

# SHOCK HUGONIOT AND MELT CURVE FOR A MODIFIED EMBEDDED ATOM METHOD MODEL OF GALLIUM

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**Abstract.** Molecular dynamics (MD) simulations have been performed on the complex material gallium using a literature modified embedded atom method (MEAM) potentials which reproduces the unusual behavior of this element. Both liquid and solid properties will be examined using the equilibrium MD "Hugoniostat" method and molecular statics. The calculated pressure dependence of the melt curve is found to agree well with experiment. The calculated Hugoniot is in reasonable agreement with the experimental Hugoniot EOS even better agreement can be obtained through a slight modification of the MEAM parameters.

## INTRODUCTION

Gallium is a complex element. It exhibits a negative Clapeyron slope between the low pressure solid phase (A11, oC8, GaI) and liquid (see Fig. 1). The equilibrium phase at low pressure is orthorhombic showing a significant amount of dimerization. The dimerization has been used to describe the existence of a slight shoulder in the structure factor for liquid Ga[1, 2]. The phase diagram shows three additional solid phases at high pressure: face centered tetragonal (fct) (cI12, GaII), A6 (tF4, tI2, GaIII), and fcc (GaIV, not shown in Fig. 1)[3]. Gallium also melts slightly above room temperature at 303 K.

Recently, a modified embedded atom method (MEAM) potential for gallium was developed[5]. Besides gallium, MEAM has been used to describe a variety of other complex materials, namely, tin[6] and plutonium[7]. In the gallium paper[5], the authors examined a variety of static and transport properties of the MEAM gallium potential. Here we will focus on the effect of pressure upon the melt curve as well as the shock behavior of liquid gallium. Using the equilibrium MD Hugoniostat technique [8], we calculate the liquid shock Hugoniot, which can be directly compared with recently available experimental data[9].

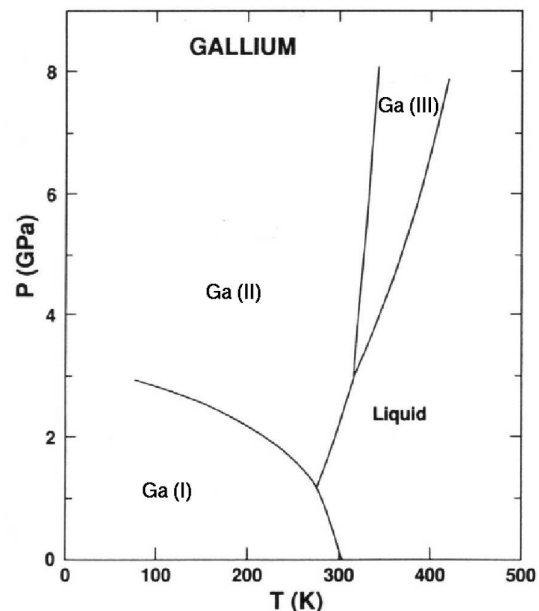


FIGURE 1. Phase diagram of gallium[4].

## MODEL

For a system containing one type of atom using the embedded atom method (EAM) formalism[10, 11, 12] the total energy is given by an expression of

the form,

$$E = \sum_i \left( F(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi(R_{ij}) \right), \quad (1)$$

where the indices  $i$  and  $j$  denote the atoms. The embedding function  $F$  is the energy to embed an atom into the background electron density,  $\bar{\rho}_i$  at site  $i$ ; and  $\phi$  is a pairwise interaction between atoms  $i$  and  $j$  whose separation is given by  $R_{ij}$ . For EAM,  $\bar{\rho}_i$  is given by a linear supposition of spherically averaged atomic electron densities, however in MEAM,  $\bar{\rho}_i$  has an angular dependence [13, 14].

By using a reference equation of state (EOS)  $E^u(R)$ , where  $R$  is the nearest neighbor distance, the pair potential  $\phi(R)$  between 2 atoms is given by

$$\phi(R) = \frac{2}{Z} \{ E^u(R) - F(\bar{\rho}^0(R)) \}, \quad (2)$$

where  $\bar{\rho}^0(R)$  is the background electron density at an atom in what is termed the reference structure, and  $Z$  is the number of first neighbors in this structure. The reference EOS is taken to be the universal EOS of Rose *et al.* [15],

$$E^u(R) = -E_c \left( 1 + a^* + \frac{r_e}{R} \delta a^{*3} \right) e^{-a^*} \quad (3)$$

with

$$a^* = \alpha \left( \frac{R}{r_e} - 1 \right), \quad (4)$$

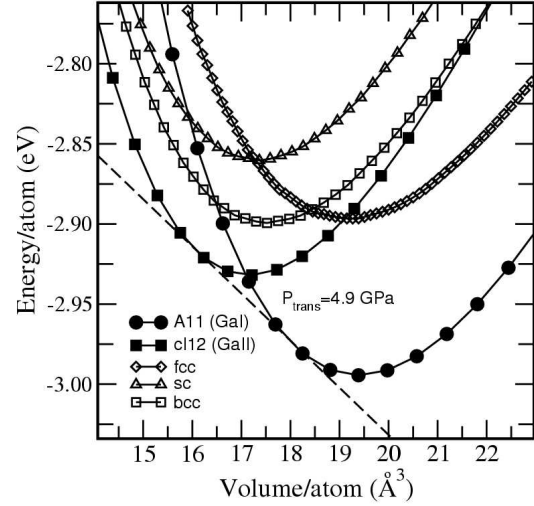
and

$$\alpha^2 = \frac{9\Omega B}{E_c}, \quad (5)$$

where  $E_c$ ,  $r_e$ ,  $\Omega$ , and  $B$  are the cohesive energy, nearest neighbor distance, atomic volume, and bulk modulus, respectively, all evaluated at equilibrium in the reference structure. The cubic anharmonicity parameter  $\delta$  has been added to better represent the pressure derivative of the bulk modulus and will be discussed further below. The specific parameters for Ga are given in Baskes *et al.* [5].

## RESULTS AND DISCUSSION

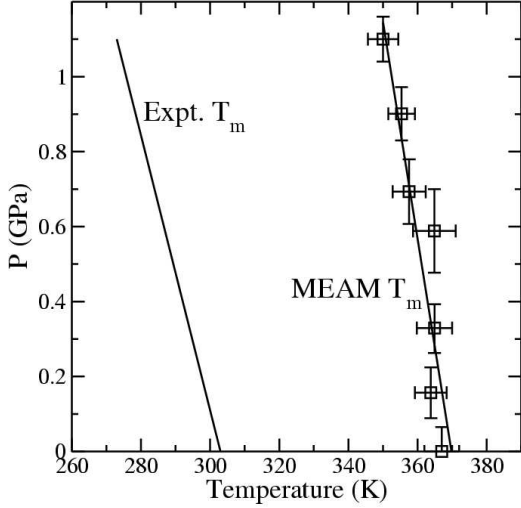
In Fig. 2, we show the calculated energy as a function of volume for a variety of structures: A11 (GaI), cI12 (GaII), bcc, sc, and fcc. For these calculations, we calculated the energy of the structure using



**FIGURE 2.** Energy diagram of various phases calculated with the MEAM gallium potential at 0 K.

a three dimensional periodic cell with approximately 250 atoms expanding the volume isotropically. Figure 2 shows that at zero pressure the most stable phase as predicted by the potential is the A11 phase which corresponds to the equilibrium phase observed experimentally. In addition to this we predict the A11 to cI12 transition pressure (triangular construction,  $-dE/dV$ ) at 0K to be 4.9 GPa. We compare this pressure with approximately 3.2 GPa from the experimental phase diagram shown in Fig. 1 [4] and the 4.0 GPa determined from Fig. 5 of reference [3]. We see that the pressure for the transition is predicted to be a little high yet very close to the experimental values. From this we are encouraged that the potential could potentially capture semi-quantitatively the phase transition behavior of gallium.

In addition to the transition pressure calculated above, we performed a series of molecular dynamics calculations to obtain the melting point at pressure. The method we used is the so called moving interface method. This method consists of a three step iterative process. The first step is to equilibrate a solid at isothermal-isobaric conditions maintaining crystal symmetries at the temperature one assumes the melting temperature to be. This step provides the necessary lattice parameters that can then be used in step two. Step two uses a periodic planar liquid-solid-liquid geometry. The simulation is performed



**FIGURE 3.** Low pressure melting temperature of MEAM gallium (A11) compared with the experimental melt curve.

maintaining a constant in-plane lattice spacing (plane parallel to the liquid-solid interface) yet allowing the out of plane box dimension to expand and contract while maintaining the desired pressure and temperature. Once the system has equilibrated its pressure and temperature we begin step three by performing a simulation for 125 ps at constant volume and energy. If the average temperature or average pressure deviates significantly from the initial temperature and desired pressure, the above process is repeated. In Fig. 3, we show the calculated melting points as a function of pressure compared with the experimental melting points of gallium. As we previously reported [5], the calculated melting point of Ga is approximately 60 K higher than experiment. We see here that the change in melting point with pressure, namely the negative Clapeyron slope, is in excellent agreement with experiment. In Table 1, we reiterate the data suggesting that the potential captures the nature of the solid- liquid phase transition[5].

The liquid Hugoniot was calculated using the method of Maillet *et al.* [8]. A liquid consisting of 1372 atoms was equilibrated at  $T = 308$  K and  $P = 0$ , which resulted in  $\rho = 5.983$  g/cm<sup>3</sup> compared with the experimental  $\rho$  of 6.078 g/cm<sup>3</sup>. The Hugoniot was then implemented with target pressures of up to 200 GPa. The results are shown in Fig. 4. The

**TABLE 1.** Properties for A11 to liquid transition in gallium. Quantities presented are the heat of fusion  $\Delta H$ , the relative volume change on melting  $\Delta V/V$ , the melting point ( $T_m$ ) at zero pressure, and the pressure derivative of the melting point ( $dT_m/dP$ ). The heat of fusion and volume change were calculated at 375 K.

	MEAM	Experiment*
$\Delta H$ (eV/atom) <sup>†</sup>	0.063	0.058
$\Delta V/V$ <sup>†</sup>	-2.5%	-3.2%
$T_m$ (K) <sup>†</sup>	$367 \pm 5$	303
$dT_m/dP$ (K/GPa)	17.3	24.4

\* Reference [16]

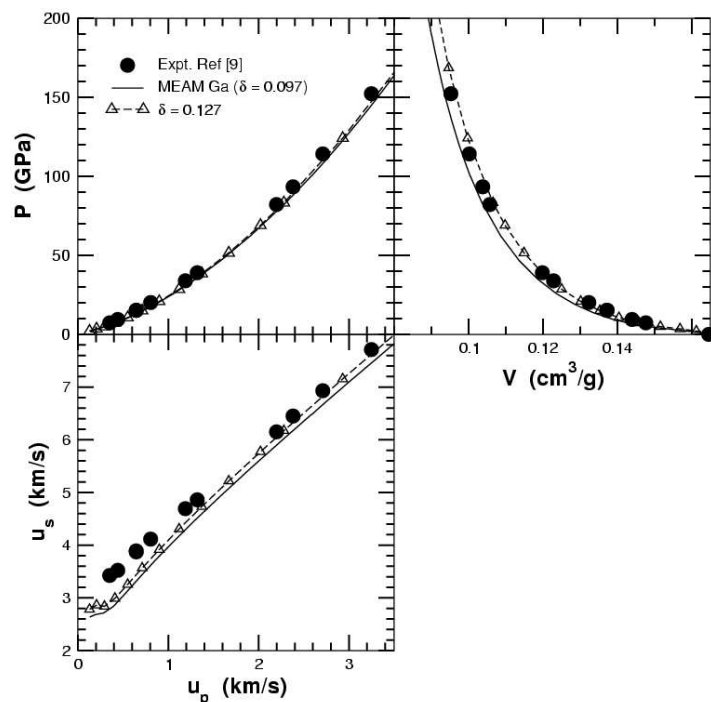
† Reference [5]

$P$  versus  $u_p$  prediction agrees almost exactly with experiment[9], but the predicted  $P$  versus  $V$  curve is slightly below (softer than) experiment. By varying the parameter  $\delta$ , we see that there is a much closer agreement could be obtained without affecting the  $P$  versus  $u_p$  curve. Furthermore, we determined that there was no size dependence by performing simulations with 10976 atoms. The  $u_s$  versus  $u_p$  curve is slightly below experiment because the predicted equilibrium bulk modulus of liquid Ga is below experiment. The sound speed calculated ( $\sqrt{B/\rho}$ ) for MEAM Ga is 2.799 km/s whereas the experimental sound speed is 2.911 km/s. The slope of the  $u_s - u_p$  curve agrees well with experiment. The slight change in the slope at the low  $u_p$  values could be attributed to structural changes due to undercooling because the simulations were begun about 60 K below the MEAM Ga  $T_m$ . Another possible explanation in the change of slope is that gallium has dimers present in its low temperature liquid. Finally, the "Hugoniot" method may not be sensitive in the low pressure regime. The variation in the  $\delta$  parameter does not appear to affect the low  $u_p$  portion of the curve, but improves the agreement with experiment at high  $u_p$ .

## CONCLUSIONS

The literature MEAM gallium model is in excellent agreement with experimental phase stability, melting point, and liquid Hugoniot as a function of pressure.

A slight modification of the MEAM parameters can improve the agreement of the liquid Hugoniot



**FIGURE 4.** Predicted liquid Hugoniot using the Ga MEAM parameters from Baskes *et al.* [5] and a slightly modified Ga MEAM potential compared with experiment[9].

with experiment with no significant change to the solid properties.

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