLES

A. C. Buckingham, W. J. Siekhaus,^{*} S. J. French,
J. O. Keller,⁺ J. Ellzey,⁺ G. Hubbard,⁺ J. W. Daily⁺⁺

- We are theoretically and experimentally investigating the interactions between turbulence and dispersed inert particles. We are interested in the apparent reduction in turbulent intensity associated with thermochemically inert solid particle dispersal in developing free shear layers. Two plane, incompressible, shear flows are studied. One forms over a rearward facing step and the other over a parallel splitter plate. Both evolve in a rectangular test section driven by a steady, mean, incompressible stream. Computations on these flow configurations are being prepared. The computations include Reynolds' averaged unsteady Navier-Stokes gas field solutions combined with separate Lagrangian particle field solutions. Random statistical interactions simulate the connection between the two fields. This study is a part of our research on fundamental mechanisms of hot gas erosion which is funded by the Department of the Army, U.S. Army Research Office.

It seems intuitively reasonable that, in a turbulent flow, particle inertial effects, fluctuating phase volume effects, and, in combustion, particle enhanced acoustical coupling should affect the dissipation and transport of turbulence energy. Our investigations, summarized here and discussed in current publications,^{39,40,41,42} isolate the purely inertial influences of the dispersed phase on reducing turbulence.

Earlier investigations on inviscid shocked flows⁴³ and laminar viscous flows⁴⁴ indicate that dispersed particles significantly influence heat, mass, and momentum transport as well as wave propagation processes in the carrier gas. Generally, a dispersal of finely divided particles acts to reduce

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molecular diffusion and attenuate wave propagation. We are looking for similar influences in turbulent flow. Back influences of moderately sparse particle concentrations have been theoretically investigated using a round turbulent jet configuration.^{39,40} In this previous work as well as in our current work^{41,42} we take advantage of Crowe's formulation for gas particle forces,⁴⁵ modifying the instantaneous interactions with a Monte Carlo randomization to simulate the turbulent motions.

In contrast to the present work, a substantial number of important flow situations exist where completely interactive coupling does not need to be considered. Generally, in these cases, consideration of particle dispersal alone is adequate. Particle populations are modest enough so that their effects on the flow can be ignored. Examples include the meteorological droplet dispersal predictions of Watson and Barr,⁴⁶ the turbulent channel flow predictions of Peskin and Kau,⁴⁷ and the droplet spray dispersal calculations of Dukowicz,⁴⁸ who predicts the dispersed phase influences on the mean but not on the fluctuating components of the flow.

In our computational method, the coupling forces between the particles and gas are accounted for using a self-consistent, control volume formulation⁴⁵ describing forces produced by fluctuations of the gas phase and the resulting particle accelerations. The particle equations of motion are re-written in a Lagrange center-of-mass system. Particle motions are treated incrementally in time, Δt . The random fluctuational gas/particle encounters are generated in an intermediate computational step.^{40,41,42} Forces considered on the particle include drag, virtual mass, Basset (boundary layer displacement), Magnus (spin), and Saffman Lift. Following determination of the particle concentrations and trajectories, void fraction weighting is applied to the particle gas mixture equations and a new set of mixture mass modified Navier-Stokes solutions are obtained for the updated mixture field.

For illustration, our previous results⁴⁰ for a round turbulent jet configuration are shown. The lateral profiles of turbulent Reynolds' stress are shown in Fig. 11 at 20 diameters from the entrance. The influence of the particles is seen to reduce significantly the Reynolds' stress relative to that obtained in a particle free gas.

The particle concentration normalized probability distributions are shown in Figs. 12 and 13 for this round jet flow configuration. The distribution traces a transverse sweep of the computed test section. These profiles were taken at a modeled axial location, $1/2$ diameter downstream from the jet entrance into the test chamber. Figure 12 shows the transverse distribution for $40\text{ }\mu\text{m}$ particles while Fig. 13 shows the much greater penetration (greater particle dispersal) for $0.4\text{ }\mu\text{m}$ particles. The sizes refer to the assumed common diameter of the dispersed spherical particles. Initial particle velocity distribution at the jet origin was assumed to be 10% of the mean gas phase velocity at the origin and is considered uniform in y , for both cases shown.

The axial auto-correlation coefficient with and without 0.1% mass loading of $40\text{ }\mu\text{m}$ spherical particles is shown in Fig. 14. The other flow conditions are given on the figure. A small, but consistent decrease in correlation and diminished turbulence integral scale, hence diminished eddy size and fine scale structural features, are predicted when the particles are present.

Our experiments on turbulence particle interactions are conducted at a University of California combustion wind tunnel facility, configured for Schlieren and LDV diagnostics.⁴⁹ Current flow configurations include low speed, steady, mean flow in a rectangular test section. Turbulent eddy structure develops at a rearward facing step and at the trailing edge of a splitter-plate which divides the test section into equally sized upper and lower channels. The former flow configuration is shown in Fig. 15(a), while the latter is shown in Fig. 15(b).

To measure particle influences on large structure features, for example the eddy shedding, we trace the eddy history and ensemble average the observations for a large number of eddies. The results are digitized from cinematographic observations using fast framing (5000 s.^{-1}) motion picture exposures of Schlieren or (for combustion flows) shadowgraph eddy field images. Figure 16 illustrates these features with histograms. Adding larger particles produces a distinctly bimodal distribution of shedding frequency indicating an increased population of smaller (less energetic) high frequency eddies. The tendency for breakdown of the large eddy structures increases with particle

mass loading. Splitter plate generated free shear turbulence power spectra LDA measurements at a mid-plane, mid-channel position just downstream of the splitter plate are shown in Fig. 17 for the three indicated Reynolds numbers, based on the channel half-depth. Our current experimental plans include measurement of the modulation of fine scale turbulent features influenced by particles using dual LDV (for particles) and LDA (for gas) diagnostics.

EXPERIMENTAL PHYSICS

THE EQUATION OF STATE OF MOLECULAR HYDROGEN AND DEUTERIUM FROM SHOCK-WAVE EXPERIMENTS TO 760 kbar

W. J. Nellis, M. Ross, A. C. Mitchell, M. van Thiel and D. A. Young

- We have carried out single shock experiments with liquid deuterium to 200 kbar ($T \sim 4500$ K) and reflected experiments to 760 kbar ($T \sim 7000$ K) as well as single shock experiments with liquid hydrogen to 100 kbar ($T \sim 3300$ K). These results enable us to determine a spherically symmetric, effective intermolecular pair potential that predicts isotherms in excellent agreement with the recent static measurement to 370 kbar of van Straaten, et al. at 5 K, but in disagreement with those of Shimizu, et al. to 200 kbar at 300 K.

The high pressure equation of state of molecular hydrogen and its transition to the metallic state is currently a subject of intense interest. In this paper we report accurate, new shock-wave results on the liquid up to a pressure of 760 kbar and a calculated temperature of about 7100 K. The high final temperatures and pressures achieved in the shock process allow us to determine an effective pair-potential for molecular hydrogen valid at small intermolecular separations. We have used this potential to calculate low temperature solid isotherms and to compare them with recent static measurements.

For these experiments shock waves were generated by accelerating a planar projectile to a velocity in the range 3.9-6.7 km/s using a two-stage light-gas gun⁵⁰ and impacting the projectile onto a target containing liquid H_2 or D_2 . The experiment is based on the Rankine-Hugoniot relations which relate measured kinematic parameters to thermodynamic variables. The diagnostic system was described previously.⁵¹ Liquid D_2 specimens were also double-shocked by reflecting a shockwave off an aluminum (alloy 1100) anvil to achieve pressures four times higher than could be achieved by a single shock. The technique has been described previously.⁵² For the double-shock D_2 experiments the mixing circuit used to multiplex two detector signals onto a single oscilloscope was modified somewhat because of the short shock transit times being measured (~ 110 ns). The cryogenic targets have also been described.⁵³ The coolant was liquid H_2 for all experiments. The cryogenic design was modified because the heat of vaporization per unit volume is significantly less for liquid H_2

than for coolants used previously, like liquid N_2 or Ar. The initial state was close to the saturation curve at 20.2 K. Au-Fe vs chromel thermocouples were calibrated in place. Sample temperature was used to obtain initial sample density.^{54,55} The Hugoniot equation of state for the metal impactors and walls or base plates were published earlier,⁵⁶ as was the calculation of the release isentrope of the aluminum base plate.⁵³ Small corrections were made for thermal contraction as previously noted.⁵³ The error analysis has also been published.^{51,56} Changes in experimental details from our other experiments will be published elsewhere.

The data are plotted in Figs. 18 and 19 and are compared with earlier work of van Thiel, et al.^{57,58,59} and Dick and Kerley.⁶⁰ Figure 18 shows the principal Hugoniot up to 0.21 Mbar and the reflected D_2 Hugoniot data near 0.76 Mbar. These higher pressure points were reflected from the lower point at 0.21 Mbar. Fig. 19 shows the H_2 principal Hugoniot points. The present shockwave experiments have the highest accuracy of any to date on H_2 and D_2 .

One goal of our work has been to determine a spherically symmetric, effective intermolecular potential which can be used with accurate theoretical models to calculate the equation of state of condensed hydrogen. In 1978 Silvera and Goldman⁶¹ (SG) carried out a very careful theoretical study of the deuterium isotherm at 4 K and up to 26 kbar using self-consistent photon theory and determined an intermolecular potential that best fit these data.⁶² Subsequently we showed that their potential would also predict the fluid isotherms of H_2 and D_2 from 75 to 300 K up to 20 kbar and the melting curves to 57 kbar in agreement with experimental data.⁶² In these calculations we used soft-sphere perturbation theory for the fluid properties and lattice dynamics for the solid with anharmonic corrections. The melting curves were computed by equating the Gibbs free energies and pressures of the two phases. However, this limited data base is insufficient to determine the short range intermolecular repulsions that dominate the high temperature-high pressure shocked states, and as a result the SG potential predicts Hugoniot curves that are too steep. We found that if this potential were modified for $r < 2.55 \text{ \AA}$ it was possible to compute the theoretical Hugoniots shown in Figs. 18 and 19, 34d still maintain the excellent fit to the lower pressure fluid, solid and melting data.

Our new potential is

$$\phi = \phi_{SG} \quad r > r_c \quad (1a)$$

$$\phi = A \exp [B(r-r_c) - C(r-r_c)^2 - D(r-r_c)^3 - E(r-r_c)^3(r-r_1)] \quad r < r_c \quad (1b)$$

where $A = 3.98823 \times 10^{-14}$ erg, $B = 4.76940 \text{ \AA}^{-1}$, $C = 2.25457 \text{ \AA}^{-2}$, $D = 0.955189 \text{ \AA}^{-3}$, $E = 0.248158 \text{ \AA}^{-4}$, $r_1 = 1.2 \text{ \AA}$, and $r_c = 2.55 \text{ \AA}$.

The calculation of the Hugoniot curve and the statistical mechanical theory used to compute the thermodynamic properties of compressed fluid hydrogen are described in previous publications.^{62,63,64} In these calculations the vibrational and rotational properties are assumed to be unaffected by compression and were calculated as in the gas phase. The actual change in the vibrational frequency under compression to pressure up to 600 kbar at 300 K reported by Sharma, *et al.*⁶⁵ is too small to be observed along the Hugoniot. Molecular dissociation is expected to be negligible at these densities. The theoretical Hugoniot curves were calculated with fluid perturbation theory and Monte Carlo calculations. Perturbation theory is particularly useful in a study of this type in which a best fit pair potential is sought and fast calculational methods are desirable. To check the accuracy of the perturbation theory we carried out Monte Carlo calculations and determined that the predicted Hugoniots were generally softer than perturbation theory by about 1% in volume, but well within the $\pm 3\%$ experimental error. The theoretical curves shown in Figs. 18 and 19 are based on Monte Carlo results. Also indicated on the figures are some of the calculated temperatures. The high temperatures achieved in these experiments provide information about the pair potential down to molecular separations of about 1.6 $\text{\AA}$, or comparable to separations at which the molecular-metallic transition is believed to take place.

Pressure versus volume measurements, made using diamond anvils, have been reported by Shimizu, *et al.*⁶⁶ up to 200 kbars at 300 Kelvins, and by van Straaten, *et al.*⁶⁷ up to 370 kbars at 5 Kelvins. These two sets of results, shown in Fig. 20, are in serious disagreement. The disagreement is somewhat

worse than it appears since the 300 K isotherm is below the 5 K curve. Also shown is a 5 K isotherm calculated using lattice dynamics and the inter-molecular potential that best fitted our shock-wave data. The theoretical curve is in very good agreement with the results of van Straaten, et al. It is worth emphasizing that the shock-wave method has nothing in common with diamond anvil experiments and represents a totally independent determination of the H_2 equation of state.

We have recalculated the molecular to monatomic metal transition using a molecular equation of state based on our new intermolecular potential and metal equations of state calculated by the APW method⁶⁸ and third order perturbation theory.⁶⁹ Zero point properties and electron correlation energy were included. These theories predict metallic transitions at 3.1 Mbar (APW) and 3.6 Mbar (third order). The new results do not differ substantially from earlier work.⁷⁰ This result assumes metallization will occur by molecular dissociation. However, experimental work on iodine⁷¹ has demonstrated that a molecular crystal can become conducting, without dissociation, as a result of the crossing of the filled valence band of the molecule with its empty conduction band. Some preliminary theoretical calculations for a solid at 0 K indicate that hydrogen may undergo the same transition.^{72,73}

NUCLEAR-EXPLOSIVE-DRIVEN EQUATION-OF-STATE EXPERIMENT

W. J. Nellis, A. C. Mitchell, R. Olness, M. van Thiel

- We are in the process of fielding a shock-impedance-match experiment driven by a nuclear explosive. This equation-of-state experiment is a joint effort between H Division, A Division (W. P. Crowley, D. Hardin), B Division (J. White, G. Repp), and L Division (R. Heinle, H. Finn, T. Valk). The experiment is similar to that described by C. Ragan.⁷⁴ A planar shockwave will be generated in Pb, transmitted into an Al baseplate, and shock-impedance-matched into samples which include Be, Cu, and Pb. Expected pressures are about 10 Mbar in Al and Be and about 20 Mbar in Cu and Pb. Measured shock transit times will be about 500 ns. The detectors will be electrical shorting pins developed in 1975.⁷⁵

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Figure Captions

- Fig. 1 Relative total energies of bcc, hcp and fcc structures vs. volume, as calculated by the GPT method. a) Na, b) Mg.
- Fig. 2 Relative total energies of the bcc, hcp and fcc structure of Al vs. volume, as calculated by (a) the LMTO method, and (b) the GPT method.
- Fig. 3 The bcc-fcc total energy difference for Al vs. volume, as calculated by the GPT method and by the LMTO method with and without d states.
- Fig. 4 Calculated zero temperature bulk moduli as function of relative volumes. Values of B and $d \ln B / dV$ derived from static and ultrasonic experimental data range over values shown by Φ and the shaded cones along right axis. Static compression data for Na up to compressions of 30% ranges over values indicated by I.
- Fig. 5 Calculated and experimental values of the Grüneisen coefficient as function of relative volume.
- Fig. 6 Electron-proton effective potentials for $kT = 1$ eV, $\rho = 0.0166$ g/cm³, $\alpha_{ep} = 80 a_0$. The Barker pseudopotential (Eq. (2)), the Deutsch pseudopotential (Eq. (4)), and the Planck-Larkin pseudopotential (Eq. (3)) are shown.
- Fig. 7 The same as Fig. 6 except $kT = 2$ eV.
- Fig. 8 Hypernetted chain electron-proton distribution functions for the Deutsch and Planck-Larkin pseudopotentials, corresponding to Fig. 7.
- Fig. 9 OCP Helmholtz free energy.
- Fig. 10 Plastic dilatation increases the pressure.
- Fig. 11 Calculated radial profiles of turbulent Reynolds stress between roundjet centerline and wall at indicated particle concentrations.
- Fig. 12 Calculated normalized 40 μ m radial particle concentration distributions between round turbulent jet centerline and wall at indicated times.
- Fig. 13 Calculated normalized 0.4 μ m radial particle concentration distributions between round turbulent jet centerline and wall at indicated times.
- Fig. 14 Calculated turbulent axial (streamwise) velocity component auto-correlation coefficient with and without particles.
- Fig. 15 (a) Experimental two-dimensional blow-down turbulent two-phase flow combustion chamber with rearward facing step turbulence generator.
(b) Experimental two-dimensional blow-down turbulent two-phase flow combustion chamber with dividing flow splitter plate turbulence generator.

- Fig. 16 Histograms of turbulent eddy shedding features from Schlieren fast framing movie records, rearward facing step configuration.
- Fig. 17 Turbulent power spectra LDA measurements in splitter plate generated mixing layer at three test flow speeds and corresponding Reynolds numbers.
- Fig. 18 Principal and reflected deuterium Hugoniot.
- Fig. 19 Principal liquid hydrogen Hugoniot
- Fig. 20 Solid hydrogen isotherms.

mpd/ks/0081Q

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15(a)

Fig. 15(b)

$Re (cm^{-1}) = 9092, U_{\infty} = 13.28 \text{ m/s}, T = 298 \text{ K}$

Fig. 16

Fig. 17

Fig. 18

Fig. 19

Fig. 20

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