

# Implementing and testing a Kinetic Phase Transition Model

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*We discuss, in general terms, the hydro-code implementation of a rather simple empirical kinetic phase transition model originating with Carl W Greeff. We focus on general issues when introducing the additional ingredient of the kinetics of phase transitions in hydro-codes, such as phase coexistence and phase equilibrium.*

## Introduction and Motivation

When comparing experimental measurements to theoretical predication, it is often the case that perfect agreement is not achieved. In particular, there are often extra features in the experimental curves. Typically, the extra features in the experimental curves are minor, but occasionally these features must be explained to gain confidence that the calculations are accurately capturing the physical phenomena observed in experimental measurements. As measuring techniques advance, and results capture more features reproducibly, it also becomes necessary to advance computational models to include the physics that gives rise to these features.

An example of such a feature in experimental velocimetry data is the appearance of shoulders as the material undergoes phase transitions as, for example, observed by Greeff et al in Reference 1. These shoulders cannot be described by standard single phase Equations of State (EoS) models used in the hydro-codes (see for example Figure 3), since single phase EoSs only describe the stable phase in each point in parameter space and assume an instantaneous transition between phases. In reality, a phase transition occurs over some finite time period. During this transition, at a given time and location, two or more phases are present simultaneously, with some or all phases being meta-stable or un-stable. In order to describe these multi-phase states computationally, a multi-phase EoS with an associated model for describing the time evolution of such mixed phases states is necessary. This kind of model is termed a Kinetic Phase Transition Model.

## Kinetics of Phase Transitions

When a phase transition is not instantaneous, but takes some time to complete, a mixture of phases may be present during the transition. In a simulation, the mixture of phases at each element will need to be described using a new set of variables: the mole fractions,  $\lambda_j$ , of each of the phases  $j$ , in an element (the element index will be suppressed throughout this article).

The Gibbs free energy,  $G$ , with natural variables pressure,  $P$ , and temperature,  $T$ , governs phase equilibrium. The general assumption is that all phases in an element at a certain time have the same pressure and temperature. New subroutines are needed for the Equation of State (EoS) package to give a pressure,  $P$ , and temperature,  $T$ , in an element, given the total density,  $\rho$ , internal energy,  $E$ , and mole fractions,  $\lambda_j$ , in this element. Finally, we need to update the mole fractions of each phase,  $\lambda_j \rightarrow \lambda_j^{new}$  at each time step due to phase transitions.

Since the Gibbs free energy,  $G(P,T) = E(V,T) - TS + P(V,T) V$ , that governs phase transitions requires more than the usually tabulated quantities of internal energy and pressure as functions of temperature and density, [ $\rho=1/V$ ] complete EoSs, with entropy,  $S$ , are necessary. Additionally each phase will require a separate EoS even in its meta-stable and un-stable regimes.

### ***New variables needed: the mole fractions of each phase***

The new parameters,  $0 \leq \lambda_j \leq 1$ ,

$$\sum_{j=1}^N \lambda_j = 1, \quad (1.)$$

describe the mole fractions of each phase  $j$  in an element. For a given set of mole fractions,  $\{\lambda_j\}_{j=1}^N$ , the specific volume and internal energy are simply the weighted sums of the same quantities in each phase:

$$V = \sum_{j=1}^N \lambda_j V_j \quad \text{and} \quad E = \sum_{j=1}^N \lambda_j E_j. \quad (2.)$$

### ***Determining pressure and temperature given density, internal energy, and mole fractions***

The pressure and temperature is assumed to be the same for all phases in an element:

$$T = T_j(V_j, E_j) \quad \text{and} \quad P = P_j(V_j, E_j) \quad \text{for all } j. \quad (3.)$$

Since the hydro-code updates only the total density,  $1/V$ , and internal energy  $E$ , the  $\{V_j\}_{j=1}^N$  and  $\{E_j\}_{j=1}^N$  are unknown. We need to construct a routine that self-consistently uses the equal temperature and pressure criteria in Equation (3), and values of  $V$ ,  $E$  and  $\{\lambda_j\}_{j=1}^N$ , to arrive at the correct sets of volumes  $\{V_j\}_{j=1}^N$  and internal energies  $\{E_j\}_{j=1}^N$ , fulfilling Equation (2). The key to a stable routine is to use *analytical* (or very accurate) thermodynamic derivatives to update  $\{V_j\}_{j=1}^N$  and  $\{E_j\}_{j=1}^N$  in the self-consistent loop. With  $V_{j_{n+1}} = C (V_{j_n} + \Delta V_{j_n})$  and  $E_{j_{n+1}} = E_{j_n} + \Delta E_{j_n} - \Delta E_n$ , ( $C$  and  $\Delta E_n$  providing adjustments for the  $n+1$  quantities to still fulfill Equation (2)), we have for step  $n$ :

$$\begin{pmatrix} \Delta V_{j_n} \\ \Delta E_{j_n} \end{pmatrix} = \begin{pmatrix} \left. \frac{\partial V}{\partial P} \right|_T & \left. \frac{\partial V}{\partial T} \right|_P \\ \left. \frac{\partial E}{\partial P} \right|_T & \left. \frac{\partial E}{\partial T} \right|_P \end{pmatrix}_{j_n} \begin{pmatrix} \Delta P_{j_n} \\ \Delta T_{j_n} \end{pmatrix} \quad (4.)$$

where  $\Delta P_j = P_j(V_j, E_j) - P_n$ ,  $\Delta T_j = T_j(V_j, E_j) - T_n$ , and  $P_n$  and  $T_n$  are suitable means calculated from the pressures and temperatures in the individual phases in that self-consistent step.

Complicating the application of the partial derivatives in Equation (4) is the reality that several different free energy frameworks using different state variables are used. The framework with pressure and temperature, used by Equation (4), as natural variables is the Gibbs free energy,  $G(P, T)$ . The natural energy used in hydro-codes is the internal energy,  $E(S, V)$ , with natural variables  $S$ , entropy, and  $V$ , volume. Equation of State work is usually performed using Helmholtz free energy,  $F(V, T)$ , with temperature and volume as natural variables. Thankfully, the fourth framework based on enthalpy,  $H(S, P)$ , with natural variables entropy and pressure is not pertinent here. Obtaining values for the thermodynamic derivatives connected to the Gibbs free energy in Equation (4), requires deriving or looking up these derivatives as functions of other thermodynamic derivatives available in the code. Based on the first and second law of thermodynamics

$$dE = -PdV + TdS \quad (5.)$$

and definitions that relate all four energy quantities ( $F = E - TS$ ,  $G = F + PV$ ,  $H = E + PV$ ), a large number of relations among thermodynamic derivatives can be derived. The choice and application of formulas depends on the availability and accuracy of these quantities in the code. As an example, if we have Helmholtz free energy quantities,

$$\left. \frac{\partial E}{\partial P} \right|_T = \left. \frac{\partial E}{\partial P} \right|_P - \frac{\left. \frac{\partial P}{\partial T} \right|_P \left. \frac{\partial E}{\partial \rho} \right|_T}{\left. \frac{\partial P}{\partial \rho} \right|_T}. \quad (6.)$$

For rapid and stable convergence very accurate values for the thermodynamic derivatives in Equation (4) must be used. We have used analytic derivatives derived from the Helmholtz free energy of our EOS models, which are of extended Vinet form<sup>2</sup>.

### ***Thermodynamic quantities***

In addition to values for the thermodynamic derivatives for each phase, as for the matrix in Equation (4), we also need to have derivatives for the mixed phase. Determining these thermodynamic derivatives in an element with mixed phases is not trivial but can be derived using their definitions together with Equation (2) and the fact that entropy is additive:

$$S = \sum_{j=1}^N \lambda_j S_j .$$

This also implies that all described energies, internal, Helmholtz, Gibbs, and enthalpy, are additive in the same way. When phases are mixed only derivatives along isobars (constant

pressure) and isotherms (constant temperature) are well defined, since these quantities are the same in all phases. Combining the relation in Equation (6) with definitions in Equation (2), we have

$$\left. \frac{\partial E}{\partial P} \right|_T = \sum_{j=1}^N \lambda_j \left. \frac{\partial E_j}{\partial P} \right|_T = \sum_{j=1}^N \lambda_j \left. \frac{\partial E_j}{\partial P} \right|_{\rho_j} - \sum_{j=1}^N \lambda_j \frac{\left. \frac{\partial P}{\partial T} \right|_{\rho_j} \left. \frac{\partial E_j}{\partial \rho_j} \right|_T}{\left. \frac{\partial P}{\partial \rho_j} \right|_T}.$$

An Equation of State model needs to output the values of some thermodynamic derivatives in each element at each time step. The length of each time step depends on sound speed,  $C_S$ , which is related to the volume derivative of the pressure along an isentrope (constant entropy) and is suited for use in hydro-codes, based on internal energy with entropy and volume as natural variables. Thus the derivative needs to be rewritten along isobars and isotherms. After some manipulations, the sound speed can be calculated if, in addition to the sound speed, Helmholtz quantities are available for the phases, and the global Helmholtz quantities are already calculated:

$$C_S^2 \frac{\left. \frac{\partial E}{\partial T} \right|_{\rho}}{\left. \frac{\partial P}{\partial \rho} \right|_T} = \sum_{j=1}^N \lambda_j C_{Sj}^2 \frac{\left. \frac{\partial E_j}{\partial T} \right|_{\rho_j}}{\left. \frac{\partial P}{\partial \rho_j} \right|_T}.$$

A more extensive discussion of thermodynamic derivatives and how to calculate them will be given elsewhere<sup>3</sup>.

## ***Updating the mole fractions***

### *Complete Equation of State needed*

Updating the mole fractions with time uses the Gibbs free energy differences,  $\Delta G_{ij} = G_i - G_j$ , between the phases, as  $\Delta G_{ij} = 0$  when the phases are at equilibrium with each other. The larger this difference is, the faster the material will transition from the higher Gibbs free energy phase to the lower Gibbs free energy phase. In order to calculate the Gibbs free energy, we need entropy in addition to the, usually provided, internal energy and pressure quantities since  $G = E - TS + PV$ . An alternative is to use Helmholtz free energy as an additional quantity since  $G = F + PV$ .

The assumptions made in both the Mie-Grüneisen and the temperature enhanced Vinet EoSs, allow for a derivation of entropy from the first and second law of thermodynamics in Equation (5). The assumptions are that the specific heat at constant volume,  $C_V$ , is constant and that the product of the Grüneisen parameter,  $\Gamma$ , and density,  $\rho$ , or isothermal linear expansion,  $\alpha$ , and isothermal bulk modulus,  $B$ ;  $C_V \Gamma \rho = \alpha B$ , is constant. The result is

$$S(V, T) = S(V_0, T_0) + \alpha_0 B_0 (V - V_0) + C_{V_0} \ln \left( \frac{T}{T_0} \right),$$

where the subscript zero denotes values at the equilibrium volume on the reference isotherm  $(V_0, T_0)$ .

While this form for the entropy violates the third law of thermodynamics, which states that the entropy of a system at zero temperature is a well-defined constant, it is appropriate for use at temperatures  $T \gtrsim T_0$ .

An additional issue is that in the numerical self-consistent loop determining pressure and temperature, described in a previous section, the temperature can become negative, which would

make the entropy imaginary, an undesirable result. In our implementation we thus add the requirement that if  $T \leq 0$ , we set  $S = 0$ .

### Updating the mole fractions

In addition to the general implementation-details discussed above, which are needed as soon as we are dealing with systems that can have elements with mixed phases, we now need to have an explicit model for updating the mole fractions with time. Carl Greeff has proposed a simple model (see, for example, Reference 1) for updating the mole fractions:

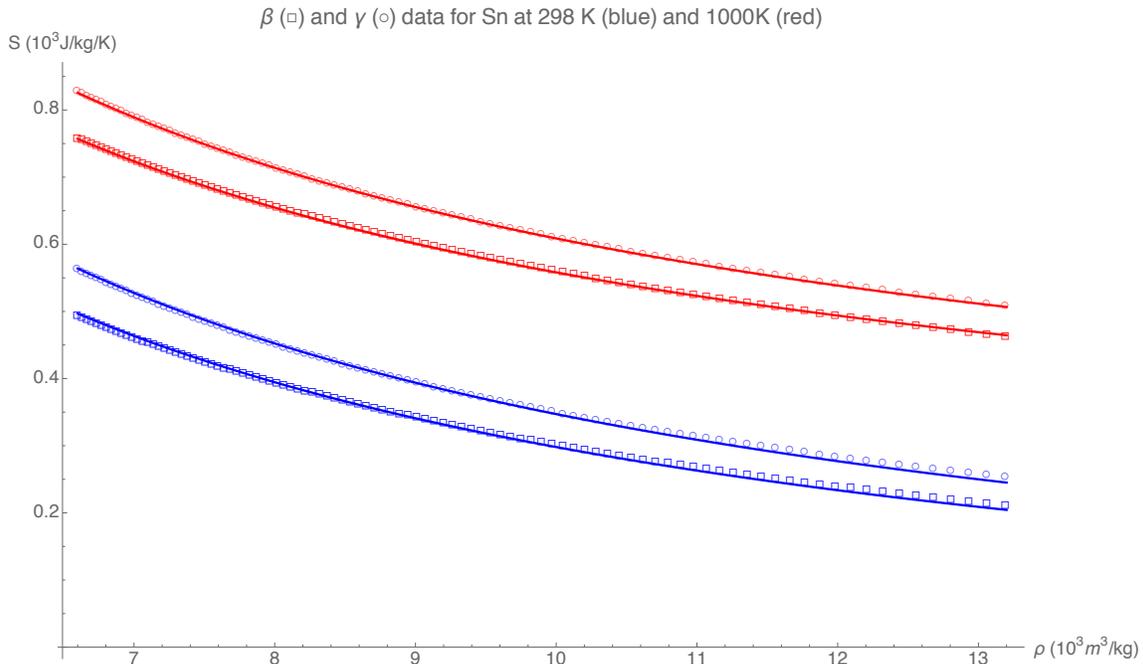
$$\lambda_j^{new} = \lambda_j + \dot{\lambda}_j \Delta t$$

$$\dot{\lambda}_j = \sum_{i=1}^N R_{ij} \lambda_i - R_{ji} \lambda_j$$

$$R_{ij} = \begin{cases} v_{ij} \frac{\Delta G_{ij}}{B_{ij}} \exp \left[ \left( \frac{\Delta G_{ij}}{B_{ij}} \right)^2 \right] & \text{if } \Delta G_{ij} > 0 \\ 0 & \text{if } \Delta G_{ij} \leq 0 \end{cases}$$

where  $\Delta t$  is the time step, and  $v_{ij}$  and  $B_{ij}$  are empirical constants. While this set of formulas maintains the relation in Equation (1), it does not prevent the mole fractions from becoming unphysical, that is, negative or larger than one. In addition, the exponential in the transition rate,  $R_{ij}$ , needs to be handled correctly to avoid overflows and other numerical issues. This, and other details, will be discussed elsewhere<sup>3</sup>.

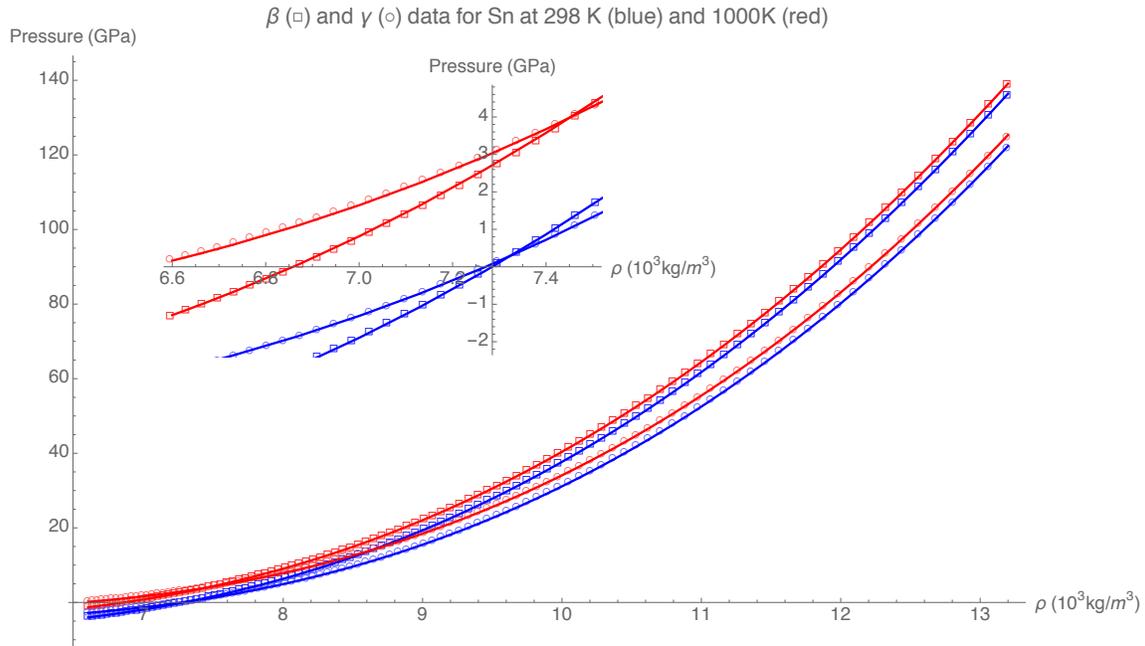
### Phase models



**Fig. 1. – Entropy on two isotherms, 298K and 1000K, for Sn  $\beta$  and  $\gamma$  phases, as a function of density. The open symbols are data from Equations of State constructed by Carl Greeff and the full lines are from the temperature enhanced Vinet model with parameters fitted to the full data set.**

We need one Equation of State model for each phase, covering not only the phase's stable regions but also the meta- and un-stable regions. For this work we have used the temperature enhanced Vinet EoS model (see Appendix 1 of Reference 2) with parameters fitted to values for a number of quantities for the  $\beta$  and  $\gamma$  phases of tin (Sn), among them pressure, internal energy, and entropy, as functions of volume, on two isotherms, 298 K and 1000 K. Since Carl Greeff tabulated these isotherms from his analytical EoS package, this allows us to compare results from our implementation to results from Carl Greeff's original implementation despite not having the same EoS capabilities in the two implementations.

In Figure 1 and 2, we see two examples of how well the temperature enhanced Vinet model can reproduce the given isotherms. We have used the Vinet EoS model to fit other multi-phase EoSs, as well, with good results.

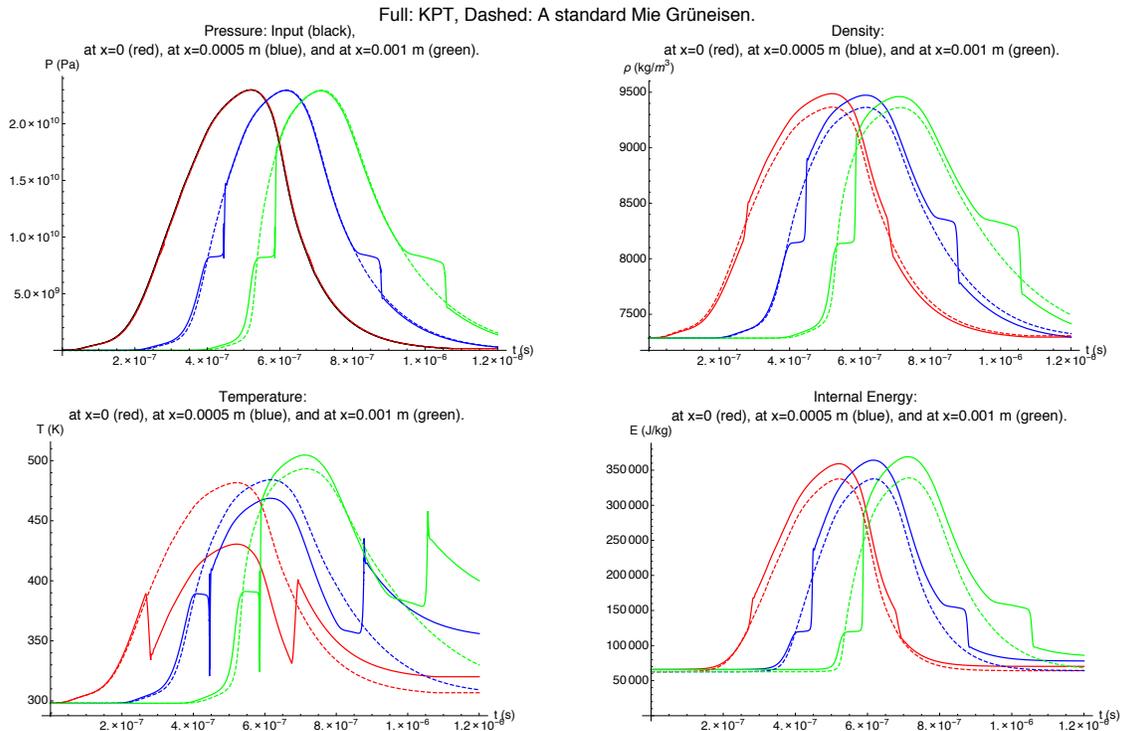


**Fig. 2. – Pressure on two isotherms, 298K and 1000K, for Sn  $\beta$  and  $\gamma$  phases, as a function of density. The open symbols are data from Equations of States constructed by Carl Greeff and the full lines are from the temperature enhanced Vinet model with parameters fitted to the full data set.**

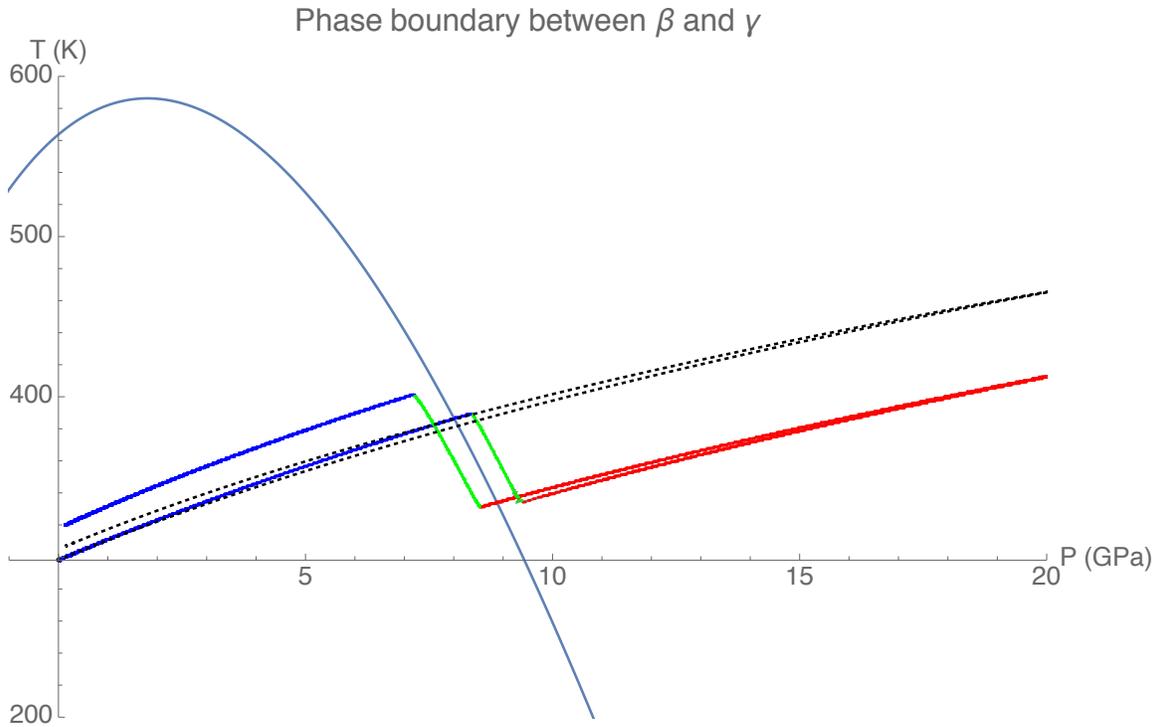
## Results

We implemented the Kinetic Phase transition model, with Carl Greeff's model for updating the mole fractions, into the LAMBDA Equation of State package, and subsequently used this package in the 1-D LASLO hydro-code. We tested the implementation on a ramp-wave problem: A ramped pressure boundary condition on the left side of a 0.003 m slab of Sn. The parameters in the mole fraction update model for Sn are:  $v_{\beta\gamma} = v_{\gamma\beta} = 1 \times 10^4 \text{ s}^{-1}$  and  $B_{\beta\gamma} = B_{\gamma\beta} = 421.2 \text{ J/kg}$ .

In Figure 3, we show results for pressure, temperature, density, and internal energy, as functions of time, using 350 elements and a small time step setting leading to an average time step of  $1 \times 10^{-10} \text{ s}$ . It is clear that a discontinuity is forming in all quantities that are not present in the pressure wave used as boundary condition (black line close to the red  $x = 0 \text{ m}$  line in the pressure panel). A closer examination reveals that this shock is forming in the phase transition.



**Fig. 3. – Pressure, density, temperature, and internal energy, as a function of time, at three different positions,  $x=0$  (red), 0.0005 (blue), and 0.001 (green) m, in a 0.003 m thick Sn sample with a pressure ramp applied to the left,  $x=0$  m, boundary (black line in the pressure plot). Full lines are the Kinetic Phase transition model results and, for comparison, dashed lines are the results using a standard one-phase Mie-Grüneisen Sn EoS.**

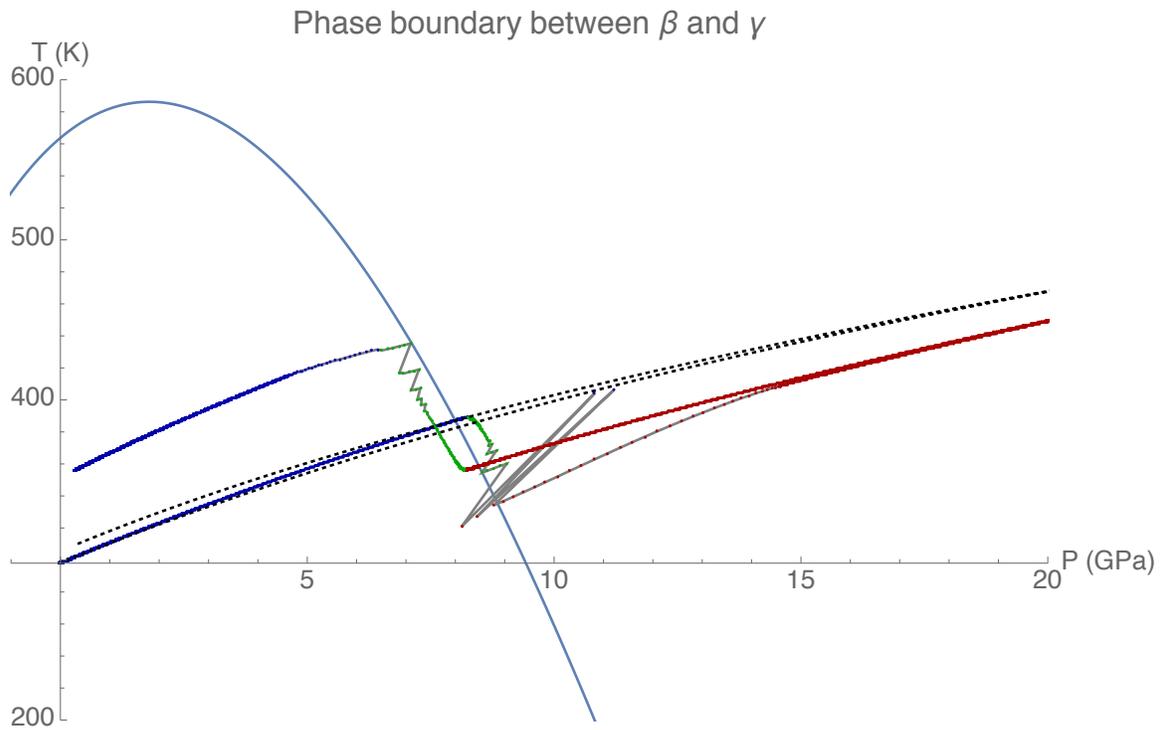


**Fig. 4. – The trace in thermodynamic phase space of the element at  $x = 0$  m (red lines in Figure 3.). The solid blue line is the equilibrium phase boundary between the two phases. In the blue dots, the mole fraction of the  $\beta$  phase is larger than 0.99, while the red dots have more than 0.99 mole fraction of the  $\gamma$  phase. In the green dots we have a mixture of  $\beta$  and  $\gamma$  phases. For comparison, the black dotted line is the trace obtained from using a standard one-phase Mie-Grüneisen EoS for Sn.**

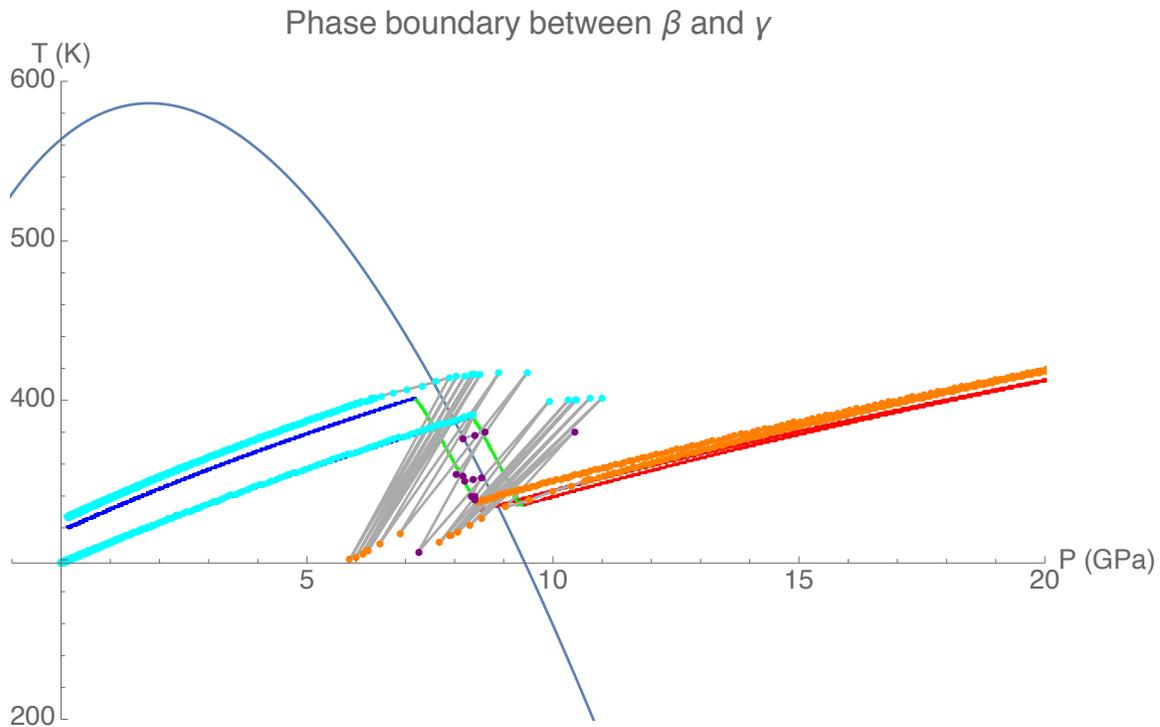
In Figure 4, we show the trace in thermodynamic phase space for the element at  $x = 0$  m (the red lines in Figure 3). The phase boundary is calculated from the separate phase EoS models on the Vinet form. We clearly see that there is latency for the phase transition to occur, and that the state follows the phase boundary until all material has transitioned. The one-phase EoS cannot permit such behavior, as is seen when comparing to the black dashed line produced with a one-phase standard Mie-Grüneisen EoS for Sn.

However, a similar plot for a position further into the material, for example the blue lines for  $x = 0.005$  m in Figure 3, reveals some numerical problems, as seen in Figure 5. This is due to the shock that is forming. The rates for transitioning between the phases are very high during shock and thus the transition time is extremely small, smaller by orders of magnitude, than is possible for any hydro-code time step. Even though we have subdivided the time step given by the LASLO code, to avoid getting negative mole fractions, the abrupt transition gives rise to numerical instabilities, in particular, slushing between the phases. This issue has recently been successfully addressed and will be described in detail elsewhere<sup>3</sup>. The solution is based on updating the mole fractions by having the Kinetic Phase transition module internally properly resolve the phase transition time within the hydro-code timestep, based on the previous and present state,  $(V, E)$ , of the element.

Lastly we want to point out that with more normal settings for element size and time step, this problem is aggravated. In Figure 6, we show the same trace as in Figure 4, but calculated with only 250 elements and allowing for a larger time step, the average time step is now  $8 \times 10^{-10}$  s.



**Fig. 5.** – The same plot as in Figure 4, but for the element at  $x = 0.0005$  m (blue lines in Figure 3.). It is clear that we have numerical instabilities in our implementation.



**Fig. 6 – The same plot as in Figure 4, but overlaid with a calculation with fewer elements, 250 elements instead of 350 and a longer average time step,  $8 \times 10^{-10}$  s instead of  $1 \times 10^{-10}$  s. The slushing between phases is because the transition rates are so large that the transition time between phases is far faster than the time step. See text for a short description of our solution to this problem.**

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## References

1. Greeff, C. W., Rigg, P. A., Knudson, M. D., Hixson, R. S. and Gray, G. T. 2004. Modeling Dynamic Phase Transitions in Ti and Zr, SHOCK COMPRESSION OF CONDENSED MATTER - 2003: Proceedings of the Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter. AIP Conference Proceedings 706: 209-212.
2. Lemke, R. W., Dolan, D. H., Dalton, D. G., Brown, J. L., Tomlinson, K., Robertson, G. R., Knudson, M. D., Harding, E., Mattsson, A. E., Carpenter, J. H., Drake, R. R., Cochrane, K., Blue, B. E., Robinson, A. C. and Mattsson T. R. 2016. Probing off-

- Hugoniot states in Ta, Cu, and Al to 1000 GPa compression with magnetically driven liner implosions. *Journal of Applied Physics* 119: 015904.
3. Mattsson, A. E., Brown, J. L. and Greeff, C. W. In preparation.