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# Calculation of open and closed system elastic coefficients for multicomponent solids

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## Abstract

Thermodynamic equilibrium in multicomponent solids subject to mechanical stresses is a complex nonlinear problem whose exact solution requires extensive computations. A few decades ago, Larché and Cahn proposed a linearized solution of the mechanochemical equilibrium problem by introducing the concept of open system elastic coefficients [Acta Metall. **21**, 1051 (1973)]. Using the Ni-Al solid solution as a model system, we demonstrate that open system elastic coefficients can be readily computed by semi-grand canonical Monte Carlo simulations in conjunction with the shape fluctuation approach. Such coefficients can be derived from a single simulation run, together with other thermodynamic properties needed for prediction of compositional fields in solid solutions containing defects. The proposed calculation approach enables streamlined solutions of mechanochemical equilibrium problems in complex alloys. Second order corrections to the linear theory are extended to multicomponent systems.

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## I. INTRODUCTION

Many phase transformations in solid materials are accompanied by significant changes in shapes and volumes of phases, producing large elastic stresses. Such stresses, in turn, can alter thermodynamic properties of the phases and affect their equilibrium chemical compositions and ultimately the structure of the material. Prediction of structures and chemical compositions of coexisting phases is a complex, nonlinear mechanochemical problem that has been discussed by several authors over the recent years.<sup>1,2</sup> Even in a single-phase solid solution, crystalline defects can create elastic strain fields that cause redistribution of chemical components and lead to the formation of solute atmospheres on dislocations,<sup>3</sup> stacking faults (Suzuki segregation)<sup>3</sup> and other defects. Such atmospheres can cause solute drag and pinning effects that drastically alter mechanical and physical properties of the material.

In a series of papers, Larché and Cahn<sup>1,4-6</sup> developed a rigorous thermodynamic theory of mechanical and chemical equilibrium in and between solid phases by generalizing Gibbs' approach<sup>7</sup> that had been primarily focused on fluid systems. Their work resulted in formulation of thermodynamic equilibrium conditions for heterogeneous solid systems, including internal equilibrium in phases containing multiple sources of elastic stress. Although their equations can, in principle, be solved knowing certain material properties as input, solutions have only been obtained for a few simple cases.<sup>1</sup>

Larché and Cahn<sup>1,4,5</sup> also proposed an approach to obtaining approximate solutions of their equations by linearizing them under the assumption of relatively small stresses and compositional variations in the material. This allowed them to decouple the equations into (i) a linear elasticity problem to find the stress field, and (ii) a chemical equilibrium problem in a known stress field. The key to decoupling the equations was the introduction of the concept of open system elastic coefficients (compliances and stiffnesses), which are different from the ordinary, closed system elastic coefficients. Knowledge of open system elastic coefficients enables theoretical prediction of compositional and stress fields (e.g., around crystalline defects) by solving two relatively simple, or at least familiar, problems.

Unfortunately, open system elastic coefficients are difficult to measure experimentally. A number of methods exist for measuring elastic moduli of alloys, ranging from traditional tensile tests, to nano-indentation experiments, to the resonant ultrasound spectroscopy (RUS).<sup>8</sup> The RUS method can now be applied for elastic constant measurements at high temperatures.<sup>9-11</sup> All such measurements, however, are conducted on samples with a fixed chemical composition and thus deliver normal, closed-system elastic coefficients. To our knowledge, measurements in which the material would be allowed to adjust the chemical composition during the deformation process under fixed chemical potentials have not been done and would be extremely difficult to implement.

In this paper we demonstrate the possibility of computational prediction of open system elastic coefficients by atomistic simulations. To set the stage, we start by reviewing the

mechanochemical problem and its linearized solution for the case of multicomponent alloys (Sec. II). We also derive second order corrections to the linear theory for both the elasticity problem and the compositional field. In Sec. III we present the results of Monte Carlo calculations of both open and closed system elastic constants of Ni-Al alloys modeled with an embedded-atom potential. It is shown that the shape fluctuation approach can generate accurate results at a reasonable computational cost. These results demonstrate the feasibility of high throughput calculations of open system elastic coefficients for binary as well as multicomponent alloys, opening the possibility of quantitative predictions of solute atmospheres and other forms of chemical heterogeneity in alloys. In Sec. IV we summarize the results and outline future work.

## II. EQUILIBRIUM IN MECHANICALLY STRESSED SOLID SOLUTIONS

### A. Equilibrium conditions

As a base model, we consider a solid solution without vacancies. Suppose the solution contains  $N_s$  mobile substitutional components and  $N_i$  mobile interstitial components. Some of the substitutional components are allowed to be immobile. Such components are assumed to have a uniform spatial distribution and their concentrations are not considered as variables of the model. Lattice sites cannot be created or destroyed. The local chemical composition of the solution is characterized by the numbers of mobile substitutional atoms ( $c_2, \dots, c_{N_s}$ ) and numbers of interstitial atoms ( $\tilde{c}_1, \dots, \tilde{c}_{N_i}$ ) per lattice site. Note that  $c_1$  has been eliminated by the constraint that the concentrations of all (mobile and immobile) substitutional components must sum to unity. The interstitial concentrations are not subject to this constraint.

The solution may contain defects, such as dislocations, that give rise to elastic strain fields and chemical inhomogeneity in some regions. Elastic deformations of the solution are treated in the approximation of linear elasticity with small strains. As a reference state for the elastic strain  $\varepsilon_{ij}$  we take the stress-free solution with a given chemical composition ( $c_2^0, \dots, c_{N_s}^0, \tilde{c}_1^0, \dots, \tilde{c}_{N_i}^0$ ) at a given temperature  $T$ . This state usually represents perfect lattice regions far away from the defects.

Thermodynamic properties of the solution are described by the equation of state

$$f = f(T, \varepsilon_{ij}, c_2, \dots, c_{N_s}, \tilde{c}_1, \dots, \tilde{c}_{N_i}), \quad (1)$$

$f$  being the Helmholtz free energy per lattice site. The differential form of this equation is

$$df = -sdT + \omega\sigma_{ij}d\varepsilon_{ij} + M_pdc_p + \mu_qd\tilde{c}_q. \quad (2)$$

Here,  $s$  is the entropy per site,  $\omega$  is volume per site in the reference state,  $\sigma_{ij}$  is the stress tensor,  $M_p$  is the diffusion potential<sup>1,4,5</sup> of substitutional component  $p$  relative to component

1, and  $\mu_q$  is the chemical potential of interstitial component  $q$ . Here and everywhere below, the stress and strain tensors are represented by Cartesian coordinates relative to a chosen laboratory system. The summation convention is adopted for repeated indices with respect to both Cartesian coordinates and the compositional variables.

The reason for treating the substitutional components differently from interstitial is that the former are subject to the network constraint<sup>1,4,5</sup>: to add an extra atom of a substitutional component  $p$  we must remove an atom of some other substitutional component  $p'$ . The accompanying change in the free energy (with other variables fixed) defines the diffusion potential  $M_{pp'}$  of  $p$  with respect to  $p'$ . Individual chemical potentials of substitutional components remain undefined. The solution is characterized by  $(N_s - 1)$  diffusion potentials, which in this work are taken with respect to the substitutional component 1 and denoted  $M_p \equiv M_{p1}$ . For interstitial components, there is no network constraint and they can be added or removed independently of each other. Hence, their chemical potentials  $\mu_q$  are well-defined quantities.

To simplify the exposition, we will denote all concentrations, both substitutional and interstitial, by the same symbol  $c_p$ ,  $p = 2, \dots, N$ , where  $N = N_s + N_i$  is the total number of mobile components. Likewise, the diffusion potentials of the substitutional components and chemical potentials of the interstitial components will be denoted by the same symbol  $M_p$  ( $p = 2, \dots, N$ ). Equation (2) can now be rewritten as

$$df = -sdT + \omega\sigma_{ij}d\varepsilon_{ij} + M_p dc_p. \quad (3)$$

If the solution is thermodynamically stable\* with respect to compositional fluctuations, then the symmetrical  $(N - 1) \times (N - 1)$  matrix

$$\left\{ \frac{\partial M_p}{\partial c_q} \right\}_{p,q=2,\dots,N} \quad (4)$$

must be positive definite. Indeed, for a small homogeneous region of the solution containing  $n$  sites and surrounded by much larger volumes, consider a fluctuation in which the region exchanges atoms with the surroundings at a fixed temperature and strain. If  $\delta f$  is the free energy change (per site) in the region, then the free energy change of the entire system is

$$n\delta f - nM_p\delta c_p \quad (\text{fixed } T, \varepsilon_{ij}), \quad (5)$$

where the second term is the free energy change of the environment. For stable equilibrium this change must be positive for all compositional variations  $\delta c_p$ . Expanding  $\delta f$  up to

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\* In this paper, the stability of the solid solution is understood as intrinsic stability, i.e., stability with respect to small perturbations of thermodynamic variables. Stability with respect to alternate phases is beyond the scope of the paper. Thus the theory discussed here can be applied to metastable solid solutions inside the miscibility gap, as long as the solution is not too close to spinodal lines or critical states.

quadratic terms in the compositional variables and considering that  $\partial f/\partial c_p = M_p$  we obtain

$$\frac{\partial M_p}{\partial c_q} \delta c_p \delta c_q > 0. \quad (6)$$

It follows that the matrix  $\partial M_p/\partial c_q$  must be positive definite.

It is convenient to transform the problem to the new variable set  $(T, \sigma_{ij}, c_2, \dots, c_N)$ . This is achieved by the Legendre transformation

$$d(f - \omega \sigma_{ij} \varepsilon_{ij}) = -s dT - \omega \varepsilon_{ij} d\sigma_{ij} + M_p d c_p, \quad (7)$$

from which we obtain the set of Maxwell relations

$$\frac{\partial M_p}{\partial \sigma_{ij}} = -\omega \frac{\partial \varepsilon_{ij}}{\partial c_p}. \quad (8)$$

These relations are used to calculate the diffusion and chemical potentials in the solution by thermodynamic integration. A given state of the solution can be thought of as obtained from the reference state by first changing the chemical composition from  $(c_2^0, \dots, c_N^0)$  to  $(c_2, \dots, c_N)$  at zero stress and a fixed temperature  $T$  followed by elastic deformation at a fixed chemical composition and the same temperature. Accordingly,

$$\begin{aligned} M_p(T, \sigma_{ij}, c_2, \dots, c_N) &= M_p(T, 0, c_2, \dots, c_N) + \int_0^{\sigma_{ij}} \frac{\partial M_p}{\partial \sigma_{ij}} d\sigma_{ij} \\ &= M_p(T, 0, c_2, \dots, c_N) - \omega \int_0^{\sigma_{ij}} \frac{\partial \varepsilon_{ij}}{\partial c_p} d\sigma_{ij}, \end{aligned} \quad (9)$$

where we utilized Eq.(8). In the small-strain approximation, the total strain is

$$\varepsilon_{ij}(T, \sigma_{ij}, c_2, \dots, c_N) = \varepsilon_{ij}^c(T, c_2, \dots, c_N) + S_{ijkl}(T, c_2, \dots, c_N) \sigma_{kl}, \quad (10)$$

where  $\varepsilon_{ij}^c$  is the compositional (stress-free) strain<sup>1,4,5</sup> and  $S_{ijkl}$  is the rank four tensor of closed-system elastic compliances. Thus

$$\frac{\partial \varepsilon_{ij}}{\partial c_p} = \frac{\partial \varepsilon_{ij}^c}{\partial c_p} + \frac{\partial S_{ijkl}}{\partial c_p} \sigma_{kl}. \quad (11)$$

Inserting this equation in Eq.(9) and performing the integration we obtain

$$M_p(T, \sigma_{ij}, c_2, \dots, c_N) = M_p(T, 0, c_2, \dots, c_N) - \omega \frac{\partial \varepsilon_{ij}^c}{\partial c_p} \sigma_{ij} - \frac{1}{2} \omega \frac{\partial S_{ijkl}}{\partial c_p} \sigma_{ij} \sigma_{kl}. \quad (12)$$

In thermodynamic equilibrium,  $M_p$  must be uniform across the system and equal to their reference values<sup>1,4,5</sup>. This gives the following mechanochemical equilibrium condition in a non-uniform solid solution:

$$M_p(T, 0, c_2, \dots, c_N) - M_p(T, 0, c_2^0, \dots, c_N^0) = \omega \frac{\partial \varepsilon_{ij}^c}{\partial c_p} \sigma_{ij} + \frac{1}{2} \omega \frac{\partial S_{ijkl}}{\partial c_p} \sigma_{ij} \sigma_{kl}. \quad (13)$$

Equations (10) and (13) constitute the conditions of mechanical and chemical equilibrium in the stressed solid solutions. This is a complex non-linear problem that for most systems requires rather extensive computations.

## B. Linear approximation

We will now linearize the problem by making the following approximations.<sup>1,4,5</sup> In Eq.(10), we replace the elastic compliance tensor (which generally depends on chemical composition) by its value  $S_{ijkl}^0$  in the reference state. Further, the compositional strain  $\varepsilon_{ij}^c$  is approximated by an isothermal linear expansion around the reference state. The total strain becomes

$$\varepsilon_{ij} = \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \Delta c_q + S_{ijkl}^0 \sigma_{kl}, \quad (14)$$

where  $\Delta c_q \equiv (c_q - c_q^0)$ ,  $q = 2, \dots, N$ . Here and everywhere below, the subscript 0 indicates that the derivatives are evaluated in the reference state. We also took into account that the reference value of  $\varepsilon_{ij}^c$  is zero by definition. Next, in right-hand side of Eq.(13) we drop the last term quadratic in stress and replace  $(\partial \varepsilon_{ij}^c / \partial c_p)$  by its value in the reference state. In the left-hand side, we approximate the stress-free diffusion and chemical potentials by linear expansions around the reference state. As a result, the linearized equilibrium condition (13) becomes

$$\left( \frac{\partial M_p}{\partial c_q} \right)_0 \Delta c_q = \omega \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_p} \right)_0 \sigma_{ij}. \quad (15)$$

We can now eliminate  $\Delta c_q$  from Eqs.(14) and (15). To this end, we solve Eq.(15) for  $\Delta c_q$ :

$$\Delta c_q = \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \sigma_{kl}, \quad (16)$$

where  $(\partial M_p / \partial c_q)_0^{-1}$  the inverse of the matrix  $\partial M_p / \partial c_q$  evaluated in the reference state. Inserting this  $\Delta c_q$  in Eq.(14) we finally obtain

$$\varepsilon_{ij} = S_{ijkl}^* \sigma_{kl}, \quad (17)$$

where

$$S_{ijkl}^* \equiv S_{ijkl}^0 + \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \quad (18)$$

is the the tensor of open-system compliances.<sup>1</sup>

Since the inverse of a positive definite symmetric matrix is also positive definite,<sup>†</sup>  $(\partial M_p / \partial c_q)_0^{-1}$  is positive definite and all components of the second term in Eq.(18) are non-negative provided that the solid solution is thermodynamically stable. Thus, all components of the open-system compliance tensor  $S_{ijkl}^*$  are larger or equal to the respective components of the ordinary, closed-system compliance tensor  $S_{ijkl}^0$ . The second term in Eq.(18) originates from changes in compositional strain in response to the applied stress by

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<sup>†</sup> Outline of the proof: all eigenvalues  $\lambda$  of a symmetric positive definite matrix  $\mathbf{A}$  are positive. The inverse matrix  $\mathbf{A}^{-1}$  exists, is symmetric and has eigenvalues  $1/\lambda$ , which are therefore also positive. Thus  $\mathbf{A}^{-1}$  is also positive definite.

exchanging atoms with the environment. Due to this additional contribution to the total strain, an open system behaves as more elastically compliant than a closed system.

The linearization described above separates the elasticity and compositional field problems. Equation (17) is Hooke's law with composition-independent elastic compliances  $S_{ijkl}^*$ , from which the stress field can be found by solving the standard linear elasticity problem. Often, existing solutions can be utilized by simply replacing  $S_{ijkl}^0$  by  $S_{ijkl}^*$ . Once the stress-field is known, the compositional field immediately follows from Eq.(16). In this approximation, all local deviations from the reference chemical composition are linear in stress.

### C. Second order approximation

It is possible to improve on the linear approximation by adding second order corrections. Such corrections were derived by Larché and Cahn<sup>6</sup> for binary alloys and are generalized to multi-component solid solutions in Appendix A. The open-system compliance tensor becomes

$$S_{ijkl}^* = S_{ijkl}^0 + \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 + \Lambda_{ijklmn} \sigma_{mn}, \quad (19)$$

where the second order correction is represented by the tensor  $\Lambda_{ijklmn}$  which depends only on the reference composition and temperature. The effects captured by this tensor include the stress and composition dependencies of  $S_{ijkl}^0$  and the second derivatives  $\partial^2 M_p / \partial c_q \partial c_r$  and  $\partial^2 \varepsilon_{ij}^c / \partial c_p \partial c_q$ . Likewise, the compositional field is given by

$$\Delta c_q = \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \sigma_{kl} + K_{klmn} \sigma_{kl} \sigma_{mn}, \quad (20)$$

where the tensor  $K_{ijklmn}$  represents the same second order effects and also depends only on the reference composition and temperature. Thus, the elasticity problem becomes nonlinear, with elastic coefficients being linear functions of stress. The compositional field becomes a quadratic function of the stress field.

Expressions for the tensors  $\Lambda_{ijklmn}$  and  $K_{klmn}$  are given in the Appendix A. Inspection shows that all ingredients of these tensors can be readily obtained from experimental data or atomistic simulations. The main difficulty in applying the above equations is in solving the non-linear elasticity problem with stress-dependent elastic coefficients. The luxury of re-using existing linear-elasticity solutions is now lost. But once the stress field is found, calculation of the compositional field from Eq.(20) is straightforward.



### III. CALCULATION OF ELASTIC COEFFICIENTS FOR ALLOYS

#### A. The isotropic approximation

In most alloys, the compositional strain can be treated as fully isotropic. In the isotropic approximation,

$$\left(\frac{\partial \varepsilon_{ij}^c}{\partial c_q}\right)_0 = \alpha_p \delta_{ij}, \quad (21)$$

where  $\delta_{ij}$  is Kronecker's delta-symbol and  $\alpha_p$  are functions of the reference (but not local) composition. Equation (18) becomes

$$S_{ijkl}^* \equiv S_{ijkl}^0 + \omega \left(\frac{\partial M_p}{\partial c_q}\right)_0^{-1} \alpha_p \alpha_q \delta_{ij} \delta_{kl}. \quad (22)$$

Note that

$$\lambda \equiv \omega \left(\frac{\partial M_p}{\partial c_q}\right)_0^{-1} \alpha_p \alpha_q \quad (23)$$

is composition-independent. Using two-index notations for elastic compliances<sup>12</sup> we have

$$S_{ij}^* = S_{ij} + \lambda, \quad i, j = 1, 2, 3; \quad (24)$$

$$S_{ij}^* = S_{ij}, \quad i \text{ and/or } j > 3. \quad (25)$$

Thus, the components  $S_{ij}^*$  ( $i, j = 1, 2, 3$ ) are shifted relative to the respective closed system components by the same amount  $\lambda$ , whereas the remaining components are unchanged. This property could be derived from crystal symmetry considerations.<sup>1,4-6</sup>

For a binary substitutional solution we recover the known result<sup>1,4,5</sup>

$$\lambda = \omega \alpha^2 \left(\frac{\partial M}{\partial c}\right)_0^{-1}, \quad (26)$$

where  $\alpha = (\partial \varepsilon^c / \partial c)_0$  is the compositional derivative of  $\varepsilon^c$  in the reference state,  $c$  is the atomic fraction of the solute and  $M$  its diffusion potential relative to the solvent. The compositional field is given by

$$\Delta c = -3\omega \alpha \left(\frac{\partial M}{\partial c}\right)_0^{-1} p, \quad (27)$$

where  $p = -\sigma_{kk}/3$  is the negative of the local hydrostatic stress ("solid pressure").

For a ternary substitutional solution,

$$\lambda = \omega \frac{\left(\frac{\partial M_2}{\partial c_2}\right)_0 \alpha_3^2 + \left(\frac{\partial M_3}{\partial c_3}\right)_0 \alpha_2^2 - 2 \left(\frac{\partial M_2}{\partial c_3}\right)_0 \alpha_2 \alpha_3}{\left(\frac{\partial M_2}{\partial c_2}\right)_0 \left(\frac{\partial M_3}{\partial c_3}\right)_0 - \left(\frac{\partial M_2}{\partial c_3}\right)_0^2}, \quad (28)$$

where  $\alpha_2 = (\partial \varepsilon^c / \partial c_2)_0$  and  $\alpha_3 = (\partial \varepsilon^c / \partial c_3)_0$ . The compositional fields of the solutes 2 and 3 can be found from

$$\Delta c_2 = -3\omega \frac{\left(\frac{\partial M_2}{\partial c_2}\right)_0 \alpha_2 + \left(\frac{\partial M_3}{\partial c_2}\right)_0 \alpha_3}{\left(\frac{\partial M_2}{\partial c_2}\right)_0 \left(\frac{\partial M_3}{\partial c_3}\right)_0 - \left(\frac{\partial M_2}{\partial c_3}\right)_0^2} p, \quad (29)$$

$$\Delta c_3 = -3\omega \frac{\left(\frac{\partial M_2}{\partial c_3}\right)_0 \alpha_2 + \left(\frac{\partial M_3}{\partial c_3}\right)_0 \alpha_3}{\left(\frac{\partial M_2}{\partial c_2}\right)_0 \left(\frac{\partial M_3}{\partial c_3}\right)_0 - \left(\frac{\partial M_2}{\partial c_3}\right)_0^2} p. \quad (30)$$

## B. Atomistic calculations

Two atomistic approaches exist for calculations of elastic properties of solids at finite temperatures.<sup>13</sup> In the finite-strain method, stress is computed for a series of fixed strains followed by a linear fit through zero. This requires a series of simulation runs to obtain each elastic coefficients. Fluctuation methods analyze statistical correlations between components of the stress and/or strain tensors fluctuating around equilibrium.<sup>14–19</sup> The advantage of the latter approach is that all elastic coefficients can be extracted from a *single* simulation run. However, the results are subject to significant statistical errors and long simulations are required for achieving a good accuracy. For single-component solids, both types of calculations can employ either molecular dynamics<sup>13–16,18,19</sup> or Monte Carlo methods.<sup>17</sup> For alloys, molecular dynamics cannot sample the configurational degrees of freedom associated with permutations of atomic species. Thus Monte Carlo remains the only feasible approach.

In this paper, a Monte Carlo fluctuation method was applied to Ni-Al alloys with atomic interactions described with an embedded-atom potential.<sup>20</sup> This potential accurately captures thermodynamic properties of the Ni-Al system, and in particular reproduces the Ni-rich part of the Ni-Al phase diagram in reasonable agreement with experiment. It also predicts the elastic constants of Ni, Al and the Ni<sub>3</sub>Al compound in close agreement with experimental data.

The simulated system was a periodic block of face centered cubic structure containing  $N_a = 2034$  atoms with approximately cubic dimensions. The lattice had the following crystallographic orientation with respect to the block edges:  $x_1$ : [001],  $x_2$ : [110],  $x_3$ :  $[\bar{1}10]$ . Semi-grand canonical Monte Carlo simulations<sup>13</sup> were implemented at the temperature of 700 K for a set of diffusion potentials  $M$  of Al with respect to Ni. In such simulations,  $T$  and  $M$  remain fixed while the system dimensions and chemical composition can vary. These simulations model an open system and can be used for direct calculations of open-system elastic properties.

The trial moves of the Monte Carlo process included displacements of randomly selected atoms by a random amount (not exceeding 0.01 nm) in a random direction with simultaneous random re-assignment of the chemical species of the chosen atom to either Ni or Al.  $N_a$  trial moves constitute one Monte Carlo step (or sweep). After each Monte Carlo step, the dimensions of the simulation block in the  $x_1$ ,  $x_2$  and  $x_3$  directions were changed independently by random amounts with corresponding re-scaling of atomic coordinates. The fluctuations of the system dimensions ensured zero values of the normal stresses  $\sigma_{11}$ ,  $\sigma_{22}$  and  $\sigma_{33}$ . Because the block remained rectangular, shear deformations of the system were not implemented.

The trial moves were accepted or rejected by the Metropolis algorithm.<sup>13</sup> Namely, a move was accepted with the probability of  $\exp(-\Phi/k_B T)$  if  $\Phi > 0$  and unconditionally if  $\Phi \leq 0$ , where<sup>21–23</sup>

$$\Phi \equiv \Delta E \pm M \pm \frac{3}{2} k_B T \ln \frac{m_{\text{Ni}}}{m_{\text{Al}}}. \quad (31)$$

Here,  $k_B$  is Boltzmann's factor,  $m_{\text{Ni}}$  and  $m_{\text{Al}}$  are atomic masses, and  $\Delta E$  is the total energy change resulting from the move. The positive sign applies when Ni is replaced by Al and negative when Al is replaced by Ni. The mass term comes from integration of the state probability over linear momenta of atoms, giving a pre-exponential factor proportional to the product of masses of all atoms to the power of 3/2. In the probability ratio of two configurations, all masses cancel out except for the masses of the atom whose species changes, producing a pre-exponential factor of either  $(m_{\text{Ni}}/m_{\text{Al}})^{3/2}$  or  $(m_{\text{Al}}/m_{\text{Ni}})^{3/2}$ .

For each value of  $M$ , the simulation started with pure Ni and continued until an equilibrium state was reached in which all parameters randomly fluctuated around constant average values. The latter was confirmed by computing the non-Gaussian parameters of statistical distributions. Equilibration usually required about  $2 \times 10^4$  Monte Carlo steps. Once equilibrium was reached, a production run was conducted comprising about  $10^6$  Monte Carlo steps. At each Monte Carlo step, the program recorded the current system dimensions  $L_1$ ,  $L_2$  and  $L_3$ , the chemical composition  $c$  (atomic fraction of Al) and other parameters. At the post-processing stage, the system dimensions were converted to fluctuating strains  $\varepsilon_{ii} = (L_i - \bar{L}_i)/\bar{L}_i$ , with the bar denoting the ensemble average.

It can be readily shown<sup>14</sup> that elastic compliances of the system are proportional to the covariances  $\overline{\varepsilon_{ii}\varepsilon_{jj}}$ :

$$\tilde{S}_{ij}^* = \frac{\bar{V}}{k_B T} \overline{\varepsilon_{ii}\varepsilon_{jj}}, \quad i, j = 1, 2, 3, \quad (32)$$

$\bar{V}$  being the average volume of the system. The asterisk indicates that these compliances are open-system type and the tilde is a reminder that they are computed for the chosen lattice orientation and are generally different from those in cubic axes. The  $3 \times 3$  matrix of elastic compliances obtained from the simulations was inverted to obtain the matrix of open-system elastic constants  $\tilde{c}_{ij}^*$  ( $i, j = 1, 2, 3$ ).

Due to the tetragonal symmetry of the system, the full  $6 \times 6$  matrix of elastic constants has the structure<sup>12</sup>

$$\tilde{c}_{ij}^* = \begin{pmatrix} \tilde{c}_{11}^* & \tilde{c}_{12}^* & \tilde{c}_{12}^* & 0 & 0 & 0 \\ \tilde{c}_{12}^* & \tilde{c}_{22}^* & \tilde{c}_{23}^* & 0 & 0 & 0 \\ \tilde{c}_{12}^* & \tilde{c}_{23}^* & \tilde{c}_{22}^* & 0 & 0 & 0 \\ 0 & 0 & 0 & \tilde{c}_{44}^* & 0 & 0 \\ 0 & 0 & 0 & 0 & \tilde{c}_{44}^* & 0 \\ 0 & 0 & 0 & 0 & 0 & \tilde{c}_{44}^* \end{pmatrix} \quad (33)$$

with five distinct elements  $\tilde{c}_{11}^*$ ,  $\tilde{c}_{22}^*$ ,  $\tilde{c}_{12}^*$ ,  $\tilde{c}_{23}^*$  and  $\tilde{c}_{44}^*$ . The present simulations recover only the upper  $3 \times 3$  block of this matrix. Furthermore, due to statistical errors, the element which were supposed to be identical by symmetry were actually slightly different, usually within  $< 1$  GPa. To restore the symmetry, such elements were replaced by their average values. For example, the slightly different  $\tilde{c}_{22}^*$  and  $\tilde{c}_{33}^*$  were assigned the same value  $(\tilde{c}_{22}^* + \tilde{c}_{33}^*)/2$ .

Finally, by rotating the axes to the cubic coordinate system we obtain the following equations for the cubic elastic constants (no tilde):

$$c_{11}^* = \tilde{c}_{11}^*, \quad c_{12}^* = \tilde{c}_{12}^*; \quad (34)$$

$$c_{44}^* = \tilde{c}_{22}^* - (\tilde{c}_{11}^* + \tilde{c}_{12}^*)/2, \quad (35)$$

$$c_{44}^* = (\tilde{c}_{11}^* + \tilde{c}_{12}^*)/2 - \tilde{c}_{23}^*. \quad (36)$$

Again, due to statistical errors, Eqs.(35) and (36) gave slightly different values of  $c_{44}^*$ , typically within  $< 1$  GPa. This provided a useful check of validity of our calculation procedure and an estimate of accuracy of the obtained elastic constants ( $\sim 1$  GPa).

The calculations were performed for a set of  $M$  values creating Al concentrations within the solubility limit at 700 K (13.9 at.% Al with this interatomic potential). An additional data point was obtained for pure Ni by implementing a canonical simulation (no switching of atomic identities). The open-system elastic constants thus obtained are plotted against the chemical composition in Fig. 1. For  $c_{11}^*$  and  $c_{12}^*$ , significant non-linearity is observed due to the thermodynamic term  $\lambda$ .

To evaluate the statistical error bar of the elastic constants, simulations at one of the compositions (5.43 at.%Al,  $M = -0.73$  eV) were repeated 6 times. The standard deviations of these results were found to be 0.59, 0.56 and 0.26 GPa for  $c_{11}^*$ ,  $c_{12}^*$  and  $c_{12}^*$ , respectively. Based on these numbers we estimate the error bar at  $\pm 1$  GPa (approximately two standard deviations).

Knowing  $c_{ij}^*$ , the closed-system elastic constants  $c_{ij}$  were back-calculated from Eqs.(24) and (25). From the simulations, we know the diffusion potential and the cubic lattice parameter  $a$  as functions of composition. These are plotted in Figures 2 and 3, respectively, where  $a$  was converted to the compositional strain  $(a - a_0)/a_0$  relative to pure Ni. The derivatives of these functions were computed using a cubic spline interpolation to obtain

the required ingredients of  $\lambda$ :  $(\partial M/\partial c)$  and  $\alpha = (\partial a/\partial c)/a$ . Knowing  $\lambda$  from Eq.(26),  $S_{ij}$  we found from Eqs.(24) and (25) and inverted to  $c_{ij}$ . Fig. 1 shows that the composition dependencies of  $c_{11}$  and  $c_{12}$  are much weaker and more linear than their open-system counterparts. This justifies neglecting the term with  $\partial S_{ijkl}/\partial c_p$  in Eq.(13) during the linearization of the problem.

For additional validation of the results, several simulation runs were performed in the canonical ensemble, in which the trial Monte Carlo moves included random atomic displacements, shape fluctuations, and swaps of randomly selected pairs of atoms. This ensemble simulates a closed system similar to experimental samples. All other simulation conditions were the same, including the lengths of the equilibration and production runs. The closed system elastic constants obtained are shown in Fig. 1 by the star markers, demonstrating close agreement with the back-calculation results from the open system simulations. It should be noted that closed system simulations involving atomic swaps are computationally slow and, by contrast to the semi-grand canonical ensemble, do not readily lend themselves to efficient parallelization. If closed system elastic coefficients are needed for some applications, it is easier to recover them from open system simulations.

#### IV. DISCUSSION AND CONCLUSIONS

We have presented a simple derivation of the linearized solution of the mechanochemical problem for multicomponent alloys<sup>1,4-6</sup> in a form suitable for computational implementation. In addition, the second order corrections to the linear proposed<sup>6</sup> for binary alloys have been extended to multi-component solid solutions. In the computational part of the work, we have performed Monte Carlo calculations of both open and closed system elastic constants of a model system (Ni-Al alloys). In these calculations, the open system elastic coefficients were extracted directly from the simulation data, whereas the closed system elastic coefficients are calculated two ways: (i) using the open system coefficients and the thermodynamic term predicted by the linear theory, and (ii) directly by closed system Monte Carlo simulations. The agreement between the two calculations found in this work (Fig. 1) confirms the correctness of the linear theory and the accuracy of our simulation methodology.

Calculation of one point in Fig. 1 (one alloy composition) required a 40 hour simulation run on 8 CPUs of a medium grade compute cluster. Given 160 CPUs, the entire dataset shown in Fig. 1 could have been generated in 40 hours. [In reality, the present calculations took much longer due to numerous exploratory runs, convergences tests and error evaluation.] Considering the rapid growth of computer speeds, high throughput calculations are possible, or may soon becomes possible, for open and closed system elastic coefficients of alloys as functions of temperature and chemical composition. For complex crystalline structures with more than six distinct elastic constants, simulations with two or

more crystal orientations will be needed, which will obviously increase the computational cost. The proposed procedure for extracting the elastic coefficients from the shape fluctuation covariances  $\overline{\varepsilon_{ii}\varepsilon_{jj}}$  can be readily extended to more complex structures along the same line as in Sec. III B. Furthermore, as a “side product”, such simulations generate data for lattice parameters and diffusion potentials (for interstitial alloys, chemical potentials) as functions of temperature and chemical composition. These data also constitute valuable information. For example,  $M(T, c)$  can be integrated to obtain the stress-free Helmholtz free energy  $f(T, c)$ . Knowing one reference value of this function each phase, solid-solid coexistence lines on the phase diagram can be calculated.

It should be reminded that the calculations discussed here utilize an atomistic potential for the system in question. The reliability of results depends on the accuracy of the potential. Once the simulations become a routine, it will be the progress in the development of high quality potentials that will become the bottleneck. But this is true for the entire field of atomistic simulations.<sup>24,25</sup>

Once the open system elastic coefficients are known, the stress field can be computed by solving a linear elasticity problem (or borrowing a known solution). Having the stress field, the compositional field is immediately obtained from the linear relation (16). An example was given by Larché and Cahn<sup>1</sup> for solute atmospheres on dislocations: the stress field is obtained by merely replacing the ordinary elastic constants by open system ones in the well-known solution,<sup>3</sup> which results in a simple expression for solute distribution around the dislocation. It should be emphasized that, although this calculation relies on linearization of the general mechanochemical problem, it does *not* use require any particular thermodynamic model of the solid solution, such as an ideal or regular solution model. Both elastic and chemical interactions between the atoms are fully included in the calculation, as was the case in the present simulations for Ni-Al alloys.

Future work may explore possible improvements over the linear theory that can be implemented in computations. At present, two nonlinear approaches can be found in the literature. One is the addition of second order corrections to the elasticity and compositional field equations,<sup>1,6</sup> see Sec. II C and Appendix A. This is equivalent to making one iteration in solving the exact problem. This approach can be applied recursively to make further improvements, producing an expansion of the form

$$S_{ijkl}^* = S_{ijkl}^0 + \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 + \Lambda_{ijklmn} \sigma_{mn} + L_{ijklmnab} \sigma_{mn} \sigma_{ab} + \dots \quad (37)$$

The coefficients of this expansion depend on the lattice parameter and diffusion/chemical potentials as functions of composition, which are automatically computed during the Monte Carlo simulations described here. The real challenge is in solving the nonlinear elasticity equations that arise from the high order corrections.

The second approach is to compute linearized open system elastic coefficients, solve the *linear* elasticity problem with these coefficients, plug the stress field in the exact (nonlinear)

equilibrium equation (13), and then solve it for the compositional field. For example, adopting an ideal solution model for a binary alloy, the compositional field obtained from Eq.(13) is

$$\frac{c(1-c_0)}{c_0(1-c)} = \exp \left[ -\frac{\omega}{k_B T} \left( \frac{\partial \varepsilon_{ij}}{\partial c} \right)_0 \sigma_{ij} \right], \quad (38)$$

which is nonlinear in stress. For a dilute solution, the left-hand side becomes simply  $c/c_0$ . Assuming isotropic compositional strain  $\alpha$ , Eq.(38) simplifies even further:

$$\frac{c}{c_0} = \exp \left[ \frac{3\alpha\omega p}{k_B T} \right]. \quad (39)$$

This equation was used by Cahn in a recent discussion of thermodynamic aspects of dislocation atmospheres.<sup>26</sup> Although Eq.(39) may look like the well-known textbook equation,<sup>3</sup> in Cahn's work<sup>26</sup>  $p$  is understood as local pressure computed with open system elastic constants. This approach has a heuristic character and does not suggest a systematic way of making further improvements. How much it improves the accuracy over the linear approximation can be clarified by future studies.

Finally, the Ni-Al solid solution studied here had relatively low Al concentrations and was far away from spinodal lines. As was pointed out earlier,<sup>4,6</sup> the difference between the two types of elastic coefficients becomes increasingly large near spinodal lines and critical points of mixing. Near such points, the thermodynamic factor  $\partial M/\partial c$  becomes infinitely small and the thermodynamic correction to the compliance tensor (18) diverges to infinity. In an open system, the material can become extremely adaptive (superelastic), resulting in complete screening of stress fields of defects by solute atmospheres. Investigation of atmospheric effects under such conditions is an interesting topic for future research.

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## Appendix A: Second order approximation

In this appendix we derive equations for a second order approximation to the mechanochemical equilibrium problem for a multicomponent solid solution.

We first note that the linearized open-system compliances could be obtained from the exact thermodynamic relation<sup>1,4–6</sup>

$$\left( \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right)_{T, M_2, \dots, M_N} = \left( \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right) + \omega \left( \frac{\partial M_p}{\partial c_q} \right)^{-1} \left( \frac{\partial \varepsilon_{ij}}{\partial c_q} \right) \left( \frac{\partial \varepsilon_{kl}}{\partial c_p} \right), \quad (\text{A1})$$

where all derivatives in the right-hand side are taken in our usual variable set  $(T, \sigma_{ij}, c_2, \dots, c_N)$ . This relation is readily derivable from the following differentials at fixed



$T$ :

$$dM_p = \frac{\partial M_p}{\partial c_q} dc_q + \frac{\partial M_p}{\partial \sigma_{ij}} d\sigma_{ij}, \quad (\text{A2})$$

$$d\varepsilon_{ij} = \frac{\partial \varepsilon_{ij}}{\partial c_q} dc_q + \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} d\sigma_{kl}. \quad (\text{A3})$$

Imposing the mechanochemical equilibrium condition  $dM_p = 0$  ( $p = 2, \dots, N$ ) and using the Maxwell relations (8) we can eliminate the differentials  $dc_q$  and obtain (A1). Equation (18) derived in the main text follows from Eq.(A1) by applying the latter to the reference state and identifying  $(\partial \varepsilon_{ij}/\sigma_{kl})_{T, M_2, \dots, M_N}$  and  $(\partial \varepsilon_{ij}/\sigma_{kl})_{T, c_2^0, \dots, c_N^0}$  with  $S_{ijkl}^*$  and  $S_{ijkl}^0$ , respectively.

To develop a second order approximation, we expand the right-hand side of Eq.(A1) around the reference state retaining linear terms in  $\Delta c_r$  and stress. We obtain

$$\begin{aligned} S_{ijkl}^* &= S_{ijkl}^0 + \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 + \left( \frac{\partial S_{ijkl}}{\partial c_r} \right)_0 \Delta c_r + \left( \frac{\partial S_{ijkl}}{\partial \sigma_{mn}} \right)_0 \sigma_{mn} \\ &- \omega \left( \frac{\partial M_p}{\partial c_s} \right)_0^{-1} \left( \frac{\partial^2 M_s}{\partial c_t \partial c_r} \right)_0 \left( \frac{\partial M_t}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}}{\partial c_p} \right)_0 \Delta c_r \\ &+ \omega^2 \left( \frac{\partial M_p}{\partial c_s} \right)_0^{-1} \left( \frac{\partial^2 \varepsilon_{mn}}{\partial c_s \partial c_t} \right)_0 \left( \frac{\partial M_t}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}}{\partial c_p} \right)_0 \sigma_{mn} \\ &+ \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial^2 \varepsilon_{ij}^c}{\partial c_q \partial c_r} \right)_0 \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \Delta c_r \\ &+ \omega \left( \frac{\partial S_{ijmn}}{\partial c_q} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \sigma_{mn} \\ &+ \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial^2 \varepsilon_{kl}^c}{\partial c_p \partial c_r} \right)_0 \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \Delta c_r, \\ &+ \omega \left( \frac{\partial S_{klmn}}{\partial c_p} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \sigma_{mn}, \end{aligned} \quad (\text{A4})$$

where we used the Maxwell relations (8) and the matrix identity  $d\mathbf{A}^{-1} = -\mathbf{A}^{-1} \cdot d\mathbf{A} \cdot \mathbf{A}^{-1}$ .

We now insert the linearized solution for  $\Delta c_r$  given by Eq.(16) in the right-hand side of Eq.(A4). This can be considered as a step in iterative solution of the equations. The final result is

$$S_{ijkl}^* = S_{ijkl}^0 + \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 + \Lambda_{ijklmn} \sigma_{mn}, \quad (\text{A5})$$

where the sixth-rank tensor  $\Lambda_{ijklmn}$  characterizes the strength of the stress correction to

$S_{ijkl}^*$  and is given by

$$\begin{aligned}
\Lambda_{ijklmn} = & \left( \frac{\partial S_{ijkl}}{\partial \sigma_{mn}} \right)_0 + \omega \left( \frac{\partial S_{ijkl}}{\partial c_q} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{mn}^c}{\partial c_p} \right)_0 \\
& + \omega \left( \frac{\partial S_{ijmn}}{\partial c_q} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 + \omega \left( \frac{\partial S_{klmn}}{\partial c_p} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \\
& - \omega^2 \left( \frac{\partial^2 M_s}{\partial c_t \partial c_r} \right)_0 \left( \frac{\partial M_p}{\partial c_s} \right)_0^{-1} \left( \frac{\partial M_t}{\partial c_q} \right)_0^{-1} \left( \frac{\partial M_a}{\partial c_r} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}}{\partial c_p} \right)_0 \left( \frac{\partial \varepsilon_{mn}^c}{\partial c_a} \right)_0 \\
& + \omega^2 \left( \frac{\partial^2 \varepsilon_{ij}^c}{\partial c_q \partial c_r} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial M_a}{\partial c_r} \right)_0^{-1} \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \left( \frac{\partial \varepsilon_{mn}^c}{\partial c_a} \right)_0 \\
& + \omega^2 \left( \frac{\partial^2 \varepsilon_{kl}^c}{\partial c_p \partial c_r} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial M_a}{\partial c_r} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}^c}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{mn}^c}{\partial c_a} \right)_0 \\
& + \omega^2 \left( \frac{\partial^2 \varepsilon_{mn}}{\partial c_s \partial c_t} \right)_0 \left( \frac{\partial M_p}{\partial c_s} \right)_0^{-1} \left( \frac{\partial M_t}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{ij}}{\partial c_q} \right)_0 \left( \frac{\partial \varepsilon_{kl}}{\partial c_p} \right)_0. \tag{A6}
\end{aligned}$$

This equation is similar to the one derived by Larché and Cahn<sup>6</sup> for a binary system. Here, it has been generalized to a multi-component system.

The tensor  $\Lambda_{ijklmn}$  describes second order effects: the stress and compositional derivatives of the closed-system elastic compliances and second derivatives of the diffusion/chemical potentials and compositional strain. Since all these effects are evaluated in the reference state,  $\Lambda_{ijklmn}$  is a constant. Thus the second order correction to  $S_{ijkl}^*$  is linear in stress.

Similar approximations are applied to find the compositional field. In the equilibrium condition (13), we expand all terms in a Taylor series keeping only linear and quadratic terms. The latter are defined as terms proportional to  $\Delta c_p \Delta c_q$ ,  $\Delta c_p \sigma_{kl}$  or  $\sigma_{ij} \sigma_{kl}$ . Eq.(13) becomes

$$\begin{aligned}
\left( \frac{\partial M_p}{\partial c_q} \right)_0 \Delta c_q = & \omega \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \sigma_{kl} - \frac{1}{2} \left( \frac{\partial^2 M_p}{\partial c_s \partial c_r} \right)_0 \Delta c_s \Delta c_r \\
& + \omega \left( \frac{\partial^2 \varepsilon_{mn}^c}{\partial c_p \partial c_r} \right)_0 \Delta c_r \sigma_{mn} + \frac{3}{2} \omega \left( \frac{\partial S_{klmn}}{\partial c_p} \right)_0 \sigma_{kl} \sigma_{mn}. \tag{A7}
\end{aligned}$$

As above, we insert the linearized solution for  $\Delta c_q$  in the right-hand side and solve for  $\Delta c_q$  from the left-hand side:

$$\Delta c_q = \omega \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_p} \right)_0 \sigma_{kl} + K_{klmn} \sigma_{kl} \sigma_{mn}, \tag{A8}$$

where

$$\begin{aligned}
K_{klmn} = & - \frac{1}{2} \omega^2 \left( \frac{\partial^2 M_p}{\partial c_s \partial c_r} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial M_a}{\partial c_s} \right)_0^{-1} \left( \frac{\partial M_b}{\partial c_r} \right)_0^{-1} \left( \frac{\partial \varepsilon_{mn}^c}{\partial c_a} \right)_0 \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_b} \right)_0 \\
& + \omega^2 \left( \frac{\partial^2 \varepsilon_{mn}^c}{\partial c_p \partial c_r} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1} \left( \frac{\partial M_a}{\partial c_r} \right)_0^{-1} \left( \frac{\partial \varepsilon_{kl}^c}{\partial c_a} \right)_0 \\
& + \frac{3}{2} \omega \left( \frac{\partial S_{klmn}}{\partial c_p} \right)_0 \left( \frac{\partial M_p}{\partial c_q} \right)_0^{-1}. \tag{A9}
\end{aligned}$$

The first term in Eq.(A8) recovers the linear result (16) while the second term is a second order corrections quadratic in stress.

In the particular case of a binary solution with isotropic compositional strain,

$$\begin{aligned}
S_{ijkl}^* &= S_{ijkl}^0 + \omega\alpha^2 \left( \frac{\partial M}{\partial c} \right)_0^{-1} \delta_{ij} \delta_{kl} + \left( \frac{\partial S_{ijkl}}{\partial \sigma_{mn}} \right)_0 \sigma_{mn} - 3\omega\alpha \left( \frac{\partial S_{ijkl}}{\partial c} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-1} p \\
&+ \omega\alpha \left( \frac{\partial S_{ijmn}}{\partial c} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-1} \sigma_{mn} \delta_{kl} + \omega\alpha \left( \frac{\partial S_{klmn}}{\partial c} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-1} \sigma_{mn} \delta_{ij} \\
&+ 3\omega^2\alpha^2 \left( \frac{\partial^2 M}{\partial c^2} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-3} p \delta_{ij} \delta_{kl} - 9\omega^2\alpha^2 \left( \frac{\partial \alpha}{\partial c} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-2} p \delta_{ij} \delta_{kl}, \quad (\text{A10})
\end{aligned}$$

where  $p = -\sigma_{kk}/3$ . The compositional field can be found from

$$\begin{aligned}
\Delta c &= -3\omega\alpha \left( \frac{\partial M}{\partial c} \right)_0^{-1} p - \frac{9}{2}\omega^2\alpha^2 \left( \frac{\partial^2 M}{\partial c^2} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-3} p^2 \\
&+ 9\omega^2\alpha \left( \frac{\partial \alpha}{\partial c} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-2} p^2 + \frac{3}{2}\omega \left( \frac{\partial S_{mnkl}}{\partial c} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-1} \sigma_{mn} \sigma_{kl}. \quad (\text{A11})
\end{aligned}$$

The above equations take a simpler form when the composition dependence of the thermodynamic factor  $\partial M/\partial c$  is the dominant second order effect. This was the case in the present Ni-Al simulations where the closed-system elastic constants and compositional strain are nearly linear functions of composition (see Figures 1-3). In this case,

$$S_{ijkl}^* = S_{ijkl}^0 + \omega\alpha^2 \left( \frac{\partial M}{\partial c} \right)_0^{-1} \delta_{ij} \delta_{kl} + 3\omega^2\alpha^2 \left( \frac{\partial^2 M}{\partial c^2} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-3} p \delta_{ij} \delta_{kl}. \quad (\text{A12})$$

In two-index notations,<sup>12</sup>

$$S_{ij}^* = S_{ij}^0 + \omega\alpha^2 \left( \frac{\partial M}{\partial c} \right)_0^{-1} + 3\omega^2\alpha^2 \left( \frac{\partial^2 M}{\partial c^2} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-3} p \quad (\text{A13})$$

if  $i, j = 1, 2, 3$ ; otherwise  $S_{ij}^* = S_{ij}^0$ . Thus, similar to the linear approximation, only the compliances with components  $i, j = 1, 2, 3$  are different for open and close systems; the remaining components are the same. For the compositional field we have

$$\Delta c = -3\omega\alpha \left( \frac{\partial M}{\partial c} \right)_0^{-1} p - \frac{9}{2}\omega^2\alpha^2 \left( \frac{\partial^2 M}{\partial c^2} \right)_0 \left( \frac{\partial M}{\partial c} \right)_0^{-3} p^2. \quad (\text{A14})$$

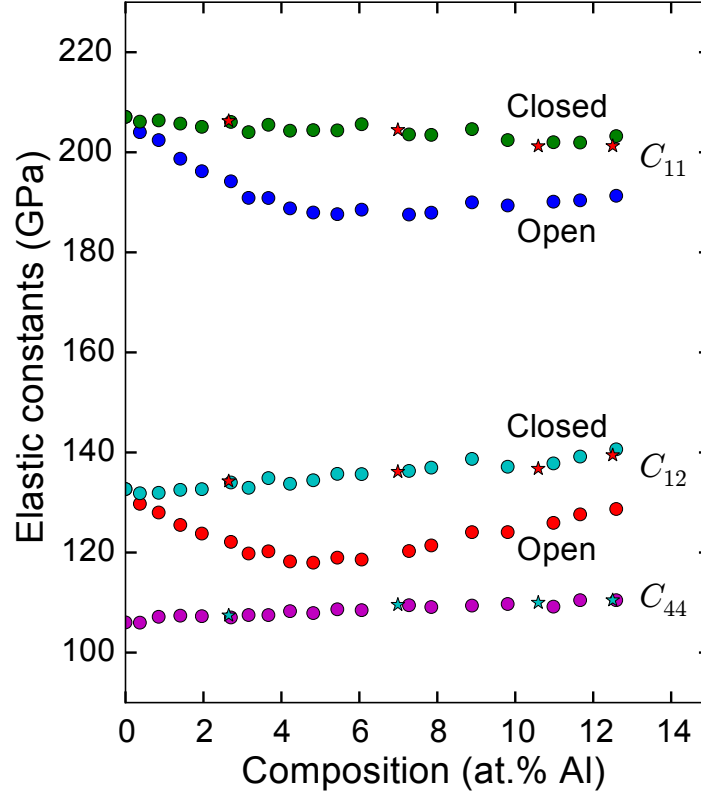


Figure 1: Calculated open and closed system elastic constants of Ni-Al solid solutions as functions of chemical composition at 700 K. For  $c_{44}$ , the closed and open system elastic constants coincide by crystal symmetry. For a closed system, the asterisk symbols are results of direct canonical simulations with atomic swaps. The statistical error bar of the elastic constants is estimated at  $\pm 1$  GPa ( $< 1\%$ ).

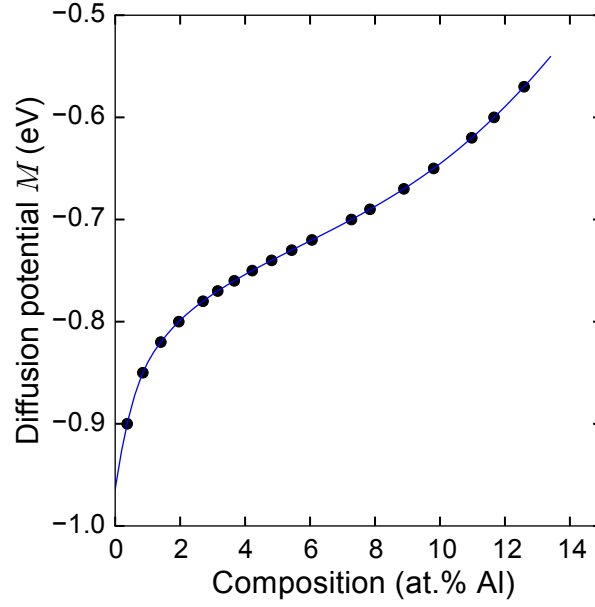


Figure 2: Calculated diffusion potential  $M$  of Al relative to Ni for Ni-Al solid solutions at the temperature of 700 K as a function of chemical composition. The points represent individual simulation runs, the line is a cubic-spline interpolation.

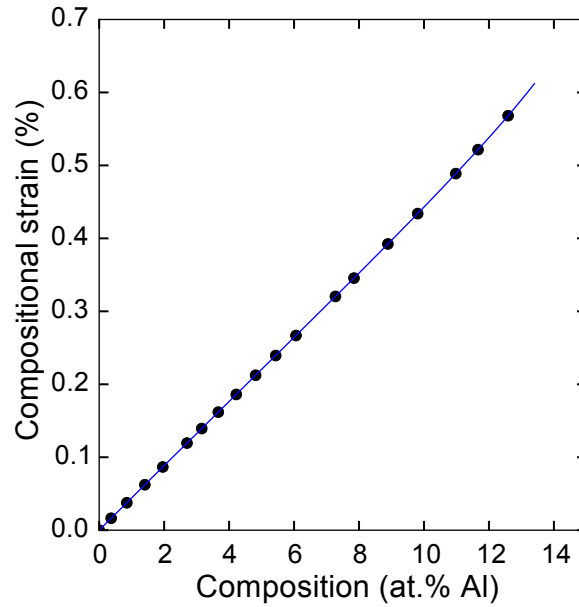


Figure 3: Calculated compositional strain (relative to pure Ni) of Ni-Al solid solutions at the temperature of 700 K as a function of chemical composition. The points represent individual simulation runs, the line is a cubic-spline interpolation.