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ALUMINUM AT $T \approx T_F$ : THEORY OF THE DYNAMICALLY COMPRESSED METALLIC
STATE *

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Résumé

Nous rendons compte ici d'une méthode de calcul de l'équation
d'état et des courbes Hugoniot des métaux simples sous haute compres­
sion, à la fois dynamique et statique. La méthode est fondée sur
l'observation que les énergies libres de Helmholtz des phases isochoriques
solide et liquide diffèrent surtout par leurs composantes entropiques
respectives. Par conséquent, nous utilisons une théorie pseudopotentielle
au second ordre pour calculer les fonctions thermodynamiques du métal
simple par une méthode variationnelle qui traite la phase solide, à des
fins structurales, comme un liquide supra-refroidi. Dans le cas de
l'aluminium, nous avons examiné des compressions de volume de l'ordre
de $V/V_0=1/3$, correspondant aux valeurs atteintes dans de récentes
mesures de choc nucléaire. Les températures associées sont dans les
environs de $T_F$ et de telles conditions requièrent que l'on tienne pleine­
ment compte de la dépendance en température de l'énergie du gaz
d'électrons et de la fonction diélectrique.

Abstract

This work reports a method for calculating the equation of state and
Hugoniot curves of simple metals under high compression, both dynamic
and static. The method is based on the observation that the Helmholtz
free energies of isochoric solid and liquid phases differ mainly in their
respective entropic components. Accordingly, we use second order pseu­
dopotential theory to calculate the thermodynamic functions of the simple
metal by a variational method that treats the solid phase, for structural
purposes, as a supercooled liquid. In the case of aluminum, we have con­
sidered volume compressions in the range $V/V_0=1/3$ which correspond
to values reached in recent nuclear shock measurements. Associated tem­
peratures are in the neighborhood of $T_F$ and such conditions require that
the temperature dependence of the electron gas energy and dielectric
function be fully taken into account.

1. Introduction

In the past decade, experimental high pressure probes have undergone both a con­
siderable refinement in precision and a considerable extension in their compressive capa­
bilities. Diamond anvil experiments have recently achieved static compression pressures
of 1.7 Mbar\cite{1}, whereas dynamic compression pressures in excess of 4000 Mbar have
recently been reported in convergent nuclear shock wave experiments\cite{2}. The challenge to
theoretically model the behavior of matter under such extreme conditions has thus
become increasingly significant. It is the purpose of this paper to present a preliminary scheme to calculate the equation of state of simple metals at ultrahigh pressures. Specifically, second order pseudopotential theory is used to calculate the room temperature isotherm, bulk modulus and binding energy, as well as the shock Hugoniot. Aluminium is chosen as the prototype system for these calculations because of its importance as a possible high pressure standard, and because of the wealth of experimental data, both static and dynamic, currently available for it.

In the following section we present our calculational scheme, emphasizing the specific approximations made. The results are presented in section 3, and we conclude with commentary in section 4.

2. Calculational Scheme

Consider a system of N ions of charge +Ze and ZN electrons of charge -e in a volume V. Because we restrict our attention to simple metals, we may treat the ions (nuclei plus core electrons) as unpolarizable particles, and consider the electron-ion interaction as describable by a local pseudopotential. The Hamiltonian can thus be written

$$H = H_e + H_i + \sum_{i,j} v_p(\vec{r}_i - \vec{R}_j),$$

where \(H_e\) and \(H_i\) are the standard electronic and ionic Hamiltonians, and where \(\vec{r}_i\) and \(\vec{R}_j\) denote the electronic and ionic coordinates, respectively. For simplicity we have used a modified Heine-Abarenkov form for the pseudopotential, i.e.

$$v_p(r) = \begin{cases} 
-Ze^2/r, & r > r_e \\
-Ze^2c/r_e, & r < r_e.
\end{cases}$$

The effective ion core radius \(r_e\) and the constant \(c\) present two free parameters, which are obtained by fitting the calculated room temperature isotherm to experimental data.

The essence of our calculation is to use second order pseudopotential theory to evaluate an approximate energy of the Hamiltonian (1). Thus, upon making the standard adiabatic approximation and assuming a linear response of the electronic density to the ionic density as a perturbation, the following “pair potential” expression is obtained for the energy:

$$E(T,V) = E_e + E_p + T_i + \frac{1}{2} \sum_{i \neq j} \phi(R_{ij}).$$

Here \(E_e\) is the energy of the fully interacting homogeneous electron gas, \(E_p\) is a structure-independent term (which contains the overall Hartree energy), \(T_i\) is the kinetic energy of the ions, and \(\phi(r)\) is the temperature and volume dependent interionic pair potential.

Because we shall be calculating high temperature properties \((T \approx T_F)\) along the Hugoniot, the full temperature dependence of the electron gas energy must be included. We thus write

$$E_e = E_e^0(T,V) + U_e(T,V).$$

The kinetic energy of the electron gas, \(E_e^0\), is approximated with the kinetic energy of a gas of ideal fermions, which is obtained, along with the chemical potential, by numerical integration. The quantity \(U_e\) is the temperature dependent interaction energy of the electron gas. We approximate it with an expression that interpolates between the exchange-correlation energy of degenerate electrons and the interaction energy of a classical one-component plasma. In the density range of interest here (where \(r_s \approx 2\)), such an expression is

$$U_e(T,V) = \frac{-\alpha r_s^{-k}}{\sqrt{1 + d \theta}} NZ Ryd,$$
where $a = 1.03937$, $b = 0.91303$, $d = 0.305$, $V / \Omega = 4 \pi (r, a_s) / 3$ and $\theta = T / T_F$. $U_e (T = 0)$ is the exchange-correlation energy as determined by Rahman and Vignale. Note that $U_e$ extrapolates into the classical ($\theta >> 1$) regime to values determined by Carley and, in the extreme weak coupling limit, by Debye-Hückel theory. The term $E_e$ in Eq. (3) is given by

$$E_e (T, V) = \frac{(N \Omega)^2}{2 V \Omega (0, T)} + \frac{N}{2 V} \sum_{k} \left( \frac{2 \Omega(k, T)}{\epsilon(k, T)} \right),$$

where $\epsilon(k, T) = 1 + 4 \pi e^2 \Pi(k, T)/k^2$ is the temperature dependent dielectric function of the electron gas, $\Pi(k, T)$ being its irreducible polarization. Finally, the state-dependent pair potential appearing in (3) is given by

$$\phi(k) = \frac{4 \pi (2 \pi e)^2}{k^2} + \frac{\epsilon(k, T)}{\epsilon(k, T)} \left( \frac{2 \Omega(k, T)}{\epsilon(k, T)} \right),$$

We use the following form for the electronic polarization:

$$\Pi(k, T) = \Pi_0(k, T) \left[ 1 + \left( \frac{4 \pi e^2}{k^2} \right) G(k) \Pi_0(k, T) \right]^{-1},$$

where $\Pi_0(k, T) = \Pi_0(0, T)$ is the free electron (RPA) polarization, $f(k)$ being the Lindhard function, i.e.

$$f(k) = \frac{1}{2} + \frac{1-z^2}{4z} \ln \left| \frac{1+z}{1-z} \right|, \quad (z = k / 2k_F).$$

We have chosen a Hedin-Lundqvist form for the correlation enhancement function $G(k)$ namely

$$G(k) = 1.01434 r_s (k / 2k_F)^2,$$

where $\alpha = 0.08607$. The prefactor of $k^2$ above has been chosen so that the resulting $T = 0$ polarization satisfies the compressibility sum rule. The quantity $\Pi_0(0, T)$ is

$$\Pi_0(0, T) = -k_F \left[ \pi^2 e^2 a_s \sqrt{1 + (3 \theta / 2)^2} \right]^{-1}.$$

Note again that because of the high temperatures reached along the Hugoniot curve, a finite temperature correction to the screening wave vector that interpolates between Thomas-Fermi at $T << T_F$ and Debye-Hückel at $T >> T_F$ is included in $\Pi_0(k = 0)^9$. To evaluate $E_e$ and $\phi(r)$, the k-space integrals are carried out analytically by using a Padé approximant for the Lindhard function $10$: $f(k) = N(k) / D(k)$, where

$$N(k) = 1 - 0.5395 z^2 + 0.0212 z^4 - 0.002048 z^6 + 0.3333 z^8,$$

and

$$D(k) = 1 - 0.2061667 z^2 + 0.01910 z^4 + 0.0191657 z^6 - 0.2061238 z^8 + 0.99999 z^{10},$$

with $z = k / 2k_F$. Upon making this approximation, $\phi(r)$ can be written in closed form as the sum of six complex Yukawa potentials.

Notice that the application of second order pseudopotential theory to the Hamiltonian (1) results in a separation of the electronic and ionic degrees of freedom, and that the electronic degrees of freedom are traced over quantum mechanically in arriving at the expression (3) for the total energy. However, within the density and temperature range of interest, the ionic thermal de Broglie wavelength is much smaller than the inter-particle spacing, and thus classical statistical mechanics can be used to trace over the ionic degrees of freedom. This classical averaging can be greatly simplified, and a variational principle admitted, if the long range positional order of the solid is neglected and the structural energy is evaluated using a liquid-like pair correlation function:

$$\frac{1}{2} \sum_{i \neq j} \phi(R_{ij}) \rightarrow \frac{N^2}{2V} \int d^3 r \phi(r) g(r).$$
Such a "supercooled-liquid" approximation has been recently applied to argon by Jones and Ashcroft\(^\text{11}\). Fluid variational theory, based on the Gibbs-Bogolubov inequality\(^\text{12}\), can then be used to evaluate the free energy in a fluid reference system:

\[
F = E_e + E_v + \frac{5}{2} N k_B T - TS_e + \min \left\{ \frac{N^2}{2 V} \int dr \phi(r) g_{\text{ref}}(r;\eta) - TS_{\text{ref}}(\eta) \right\},
\]

(15)

where \(\eta\) is the variational parameter. An approximate expression for the electron gas entropy \(S_e(T, V)\) is obtained by a first order finite temperature perturbation theory calculation, which gives

\[
TS_e = \frac{5}{2} P_e^0 - \mu N .
\]

(16)

For calculations of the crystalline state we use a hard sphere reference system, where the variational parameter \(\eta\) is the hard sphere packing fraction. Because the pair potential can be expressed as the sum of complex Yukawa potentials, the energy integral in (15) can be evaluated in closed form within a Percus-Yevick approximation\(^\text{13}\). The excess hard sphere entropy is obtained from molecular dynamics as

\[
S_{\text{es}}(\eta) = \left[ \ln(\eta a^3) + a^2 - 0.44 a - 2.1559 \right] N k_B ,
\]

(17)

where \(a = (V - V_{cp})/V_{cp}\), \(V_{cp}\) being the close-packed volume. For calculations of the liquid state (at compressions beyond the point where the Hugoniot crosses the melting curve), we use the soft sphere model of Ross\(^\text{15}\), which has been shown to be the preferred reference system for liquid aluminum\(^\text{16}\). The soft sphere system uses the same pair correlation function as the hard sphere system, but the hard sphere Carnahan-Starling excess entropy is modified to the form

\[
S_{\text{es}}(\eta) = \left[ \frac{3 \eta^2 - 4 \eta}{(1-\eta)^2} + \eta^2 + \eta^2 + \frac{\eta}{2} \right] N k_B ,
\]

(18)

where \(\eta\) is again the packing fraction.

Our calculational scheme thus consists of two parts. First, second order pseudopotential theory is employed to express the total energy in the pair potential form of Eq. (3); second, by treating the solid for certain structural purposes as a supercooled liquid, fluid variational theory can be used to calculate the final thermodynamics. In the following section we report the results of our calculations on the equation of state of aluminum.

3. Results of Calculations

The first step in implementing the above calculational scheme is to obtain the two pseudopotential parameters \(c\) and \(r_e\) of Eq. (2) by fitting the calculated room temperature isotherm to experimental data\(^\text{17}\). The resulting theoretical curve plotted in Fig. (1) is seen to agree quite well with experiment. The values of the pseudopotential parameters obtained are \(c = 0.437\) and \(r_e = 1.424 a_0\).

The bulk modulus of aluminum is easily obtained by differentiating the \(p(V)\) relation shown in Fig. (1). At \(V = V_0\) and \(T = 300\) K, we obtain a value \(B_0 = 0.66\) Mbar, which is to be compared to the experimentally observed value 0.794 Mbar\(^\text{18}\).

Because we have used pseudopotential theory, the results of our total energy calculations give the binding energy of aluminum, which is the total energy relative to its triply charged ions and valence electrons separated at infinity. At room temperature and zero pressure, we obtain \(E = -4.12\) Ryd/atom, which is indeed quite close to the experimental value of -4.14 Ryd/atom\(^\text{19}\).

The major goal of this calculation, however, is the determination of the shock Hugoniot curve, which is the locus of states in the \(p-V\) plane attainable by a shock compression. The Hugoniot of course lies above the isotherm, by virtue of the heating...
that occurs during shock loading. Because the compressive stresses attained in the shock front so exceed the yield strength of the metallic sample, it is common to neglect the shear stresses produced and to treat the shocked material as a fluid. The conservation laws of mass, momentum and energy can then be straightforwardly applied to describe the Hugoniot curve by the Rankine-Hugoniot equation\(^\text{20}\) for isotropic systems:

\[
E - E_o = \frac{1}{2} (V_o - V) (p + p_o).
\]

(19)

Here \((E_o, V_o, p_o)\) is the initial thermodynamic state, while \((E, V, p)\) describes the thermodynamic state of the shock front.

In Fig. (2) is plotted the theoretical Hugoniot curve, obtained by solution of Eq. (19), along with the experimental data of Mitchell and Nellis\(^\text{21}\) and Ragan\(^\text{22}\). In the insert is shown data up to 2 Mbar obtained by impact loading, along with the experimental\(^\text{16}\) and theoretical regions in which melting occurs. This region was calculated theoretically by plotting the Hugoniot pressures of both the solid and liquid phases against the melting curve of Moriarty, Ross and Young\(^\text{16}\). In the larger plot of Fig. (2), the Hugoniot curve is extended up to 30 Mbar, in order to compare theory with a data point recently obtained by Ragan using nuclear explosive shock loading. The theoretical curve is found to lie within the 5\% error bars on compression about the Ragan point at 29.33 Mbar, and in general the calculated Hugoniot agrees quite well with experiment. At a compression of \(V/V_o=0.3\), we obtain a Hugoniot temperature of 331,000 K, which is about 1.1 \(T_F\). The slight discrepancy in melting along the Hugoniot is to be expected because of our neglect of the structural aspects of the free energy.

\section{Conclusion}

We have presented a simplified scheme to calculate the bulk properties of simple metals at high static and dynamic compression. By applying the “supercooled liquid” approximation of Jones and Ashcroft to a second order pseudopotential Hamiltonian, we are able to successfully model the isotherm, binding energy and shock Hugoniot curve of
aluminum. Significantly, in calculating the high temperature properties along the Hugoniot, we have noted that the temperature dependence of the electron gas energy and polarization must be fully included. Future work will aim at a more systematic interpolation of these quantities between their degenerate quantum mechanical values and classical high temperature values. Note that this method does not require the introduction of a phenomenological Grüneisen parameter.

References

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