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A Model For The Shock-Induced Phase Transition In Iron

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Abstract

It has long been known that the shock-induced α to ϵ phase transition in iron exhibits significant metastability in the two-phase region above 13 GPa. We have developed a simple, physically-motivated model that accurately describes the metastable phase transition surface for shock-loaded iron during numerical simulations. It is demonstrated here that the metastability of Fe can have a substantial impact on numerical simulations of time-resolved experiments.

Theoretical interpretation of shock-wave data is frequently complicated by the existence of shock-induced, solid-solid phase transitions in the transmitting medium. For this reason, there has been a long-standing interest in developing techniques for accurately modelling such transitions during simulations of shock processes. One of the more difficult issues to be addressed in this context is the possible metastability of a low-pressure phase beyond its equilibrium phase-boundary. One of the best studied examples of such a transition is the $\alpha \rightarrow \epsilon$ transition in iron [1–5], which begins on the principal Hugoniot at about 13 GPa, but is not completed until a shock-stress greater than 20 GPa is achieved. We have recently developed a simple, physically-motivated model for describing the shock-induced $\alpha \rightarrow \epsilon$ transition in iron during numerical simulations [6]. In the present work, we will first review the basic features of our model. We will then use simulations of a time-resolved shock-wave experiment [5] to demonstrate the large impact that metastability can have on such calculations.

Accurate simulations of a solid-solid phase transition require high-quality equations-of-state (EOS) for the two phases involved in the transition. Here we utilize a highly accurate analytical EOS developed by Wallace [7]. The Helmholtz free energy $F(V, T)$ for each crystal structure is written as

$$F = \Phi_0 + F_H + F_A + F_E \quad (1)$$

where Φ_0 is the static-lattice potential, F_H is the quasiharmonic phonon free energy, F_A is the anharmonic contribution to the lattice free energy, and F_E is the free energy due to thermal excitation of electrons. All other needed thermodynamic functions can then be obtained from the usual thermodynamic relationships involving partial derivatives of the free energy.

The exact expressions used here for the various contributions to $F(V, T)$, and the values of all required parameters, have been provided elsewhere [6] and, hence, are only briefly discussed here. The static-lattice potential is fitted with a modified version [8] of the Vinet-Ferrante-Rose-Smith universal EOS [9]. The quasiharmonic phonon free energy is described

by a high-temperature expansion based on moments of the V -dependent phonon frequencies, that should be quite accurate for the temperatures of interest here, room temperature and above. The anharmonic contribution to the free energy is assumed to be negligible for iron. Finally, the thermal electronic contribution is expressed as the sum of two parts, a normal conduction-electron contribution (F_{cond} ; approximated with its low-temperature form) and a contribution due to the magnetic ground state of α iron (F_{mag} ; obtained from Andrews' fit to the magnetic specific heat of α iron [3]). The analytical EOSs used here for the α and ϵ phases provide a good fit to the experimental α - ϵ phase boundary of iron [10–12] and the 300 K isotherm measured by Mao *et al* [13,14].

Our analytical EOSs for the α and ϵ phases of iron have been implemented in the one-dimensional numerical simulation code HYDROX [15]. A dynamic phase mixing scheme described by Boettger *et al.* [16] is then used to determine the state of the iron in the mixed-phase region. It is assumed during the mixing that: (1) the two phases are in local pressure and temperature equilibrium ($P_\alpha = P_\epsilon$ and $T_\alpha = T_\epsilon$) at all times; (2) for any given P and T , the metastable mass fraction of the ϵ phase, λ_m , is a function of the Gibbs free energy difference between the phases, $\Delta G(P, T) = G_\alpha - G_\epsilon$; and (3) all extensive thermodynamic functions can be expressed as sums of α and ϵ phase contributions; for example, $V = (1 - \lambda)V_\alpha + \lambda V_\epsilon$, where λ is the instantaneous mass fraction of the ϵ phase.

For the dynamic mixing scheme employed by HYDROX to be useful, λ_m must be simply related to ΔG in the mixed phase region. Ignoring any time dependence of the transition, for the moment, the necessary equation can be developed from a balance of forces. At any instant during the forward transition, the fraction of the material that has not yet been transformed ($1 - \lambda$) will be driven to transform by a thermodynamic force ΔG . Because of the volume change associated with the transformation, the already transformed fraction of the material (λ) will exert a stress that resists any further transformation. The metastable mass fraction (λ_m) will then be the mass fraction at which the driving force and the resisting force just balance;

$$d\lambda_m \propto (1 - \lambda_m)d\Delta G. \quad (2)$$

Integrating this gives

$$\lambda_m = 1 - \exp[(A_F - \Delta G)/B_F], \quad (3)$$

where A_F plays the role of an activation energy and B_F determines the range of ΔG over which the transition occurs. An analogous equation can be developed for the reverse transition with parameters A_R and B_R [6],

$$\lambda_m = \exp[(\Delta G - A_R)/B_R]. \quad (4)$$

Although Eq. 3 was developed under the assumption that the phase transition is metastable, it can also be used to model an equilibrium transition by setting A_F to zero and using a very small value for B_F . Following this procedure, equilibrium Hugoniot states were obtained for iron by generating compressive waves with constant velocity boundary conditions. (Here, and throughout the remainder of this work, the strength effects in iron were modelled with a simple elastic-plastic model with a constant yield strength of 3 kbar.) In Figure 1, the theoretical equilibrium Hugoniot of iron (dashed line), generated as described, is compared with experimental data [2,5]. In the single-phase regions, the theoretical Hugoniot is in excellent agreement with the data, demonstrating the quality of the analytical EOSs being used here. In the mixed phase region, however, there is a significant difference between the equilibrium Hugoniot and the data, due to metastability.

The metastable mixed-phase region on the principal Hugoniot of iron can be fitted rather well with Eq. 3 by choosing $A_F = 0$ and $B_F = 642$ J/mol [6]. The metastable Hugoniot obtained with these parameters is shown in Fig. 1 (solid line). Since $\Delta G = 0$ on the equilibrium phase boundary, the fitted value $A_F = 0$ implies that the shock transition begins at the equilibrium phase boundary, near 13 GPa. The fitted value for B_F ensures that the transition is not completed until after 20 GPa.

Diamond anvil cell (DAC) measurements at room temperature have shown that, even under quasistatic conditions, the $\alpha \rightarrow \epsilon$ transition in iron does not proceed on the equilibrium

surface [17]. Indeed, the DAC data for λ vs P is remarkably similar to what we find along the Hugoniot. To allow a direct comparison between the data and the theoretical metastable surface for the forward transition, we used Eq. 3 to determine λ vs P along the 300 K isotherm, with the results shown in Fig. 2. With the exception of the rather small amount of ϵ phase seen in the DAC data below 13 GPa, the theoretical results provide a good fit to the data.

Between the initial and final states of a shock, the medium passes through a series of nonequilibrium states. To lowest-order, the transition rate will be linear in the distance between the current state and the metastable surface. That is, $\dot{\lambda} = (\lambda_m - \lambda)/\tau$, where τ is the relaxation time for the transition. This relationship is not unique, as written, since the distance to the metastable surface depends on the path along which $\lambda_m - \lambda$ is evaluated. Since the driving force is proportional to $\Delta G(P, T)$, the distance $\lambda_m - \lambda$ should be measured at constant P and T , giving

$$\frac{d\lambda}{dt} = \frac{\lambda_m(P, T) - \lambda(P, T)}{\tau}. \quad (5)$$

This result differs from previous models, in that Andrews [3] measured $\lambda_m - \lambda$ at constant V and U , Horie and Duvall [18] measured $\lambda_m - \lambda$ at constant V and T , and both used the equilibrium value of λ in place of λ_m .

In our earlier work [6], we tested our phase transition model by simulating four time-resolved impact experiments on iron that were carried out by Barker and Hollenbach [5], with peak stresses ranging between 17 and 30 GPa, roughly the range of the mixed-phase region. We found that Eq. 5 provides an excellent representation of the experimental data, so long as the relaxation time τ was optimized for each experiment. The optimum values of τ ranged from 20 ns to 50 ns for the four experiments considered. Surprisingly, the optimum values of τ obtained for two experiments that were identical other than the sample thickness differed by nearly a factor of two (30 ns vs 50 ns), indicating that the $\alpha \rightarrow \epsilon$ transition in iron exhibits a nonlinear transition rate.

One issue that was not addressed in our earlier work is the question of how important

it is to use the metastable surface as the reference for the transition rate equation, Eq. 5, rather than the equilibrium surface used in previous models [3,18]. To answer this important question, we have repeated our calculations for experiment 1 of Barker and Hollenbach [5] with λ_m in Eq. 5 replaced by λ_{eq} . In this experiment, a 6.330 mm thick iron flyer plate was impacted on a 6.317 mm thick iron target at a velocity of 0.9916 km/s, producing a peak stress of 17.3 GPa. The velocity of the free surface of the target was then monitored for 3 μ s after the impact. As in our previous work, a relaxation time of 36 ns was used during the simulation, and the parameters for the reverse transition, A_R and B_R , were set equal to the forward transition parameters, A_F and B_F .

In Figure 3, the free surface velocity profile obtained here using λ_{eq} in Eq. 5 is compared with the experimental data of Barker and Hollenbach [5] and the free surface profile calculated using λ_m in Eq. 5. The profile obtained with λ_m is in near perfect agreement with the experimental data. In contrast, use of λ_{eq} in Eq. 5 produces a significant delay in the arrival time of the P2 wave relative to the experimental data. This rather large discrepancy between the current simulation and the data is quite significant, since the arrival time of the midpoint of the P2 wavefront can not be adjusted by simply varying the value of τ , which primarily effects the width of the P2 wave. Thus, it seems clear that the driving force for the time-dependent $\alpha \rightarrow \epsilon$ phase transition in iron should be determined from the metastable transition surface, not the equilibrium transition surface that has been used in the past.

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FIGURES

FIG. 1. Iron Hugoniot. Experimental data are from Bancroft, *et al.* (Ref. 2; squares) and Barker and Hollenbach (Ref. 5; circles). Dashed line is theoretical equilibrium Hugoniot, and solid line is theoretical metastable Hugoniot.

FIG. 2. λ vs P for the forward transition in iron at 300 K.

FIG. 3. Free surface velocity vs time for experiment 1 of Barker and Hollenbach (Ref. 5; circles), compared with calculations using λ_m (solid line) and λ_{eq} (dashed line) in the transition rate equation (Eq. 5).

Fig. 1

Fig. 2

Fig. 3

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