Minimization of Gibbs Energy in High-Pressure Multiphase, Multicomponent Mixtures through Particle Swarm Optimization

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1. INTRODUCTION

The thermodynamics of multicomponent mixtures at high pressures is a topic of great interest in a number of fields. By components, we mean “atom types” (elements) or possibly assumed indivisible “molecular units” in certain special cases. Planetary science is awash with such systems, and prominent examples include hydrogen/helium mixtures in giant planets; aqueous solutions of organic compounds, ammonia, carbon dioxide, and/or salts in icy moons and ocean planets; and mixtures that may form as a result of carbon dioxide dissociation in Earth’s mantle. Other examples are those produced from the detonation of diatomic and polyatomic species. Moreover, there is a growing need to understand the behavior of additively manufactured alloys under high-pressure static and dynamic loading in order to certify them for use in aerospace and automobile applications.

Like their single-component counterparts, multicomponent mixtures do not necessarily exist as homogeneous substances and can instead split up into two or more phases. Therefore, determining the equilibrium state for a given set of conditions requires finding which phases are thermodynamically stable and the relative amounts (mole fractions) of each phase. This procedure in single-component systems is often referred to as a Maxwell construction. The key distinguishing feature of multicomponent mixtures is that the various components may segregate preferentially into different phases, so that determining the mixture’s equilibrium state also requires finding the composition (mole fraction of every component) of each of the stable phases. This may be done by minimizing a particular free energy or maximizing the entropy, depending on the conditions that are specified. We present an optimization procedure to minimize the Gibbs energy of a multicomponent mixture, which reveals the relative amounts of the different phases and the composition of each phase, when the temperature, pressure, and overall composition of the mixture are specified. Our minimization scheme is based on particle swarm optimization (PSO), which is a stochastic method introduced in its modern-day form over 25 years ago. PSO is highly versatile because it is a gradient-free method that places few requirements on the nature of the objective function that is to be minimized. As a
result, it has since been applied to a wide variety of optimization problems. A crucial feature of PSO is that it is a global optimization method which, unlike local optimization methods, does not require good initial guesses for the phase mole fractions and compositions. This is an important requirement for mixtures at high pressures because under such conditions, experimental and theoretical data on the phase diagram will likely not be available. We apply our method—which may be thought of as a multicomponent extension of a Maxwell construction—to generate phase diagrams and construct equation-of-state tables that are compatible with continuum-scale, multiphysics codes that are widely used in high-pressure science.

We expand on the statements mentioned above by considering the case of single-component materials, for which a widely adopted thermodynamic formalism has already been established by the high-pressure science community. In this particular formalism, the equation of state (EOS) for each phase of a single-component material is represented with a separate Helmholtz-energy model, which is subsequently divided into three contributions: a cold energy that designates the energy of the phase at 0 K, an ion-thermal free energy that accounts for the motion of the nuclei, and an electron-thermal free energy that reflects electronic excitations and ionization processes. (In some cases, it may be important to also include terms representing phenomena such as magnetism or electron–phonon interactions, but this is not necessary for the vast majority of materials under most conditions.) Variants on this formalism have produced, for example, the large collection of EOSs that make up the LEOS and SESAME libraries. Section 2 and the Appendix provide a largely self-contained outline of key thermodynamic concepts and quantities relevant to mixtures that we refer to throughout the rest of the study, with an eye toward building on the very successful, high-pressure EOS framework encapsulated in the LEOS and SESAME tables. Details of our PSO algorithm and its suitability for high-pressure applications are explained in section 3. This is followed by section 4, which tests and demonstrates our PSO method with different example mixing models for the iron/gallium (Fe/Ga) system at high pressures. We show that it can reliably capture nontrivial features of the Fe/Ga phase diagrams dictated by the models, such as eutectic and peritectic points. We then demonstrate how PSO may be used to construct EOS tables of the type mentioned earlier. That is, we produce multiphase tables of Helmholtz energy as a function of temperature and density; for multicomponent mixtures, this means that each such table corresponds to a fixed overall composition. We produce tables for Fe/Ga mixtures and use them to perform EOS-related calculations (e.g., compute isentropes and Hugoniot curves), just like we may do with any table from the LEOS or SESAME libraries. We apply this formalism to develop different example models that we subsequently use in the minimization calculations. This is somewhat akin to how one might demonstrate a new free-energy minimization technique in classical molecular dynamics simulations with representative interatomic potentials.

We organize the rest of this study in the following manner. Section 2 and the Appendix provide a largely self-contained outline of key thermodynamic concepts and quantities relevant to mixtures that we refer to throughout the rest of the study, with an eye toward building on the very successful, high-pressure EOS framework encapsulated in the LEOS and SESAME tables. Details of our PSO algorithm and its suitability for high-pressure applications are explained in section 3. This is followed by section 4, which tests and demonstrates our PSO method with different example mixing models for the iron/gallium (Fe/Ga) system at high pressures. We show that it can reliably capture nontrivial features of the Fe/Ga phase diagrams dictated by the models, such as eutectic and peritectic points. We then demonstrate how PSO may be used to construct EOS tables of the type mentioned earlier. That is, we produce multiphase tables of Helmholtz energy as a function of temperature and density; for multicomponent mixtures, this means that each such table corresponds to a fixed overall composition. We produce tables for Fe/Ga mixtures and use them to perform EOS-related calculations (e.g., compute isentropes and Hugoniot curves), just like we may do with any table from the LEOS or SESAME libraries. Section 5 concludes with a summary of our study. This section also presents a critical evaluation of our approach, gives suggestions on future work, and compares our approach with others that have been developed for multiphase, multicomponent mixtures.

2. THERMODYNAMIC DESCRIPTION OF MIXTURES

2.1. Overview. For a multiphase mixture with \( P \) different phases, its molar internal energy \( E \), entropy \( S \), and volume \( V \) are given by

\[
E = \sum_{i=1}^{P} \chi_i E_i
\]
\[ S = \sum_{i=1}^{p} \chi_i S_i \]  
\[ V = \sum_{i=1}^{p} \chi_i V_i \]

where \( \chi_i \) is the mole fraction of phase \( i \) and denotes the moles of phase \( i \) divided by the moles of the mixture. In this work, we will introduce four different kinds of mole fractions, and so for the purposes of clarity, we will be very explicit when defining each of them. If phase \( i \) is at a temperature \( T \) and pressure \( P \), we apply standard thermodynamic relations to define the molar Helmholtz energy, enthalpy, and Gibbs energy of the phase as

\[ F_i = E_i - T S_i \]  
\[ H_i = E_i + PV_i \]  
\[ G_i = E_i - TS_i + PV_i \]

respectively. For the multiphase mixture as a whole, we have

\[ F = \sum_{i=1}^{p} \chi_i F_i \]  
\[ H = \sum_{i=1}^{p} \chi_i H_i \]  
\[ G = \sum_{i=1}^{p} \chi_i G_i \]

If all phases are at a common temperature \( T \) and pressure \( P \) (which are fundamental requirements for the mixture to be in thermodynamic equilibrium\(^{36} \)), eqs 1-9 lead to

\[ F = E - TS \]  
\[ H = E + PV \]  
\[ G = E - TS + PV \]

To proceed further, we must have a prescription for the thermodynamic properties of the individual phases, so that we can compute \( G_i, E_i, S_i, V_i, F_i \), and \( H_i \) of each phase \( i \). It is useful at this point to draw a distinction between solutions and compounds. A compound is a covalently or ionically bonded substance with a fixed stoichiometric ratio between its constituent elements; it remains fixed in this ratio even when it is melted to a liquid or vaporized to a gas. In contrast, a solution—which includes fluid mixtures, substitutional alloys, and interstitial alloys—may have a variable composition. If \( Q \) denotes \( G, E, S, V, F, \) or \( H \), then \( Q \) of a compound can be represented as a linear combination of the \( Q \) of its elements (with the weights coming from the stoichiometric ratios) plus \( \Delta Q_i \) of formation. In practice, this representation is likely to be useful only at ambient pressure, where an abundance of experimental data tends to be available even for difficult-to-compute quantities like the entropy of formation \( \Delta S_i \). If we are instead interested in the compound’s properties over a wide range of pressures where such data are no longer available, a better approach is to construct a multiphase EOS specific to that compound that is separate from the EOSs for the constituent elements. Thus, if \( i \) represents a particular phase of a compound, then \( G_i, E_i, S_i, V_i, F_i \), and \( H_i \) denote the properties extracted from the EOS corresponding to that phase. A prime example of a compound is water, for which the development of a wide-ranging, accurate EOS that covers its multiple solid and fluid phases is still an ongoing area of work. Because water has very different properties from a solution of hydrogen and oxygen, its EOS will bear little resemblance to those of its constituent elements and can be developed independently of the EOSs for those elements.

In contrast, if phase \( i \) is a solution (e.g., a fluid mixture or an alloy), a good approach is to represent \( G_i, E_i, S_i, V_i, F_i, \) and \( H_i \) in terms of the corresponding properties of the constituent components, rather than developing a separate EOS altogether like in the case of a compound. A standard prescription from chemical thermodynamics is to model the properties of each solution phase as a linear combination of the properties of the pure components that make up the phase plus additional mixing terms.\(^{36-40} \) In the rest of this study, we neglect compounds and assume that each phase is a solution that is composed of up to \( c \) components. This implies that for the Fe/Ga mixture examples in section 4, our analysis excludes compounds like Fe\(_3\)Ga, Fe\(_6\)Ga\(_5\), Fe\(_3\)Ga\(_4\), and FeGa\(_3\) that exist at ambient pressure\(^{41} \) and are presumably still stable at higher pressures. We have noted in the Introduction that the goal of the present study is not necessarily to develop a set of free-energy models for Fe/Ga or for any other mixture. Our objective is to instead demonstrate PSO as a reliable means to perform a free-energy minimization given a set of such models. Section 4 does this with different example Fe/Ga solution mixing models. Section 5.1 includes a discussion of how the PSO algorithm may be adapted in the future to handle compounds like the ones listed above, which can then be tested once an EOS has been developed for them. Although the present study does not focus on model development per se, the formulation we outline in the rest of this section builds on existing high-pressure, single-component EOS models (e.g., those in the LEOs and SESAME tables), and so, it can be an effective basis for future development of EOSs for a diverse selection of multicomponent mixtures.

Using the index \( j \) to label the \( c \) components of phase \( i \), we can express the molar Gibbs energy of that phase as

\[ G_i = \sum_{j=1}^{c} z_{ij} \mu_{ij} \]

where \( z_{ij} \) is the mole fraction of component \( j \) in phase \( i \) and is defined as the moles of \( j \) in \( i \) divided by the total moles of phase \( i \). Here, \( \mu_{ij} \) is the chemical potential of component \( j \) in phase \( i \), and it is clear from eq 13 why \( \mu_{ij} \) is also commonly referred to as the partial molar Gibbs energy of \( j \) in \( i \). The concept of a partial molar Gibbs energy (or more generally, any partial molar property) appears prominently in the chemical thermodynamics of multicomponent solutions.\(^{36-40} \) A rather general expression for \( \mu_{ij}(T, P, z_i) \) is

\[ \mu_{ij}(T, P, z_i) = G_j(T, P) + RT \ln z_{ij} + \overline{G_{ij}}^{\text{excess}}(T, P, z_i) \]

in which \( z_i = (z_{i1}, z_{i2}, ..., z_{ic}) \) denotes the composition (mole fractions of the \( c \) components) of phase \( i \), \( R \) is the gas constant, and \( G_j(T, P) \) is the molar Gibbs energy of component \( j \) when it exists by itself as a pure substance but is evaluated at the same \( T \) and \( P \) of the mixture. The subscript \( i \) in \( G_i \) indicates that this pure-component property is to be evaluated in the same state of matter as phase \( i \). For instance, if \( i \) is a liquid, \( G_i \) is the molar Gibbs energy of pure \( j \) in the liquid phase.
The second and third terms on the right-hand side of eq 14 represent contributions of mixing to the free energy. The second term, \( RT \ln z_i \), is the ideal-mixing contribution of \( j \) in \( i \), while \( G_i^{\text{excess}}(T,P,z_i) \) is the excess partial molar Gibbs energy of \( j \) in \( i \) and represents the nonideal-mixing contribution. It is evident that \( G_i^{\text{excess}}(T,P,z_i) \) may in general be far more complicated than the ideal contribution \( RT \ln z_i \). For instance, the former may depend on pressure, while the latter does not. Furthermore, \( RT \ln z_i \) depends only on the mole fraction \( z_i \) while \( G_i^{\text{excess}}(T,P,z_i) \) may involve the mole fractions of the other components in phase \( i \) as well. As with any EOS, developing a model for \( G_i^{\text{excess}} \) requires fitting a set of parameters to a combination of experimental and theoretical data. For high-pressure applications, this represents a great challenge because we must fit to data that span an enormous range of temperatures, pressures, and potentially also compositions.

Substituting eqs 14 into 13 and 9, we obtain

\[
G_i = \sum_{j=1}^{c} z_j [G_j(T,P) + RT \ln z_j + G_j^{\text{excess}}(T,P,z_j)]
\]

(15)

\[
G = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_j [G_j(T,P) + RT \ln z_j + G_j^{\text{excess}}(T,P,z_j)]
\]

(16)

The molar entropy and molar volume of each phase are given by

\[
S_i = \left[ \frac{\partial G_i}{\partial T} \right]_{P,z_i} = \sum_{j=1}^{c} z_j \left[ S_j(T,P) - R \ln z_j - \left( \frac{\partial G_j^{\text{excess}}}{\partial T} \right)_{P,z_j} \right]
\]

(17)

\[
V_i = \left[ \frac{\partial G_i}{\partial P} \right]_{T,z_i} = \sum_{j=1}^{c} z_j \left[ V_j(T,P) + \left( \frac{\partial G_j^{\text{excess}}}{\partial P} \right)_{T,z_j} \right]
\]

(18)

where \( S_j(T,P) = -\langle \partial G_j/\partial T \rangle_p \) and \( V_j(T,P) = \langle \partial G_j/\partial P \rangle_T \) are the molar entropy and volume of pure \( j \) evaluated in the same state of matter (solid, liquid, etc.) as phase \( i \), and the quantities in the square brackets are referred to as the partial molar entropy and partial molar volume of component \( j \) in phase \( i \). The derivatives in these brackets are the excess partial molar entropy \( S_j^{\text{excess}} = -\langle \partial G_j^{\text{excess}}/\partial T \rangle_{P,z_j} \) and the excess partial molar volume \( V_j^{\text{excess}} = \langle \partial G_j^{\text{excess}}/\partial P \rangle_{T,z_j} \) of \( j \) in \( i \). From these equations, one may compute the internal energy \( E_i = G_i + TS_i - PV_i \), Helmholtz energy \( F_i = G_i - PV_i \), and enthalpy \( H_i = G_i + TS_i \) of the individual phases. The molar internal energy \( E_i \), entropy \( S_i \), volume \( V_i \), Helmholtz energy \( F_i \), and enthalpy \( H_i \) of the entire multiphase, multicomponent mixture may then be calculated from eqs 1–3 and 7 and 8, respectively. Other thermodynamic properties of interest, such as the sound speed, may be derived by taking one or more derivatives of \( G, E, S, V, F, \) or \( H \). This seemingly straightforward task can actually be quite complicated for the reasons explained in the Appendix, where we suggest an approximation to greatly simplify the computation of these thermodynamic derivatives.

2.2. Ideal and Nonideal Mixtures. An ideal multiphase, multicomponent mixture is defined to be one in which \( G_j^{\text{excess}} = 0 \) for every component \( j \) and phase \( i \) over all conditions. The Gibbs energy \( G \), Helmholtz energy \( F \), and entropy \( S \) of such a mixture are

\[
G = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_j [G_j(T,P) + RT \ln z_j]
\]

(19)

\[
F = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_j [F_j(T,P) + RT \ln z_j]
\]

(20)

\[
S = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_j [S_j(T,P) - R \ln z_j]
\]

(21)

while its volume \( V \), internal energy \( E \), and enthalpy \( H \) are

\[
V = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_j V_j(T,P)
\]

(22)

\[
E = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_j E_j(T,P)
\]

(23)

\[
H = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_j H_j(T,P)
\]

(24)

An ideal mixture is imagined as being a lattice in which the components are randomly distributed on the lattice sites. An analysis of the number of additional lattice configurations in the mixture leads to the well-known terms of the form \( -RT \ln z_i \) (for entropy) or \( RTz_i \ln z_i \) (for free energies). In addition, one assumes in an ideal mixture that a component experiences the same interatomic interactions, on average, in the mixture that it would experience if it were instead surrounded by other like components, that is, in the pure substance. This also implies that there is no short-range ordering (preferential mixing or bonding) or any other phenomena that lead to a deviation away from the idealized, random-distribution-on-a-lattice picture described above. As a result, \( V, E, \) and \( H \) of an ideal mixture depend only on the pure-component contributions, with no contribution from the mixing itself. [The additivity of volumes in eq 22 has been referred to in different contexts as the “linear mixing approximation” or Amagat’s law.] Although the assumptions inherent in ideal mixing appear to be rather severe, if the components in the mixture are similar in nature, it can actually provide a fairly good approximation. For instance, a binary mixture of toluene and benzene (both of which are large, but similar organic molecules) behaves ideally, and a recent study has found that ideal mixing may also hold for certain shock-compressed mixtures in a particular range of conditions.

We note that if a phase \( i \) is almost pure in a particular component \( j \), so that \( z_i \approx 1 \), then \( G_j^{\text{excess}} \approx 0 \) (though \( G_k^{\text{excess}} \) for \( k \neq j \) is not necessarily close to zero) because the environment that \( j \) experiences in this phase is very similar to what it would experience as a pure substance. In a largely phenomenological way, the goal of an accurate excess free energy model is to account for the aforementioned processes that are neglected in the ideal-mixing approximation.

We clarify that to be precise in our terminology, the definition of an ideal mixture that we have adopted is based on Raoult’s law and may be referred as an ideal Raoultian mixture. In this definition, the \( G_j \) that appears in eq 14, which is the molar Gibbs...
energy or chemical potential of pure \( j \), may be thought of as a reference state onto which the mixing terms are added to obtain the true chemical potential \( \mu_j \) of \( j \) when it is mixed with the other components that make up phase \( i \). This is the most convenient reference state to adopt for our purposes because it allows us to directly use high-pressure-oriented EOSs that have already been developed for the individual components, like the EOS tables in the LEOS and SESAME libraries, to compute \( G_i \) and other pure-component properties. An alternative reference state is the chemical potential of \( j \) in the ideal-gas state, for which the analogues to the excess properties are called residual properties or departure functions. (These are associated with the concepts of fugacity and fugacity coefficients, while excess properties are more closely associated with activity and activity coefficients.) While EOSs involving departure functions are often easier in some ways than the formulation we have chosen here, they are not convenient for our purposes because under the conditions achieved in typical high-pressure applications (e.g., ramp-compression experiments), ideal gases are often times very far away in terms of their properties from the real mixture of interest.

3. APPLICATION OF PSO TO PHASE EQUILIBRIA

3.1. Algorithm Details. The main objective of this study is to develop an optimization method that enables one to construct phase diagrams for multiphase, multicomponent mixtures and produce EOS tables that can be used in high-pressure, continuum-scale simulations. In order to achieve this goal, we aim to solve the following problem: given the temperature \( T \), pressure \( P \), and overall composition \( X = (X_1, X_2, \ldots, X_P) \) in a mixture of \( P \) phases and \( c \) components determine the mixture’s equilibrium state. The variable \( X \) is the third distinct set of mole fractions that we have introduced so far; the other two sets defined earlier are the phase mole fractions \( \chi = (\chi_1, \chi_2, \ldots, \chi_P) \) and phase compositions \( z = (z_1, z_2, \ldots, z_P) = (z_{11}, z_{12}, \ldots, z_{1c}, z_{21}, z_{22}, \ldots, z_{2c}, \ldots, z_{p1}, z_{p2}, \ldots, z_{pc}) \). The mole fraction \( X_j \) denotes the total moles of component \( j \) in the mixture (moles of \( j \) in each phase summed over all \( P \) phases) divided by the total moles in the mixture. Constraining \( T, P, \) and \( X \) to some fixed set of values provides a complete thermodynamic specification of the mixture, corresponding to a description of the system in the isothermal–isobaric ensemble, and therefore, it should be possible in principle to determine the mixture’s equilibrium state from this specification. The well-known condition for equilibrium in this particular situation is that the Gibbs energy \( G \) must attain a global minimum. From eq 19 for \( G \) of an ideal mixture or the more general expression in 16 for \( G \) of a nonideal mixture, it is clear that if \( T \) and \( P \) are fixed, the only freedom one has in adjusting the value of \( G \) is to vary \( \chi \) and \( z \). Therefore, we find the equilibrium state of a mixture by adjusting the relative amounts of the different phases \( \chi \) and the compositions of the phases \( z \) to minimize \( G \) subject to the constraints that all phases must remain fixed at \( T \) and \( P \), and the following mole-balance (mass-conservation) equations

\[
\sum_{j=1}^{P} \chi_j z_{ij} = X_j, \quad j = 1, 2, \ldots, c
\]  

(25)

We will show later in this study that the mole-balance constraints are much easier to enforce if we introduce an auxiliary set of mole fractions \( y = (y_1, y_2, \ldots, y_1, y_2, \ldots) \), where \( y_j \) is defined as the moles of component \( j \) in phase \( i \) divided by the total moles of the mixture. The information content in \( y \) is the same as that in the set \((\chi, z)\), so that we can obtain the latter from the former, and vice-versa, through the following relations

\[
\chi_i = \sum_{j=1}^{c} y_{ij} X_j
\]  

(26)

\[
\tau_j = \frac{y_j}{\sum_{i=1}^{P} y_{ij} X_i} = \frac{y_j}{X_j} \chi_i
\]  

(27)

\[
y_j = X_j \tau_j
\]  

(28)

The mole-balance constraints, when expressed in terms of \( y \), take on the simpler form

\[
\sum_{i=1}^{P} y_{ij} = X_j, \quad j = 1, 2, \ldots, c
\]  

(29)

Thus, the maximum value that \( y_j \) can take is \( X_j \), corresponding to the situation where all of component \( j \) resides in phase \( i \). In each iteration of our optimization process, we convert \( y \) to \( \tau \) and \( \chi \), so that we can evaluate our objective function (the Gibbs energy \( G \)) according to eq 16, then we proceed to the next iteration by adjusting \( y \) via some prescription that obeys (29).

As stated in the Introduction, we perform the Gibbs-energy minimization using PSO, which is a stochastic method whose modern-day form is attributed to the seminal work by Kennedy and Eberhart. PSO simulates the trajectory of a large number \( N_p \) of particles (points) that reside in the search space. The particles together comprise the swarm. (Kennedy and Eberhart were motivated by a desire to model collective social behavior in animals, and they imagined the swarm as being a flock of birds in their original study.) In the problem of interest in this study, the search space is the Gibbs-energy surface, and each of the particles in the swarm represents—in general—a multiphase, multicomponent mixture that is fixed at the given \( T, P, \) and \( X \). If \( N_p \to \infty \), the swarm signifies an isothermal–isobaric ensemble. Each particle is initially assigned to a location on the Gibbs-energy surface, meaning that it is assigned to some set of \( y \) and consequently also some set of \( \chi \) and \( z \). The \( y \) of each particle is then adjusted iteratively in a manner that depends on the particle’s current \( y \), its best ever \( y \) (corresponding to the lowest \( G \) it has ever achieved), the best ever \( y \) achieved by any of the particles in the swarm, and potentially other quantities. The iterations are carried out until a termination criterion is met. PSO has enjoyed widespread usage since its introduction over 25 years ago, and many variants have been developed. The assortment of PSO flavors may differ in their choice of particle initialization, the method by which the particles are moved in the search space, the termination criteria, and the various hyperparameters that influence the optimization process. A perusal of the literature reveals the perhaps obvious fact that there does not seem to be a “magic bullet”; different variants work better for different applications.

PSO has been used in a number of thermodynamic modeling studies. Cox and Christie report it to be an effective tool for optimizing EOS parameters to fit experimental data, and they have applied it to develop high-pressure-oriented, multiphase EOSs for four single-component materials: aluminum, tantalum, lead, and titanium. PSO has also been tested along certain select \((T, P, X)\) points under ambient or near-ambient conditions in multicomponent systems, including mixtures of
energetic materials,50 petrochemical fluids,51,52 and complex microemulsions.53 Although none of these studies have applied PSO toward our goal of producing whole phase diagrams covering multiple phase boundaries of a mixture, they suggest that if extensive and careful testing is done to properly tune the optimization details, it can be a reliable method for achieving our goal.

Now that we have provided an overview of PSO, the rest of this section focuses on the specific details of our particular algorithm. The first step is to initialize the location of the particles (mixtures) along the Gibbs-energy surface by assigning mole fractions \( y \) to each. Let \( y_{ij}^0 \) denote the value of the mole fraction \( y_{ij} \) for particle \( k \) at iteration \( l \). Initializing the particle locations entails setting the mole fractions \( y_{ij}^0 \) for all phases \( i = 1, 2, ..., P \) and all components \( j = 1, 2, ..., N_p \) at \( l = 0 \). To do this, we first randomize the order of the \( P \) phases (so as to not bias any particular one) by creating the set \( r = (r_1, r_2, ..., r_P) \), in which \( r_i \) is a random integer between 1 and \( P \) and is different from the other \( P - 1 \) integers in \( r \). For each particle \( k \), its mole fractions in the phase corresponding to \( r_i \) are assigned as follows:

1. Calculate \( d_j = X_j / N_p \) for each component \( j \).
2. Set \( y_{ij}^0 \) to be a random real number between \((k - 1)d_j\) and \(kd_j\) for each \( j \).

Thus, the \( k = 1 \) particle has mole fractions in its \( r_1 \) phase that lie between 0 and dy, for each component \( j \), while the \( k = N_p \) particle has mole fractions in that same phase that lie between \((N_p - 1)d_y\) and \(X_j \) for each component \( j \). This ensures that, at least for the \( r_1 \) phase, the particles in the swarm collectively provide a representative sampling of the search space. Our initialization approach is adapted from the Latin-hypercube sampling technique used in the recent study by Sterbenz et al.,54 who have applied another stochastic method called differential evolution optimization to determine the input drive in high-pressure, ramp-compression experiments. (Incidentally, we have also tried differential evolution optimization for our problem, but we have not been able to get it to work as reliably as PSO.) If we let \( i \in (2, ..., P - 1) \), so that we consider all of the remaining phases except for the \( r_p \) phase in the sequential order given by \( r \), we set the mole fractions of the \( r_i \) phase in all \( N_p \) particles in a similar manner:

1. Calculate \( dy_j^k = \left( X_j - \sum_{m=1}^{N_p-1} x_{m}^{k} \right) / N_p \) for each \( j \) and \( k \).
2. For each \( j \) and \( k \), set the mole fraction \( y_{ij}^0 \) to be a random real number between \((q - 1)dy_j^k\) and \(qdy_j^k\), where \( q \) is a random integer between 1 and \( N_p \).

Finally, the mole fractions of the \( r_p \) phase in all \( N_p \) particles are initialized by setting \( y_{ij}^0 = X_j - \sum_{m=1}^{N_p-1} x_{m}^{k} \) for each \( j \) and \( k \). This enforces the mole-balance constraints in eq 29.

In every iteration, each particle’s fitness is examined by evaluating its Gibbs energy using eq 16. Evaluation of \( G \) requires converting each particle’s \( y \) to \( \chi \) and \( z \) by applying eqs 26 and 27. As mentioned earlier, we track \( y_{\text{best}}^k \), the best ever \( y \) achieved by any of the particles in the swarm, \( y_{\text{warm,best}}^k \). We also track \( G_{\text{warm,best}}^k \), which is the lowest value of \( G \) ever achieved by any of the particles in the swarm and corresponds to \( y_{\text{warm,best}}^k \). All of these quantities are updated, if necessary, in each iteration.

A critical part of any PSO algorithm is in updating the locations of the particles from one iteration to the next, and many of the studies in the literature17,18,52,55 focus on proposing new ways to perform this update. If we designate the mole fractions \( y \) for particle \( k \) at iteration \( l \) as \( y^{kl} = (y_{11}^{kl}, y_{12}^{kl}, \ldots, y_{i1}^{kl}, y_{i2}^{kl}, \ldots, y_{l1}^{kl}, y_{l2}^{kl}, \ldots, y_{pj}^{kl}) \), then the mole fractions at the next iteration are given by \( y^{k,l+1} = y^{kl} + \Delta y^{kl} \), where we calculate \( \Delta y^{kl} \) according to the formula

\[
\Delta y^{kl} = w \Delta y^{k,l-1} + a(y^{kl} - y_{\text{best}}^k) + b(y^{kl} - y_{\text{warm,best}}^k)
\]

in which \( \Delta y^{k,l-1} \) from the previous iteration is set to zero for all \( N_p \) particles if we are in the initialization step, where \( l = 0 \); and \( w \), \( a \), and \( b \) are weighting factors. All three weighting factors are based on real random numbers that lie between two specified bounds. After much testing, bounds that we have found to be effective are \((-0.02, 0.05)\), \((0, 1)\), and \((0, 3)\) for \( w \), \( a \), and \( b \) respectively. These random numbers are generated separately for each particle in every iteration, and so, \( w \), \( a \), and \( b \) will in general be different across particles and across iterations. The fact that \( w \) can be a negative number helps the algorithm escape local minima. In addition, we apply a “constriction factor”17,18,52 on \( w \), so that the complete expression for \( w \) is

\[
w = \ln \left( \frac{l_{\text{max}}}{l + 1} \right) \ \text{rand}(−0.02, 0.05)
\]

where \( l_{\text{max}} = 100 \) is the maximum number of iterations allowed (see below for a discussion on how we decided on this particular value), and \( \text{rand}(−0.02, 0.05) \) is a random number between the specified bounds. The constriction factor is always positive, and its role is to gradually decrease the magnitude of \( w \), as PSO iterates and settles in on a minimum, with \( w \) becoming zero if \( l = l_{\text{max}} \).

The mole fractions that we obtain from the sum \( y^{k,l+1} = y^{kl} + \Delta y^{kl} \) may sometimes be unphysical because one or more of the resulting \( y^{k,l+1} \) might be negative or might exceed the bounds set by the mole-balance constraints in eq 29. Some adjustment on \( y^{k,l+1} \) may therefore be necessary to make these mole fractions physically viable. For each particle \( k \), we apply the following adjustment procedure on \( y^{k,l+1} \) that resembles the initialization procedure described above:

1. Randomize the order of the phases by creating the set \( r = (r_1, r_2, ..., r_P) \) as discussed earlier. Carry out the steps below for each component \( j \).
2. Let \( i \in (1, ..., P - 1) \), so that we traverse through all but the last phase in the order given by \( r \) and perform the following for each phase \( r_i \). We remind the reader that if the phase mole fractions are set in the order dictated by \( r \), the maximum possible value for \( y_{ij}^{k,l+1} \) allowed by the mole-balance constraints is \( X_j - \sum_{m=1}^{i-1} y_{mj}^{k,l+1} \). We multiply this maximum value by scaling factors \( a \) and \( \beta \)—whose values we determine as explained below—to obtain

\[
a(X_j - \sum_{m=1}^{i-1} y_{mj}^{k,l+1}) + \beta(X_j - \sum_{m=1}^{i} y_{mj}^{k,l+1})
\]

which we subsequently use to adjust \( y_{ij}^{k,l+1} \) as necessary in the following manner:

- If \( y_{ij}^{k,l+1} < 0 \) (is negative), set \( y_{ij}^{k,l+1} \) to a random number between 0 and \( a(X_j - \sum_{m=1}^{i-1} y_{mj}^{k,l+1}) \).
• If $y_{ij}^{k+1} > X_j - \sum_{m=1}^{r-1} y_{mj}^{k+1}$ (exceeds the maximum), set $y_{ij}^{k+1}$ to a random number between $\beta \left( X_j - \sum_{m=1}^{r-1} y_{mj}^{k+1} \right)$ and $X_j - \sum_{m=1}^{r-1} y_{mj}^{k+1}$.

3. Finally, in order to satisfy eq 29, the mole fractions of the $r_p$ phase are determined by setting $y_{ij}^{k+1} = X_j - \sum_{m=1}^{r_p-1} X_{mj}^{k+1}$.

We have done extensive testing to determine the most effective values for the scaling factors $\alpha$ and $\beta$. From this testing, we conclude that it is best to set $\alpha \approx 0$ and $\beta \approx 1$. In retrospect, this seems reasonable because if $y_{ij}^{k+1}$ is found to be negative, it is an indication that component $j$ is likely not present in great amounts in phase $r_p$ and so, its value should be adjusted to be close to zero. Likewise, if $y_{ij}^{k+1}$ exceeds the maximum $X_j - \sum_{m=1}^{r-1} X_{mj}^{k+1}$, it seems reasonable to adjust it to a number that is only slightly smaller than this maximum. Specifically, we set $\beta = 0.99$ and $\alpha = 10^{-9}$. We find that small values of $\alpha$ are required in single-phase regions to prevent the spurious appearance of other phases that should not be present. However, if $\alpha$ is too small, it reduces the efficiency in two-phase regions, especially when significant amounts of both phases are present. The value we have chosen appears to be a good compromise between these two competing needs. We have tried setting $\alpha$ closer to 1 and $\beta$ closer to 0 and have found that this choice does not lead to lower values of $G_{\text{warm, best}}$; in fact, this choice only reduces the efficiency of the algorithm, so that it requires more iterations to converge to the same $G_{\text{warm, best}}$ and $y_{ij}^k$.

We terminate the optimization process if one of two criteria are met. One criterion is satisfied if the maximum number of iterations $l_{\text{max}}$ is exceeded. For the Fe/Ga examples that we show in section 4, we have found that a good compromise between reliability and computational efficiency is to set the number of particles $N_p = 60$. With this choice of $N_p$, we have found that PSO always terminates in less than 100 iterations, which is why we have set $l_{\text{max}} = 100$ as stated above. In single-phase regions, it usually converges within 15–20 iterations, while in two-phase regions, it usually does so in under 40 iterations, but in rare instances can take up to 80 iterations. A second termination criterion we check is if the method stops producing meaningful improvements. We define this as having occurred when $G_{\text{warm, best}}$ at the current iteration minus the running average of this quantity over the past 10 iterations converges to within a very tight tolerance of $10^{-10} RT$. We evaluate whether or not this criterion is met starting in the 15th iteration.

Once the optimization process has terminated, we use eqs 26 and 27 to translate $y_{ij}^k$ to $\chi$ and $z$, and we take the resulting set $(\chi, z)$ as being the equilibrium state that corresponds to the given $T$, $P$, and $X$. If component $j$ is insoluble in phase $i$, this will be revealed by the fact that the equilibrium value of the mole fraction $z_j$ will be a very small number, typically $10^{-9}$ or less. Likewise, if phase $i$ is not present in the equilibrium state (this state may lie in a single-phase region for instance), $\chi_i$ will be a negligibly small number. From knowledge of the equilibrium $\chi$ and $z$, one can compute other properties of the mixture (internal energy, density, sound speed, etc.) by applying the formulas in section 2 and the Appendix to the chosen EOS for the mixture of interest.

3.2. Suitability of PSO for High-Pressure Phase Equilibria. A key set of equations that we use in our testing of PSO is the equality of chemical potentials in eq 32, which is a fundamental thermodynamic requirement for equilibrium. Suppose that the equilibrium state for a given $(T, P, X)$ is an $N$-phase state, where $N$ is an integer that is less than or equal to the maximum possible number of phases $P$. The chemical potentials across the various phases must then satisfy

$$\mu_j(T, P, z_j) = \mu_k(T, P, z_k) = ... = \mu_N(T, P, z_N),$$

$j = 1, 2, ..., \epsilon$

We may solve these equations with a direct numerical method (e.g., a Newton–Raphson solve) to obtain the phase compositions $z = (z_1, z_2, ..., z_N) = (z_{11}, z_{12}, ..., z_{1\epsilon}, z_{21}, z_{22}, ..., z_{N1}, ..., z_{N\epsilon})$. A crucial point we emphasize is that we do not explicitly enforce these constraints in PSO, but the equilibrium state that it converges to must nevertheless satisfy these equations because they are necessary but not sufficient conditions for the Gibbs energy to achieve a minimum. Thus, they serve as an important check on the phase boundaries predicted by PSO.

Direct numerical solutions of eq 32 offer a potentially simple and computationally efficient means to infer phase boundaries and construct phase diagrams, but they have certain limitations that a more sophisticated approach like PSO is able to overcome. One limitation is that the direct solutions reveal information only about the phase compositions $z$, but not the relative amounts of the different phases encapsulated in the mole fractions $\chi$ whereas PSO reveals the complete set $(\chi, z)$. Another issue is that a direct method for solving eq 32 will converge to a sensible solution only if there actually are $N$ phases in equilibrium at the given $(T, P, X)$. It will fail to converge if this is not the case, especially if a gradient-based method is used. This means that number of phases must be known a priori if using a direct method. Contrast this with PSO, which requires input only about the maximum possible number of phases $P$ and free-energy models for these phases. Given this input, PSO will determine the actual number of phases $N$ in the equilibrium state and will thereby eliminate much of the guesswork that would be required if one were to instead piece together a mixture’s phase diagram from the direct solutions alone.

Furthermore, it is important to reiterate that the equations in eq 32 represent necessary but not sufficient conditions for equilibrium; they cannot distinguish between local minima and the global minimum. Direct solutions of those equations therefore cannot resolve ambiguities when there are multiple different sets of $N$ phases that can be in equilibrium (each set represents a different minimum) at the given $T$, $P$, and $X$, meaning multiple different ways for the resulting phase boundaries to combine together to form the phase diagram. An example of this kind of ambiguity will be presented in Figure 7. The direct solutions tend to be useful only when the “right answer” is known in some sense. For instance, we will apply them in this study as an a posteriori check on the PSO-predicted phase diagrams. Direct solutions also enjoy usage when experimental data on the phase diagram are readily available, which is the case for some mixtures at ambient pressure. In such situations, eq 32 may be solved directly to verify whether phase boundaries predicted by EOS models developed for these mixtures can reproduce the experimental data. One of the authors of this paper has in fact done this in condensed-phase mixtures of unreacted high explosives at ambient and near-ambient pressures. However, in the Introduction, we have
alluded to a quite different reality that exists at higher pressures, where data regarding phase boundaries are not available for the vast majority of mixtures. For these mixtures, the only such information that one may reasonably hope to obtain are predictions from atomistic simulations at a few select points along a particular phase boundary. Consequently, the free-energy models for these mixtures will have to be fit to more readily available data, such as isotherms, Hugoniot curves, and isentropes. Thus for high-pressure applications, one must be able to reliably generate phase diagrams with little a priori knowledge about the appearance of the phase diagram, that is, how the phase boundaries are connected together. This is precisely what a global optimization method like PSO, which does not require one to specify good guesses for the phase fractions \( \chi \) and compositions \( z \), is intended to do. As long as it is given EOS models for the different phases of the mixture that might be present, it will automatically sort out the different possibilities for the phase boundaries to find the one that minimizes the Gibbs energy represented by those models.

**4. RESULTS AND DISCUSSION**

Here, we demonstrate our PSO algorithm on the Fe/Ga system, using LEOS tables for pure Fe and pure Ga combined with different example models for the mixing free energy. We verify through different ways that it can reliably locate the minimum on the Gibbs-energy surface fashioned by these models. We illustrate this by producing temperature–composition phase diagrams at different fixed pressures. (Although not shown in this study, we could also apply the same algorithm to fix the temperature and generate pressure–composition diagrams instead.) Finally, we explain how PSO may be used to construct multiphase LEOS- or SESAME-style tables for a mixture at a particular overall composition \( X \), again using the Fe/Ga system to demonstrate the construction process. In this process, we first produce a temperature–pressure phase diagram for the mixture using PSO and then apply post-processing steps to obtain a table of Helmholtz energy versus temperature and density, which may be graphically visualized in the form of a temperature–density diagram. We compare Hugoniot and isentrope curves obtained from the resulting Fe/Ga tables with those from the pure Fe table.

Before proceeding to the mixtures, we briefly introduce the EOSs we use for pure Fe and Ga, along with their phase diagrams. For Fe, we use a new two-phase EOS developed by Benedict et al., which is intended for temperatures above roughly 3200 K and pressures above around 100 GPa. A recent study on shock-compressed Fe reports that the solid under these conditions is in the hexagonal closed-pack (hcp) phase. As a result, the two phases modeled by the EOS developed by Benedict et al. are fluid and hcp. To keep the nomenclature simple, we use “fluid” as a general term to indicate liquid or supercritical fluid or any other fluid-like phase, all of which are represented by the same set of free-energy models in the EOS. The temperature–pressure phase diagram predicted by this EOS is shown in Figure 1a. For Ga, we use the five-phase EOS developed by Wu et al., though only three phases—the fluid plus two solids, Ga-III (which has a body-centered tetragonal [bct] structure) and Ga-IV (face-centered cubic [fcc])—are thermodynamically stable in the applicable temperature–pressure range of the Fe EOS developed by Benedict et al. The phase diagram of the Wu et al. Ga EOS is shown in Figure 1b–d.

4.1. Temperature–Composition Phase Diagrams. 4.1.1. Ideal Mixtures. When considering a mixture of two or more components, a question naturally arises as to what are the possible number of phases \( P \) and the identity of these phases. In the Fe/Ga system at the pressures shown in Figure 1, obvious choices are the fluid phase, which is a mixture of fluid Fe and fluid Ga, and three terminal solid solutions: hcp, bct, and fcc. In the first of these solid solutions, Fe in the hcp phase would serve as a solvent for Ga solutes in that same phase. Likewise, the bct and fcc phases would be composed of Fe solute in those phases dissolved in a Ga-III or Ga-IV solvent, respectively. At intermediate compositions, there might also be compounds (e.g., Fe<sub>3</sub>Ga, Fe<sub>5</sub>Ga<sub>3</sub>, Fe<sub>7</sub>Ga<sub>4</sub>, and FeGa<sub>3</sub>) and potential secondary solid solutions—such as a body-centered cubic (bcc) phase—that have yet to be discovered. Developing a complete set of free-energy models to cover all of these possibilities is not the purpose of this study, nor is it necessary to demonstrate the efficacy of PSO. Given the lack of currently available EOSs (e.g., high-pressure EOSs have not yet been developed for any of the compounds, nor do we have a bcc-phase EOS for either Fe or Ga that is usable under such conditions), we take \( P = 3 \) in which the three phases include the fluid and two solid solutions that we refer to as the Ga-III/Fe and Ga-IV/Fe phases. In both of these solid solutions, the properties of pure Fe are modeled with the hcp-phase EOS from Benedict et al. We present various mixing models and demonstrate that PSO may be used to reliably locate the minimum on the Gibbs-energy surface represented by these models to produce coherent phase diagrams.

The simplest test of PSO is the case of ideal mixing. Under this assumption, the Gibbs energy that we minimize is taken from eq 19 and may be expressed as

\[
G = \sum_{i=1}^{P=3} \sum_{j=1}^{2} \chi_i z_i \mu_j \left[ G_i(T, P) + RT \ln z_i \right]
\]  

where the phase index \( i \) covers the fluid, Ga-III/Fe, and Ga-IV/Fe phases (in that order), while the component index \( j = 1 \) stands for Fe and \( j = 2 \) denotes Ga. We have used PSO to produce temperature–composition diagrams at two different pressures: 205 GPa and 700 GPa; see Figure 2. The fluid–solid region (colored in red) in this figure is lens-shaped, which is a characteristic feature of ideal mixing. In these two-phase regions, the equilibrium conditions in eq 32 require that the chemical potentials satisfy

\[
\mu_{ij} = \mu_{i'j'} \quad j = 1, 2
\]  

in Figure 2a,b, where the fluid \((i = 1)\) is in equilibrium with Ga-III/Fe \((i = 2)\), while they must satisfy

\[
\mu_{ij} = \mu_{i'j'} \quad j = 1, 2
\]  

in Figure 2c,d, where the fluid is in equilibrium with Ga-IV/Fe \((i = 3)\). The PSO-predicted two-phase regions in Figure 2 satisfy these equations, without requiring any explicit enforcement, to within \( 10^{-3} \) RT (the left- and right-hand sides agree to about 0.00005% or better). We have also verified that the liquidus and solidus curves illustrated in the figure are essentially indistinguishable from what we would obtain if eq 34 or eq 35 were explicitly solved with a direct numerical method to a very tight tolerance of \( 10^{-9} \) RT.

PSO is also able to correctly describe the solid-phase equilibria dictated by the Gibbs-energy surface in eq 33. We
can see from Figure 1d that at 205 GPa, Ga-IV is more thermodynamically stable than Ga-III at low temperatures, but there is a relatively narrow temperature band of about 100 K directly below the melt temperature, where Ga-III is more stable than Ga-IV. Thus, we would expect both the Ga-III/Fe and Ga-IV/Fe phases to be present in the temperature–composition diagram at this pressure, and that is indeed what we observe in Figure 2a,b. These PSO-generated phase diagrams suggest that there is no two-phase, solid–solid region, and instead, there is an abrupt transition from Ga-IV/Fe to Ga-III/Fe or vice-versa. The absence of a solid–solid region may be understood from the following arguments. If such a region were to exist, all points in it would satisfy

\[ \mu_{j} = \mu_{j}^{*}, \quad j = 1, 2 \]  

(36)

which means that for Fe \((j = 1)\), we have from eq 33 that

\[ G_{21}(T, P) + RT \ln z_{21} = G_{31}(T, P) + RT \ln z_{31} \]  

(37)

and because \(z_{22} = 1 - z_{21}\) and \(z_{32} = 1 - z_{31}\), we have for Ga \((j = 2)\) that

\[ G_{22}(T, P) + RT \ln(1 - z_{21}) = G_{32}(T, P) + RT \ln(1 - z_{31}) \]  

(38)

Because the pure-component Gibbs energies of Fe in both solid solutions are described by the same free-energy model (see our discussion at the beginning of this subsection), we have \(G_{21} = G_{31}\), which therefore implies that \(z_{21} = z_{31}\) and \(G_{22} = G_{32}\). The last equality indicates that under the assumption of ideal mixing, the two solid solutions can be equilibrium only at the transition temperature between pure Ga-III and Ga-IV, which is represented by the dotted lines in Figure 2a,b. Moreover, at 700 GPa, the Ga-III/Fe phase is absent, as we would expect from Figure 1.

The phase diagrams that we generate in this study are produced through an iterative procedure that resembles the process of how one might put together a jigsaw puzzle. In the first iteration, a set of overall mole fractions \(X\) is chosen, and for each \(X\), we perform PSO calculations over a coarsely spaced set of temperatures. This produces a rough overview of the phase diagram. In subsequent iterations, we refine it by performing calculations over additional choices of \(X\) and/or homing in on
multiphase regions with a more closely spaced temperature grid. Two iterations are sufficient for the phase diagrams in Figure 2, but multiple rounds of refinement may be needed for more complicated ones. Results for some of the points are omitted in order to improve the visual appearance/ clarity.

4.1.2. Nonideal Mixtures. If we relax the assumption of ideal mixing, the expression for the Gibbs energy becomes

\[ G = \sum_{i=1}^{P} X_i \sum_{j=1}^{c} z_j(G_i(T, P) + RT \ln z_j + G_{ex}(T, P, z_j)) \]

(39)

It is conceptually useful to decompose 39 so that

\[ G = \sum_{i=1}^{P} X_i (\Delta G_i^{pure} + \Delta G_i^{mix}) \]

(40)

in which \( \Delta G_i^{pure} = G_i^{pure}(T, P, z_j) \) is the change in Gibbs energy that occurs when the components of phase \( i \) are physically brought together in the proportions indicated by \( z_i \)

\[ \Delta G_{ij}^{mix} = \sum_{j=1}^{c} z_j \left[ RT \ln z_j + G_{ex}(T, P, z_i) \right] \]

(41)

and \( \Delta G_{ij}^{mix} = \Delta G_{ij}^{mix}(T, P, x) \) is the change in Gibbs energy that occurs when the components are chemically mixed together (dissolved) in phase \( i \)

\[ \Delta G_i^{mix} = \sum_{j=1}^{c} z_j [RT \ln z_j + G_{ex}(T, P, z_i)] \]

(42)

In order for any functional form of \( \Delta G_i^{mix} \) to be physically valid, it must go to zero if phase \( i \) is pure in any component \( j \), so that \( z_j = 1 \) and \( z_k = 0 \) for \( k \neq j \). Furthermore, the nonideal-mixing effects encapsulated in the excess Gibbs energy must vanish in the limit, as \( T \to \infty \). The excess Gibbs energy may be nonzero at \( T = 0 \), reflecting “cold” contributions to the mixing that may be computed from \textit{ab initio} quantum simulations or inferred from high-pressure cell experiments conducted at low temperatures. For the Fe/Ga examples in this study, we employ the functional form

\[ \Delta G_i^{mix} = G_{M} z_i^{2} z_2 + RT z_1 \ln z_1 + RT z_2 \ln z_2 \]

(43)
Here, nonideal mixing is represented in terms of a Margules model of the form
\[ G_{\text{M}} = \eta_1 P \left[ 1 - \ln \left( \frac{P}{\sigma_1} \right) \right] \frac{1}{\cosh(T/\theta_1)} \]
where \( \eta_1, \sigma_1, \) and \( \theta_1 \) are phase-specific constants.

As a first step toward nonideal mixing, we consider the situation where the fluid phase is a nonideal mixture described by eqs 43 and 44, while the two solid solutions still undergo ideal mixing (which essentially implies that for the time being, we set \( \eta_2 = \eta_3 = 0 \)). We set \( \eta_1 = 0.5 \text{ cm}^3/\text{mol}, \sigma_1 = 100 \text{ GPa}, \) and \( \theta_1 = 2000 \text{ K} \) for the fluid. With this choice of \( \sigma_1 \) and \( \theta_1 \), the Margules coefficient \( G_{\text{M}} \) is positive (negative) for all temperatures and compositions if the pressure \( P \) is below (above) \( 100 \exp(1) \approx 271.8 \text{ GPa} \). Therefore, we expect nonideal mixing to destabilize (and thus contract the stability field of) the fluid at 205 GPa, while it should have the opposite effect at 700 GPa. This is exactly the behavior depicted in Figures 3 and 4, respectively.

Again, we can validate the results predicted by PSO with a direct numerical solution of the equilibrium conditions in eq 34 or 35. The liquidus and solidus curves that we obtain from this direct solution overlap with those predicted by PSO. This includes the behavior on both sides of the minimum at 700 GPa that occurs around an Fe mole fraction of \( X_1 = 0.1 \), which is a particular two-phase state where the coexisting fluid and solid [Ga-IV/Fe] happen to have the same composition.

We may add a degree of complexity by allowing for nonideality in one of the two solid solutions, the Ga-IV/Fe phase. We model the Gibbs energy of mixing in Ga-IV/Fe with eqs 43 and 44, and we set two out of the three parameter values to be the same as in the fluid, so that \( \sigma_3 = \sigma_1 = 100 \text{ GPa} \) and \( \theta_3 = \theta_1 = 2000 \text{ K} \). However, we choose \( \eta_3 = -0.1 \text{ cm}^3/\text{mol}, \) and because \( \eta_3 \) has a different sign and is smaller in magnitude than \( \eta_1 = 0.5 \text{ cm}^3/\text{mol}, \) this particular nonideal-mixing model has the opposite, though weaker, effect as in the fluid. Therefore, nonideal mixing at 205 GPa increases the thermodynamic stability of Ga-IV/Fe, while it destabilizes Ga-IV/Fe at 700 GPa. Results at these two pressures are presented in Figures 5 and 6, respectively. Comparing Figures 5 with 3, both of which are at 205 GPa, we see that nonideal mixing in Ga-IV/Fe at this pressure results in a significant expansion in the stability field of that phase, to the extent that it almost entirely displaces Ga-III/Fe. The Ga-III/Fe phase appears in only a narrow range of low Fe concentrations (high Ga concentrations), as shown in Figure 5d. Ga-III/Fe and Ga-IV/Fe are separated by a two-phase, solid–solid region that we have colored in cyan. All points in this
region satisfy the equality of chemical potentials in eq 36, which when we substitute the Margules model eqs 43 and 44 for the excess Gibbs energy, may be written as

\[ G(T, P) + RT \ln z_{21} = G_{31}(T, P) + RT \ln z_{31} + G_M(1 - z_{31})^2 \]  

(45)

and

\[ G(T, P) + RT \ln(1 - z_{21}) = G_{32}(T, P) + RT \ln(1 - z_{31}) + G_M z_{31}^2 \]  

(46)

The behavior of the solid-phase equilibria in Figure 5 may be rationalized by considering the term \( G_M z_{31}^2 \) that appears in eq 46, which is negative at 205 GPa (because \( G_M < 0 \) at this pressure) for all compositions. At very low Fe concentrations where \( z_{31} \approx 0 \), this term is small in magnitude, and so, it cannot compensate for the fact that the Gibbs energy \( G_{32} \) of pure Ga-IV is larger than \( G_{32} \) of pure Ga-III for most temperatures at this pressure. This explains why Ga-III/Fe persists at very low Fe concentrations, where the magnitude of the excess mixing term \( G_M z_{31}^2 \) that appears in eq 46 is small. The liquidus curve in Figure 4 exhibits a minimum, and when combined with the two-phase, solid–solid region, the result is a eutectic point that can be seen in Figure 6c. This is a three-phase equilibrium state that represents lowest temperature where the fluid can exist at 700 GPa.

Like we have done for Figures 2–4, we can compare the PSO-predicted phase diagrams in Figures 5 and 6 against direct numerical solutions of the equilibrium conditions eqs 34–36. Solving those equations produces the liquidus, solidus, and solvus curves that enclose the two-phase regions, and we have verified that in all cases, results for these phase boundaries from the two methods are indistinguishable from each other. However, because Figures 5 and 6 have a fair degree of complexity, and there are different possibilities for these phase diagrams, it is worth doing a more thorough investigation to ensure that PSO does indeed yield the true equilibrium state.
For example, Figure 5 shows that above the peritectic temperature, Ga-IV/Fe dominates over Ga-III/Fe due to the particular nonideal-mixing model we have chosen. If we assume that the phase along the solidus is actually Ga-III/Fe instead of Ga-IV/Fe, the phase boundaries that we obtain from a direct numerical solution— which represent local minima in the Gibbs energy— turn out to be similar (displaced toward higher Fe concentrations by about 2 mol % or less) to those displayed in the figure. Perhaps surprisingly, the Gibbs energies along the liquidus and solidus in that hypothetical scenario are actually lower for most conditions than the Gibbs energies along those same boundaries in the figure. Thus, based on the direct numerical solution alone, one might be led to conclude that Ga-III/Fe is actually the true equilibrium phase along the solidus.

However, an examination of the Gibbs energy as a function of composition at a fixed temperature reveals that this is not the case. Figure 7a,b illustrates results for the 4500 K isotherm in Figure 5. The hypothetical scenario that we have laid out above, which is represented by the black solid curve, is always equal to or higher in Gibbs energy than the PSO result. This occurs because the liquidus and solidus in the PSO result (the vertical dashed lines) are shifted to the left compared to those boundaries in the hypothetical scenario (the vertical dotted lines). As a result, for any set of $X$ that lies within both of these two-phase regions, the solid phase fraction will be larger in the PSO case than in the hypothetical scenario. The differing relative amounts of fluid versus solid works out such that the two-phase state predicted by PSO has a lower Gibbs energy than the two-phase state in the hypothetical scenario, despite the fact that the latter may have lower free energies along its liquidus and solidus.

Figure 7c shows a similar analysis for 3450 K and 205 GPa, which is slightly below the peritectic temperature of 3458 K at that pressure. The black curve in this figure represents the hypothetical scenario where we ignore the solid—solid transition and assume that the phase that is present along the solidus is Ga-IV/Fe instead of Ga-III/Fe. Figure 7d demonstrates results for the 7150 K isotherm at 700 GPa, which lies a little above the eutectic temperature of 7106 K at that pressure (see Figure 6). Here, the black curve denotes the local minimum, where the branch of the solidus that lies to the right of the eutectic point is...
composed of Ga-IV/Fe rather than Ga-III/Fe. We note that in all the hypothetical scenarios depicted in Figure 7, the free-energy differences are rather small; even well into the two-phase regions, \( \Delta G/RT \) for the black curves in most instances is less than \( 10^{-3}RT \). This suggests that PSO reliably yields the true equilibrium state even when there are competing local minima that are close in free energy to the equilibrium state. It illustrates the point we mentioned in the previous section about how PSO, being a global optimization scheme, is able to resolve ambiguities in phase boundaries and diagrams, whereas direct numerical solutions of eqs 34—36 [and (32) in the general case] cannot do this.

As an additional way to verify the results of the Gibbs-energy minimization, we have developed a separate version of PSO that minimizes the Helmholtz energy instead and have used it to cross-check the results of Gibbs-energy minimization. The details and motivation behind this second PSO method is best explained in the context of EOS table generation, which is the subject to which we now proceed.

### 4.2. Generation of EOS Tables

We have discussed in the Introduction the practical need for EOS tables in high-pressure science. An EOS table for a single-component system is simply an array of numbers representing the Helmholtz energy of the equilibrium (possibly multiphase) state on a grid of temperatures \( T \) and densities \( \rho \). For a mixture, we would also have to fix the overall composition \( X \). Thus, table construction involves finding the equilibrium state for a given set of \( (T, \rho, X) \), much like how we have used PSO to find the equilibrium state for a given set of \( (T, P, X) \). Basic thermodynamics dictates that one must minimize the Helmholtz energy in the former situation. Currently, there does not exist a method to rigorously produce multiphase EOS tables for mixtures in this manner, and so, we have explored PSO as a means to do that. Our algorithm for Helmholtz-energy minimization is very similar to that for Gibbs-energy minimization outlined in section 3 (indeed, this flexibility of PSO is one of the reasons we have chosen it in the first place), with the swarm representing a canonical ensemble instead of an isothermal—isobaric ensemble. The only procedural difference is that Helmholtz-energy minimization requires one additional step, where the pressure \( P \) of each particle in the swarm—here, each particle represents a multiphase, multicomponent mixture that is fixed at the specified \( T, \rho \), and \( X \)—must be computed in every iteration. This \( P \) is common to all \( P \) phases in the particle and is the pressure corresponding to the particle’s \( \chi \) and \( z \) at the current iteration plus also the specified \( T \) and \( \rho \). Unfortunately, while this additional step is conceptually simple, it is computationally expensive. A minimization over one set of \( (T, \rho, X) \) for the Fe/Ga examples is 2 orders of magnitude slower than an equivalent calculation for a set \( (T, P, X) \) in...
Gibbs-energy minimization. As a result, our Helmholtz-energy minimization algorithm cannot, in its present form, construct multiphase EOS tables for mixtures in a reasonable amount of time. This may become possible with the speedup options discussed in section 5.1, but its usage is currently limited to serving as a cross-check for the Gibbs-energy minimization through the following process:

1. Select a particular TP \( \mathbf{X} \) and perform a Gibbs-energy minimization with PSO to obtain the equilibrium values of the phase fractions \( \chi \) and compositions \( z \).
2. Input this \( \chi \) and \( z \), as well as \( T \) and \( P \), into the given free-energy models to compute \( \rho \).
3. Perform a Helmholtz-energy minimization with PSO on \( (T, \rho, \mathbf{X}) \) and verify that its predicted equilibrium state reproduces the \( P, \chi \) and \( z \) from step 1.

We have cross-checked several \( (T, P, \mathbf{X}) \) points with both ideal and nonideal-mixing models and have found that the two minimization procedures yield the same equilibrium state for all the points that we have tested.

It is still possible to produce EOS tables with the more indirect procedure that we now describe. In this procedure, we first produce a temperature–pressure phase diagram for a fixed overall composition \( \mathbf{X} \) through Gibbs-energy minimization with PSO. Figure 8 shows such diagrams for the case of a 90% Fe and 10% Ga mixture. A feature we point out is that the one-dimensional melt curve in a single-component system like pure Fe transforms to a two-dimensional, fluid–solid region in the binary Fe/Ga mixture. (These two-phase regions in iron-silicate alloys have practical importance in studying the structure of the inner Earth.) The increased dimensionality compared to the single-component case is a natural consequence of mixing and is manifested in the well-known Gibbs phase rule. Simple mixing protocols that combine different single-component EOSs without properly accounting for changes in phase boundaries would inherently not be able to capture the increased dimensionality. After the temperature–pressure diagrams are produced, we use our free-energy models to compute different properties like the density \( \rho \) and Helmholtz energy \( F \) at each \( T \) and \( P \) point, and we fit these results to two-dimensional splines of \( T \) and \( P \). We find the lowest and highest densities spanned by these diagrams, which are represented by the dashed curves in Figure 8. We then employ the splines over...
the temperature and density range to generate a table of $S$ as a function of $T$ and $\rho$ for the specified $X$. This table will necessarily be multiphase and will properly reflect the increased dimensionality (in the Gibbs phase rule sense) that arises from mixing.

We may use the EOS tables produced by PSO to perform calculations, just like we can with any EOS from the LEOS or SESAME libraries mentioned in the Introduction. As an example, Figure 8 compares Hugoniot and isentrope predictions from the Fe/Ga mixture tables with those from the pure Fe table by Benedict et al.59 The initial pressure and density in all cases are 240 GPa and 12.15 g/cm³, respectively, which is in the fluid phase and could represent the result of a shock-melting experiment. The Hugoniot curves and isentropes in the figure might therefore represent double-shock or shock–ramp experiments, respectively. Interestingly, the effect of introducing Ga solute particles to the Fe solvent appears to be much more pronounced on the temperature than it is on the pressure or the shock speed–particle speed relation. Part of this is due to the ideal-mixing entropy terms of the form $-R\sum \ln z_i$, but nonideal contributions to the entropy and the heat capacity also have a noticeable effect. This suggests that obtaining reliable temperature measurements along dynamic-compression paths, which is an ongoing and extremely challenging area of work,63 could be important toward discerning the effect of impurities under relevant high-pressure conditions.

5. CONCLUSIONS

5.1. Critical Evaluation of Our Approach and Future Work. Now that we have demonstrated the reliability and utility of PSO with the examples in the previous section, we are in a position to suggest future work to address the current limitations of our approach and expand its capabilities. We focus on limitations that we believe can be overcome in the near future. One topic that we do not dwell on at length here is chemical-reaction equilibria, which broadly includes ionic equilibria (salt solutions), acid–base equilibria, and other redox reactions that are of relevance to planetary science in particular. While PSO can describe chemical-reaction equilibria (e.g., Bonilla-Petriciolet and Segovia-Hernández52 have applied it to model equilibria in reacting fluid mixtures at low pressures), we anticipate that for high-pressure applications, this will be more of a long-term challenge than the other topics that we describe below. The main difficulty is that reactions tend to occur not in isolation, but in a complex network that can involve hundreds of species linked through several different reactions. Each reaction, whose mechanism will likely not be well characterized, introduces additional mass-conservation constraints and constraints on the chemical potentials due to the requirement for vanishing entropy production at equilibrium.64 These constraints will have to be verified, just like how we have verified that our PSO-predicted phase boundaries satisfy the equality of chemical potentials in eq 32. Moreover, EOS models will need to be supplied for each species in order to do a proper calculation of the equilibrium state. This will be a challenge for ionic and possibly also for acid–base equilibria because the charged species involved in them are notoriously difficult to model.65 All of these difficulties will be exacerbated at high pressures because the application of pressure can introduce additional reactions and species in the complex network and cause the species to become more closely packed (and thereby interact more strongly), so that, for example, simple electrolyte models like Debye–Hückel that work well for dilute mixtures are not applicable. thermochemical codes such as Magpie13 and Cheetah12,66–68 are able to model high-pressure, chemical-reaction equilibria of certain select mixtures (see section 5.2), but they necessarily have to adopt some simplifications in order to make the problem tractable.

One way to extend our algorithm, which is currently limited to solutions, is to enable it to handle compounds of the type discussed in section 2. Because these compounds have a fixed stoichiometry, each possible phase of the compound brings in an additional phase mole fraction—but not an additional set of phase compositions—whose value is to be adjusted during the
minimization process. For example, suppose that Fe₃Ga is the first compound to appear on the Fe-rich side of the Fe/Ga phase diagram and that it can exist in seven different possible phases. Then, for a given \( T \) and \( P \) and for all Fe/Ga mixtures where the Fe overall mole fraction \( X_1 \) is greater than 0.75, we can generalize the Gibbs energy that is to be minimized via PSO from its form in eq 39 to

\[
G = \sum_{i=1}^{P=3} \chi_i \sum_{j=1}^{c=2} z_j [G_j(T, P) + RT \ln z_j] + \sum_{k=1}^{P_{FeGa}} \chi_k G_k(T, P)^{excess}
\]

(47)

where the double sum over \( i \) and \( j \) concerns the three solution phases (fluid, Ga-III/Fe, and Ga-IV/Fe) considered in the previous section, and the summation over \( k \) is performed over the \( P_{FeGa} \) phases of Fe₃Ga. Here, \( \chi_i \) is the mole fraction of phase \( i \) of Fe₃Ga, and \( G_j(T, P) \) is the Gibbs energy of that phase obtained from the chosen multiphase EOS for Fe₃Ga. Clearly, this EOS must be constructed beforehand if it is to be used in eq 47, which speaks to the issue we raised earlier about the challenging need to construct separate multiphase EOSs for each compound of interest. In order to account for the presence of the compound Fe₃Ga, the mole-balance constraints in eq 25 must be modified to

\[
\sum_{i=1}^{P=3} \chi_i z_{i1} + \sum_{k=1}^{P_{FeGa}} \chi_k G_k(T, P) = X_i
\]

(48)

\[
\sum_{i=1}^{P=3} \chi_i z_{i2} + \sum_{k=1}^{P_{FeGa}} 0.75 \chi_k = X_2
\]

(49)

We may apply PSO to minimize the Gibbs energy in eq 47 subject to these mole-balance constraints to obtain the equilibrium state corresponding to the given \( T, P \), and \( X \). The equilibrium state indicates the mole fractions \( \chi \) and compositions \( z \) of the three solution phases and the mole fractions of the \( P_{FeGa} \) different phases of Fe₃Ga. If the PSO algorithm is working correctly, the equilibrium mole fraction of all Fe₃Ga phases except for that of the most stable phase(s) at the given \( T \) and \( P \) should be virtually zero, much like how PSO is able to select out and eliminate all unstable solution phases, as illustrated in the previous section. The same procedure may be followed for \( X_1 \) less than 0.75 with other compounds (such as Fe₆Ga₅, Fe₃Ga₄, and so on).

Figure 9. Comparison of Hugoniot curves and isentropes of pure Fe vs those of Fe/Ga mixtures at two different overall compositions (90% Fe and 95% Fe) and described by different mixing models: (a−c) pressure, temperature, and shock speed along the Hugoniot and (d) temperature along the isentrope. (We have not included pressure−density results for the isentrope in the figure because the differences are even smaller than they are for the Hugoniot.) All of the curves are initiated at an initial pressure and density of 240 GPa and 12.15 g/cm³, respectively. As explained in the text, the results for Fe/Ga mixtures are calculated from the multiphase EOS tables for these mixtures that are produced from PSO-generated temperature−pressure phase diagrams like the ones shown in Figure 8.
and FeGa₃), as long as multiphase EOSs are available for these compounds, so that we can compute their Gibbs energy.

A limitation of our PSO-based approach as presently designed is the computational efficiency. This is true in general for global optimization methods applied to phase-equilibria computations. For each set \((T, P, X)\), the Fe/Ga examples we have presented take a few seconds to converge on a laptop equipped with a 2.8 GHz Intel Core i7 processor. The exact amount of time varies due to the stochastic nature of the optimization process, and it also depends on the number of phases present in the equilibrium state; fewer iterations are generally required to achieve convergence in single-phase regions than in two-phase regions. Construction of the phase diagrams in Figures 2–6 typically takes several hours because each diagram involves performing a Gibbs-energy minimization for thousands of different sets of \((T, P, X)\). While the speed could certainly be improved significantly along the lines suggested below, PSO is still a practical means for Gibbs-energy minimization. It is significantly slower, however, for Helmholtz-energy minimization. Each set \((T, P, X)\) for the Fe/Ga examples takes hundreds of seconds to complete, which is 2 orders of magnitude slower than an equivalent calculation for a set \((T, P, X)\) in Gibbs-energy minimization. Part of the computational inefficiency of our code may be attributed to the fact that we are running a development version (not a production version) that is written in Python, an interpreted language. If it were instead to be optimized and rewritten in a compiled language like C++, it is reasonable to expect a several-fold (perhaps even more than a 10-fold) increase in efficiency. A more significant speedup could be achieved through parallelization in which the particles of a swarm are divided up among different processors. We note that PSO is amenable to architectures involving graphics processing units because the particles move largely independently of each other, with the only communication necessary being the need to track \(x^{\text{swarm, best}}\), which is the most optimal position in the search space ever accessed by any of the particles. Once the necessary speedup has been achieved, we aim to perform Helmholtz-energy minimization to construct temperature—density phase diagrams (for a fixed overall \(X\)) from which we can readily obtain EOS tables. This is a more direct way of producing these tables than the Gibbs-based procedure followed in this study, which requires post-processing steps to convert temperature—pressure phase diagrams to the desired tabular format.

Improving the computational efficiency will also be a necessary step toward developing a PSO capability for entropy maximization. The goal of entropy maximization is to find the equilibrium state of a multicomponent mixture for a given set of \(E, \rho, \text{ and } X\), where \(E\) is the total molar internal energy of the mixture. The swarm in this case symbolizes a microcanonical ensemble because each PSO particle represents a mixture that is fixed at the specified \(E, \rho, \text{ and } X\). The equilibrium state reveals the compositions of the solution phases and the mole fractions of all phases (both solutions and compounds) and the temperature and pressure that are common to all phases. Adapting the Gibbs-energy minimization to Helmholtz-energy minimization requires only one additional step; the same is true for entropy maximization, where the additional step in this case involves a simultaneous determination of both temperature and pressure (instead of only pressure like in Helmholtz-energy minimization) for each PSO particle at every iteration. While conceptually simple, this additional step will again be numerically expensive, even more so than the pressure-only solution required in Helmholtz-energy minimization. One possible way to ease the computational burden is to apply the scheme we have developed for a related problem, where we map our chosen set of free-energy models for the mixture onto a more simple EOS in which pressure depends linearly on volume. The functional form of this simple EOS is specifically designed, so that the \(T\) and \(P\) consistent with the given \(E\) and \(\rho\) can be found analytically. This mapping onto the analytically invertible EOS would have to be performed for each PSO particle at every iteration, but we expect that it will be much more computationally efficient to do this than to carry out a direct numerical solve for \(T\) and \(P\). The motivation for developing an entropy-maximization capability comes from the needs of the continuum-scale, multiphysics codes for high-pressure applications that we have mentioned in the Introduction. These codes track and update \(E, \rho, \text{ and } X\) along the different mesh points, but they do not track \(T\) and \(P\) or the phase mole fractions and compositions. Although this latter set of information is not tracked, the codes do need to extract this information from the given EOS models because it is of interest (especially \(T\) and \(P\)) to the various constitutive models in these codes, like those for strength effects, kinetics, transport coefficients, and so forth. If the computational efficiency can be sufficiently improved, it may be possible to implement a PSO-based, entropy-maximization procedure directly into these codes, so that they can perform on-the-fly, phase-equilibria calculations of multicomponent mixtures. This would be a thermodynamically rigorous alternative to simplified, albeit more pragmatic, approaches that treat these mixtures as if the components were homogeneously mixed (i.e., neglects the fact that they can separate into multiple phases with different compositions).

As the first demonstration in the literature of PSO on high-pressure phase equilibria, we have chosen to work with a binary system (Fe/Ga) of up to three phases because it is relatively easy to explain, validate, and visualize the performance of our method on such a system. Our algorithm is nonetheless designed to be applicable more generally to mixtures with an arbitrary number of components \(c\) and (solution) phases \(\mathcal{P}\). Part of our future work will be to test its performance on true multicomponent mixtures. In anticipation of this future testing, we have performed a computational-cost analysis of Gibbs-energy minimization of ternary and quaternary mixtures. We have mimicked the additional components in the cost analysis by creating fictitious secondary Fe and Ga components with different molar masses. Table 1 indicates an approximately linear scaling in both \(c\) and \(\mathcal{P}\). The table gives only a rough idea of the

| \(\mathcal{P}\)  | \(c = 1\) | \(c = 2\) | \(c = 3\) | \(c = 4\) |
|---|---|---|---|---|
| \(\mathcal{P} = 2\) | 1.00 | 1.79 | 2.89 | 3.63 |
| \(\mathcal{P} = 3\) | 1.35 | 2.72 | 4.32 | 5.42 |
| \(\mathcal{P} = 4\) | 3.66 | 5.82 | 7.50 |

*Each entry indicates the average time it takes to perform a Gibbs-energy minimization for a given \((T, P, X)\) relative to the simplest case of \((c = 1, \mathcal{P} = 2)\). Each listed time is an average over 20 PSO runs carried out with a fixed number of \(N_p = 60\) particles in the swarm. The \((c = 1, \mathcal{P} = 4)\) case is not examined because it is forbidden by the Gibbs phase rule.*
minimization, a flash calculation tends to be several times faster than PSO. The disparity becomes even greater for Helmholtz-energy minimization and entropy maximization; the computational cost of a flash calculation for these more complicated problems increases by an order of magnitude or less, whereas it increases by at least 2 orders of magnitude for PSO. However, PSO offers distinct advantages that may make it a more attractive option under certain circumstances. First of all, it is far more suited to parallelization, which could potentially allow it to make up for a significant part of its extra computational requirements. It also does not perform the arbitrary separation into stability and phase-split steps. We have seen that going from Gibbs-energy minimization to Helmholtz-energy minimization to entropy maximization is conceptually a straightforward matter in PSO. In contrast, for flash calculations, these transformations often require a substantial reformulation of the algorithms. Perhaps most importantly, one does not need to supply PSO with a good initial guess for quantities like phase mole fractions and compositions (though the tradeoff for this robustness is the higher computational load). This is essential for high-pressure applications, as we have discussed in section 3.2. Flash calculations are the opposite in that they are very much reliant on a good initial guess for such quantities (this is especially true for Helmholtz-energy minimization and entropy maximization as explained in a recent study\(^\text{78}\)), without which they are prone to failures like converging to an unphysical solution or not even converging to a solution at all. Correlations and recipes for initial guesses have been developed for a variety of fluid mixtures under low-pressure industrial conditions, but ultimately they are all based on trial-and-error and may not be applicable to higher pressures or to solid mixtures. As a result, it is not uncommon in a flash calculation to have to cycle through different initial guesses until finding one that works, which can significantly impact the robustness of these methods and add to the computational cost.

Cheetah\(^{66,67}\) is widely used for modeling thermodynamics under detonation, which includes chemical-reaction equilibria. It does this by representing the interatomic interactions between the different species in a mixture with exponential-six potentials\(^{12,68}\), whose parameters are fit to experimental data. These interactions are translated to a free energy via the application of mixing rules and statistical—mechanical models, and the free energy is minimized to obtain the equilibrium state for a given set of conditions. Cheetah has been coupled with high-pressure continuum-scale codes, so that it can feed information directly to these codes. It can model systems ranging in complexity from monatomic materials to large organic molecules like high explosives and plastics. However, Cheetah cannot describe regimes where there is significant electronic ionization (recall from the Introduction that the LEOS and SESAME tables that we use for the pure components account for this through an electron-thermal term) and is limited in its applicable temperature and pressure range as a result. It is also not intended to model dense metals like pure Fe, pure Ga, and Fe/Ga mixtures because the exponential-six potentials are not expected to give accurate predictions for such materials over most conditions of interest.

CALPHAD\(^{79–84}\) is the most well-known methodology for multiphase, multicomponent mixtures in materials science. It follows the standard prescription from chemical thermodynamics\(^{36–40}\) outlined in section 2, in which the Gibbs energy of each solution phase is expressed as a linear combination of the Gibbs energies of the pure components that make up the phase.

### Table 2. Computational Cost of PSO Calculations as a Function of \(N_p\) for a Binary \((c = 2)\) Mixture that can Exist in up to \(P = 3\) Phases\(^{46}\)

| \(N_p\) | 1.00 | 2.06 | 3.82 | 7.56 | 15.20 |
|--------|------|------|------|------|------|
| 50     |      |      |      |      |      |
| 100    |      |      |      |      |      |
| 200    |      |      |      |      |      |
| 400    |      |      |      |      |      |
| 800    |      |      |      |      |      |

*Each entry indicates the average time (averaged over 20 runs) it takes to perform a Gibbs-energy minimization for a given \((T, P, X)\) relative to the fastest case of \(N_p = 50\) particles.*
plus some additional mixing terms. CALPHAD applies an optimization procedure (which could be a Newton-based method or a regression approach or a Bayesian technique) to fit the parameters of the mixing models, and potentially also those of the pure-component Gibbs energies, to reproduce experimental data on the phase diagrams. Unlike Cheetah, it is designed to handle dense metallic systems, and in fact, producing phase diagrams for metallurgical applications is probably the most common use of CALPHAD. However, the vast majority of CALPHAD studies focus only on ambient pressure, where experimental phase-diagram data are far more readily available than at higher pressures. Some relatively recent studies have attempted to extend CALPHAD to higher pressures, in which most of the pressure dependence is introduced by adding a cold energy and an ion-thermal term (an Einstein model with a pressure-dependent Einstein temperature), but again no electron-thermal term, to the ambient pure-component Gibbs energies. These high-pressure extensions are tied to the legacy of the earlier, ambient-pressure database through the use of an ad hoc interpolation function, and this constraint to the ambient-pressure models can in some cases make it difficult to obtain agreement with experimental data at higher pressures, such as those pertaining to melt curves. While CALPHAD could be a good option for high-pressure applications, it is not widely used within high-pressure science at the moment because the details regarding the implementation of the underlying models and algorithms are obscured behind proprietary software packages (e.g., Thermo-Calc, FactSage). Thus in practice, it requires an experienced user of these packages to make the modifications necessary to adapt the underlying databases to high pressures. Furthermore, to the best of our knowledge, the high-pressure CALPHAD-based models have remained as standalone objects in the sense that there has been no attempt to construct EOS tables from them or to otherwise connect CALPHAD to the continuum-scale codes mentioned in the Introduction.

5.3. Summary. This study is motivated by a number of practical needs for thermodynamic modeling of multicomponent mixtures at high pressures. One is the desire to have a framework for these mixtures that directly uses existing EOS models specifically designed for high-pressure conditions, with prominent examples being the EOSs that make up the LEOS and SESAME libraries. Section 2 and the Appendix outline such a formulation in which mixing terms are added onto the pure-component properties that are obtained from the existing high-pressure EOSs. Our study is also motivated by the fact that multicomponent systems, like their single-component counterparts, can exist in a multiphase state when in equilibrium. A complete determination of the equilibrium state therefore requires finding the relative amounts of the different phases and the composition of each phase. This may be achieved through a free-energy minimization procedure. Such a capability would also be needed to generate phase diagrams because a phase diagram is merely a visual depiction of the equilibrium states of a mixture across a range of conditions. A crucial point that we reiterate here is that unlike the situation at ambient pressure, available data on phase diagrams at high pressures tend to be extremely limited. A free-energy minimization method that is suitable for high-pressure conditions must therefore be able to generate phase diagrams with little information (minimal input from the user regarding initial guesses, actual number of phases in equilibrium, etc.) on how the phase boundaries are connected together.

Our PSO-based minimization scheme described in section 3 satisfies this important criterion. Another key reason why we have chosen PSO is because it is a simple method that does not require expertise in or access to any specialized software. As long as it is given free-energy models for each of the possible phases that might be present in the equilibrium state, it will iteratively adjust the relative amounts of these phases and the compositions of the individual solution phases to find the minimum on the Gibbs-energy surface provided by the models. In doing so, it will reveal the equilibrium state for a given temperature $T$, pressure $P$, and overall composition $X$. If it turns out, for example, that a particular phase is not present in the equilibrium state at the specified ($T, P, X$), PSO will determine its mole fraction to be very close to zero, typically $10^{-9}$ or less. Section 4 tests and demonstrates the reliability of our method with different example mixing models by generating temperature–composition phase diagrams. It is able to capture the fact that the particular nonideal-mixing models we have used for demonstration purposes in this study result in nontrivial features like eutectic and peritectic points. Moreover, we have applied PSO to produce EOS tables for mixtures that rigorously account for changes in phase boundaries due to mixing. As far as we know, this is the first demonstration of such a capability.

In addition to its reliable and readily accessible nature, PSO is also highly adaptable. We have discussed how our method, which is currently limited to mixtures involving fluid or solid (e.g., alloy) solutions, may be extended to allow for stoichiometric compounds. This is a topic that we intend to work on in the near future. With minor modifications, the PSO algorithm may also be adapted to minimize the Helmholtz energy or maximize the entropy instead of minimizing the Gibbs energy. In fact, we have done this already for Helmholtz-energy minimization and have used it to cross-check results of the Gibbs-energy minimization. A limitation, however, is that our current Helmholtz-energy minimization procedure is too computationally inefficient to be used for its original intended purpose of constructing EOS tables in a direct manner through the generation of temperature–density phase diagrams. We have given suggestions on how to improve the efficiency in the previous section, though there are likely to be other avenues for speedup as well. We note that PSO is amenable to parallelization, and our tests show that it scales well (linearly) with respect to the number of components, phases, and particles in the swarm. With sufficient improvements in the efficiency, we hope to use PSO to produce multiphase EOS tables for mixtures via Helmholtz-energy minimization. It may also be possible to implement a PSO-based entropy-maximization procedure directly into continuum-scale codes for high-pressure applications to enable them to perform on-the-fly, phase-equilibria calculations of mixtures in a thermodynamically rigorous fashion.

### APPENDIX

#### Quasistatic Phase Equilibrium in the Computation of Thermodynamic Derivatives

Section 2 describes how one may compute the molar Gibbs energy $G$, internal energy $E$, entropy $S$, volume $V$, Helmholtz energy $F$, or enthalpy $H$ of a multiphase, multicomponent mixture. Other thermodynamic properties of interest, such as the sound speed and the heat capacity, may be obtained by taking derivatives of $G, E, S, V, F,$ or $H$. However, we have mentioned that evaluating such derivatives can be complicated...
for mixtures. We illustrate this point by considering the sound speed $c_s$. The definition of the bulk thermodynamic sound speed is

$$c_s = \sqrt{\frac{B_S}{\rho}} = \sqrt{-\frac{V^2 (\partial P/\partial V)_S}{M}}$$

(50)

where $M$ is the molar mass, $B_S = -V(\partial P/\partial V)_S$ is the isentropic bulk modulus, and $\rho = M/V$ is the mass density. Evaluating this derivative is a simple matter in a single-phase, single-component system. However, in a multiphase, multicomponent mixture, a complication arises when evaluating this derivative: the passage of the sound wave disturbs the phase equilibrium within the mixture. That is, when the sound wave propagates through the mixture and changes its pressure from $P$ to $P + dP$ and temperature from $T$ to $T + dT$, the phase mole fractions $\chi = (\chi_1, \chi_2, \ldots, \chi_p)$ and compositions $z = (z_{11}, z_{12}, \ldots, z_{pp})$ change from their values at $T$ and $P$ to some other set of values $\chi'$ and $z'$ that correspond to the equilibrium state at $T + dT$ and $P + dP$.

Even if a closed-form expression exists for the terms that account for the perturbation of the phase equilibrium, they may not be simple to compute. For instance, by adapting ideas from Kieffer,\cite{90} one may show that the square of the sound speed in a two-phase, single-component system is

$$c_s^2 = \frac{B_S}{\rho} = -\frac{V^2 (\partial P/\partial V)_S}{M} = \frac{V^2}{M \sum_{i=1}^{2} \chi_i \left[ \frac{V}{B_{S,i}} - \left( \frac{\partial T}{\partial S} \right)_S - \frac{\partial V}{\partial S} \left( \frac{\partial S}{\partial T} \right)_S \right]}$$

(51)

Here, $\Delta V = V_1 - V_2$ and $\Delta S = S_1 - S_2$ are the differences between the molar volumes and molar entropies of the two phases. It is straightforward to employ an EOS to compute all the quantities that appear in eq 51 except the last one in the denominator: $(\partial S/\partial P)_S$. The terms that depend on $(\partial S/\partial P)_S$ account for the perturbation in the equilibrium phase mole fractions $\chi$ due to the sound wave. Perhaps the easiest approach to calculate $(\partial S/\partial P)_S$ is through numerical finite differences in which we apply a small pressure perturbation $\Delta P$ and iteratively find what the temperature $T$ of this perturbed state has to be, so that the total entropy $S$ is the same as that of the original state. Determination of the pressure and temperature in this way will then allow us to find the entropy $S_i$ of phase $i$ of the perturbed state. Studies that have derived multiphase, multicomponent extensions of eq 51 to the specialized case of fluid mixtures\cite{91,92} show that the calculations can become rather involved if one rigorously accounts for the changes in $\chi$ and $z$.

In light of the complications illustrated above, we suggest for practical purposes to hold $\chi$ and $z$ fixed when evaluating the derivatives of $G$, $E$, $S$, $V$, $F$, or $H$. When applied to the sound speed, this assumption of quasi-static phase equilibrium implies that the timescale of the disturbance itself (the sound wave) is fast compared to any nonequilibrium process (phase-transition kinetics,\cite{93,94} diffusion, convection in fluids, dislocations in solids, etc.) that contributes to the re-establishment of equilibrium. If we redefine the isentropic bulk modulus as $B_S = -V(\partial P/\partial V)_{S,x} = -V/(\partial V/\partial P)_{S,x}$ so that the sound speed becomes

$$c_s = \sqrt{\frac{B_S}{\rho}} = \sqrt{-\frac{V^2 (\partial P/\partial V)_{S,x}}{M}} = \sqrt{-\frac{V^2}{M (\partial V/\partial P)_{S,x}}}$$

(52)

Equation 51 simplifies to

$$c_s^2 = \frac{B_S}{\rho} = -\frac{V^2 (\partial P/\partial V)_{S,x}}{M} = \frac{V^2}{M \sum_{i=1}^{2} \chi_i \frac{V}{B_{S,i}}}$$

(53)

The troublesome terms involving $(\partial S/\partial P)_S$ no longer appear because the phase mole fractions $\chi$ are now fixed in the evaluation of the bulk modulus. Equations 51 and 53 are applicable to a two-phase, single-component system. In a multiphase, multicomponent mixture, we have eqs 3 and 18 that

$$\left( \frac{\partial V}{\partial P} \right)_{S,x} = \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_{ij} \left[ -\frac{V_{ij}}{B_{S,ij}} + \frac{\partial}{\partial P} \left( \frac{\partial S_{ij}^{\text{excess}}}{\partial P} \right) \right]$$

(54)

where the pure-component volumes $V_{ij}$ and bulk moduli $B_{S,ij}$ are to be evaluated at the same temperature, pressure, and state of matter as phase $i$. Substitution of eq 54 into 52 yields a formula for the sound speed of a multiphase, multicomponent mixture under the assumption of quasistatic phase equilibrium, and this formula reduces to (53) if the number of phases $p = 2$ and the number of components $c = 1$ (remembering that all mixing free energies such as $G_{ij}^{\text{excess}}$ vanish when $c = 1$). We have tested this expression by using the Fe EOS developed by Benedict et al.\cite{95} described in section 4 to compute the two-phase (fluid—hcp solid) sound speed with the full expression in eq 51 and with the quasistatic approximation in (53). We have found that the two expressions yield similar results and fall within the experimental error bars from Nguyen and Holmes.\cite{96} (A slight caveat is that we have to add a contribution from the shear modulus of the solid\cite{97} when comparing the sound speed in that phase to experimental data.) Thus, at least in this particular example, the small errors that one incurs in making the quasistatic approximation are well worth the practical benefit of greatly simplifying the computations. Perhaps, this approximation may be valid for most multiphase regions involving condensed phases, where processes that re-establish equilibrium (e.g., diffusion) tend to be slow compared to those in the gas phase.

Other thermodynamic derivatives that are frequently of interest in various applications include the isochoric heat capacity $C_V$ and isobaric heat capacity $C_P$. If we assume quasistatic phase equilibrium, we may combine eqs 2 and 17 to obtain the following expression for $C_V$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_{V,x} = \left( \frac{\partial E}{\partial T} \right)_{V,x}$$

$$= \sum_{i=1}^{p} \chi_i \sum_{j=1}^{c} z_{ij} \left[ C_{V,ij} - T \frac{\partial}{\partial T} \left( \frac{\partial S_{ij}^{\text{excess}}}{\partial T} \right)_{P,x} \right]$$

(55)

where $C_{V,ij} = T(\partial S_{ij}/\partial T)_V$ is $C_V$ of pure $j$ evaluated at the same $T$, $P$, and state of matter as phase $i$. Similarly, it is easy to show that
\[ C_p = T \left( \frac{\partial S}{\partial T} \right)_{P,X} = \left( \frac{\partial H}{\partial T} \right)_{P,X} \]

\[ = \sum_{i=1}^{P} \sum_{j=1}^{C} \frac{C_{P,ij}}{T^2} \left[ \frac{\partial^2 H^\text{e}}{\partial T^2} \right]_{P,X} \]

(56)

By definition all excess free energies of mixing vanish in an ideal mixture, these expressions for an ideal mixture simplify to

\[ C_V = \sum_{i=1}^{P} \sum_{j=1}^{C} \frac{C_{V,ij} T^2}{2} \]

(57)

\[ C_P = \sum_{i=1}^{P} \sum_{j=1}^{C} \frac{C_{P,ij}}{T} \]

(58)

Thus, the heat capacity of an ideal mixture is a linear combination of the pure-component heat capacities, where the weighting coefficients come from \( \chi \) and \( z \), much like the case with \( V, E \), and \( H \) in eqs 22–24. All other thermodynamic derivatives of a general multiphase, multicomponent mixture, such as the isobaric thermal-expansion coefficient \( (1/V) \partial V / \partial T \)\( \delta P \) \( \delta \chi \), and the Grüneisen parameter \( \Gamma = -V \partial (\partial V / \partial T)_{\delta P \delta \chi} / \partial T_{\delta P \delta \chi} \) may be derived in the same manner as that illustrated above.

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