Calculation of the $\gamma/\gamma'$ interface free energy in the Ni–Al system by the capillary fluctuation method

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Abstract
Monte Carlo computer simulations with an embedded-atom potential are applied to study coherent $\gamma/\gamma'$ interfaces in the Ni–Al system. The (1 0 0) interface free energy has been extracted from the power spectrum of equilibrium shape fluctuations (capillary waves) and found to decrease with temperature from about 20 mJ m$^{-2}$ at 550 K to about 10 mJ m$^{-2}$ at 1200 K. These numbers are in reasonable agreement with existing experimental data. Strengths and weaknesses of the capillary wave method are discussed.

Keywords: interface free energy, capillary fluctuations, Monte Carlo simulation, Ni–Al system

(Some figures may appear in colour only in the online journal)

1. Introduction
Interfaces between different phases control the microstructural stability of many precipitation-hardened alloys. In particular, the coarsening kinetics of $\gamma'$-phase precipitates in the $\gamma$-phase matrix in Ni-based superalloys is largely controlled by the free energy $\sigma$ of the $\gamma/\gamma'$ interfaces [1]. Because making reliable computational predictions of $\sigma$ for multi-component commercial alloys is extremely difficult, attention has been focused on $\gamma/\gamma'$ interfaces in the binary Ni–Al system as a model of superalloys. In the latter case, the $\gamma$-phase is an atomically disordered Ni-based solid solution whereas the $\gamma'$-phase is the intermetallic compound Ni$_3$Al (L1$_2$ structure) accommodating a few atomic per cent of off-stoichiometry. Even in this simpler case, calculations of $\sigma$ are challenging due to the complexity of the underlying interface thermodynamics [2, 3], issues with reliability of atomic interaction models and the sheer volume of computations [2–5].
To further simplify the problem, several authors focused on coherent interfaces between pure Ni and perfectly stoichiometric Ni$_3$Al employing either first-principles calculations [6, 7] or atomistic simulations with empirical potentials [4, 8, 9]. In particular, Mao et al. [7] applied density functional theory calculations to compute $\sigma$ as a function of temperature for three different low-index orientations of the interface. Their calculations include the ferromagnetic ordering, coherency strain energy and atomic vibrations. They predict that $\sigma$ significantly decreases with temperature. For example, the (1 0 0) interface free energy decreases from 27 mJ m$^{-2}$ at 0 K to about 23 mJ m$^{-2}$ at the temperature of 1000 K, demonstrating that the temperature effect should be taken into account for accurate calculations of $\sigma$.

An equally important factor that should also be taken into account is that at finite temperatures, the $\gamma$-phase is not pure Ni and the $\gamma'$-phase is not stoichiometric Ni$_3$Al. The actual chemical compositions of both phases and long-range order in the $\gamma'$-phase vary with temperature according to the Ni–Al phase diagram [10]. First-principles-based calculations of the thermodynamic equilibrium between the $\gamma$ and $\gamma'$-phases could be pursued by the cluster expansion approach [11–13]. An alternate, and computationally more efficient, approach is offered by atomistic simulations with empirical potentials [4, 5]. For coherent $\gamma/\gamma'$ interfaces, accurate but rather tedious calculations of $\sigma$ could be performed by the thermodynamic integration method based on rigorous interface thermodynamic relations developed in previous work [2, 3]. In this paper, we explore a different route involving the analysis of capillary waves on the interfaces.

For rough interfaces supporting capillary waves, their equilibrium power spectrum can be analyzed to extract the interface free energy, or more accurately, the interface stiffness ($\sigma + \sigma''$), where $\sigma''$ is the second derivative of $\sigma$ with respect to the interface inclination angle. For a narrow, ribbon-like interface geometry, the mean square amplitude (power) of capillary waves at a given temperature $T$ is given by [14]

$$\langle a^2(k) \rangle = \frac{k_B T}{(\sigma + \sigma'') A k^2},$$

where $k_B$ is Boltzmann’s factor, $k$ is the wavenumber of the wave, and $A = wL$ is the interface area with $L$ being the interface length and $w \ll L$ the interface ribbon width. Using the computed power spectrum, $(\sigma + \sigma'')$ can be determined from the slope of the plot $1/\langle a^2(k) \rangle$ versus $k^2$. The capillary fluctuation method was applied to compute the free energies and stiffnesses of solid–liquid interfaces [14–22] and grain boundaries in single-component systems [23–25].

In this paper, we apply this method to solid–solid phase boundaries in a binary system. This extension required solving the following problem. The previous applications of the method employed molecular dynamics simulations to measure the equilibrium fluctuation spectrum. Due to the well-known computational limitations, molecular dynamics simulations are usually run for times no longer than tens of nanoseconds. This time scale is too short for observing a significant amount of substitutional solute diffusion in the crystalline lattice even at high temperatures approaching the melting point. As a consequence, the computed capillary wave spectrum does not include fluctuation modes requiring diffusion-controlled redistribution of the solute between the crests and troughs of the waves. A possible answer would be to resort to lattice-free semi-grand canonical Monte Carlo simulations [26]. In this case, redistribution of the solute occurs by an artificially fast process involving random changes of the chemical species of the atoms. Although the dynamics of this process are unphysical, the simulation quickly and correctly samples numerous configurations representing the equilibrium state of the systems. This permits a fast calculation of the ensemble average value of $\langle a^2(k) \rangle$. In practice, however, it is impossible to adjust the chemical potential difference $\Delta \mu$ between the species to exactly match the phase equilibrium condition. Consequently, the interface will
always migrate towards one of the phases, creating a dynamic situation that may affect the fluctuation spectrum. This unavoidable interface motion reflects the fact that the semi-grand canonical Monte Carlo method represents an open system with neutral equilibrium between the phases. In this work, this problem was addressed by imposing an additional constraint maintaining a fixed average composition of the two-phase system.

2. The methodology

The simulation block had the approximate dimensions of 28.6 by 50.0 by 1.4 nm with all-periodic boundary conditions and contained about 180,000 atoms. The z-dimension was relatively small, to realize the ribbon-like geometry of the interface. The block initially contained two plane coherent (1 0 0) Ni/Ni$_3$Al interfaces normal to the y-axis. Atomic interactions were modeled by the embedded-atom potential developed in previous work [4]. While a newer potential for the Ni–Al system has recently been developed [27], the potential of [4] had been extensively tested in the $\gamma$–$\gamma'$ region of the phase diagram [4, 28] and was a safer choice for this work.

Monte Carlo simulations were run to equilibrate the system at a chosen temperature $T$. The trial moves of the Monte Carlo algorithm included (1) displacement of a randomly chosen atom by a random amount in a random direction and (2) reassignment of the chemical species of the chosen atom at random to either Ni or Al. The trial move was accepted or rejected according to the Metropolis algorithm, namely, with the probability $\exp(-\Phi/k_B T)$ if $\Phi > 0$ and unconditionally if $\Phi \leq 0$. Here

$$\Phi \equiv \Delta E \pm \Delta \mu \pm \frac{3}{2} k_B T \ln \frac{m_{Ni}}{m_{Al}}, \quad (2)$$

where $m_{Ni}$ and $m_{Al}$ are the atomic masses [29, 30]. The positive sign is used when Ni is replaced by Al and the negative one when Al is replaced by Ni. The logarithmic term comes from integration of the probability distribution over the momenta of all atoms, producing a pre-exponential factor proportional to the product of all atomic masses to the power of $3/2$. In the probability ratio of two configurations, all masses cancel out except for the atom whose species changes, producing a pre-exponential factor of either $(m_{Ni}/m_{Al})^{3/2}$ or $(m_{Al}/m_{Ni})^{3/2}$.

The energy and force calculations were performed in the parallel mode using the standard domain decomposition approach typically implemented in massively parallel codes such as LAMMPS [31].

To constrain the average fraction of Al atoms $c$ in the system to a preset target value $c_0$, a feedback loop was created between the current value of $c$ and the imposed chemical potential difference $\Delta \mu$. Namely, at each Monte Carlo step $i$, $\Delta \mu_i$ was modified as follows:

$$\Delta \mu_i = \Delta \mu_{i-1} - \alpha \left( \frac{c_{i-1} + c_{i-2}}{2} - c_0 \right), \quad (3)$$

where $\alpha$ is a constant. After a short transient, the system reached a regime in which its composition slightly fluctuated around $c_0$, accompanied by fluctuations in $\Delta \mu_i$ around a value $\Delta \mu_0$ corresponding to two-phase coexistence. At each temperature, $c_0$ was chosen to create an equilibrium structure with nearly equal amounts of the phases. Once phase equilibrium was reached, the Monte Carlo run was continued for approximately $10^6$ steps per atom to save a set of statistically independent snapshots and accurately compute average values of fluctuating parameters.

As discussed in the appendix, the feedback loop (3) implements the so-called Gaussian ensemble [32, 33] representing a system coupled to a finite reservoir of atoms. The Gaussian ensemble interpolates between the semi-grand canonical ensemble arising in the limit of
\( \alpha \rightarrow 0 \) and the canonical ensemble obtained at \( \alpha \rightarrow \infty \). At intermediate values of \( \alpha \), the Gaussian ensemble stabilizes neutrally stable two-phase systems as well as unstable single-phase systems \([32–37]\) by imposing an external harmonic potential proportional to \((c - c_0)^2\). Sadigh et al \([34]\) have recently proposed a highly efficient parallel Monte Carlo algorithm, referred to as the variance-constrained (VC) method, implementing the Gaussian ensemble for binary systems. The feedback method based on equation (3) is closely related to the VC Monte Carlo method \([34]\); namely, it can be shown that the latter realizes an over-damped regime of the more general equation (3). An advantage of equation (3) is that the exact value of \( c_0 \) is preset as input to the simulation, whereas in \([34]\) \( c_0 \) is related to the simulation parameters in a less direct way. However, the parallel implementations of the two methods are different. While the computer code used in this work moves one atom at a time, the code developed by Sadigh et al \([34]\) implements simultaneous trial moves on multiple compute nodes, which increases the computational efficiency.

Several values of the parameter \( \alpha \) were tested. It was determined that the values in the interval of 0.005 to 0.1 eV did not affect the power spectrum of capillary waves obtained within the statistical scatter of the results. On the basis of these tests, a fixed value of \( \alpha = 0.05 \) eV was chosen and used throughout this work. For this \( \alpha \), the rms variation of \( \Delta \mu \) around \( \Delta \mu_0 \) was on the order of 5 meV \((\ll k_B T)\), with the rms variation of the chemical composition at around 0.01 at\%. This regime is very close to a canonical simulation. It should be noted that equation (1) was derived by postulating thermal equilibrium between the capillary waves and a thermostat and assigning the energy \( k_B T \) to each vibrational mode. The fact that our simulation results do not sensitively depend on the choice of \( \alpha \) suggests that under the chosen simulation conditions, the capillary waves are dominated by energy fluctuations due to atomic vibrations and are not significantly affected by fluctuations in \( c \) or \( \Delta \mu \).

At the post-processing stage, every snapshot was quenched to 0 K to eliminate thermal noise. It was checked that the interfaces always remained perfectly coherent. For each atom in a given snapshot, the local chemical composition \( \xi \) was computed as the fraction of Al atoms in a sphere of a radius 4 Å centered at the atom. The \( \xi \) numbers were then averaged over bulk regions unaffected by the interfaces to obtain the chemical compositions, \( c_y \) and \( c_{y'} \), of the phases. To compute the interface shape, the \( x\!-\!y \) cross-section of the block was partitioned into imaginary cells (pixels) of equal size using a \( 300 \times 400 \) mesh. The \( \xi \) numbers were averaged over each cell (including the \( z \)-direction) to obtain a coarse-grained chemical composition \( c \) assigned to each pixel \((x_i, y_i)\). In each row of pixels parallel to the \( y \)-direction (normal to the interface), \( c \) was a function of the pixel ordinate \( y_i \). Namely, it remained nearly constant and equal to either \( c_y \) or \( c_{y'} \) inside the phases and changed rapidly from one composition to the other in the interface regions. Using linear interpolation between neighboring pixels, for each interface the coordinate \( Y_i \) was found at which \( c = (c_y + c_{y'})/2 \) and was identified with the interface position at the given \( x_i \). An example of interface profiles \((x_i, Y_i)\) is shown in figure 1 where the points are connected by straight segments for clarity. The protrusions and zigzags of the profile on the scale comparable to the crystal unit cell size depend on the visualization parameters and do not necessarily reflect the physical shape of the interface. (The physical interface width could be evaluated from composition profiles across the interface averaged over the snapshots, which was not pursued in this work.) The discrete Fourier transformation was then applied to the discrete function \( Y_i(x_i) \) for each interface and the Fourier amplitudes were averaged over a few hundred snapshots and both interfaces to obtain \( \langle a^2(k_i) \rangle \) for a set of wavenumbers \( k_i \). The phase compositions were also averaged over the same set of snapshots.

We assumed that the term \( \sigma'' \) could be neglected in comparison with \( \sigma \). This cannot be proven rigorously but is consistent with the very rough shape of the interface studied here.
The interface free energy was found from
\[ \sigma = \frac{k_B T}{A \langle a^2(k) \rangle k^2}, \] (4)
where the right-hand side is the slope of the plot \(k_B T / A \langle a^2(k) \rangle\) versus \(k^2\).

### 3. Results and conclusions

Figure 2 shows typical plots of \(k_B T / A \langle a^2(k) \rangle\) versus \(k^2\) and their mean square linear fits. Significant deviations from linearity are observed at large \(k\) values when the amplitudes become comparable to the pixel size and cannot be resolved accurately. Therefore, the points which deviated from the linear fit to the small \(k\) portion of the plot by more than two standard
deviations were omitted and the linear fit was repeated until convergence was achieved. The linearity in the small $k$ region confirms that equation (4) is a reasonable approximation. The computed interface free energies are summarized in figure 3. The plot starts at the temperature of 550 K because the amplitudes of the capillary waves decrease with temperature and could not be accurately resolved below 550 K. At the high-temperature end, the simulations above 1200 K resulted in the rupture of the layers of the phases (figure 1) and the formation of a single circular $\gamma'$ particle in the $\gamma$ matrix. In the future, the temperature interval could be extended to higher temperatures by using wider layers of the phases to avoid their breakup.

Comparison of the calculated interface free energies with experiment is not straightforward for a number of reasons. The experimental values of $\sigma$ are back-calculated from observations of coarsening kinetics of $\gamma'$ particles. Such calculations rely on a kinetic model and a thermodynamic description of the alloy. Different $\sigma$ values have been reported in the literature, depending on the choice of the kinetic and thermodynamic models. This can partially explain the significant scatter of the experimental data. For example, figure 3 includes earlier results [38] based on the Lifshitz–Slyozov–Wagner (LSW) [39, 40] model of coarsening together with more recent calculations [41] employing the trans-interface-diffusion-controlled (TIDC) model [42] with more accurate thermodynamics, the two calculations utilizing the same set of experimental data. The plot also includes $\sigma$ values for two ternary Ni–Al–Cr alloys obtained by applying the Kuehmann and Voorhees model [43] of coarsening to data measured by atom-probe tomography [44, 45]. Another factor to consider is the possible anisotropy of $\sigma$ suggested by previous calculations [4, 6, 7]. The experiments give $\sigma$ averaged over all possible orientations. There is at present no experimental evidence of anisotropy in $\sigma$. Small $\gamma'$ particles are spherical and transform to a cubic shape with (1 0 0) faces when they reach a certain size. However, this shape transformation is caused by misfit strains and the elastic anisotropy of the material, and cannot be interpreted as evidence that $\sigma_{(100)}$ is smaller than for other crystallographic orientations (see the discussion by Ardell [41]). On the other hand, the magnitude of $\sigma$ is so small that it might still be anisotropic without affecting the particle shape. This possible anisotropy of $\sigma$ makes the comparison of the computed $\sigma_{(100)}$ values with average experimental values somewhat ambiguous.
Nevertheless, the computed $\sigma$ values are approximately in the same ballpark as the known experimental data: 10 to 20 mJ m$^{-2}$. Although the agreement is imperfect, it is non-trivial given the extremely small magnitude of $\sigma$. Indeed, the computed $\sigma$ is about 1–2% of the Al surface energy, below 1% of the Ni surface energy, and less than a third of the surface tension of water at room temperature.

The main source of error in the reported $\sigma$ is probably rooted in the inaccuracy of the atomistic potential [4]. As an illustration, figure 4 displays the computed $\gamma$ and $\gamma'$ solvus lines on the Ni–Al phase diagram. The phase compositions $c_\gamma$ and $c_{\gamma'}$ at different temperatures were obtained as a side product in the calculations of the interface profiles. Both solvus lines agree with the previous calculation [4] obtained by a different method using the same potential, but show significant deviations from the experimental phase diagram [46–48]. In particular, the compositional width of the $(\gamma + \gamma')$ field on the phase diagram is narrower than in experiment, suggesting that the computed $\sigma$ values are likely to be slightly underestimated. The accuracy of the calculations could be improved by developing a potential capable of reproducing the solvus lines in better agreement with experiment. Another factor neglected in this work is the effect of coherency strains. At several temperatures, the calculations were repeated by fixing the $x$-dimension of the simulation block at values creating slight lateral tensions or compressions on the level of $\pm0.2\%$, modifying the coherency strains in the phases. No effect on $\sigma$ was detected within the statistical errors of the calculations. However, if the accuracy of the method can be improved in the future, a way should also be found to take into account the coherency strains.

In conclusion, this work demonstrates that the capillary fluctuation method in conjunction with Monte Carlo simulations has potential as a means of predicting free energies of $\gamma/\gamma'$ interfaces and possibly other solid–solid interfaces with low free energies. The small magnitude of $\sigma$ which makes it difficult to compute by thermodynamic integration or similar methods...
leads to relatively large amplitudes of capillary waves and makes them amenable to spectral analysis allowing the extraction of $\sigma$. The values of $\sigma$ computed in this work are in reasonable agreement with existing experimental data and show a significant decrease with temperature, approaching $\sim 10 \text{ mJ m}^{-2}$ at high temperatures (figure 3).

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Appendix

This appendix provides additional information related to the Monte Carlo algorithm applied in this work. In section A.1 of this appendix, we define the statistical ensemble implemented by the algorithm. Section A.2 of this appendix presents a set of fluctuation relations computed in this ensemble using a simple fluid as a model. It is shown that these fluctuation relations describe both canonical and grand-canonical ensembles as limiting cases, as well as intermediate situations when the system is coupled to a finite reservoir of particles. In section A.3 of this appendix, we discuss possible implementations of this ensemble in Monte Carlo simulations. We provide a justification of the Monte Carlo algorithm implemented in this paper and compare it with the recently proposed ‘VC’ Monte Carlo method [34].

A.1. The Gaussian ensemble

Consider a single-component system embedded in a reservoir. Suppose the volume of the system is fixed but it can exchange energy and particles with the reservoir. The reservoir is treated as an infinite source of heat (thermostat) but a finite source of particles. Skipping the appropriate derivations, it can be shown that the micro-state probability distribution of this system depends on its energy $E$ and number of particles $N$ according to the equation

$$P = A \exp \left[ -\frac{E - \mu_0 N}{k_B T_0} - R(N - N_0)^2 \right].$$

(5)

Here $A$ is a normalization constant and $T_0, \mu_0, N_0$ and $R$ are fixed parameters of the reservoir. It can be shown that the equilibrium temperature, chemical potential and the number of particles in the system coincide, respectively, with $T_0, \mu_0$ and $N_0$.

When the reservoir is an infinite source of particles, we have $R \to 0$ and equation (5) recovers the grand-canonical distribution. When the reservoir cannot supply or absorb particles, $R \to \infty$ and the probability distribution is strongly dominated by the quadratic term. In this case, all micro-states whose $N$ displays any significant deviation from $N_0$ are extremely improbable and the system behaves as closed. Thus, equation (5) interpolates between the canonical ($NVT$) and grand-canonical ($\mu VT$) distributions; one can smoothly transition from one to the other by varying the reservoir parameter $R$.

An equation similar to equation (5) can be obtained for a system with a fixed number of particles coupled to a thermostat with a finite heat capacity. In this case, the role of the number of particles is played by the energy, so that the additional term contributed by the thermostat
is quadratic in \((E - E_0)\):
\[
P = A \exp \left( - \frac{E}{k_B T_0} - R(E - E_0)^2 \right).
\]
(6)

This case has long been known in the literature as the Gaussian ensemble \([32, 33]\). By analogy, formula (5) can also be referred to as the Gaussian ensemble distribution.

Equation (5) can be rewritten in the form
\[
P = A \exp \left( - \frac{E - \mu N}{k_B T_0} \right),
\]
(7)
where
\[
\mu \equiv a - bN
\]
with the constant parameters
\[
a = \mu_0 + 2RkT_0N_0,
\]
(9)
\[
b = RkT_0.
\]
(10)
Equation (7) looks similar to the grand-canonical distribution, except that the fixed reservoir parameter \(\mu_0\) is replaced by an 'effective' chemical potential \(\mu\) linearly dependent on the current number of particles \(N\). In the limit of \(R \to 0\), this dependence disappears and we return to the grand-canonical distribution with a fixed \(\mu_0\).

### A.2. Fluctuations in the Gaussian ensemble

Mean-square fluctuations and correlation moments (covariances) of various properties can be readily calculated in the Gaussian ensemble using the standard methods of fluctuation theory \([50]\). As a simple example, consider fluctuations in a single-component fluid. To simplify the equations, we will neglect the temperature dependence of the chemical potential, treating it as only a function of the particle density \(n\) (number of particles per unit volume). It can be shown that

\[
\frac{\langle \Delta E \rangle^2}{k_B T_0} = N_0k_B T_0^2c_v \left( \frac{\partial \mu}{\partial n} \right)_T + k_B T_0^3 V \left( \frac{\mu_0}{T_0} + 2N_0k_Bc_vR \right)
\]
\[
+ k_B T_0^3 V R \left( \frac{\partial^2 \mu}{\partial n^2} \right)_T + 2k_B T_0 V R
\]
(11)

\[
\frac{\langle \Delta N \rangle^2}{k_B T_0} = k_B T_0 V \left( \frac{\partial \mu}{\partial n} \right)_T + 2k_B T_0 V R
\]
(12)

\[
\frac{\langle \Delta \mu \rangle^2}{k_B T_0} = k_B T_0 \left( \frac{\partial \mu}{\partial n} \right)^2 \left( \frac{\partial^2 \mu}{\partial n^2} \right)_T + 2k_B T_0 V R
\]
(13)

\[
\frac{\Delta \mu \Delta N}{\langle \Delta \mu \rangle \langle \Delta N \rangle} = \frac{\mu_0k_B T_0 \left( \frac{\partial \mu}{\partial n} \right)_T}{k_B T_0 \left( \frac{\partial \mu}{\partial n} \right)_T + 2k_B T_0 V R}
\]
(14)

\[
\frac{\Delta \mu \Delta E}{\langle \Delta \mu \rangle \langle \Delta E \rangle} = \frac{\mu_0k_B T_0 \left( \frac{\partial \mu}{\partial n} \right)_T}{k_B T_0 \left( \frac{\partial \mu}{\partial n} \right)_T + 2k_B T_0 V R}
\]
(15)

Here \(c_v\) is the constant-volume specific heat per particle.
When \( R \to 0 \) (the reservoir is an infinite source of particles), we exactly recover the known fluctuation relations for the grand-canonical ensemble \([50]\). When \( R \to \infty \) (the reservoir cannot supply or absorb particles), the energy fluctuation (11) reduces to

\[
(\Delta E)^2 = N_0 k_B T_0^2 c_v,
\]

which is the familiar result for the NVT ensemble \([50]\). All other mean-square fluctuations and correlation moments tend to zero as \( 1/R \), which is also in agreement with fluctuation properties of the NVT ensemble \([50]\). The only exception is \( (\Delta \mu)^2 \). Generally, the chemical potential fluctuation need not be zero in NVT systems; namely, it can be shown that in such systems

\[
\frac{(\Delta \mu)^2}{(\Delta N)^2} = \frac{k_B T_0^2}{N c_v} \left( \frac{\partial \mu}{\partial T} \right)_n > 0.
\]

In our case, however, \( (\Delta \mu)^2 \) vanished because we neglected the temperature dependence of \( \mu \). A more accurate calculation within the Gaussian ensemble taking into account the temperature dependence of \( \mu \) exactly recovers equation (17) in the limit of \( R \to \infty \).

For unstable systems with \( (\partial \mu/\partial n)_T \leq 0 \), the grand-canonical fluctuations \( (\Delta \mu)^2 \) and \( (\Delta N)^2 \) diverge to infinity, whereas the Gaussian ensemble keeps them finite provided that \( R \) is chosen large enough to stabilize the system. This gives access to calculations of thermodynamic properties of unstable phases \([34–37]\).

A.3. Implementations of the Gaussian ensemble in Monte Carlo simulations

Equations (7)–(10) can be implemented in Monte Carlo simulations using a grand-canonical or semi-grand canonical algorithm modified to make the chemical potential a variable parameter adjustable on the fly. There are many ways to do so. For example, Sadigh et al \([34]\) have recently developed a highly efficient parallel algorithm implementing the Gaussian ensemble for binary solid mixtures, which they call the ‘variance-constrained’ (VC) Monte Carlo method. Related Monte Carlo algorithms were earlier developed for closed systems coupled to a finite-capacity thermostat. The initially proposed ‘dynamical ensemble’ method \([51, 52]\) later evolved into more sophisticated and computationally more efficient iterative Monte Carlo schemes based on equation (6) \([35, 36]\).

As an example, let us consider a simple fluid with a fixed volume coupled to a thermostat and a finite reservoir of particles. A Monte Carlo trajectory sampling the configuration space is typically generated by repeated implementations of the following trial moves: (i) random displacement of a randomly selected particle, (ii) random change of the chemical species of this particle. A move between two configurations \( i \) and \( i + 1 \) is accepted or rejected according the Metropolis probability

\[
\min \left( 1, \exp \left[ -\frac{1}{k_B T_0} (\Delta U_i - \mu_i \Delta N_i) \right] \right),
\]

where \( \Delta U_i = U_{i+1} - U_i \) and \( \Delta N_i = N_{i+1} - N_i \) are the changes in the potential energy and number of particles, respectively, during the move.

Different algorithms differ from one another in how \( \mu_i \) is selected and if and how it is re-adjusted between trial moves. For example, in the VC Monte Carlo method \([34]\),

\[
\mu_i = a - 2b\tilde{N}_i,
\]

where \( \tilde{N}_i \equiv (N_{i+1} + N_i)/2 \) is the average number of particles in the system before and after the move (we use our notations and omit details of parallel implementation \([34]\)). Note that the change in the effective chemical potential between two moves is

\[
\mu_{i+1} - \mu_i = -b(N_{i+2} - N_i).
\]
Thus, the VC algorithm could be formulated as a grand (or semi-grand) canonical simulation with the effective chemical potential updated between trial moves according to the rule

$$\mu_{i+1} = \mu_i - b(N_{i+2} - N_i).$$  (21)

For the following discussion, it will be convenient to interpret the number of Monte Carlo attempts $i$ as the elapsed ‘time’ of the simulation. (Of course, no relevance to the CPU, wall-clock or any other physical time is implied here.) For example, equation (20) can be written in terms of the ‘time’ derivatives as

$$\dot{\mu} = -2b\dot{N}.$$  (22)

The idea behind the Monte Carlo algorithm used in this paper is to generate a Monte Carlo trajectory by analogy with fluctuation dynamics in a real physical system. Namely, in an open physical system subject to fixed temperature $T_0$ and chemical potential $\mu$, the particle density $n$ eventually converges to an equilibrium value $n_e$ satisfying the equation of state $\mu = \mu(n_e, T_0)$. Based on the fluctuation-dissipation theorem, we expect that the convergence will be exponential with a characteristic relaxation time $\tau$. The dynamic equation leading this exponential decay can be written as

$$\ddot{x} = -\omega^2 x - \frac{1}{\tau} \dot{x}.$$  (23)

Interestingly, the convergence of grand-canonical Monte Carlo simulations does actually follow the exponential law as a function of $i$. Equation (23) continues to be valid if $\mu$ changes with time, causing variations in $n_e$. Taking the time derivative of equation (23), we have

$$\ddot{n} = -\frac{1}{\tau} \left( \dot{n} - \frac{1}{(\partial \mu/\partial n_e)_T} \dot{\mu} \right).$$  (24)

The algorithm used is this paper updates $\mu$ after each Monte Carlo step according to the iteration scheme

$$\mu_{i+1} = \mu_i - \alpha \left( \frac{n_i + n_{i-1}}{2} - n_0 \right),$$  (25)

where $n_0$ is a preset target value of the equilibrium density. To understand the behavior of the system produced by this algorithm, we rewrite equation (25) using the analogy with time, with

$$\dot{\mu} = -\alpha(n - n_0),$$  (26)

and insert this relation in equation (24). Denoting $x \equiv n - n_0$, we obtain the equation

$$\ddot{x} = -\omega^2 x - \frac{1}{\tau} \dot{x}.$$  (27)

This equation describes the motion of a particle of unit mass in a harmonic potential with friction. The friction coefficient is $1/\tau$ and resonant frequency $\omega$ is given by

$$\omega^2 = \frac{\alpha}{(\partial \mu/\partial n_e)_T}.$$  (28)

However, we know that $\omega^2$ is proportional to the curvature at the bottom of the potential well. In other words, the coupling constant $\alpha$ defined by equation (25) is proportional to the reservoir parameter $R$ appearing in equation (5). Whatever the initial state, the particle always ends up in the equilibrium position at $x = 0$, i.e. $n = n_0$. Fluctuations of the particle around the equilibrium position can be captured by adding a random force to the right-hand side of equation (27), giving rise to a Langevin equation.

Thus, the iteration scheme (25) implements the Gaussian ensemble and ensures that the system converges to the desired equilibrium density $n_0$. Accordingly, the chemical potential
Figure 5. Typical snapshot of Monte Carlo simulations of the $\gamma/\gamma'$ system at the temperature of 1000 K used as a test of two simulation methods. The periodic simulation block is projected on the $x$-$y$ plane showing only Al atoms. The block contains 8192 atoms and has the chemical composition of 18 at% Al. The arrows indicate approximate positions of the $\gamma/\gamma'$ interfaces.

converges to $\mu(n_0, T_0)$. In this method, the target equilibrium density $n_0$ constitutes direct input to the simulation, by contrast to the VC method in which $n_0$ is related to the simulation parameters $a$ and $b$ in a less direct way. The simulation parameter $\alpha$ affects the fluctuations of $n$ and $\mu$ but not their equilibrium values.

In the limit of a large friction coefficient, the inertia term $\ddot{n}$ can be neglected and equation (24) predicts a linear relation between $\mu$ and $\dot{n}$, which is equivalent to the VC iteration scheme (22). In other words, the VC Monte Carlo algorithm is the over-damped case of the algorithm used in this paper.

To summarize, both Monte Carlo algorithms implement the Gaussian ensemble describing a system coupled to a finite reservoir of particles. The algorithm used in this paper generates a Monte Carlo trajectory emulating relaxation and fluctuation dynamics in a physical system, interpreting the number of Monte Carlo steps $i$ as a ‘time’ variable. This is achieved by adjusting the chemical potential on the fly according to the iteration scheme (25). The recently proposed VC algorithm [34] can be formulated as the iteration scheme (21) and represents the over-damped limit of our algorithm.

It is worth mentioning that approaches in which a particular statistical ensemble is implemented by emulating a physical fluctuation process are common in atomistic simulations. For example, constant-pressure molecular dynamics simulations can be implemented by the Nosé–Hoover Langevin piston algorithm [53] combining the Nosé–Hoover constant-pressure method with piston fluctuations modeled by Langevin dynamics.

A.4. Numerical example

To illustrate the fluctuation behavior predicted by the two Monte Carlo algorithms, additional simulations have been conducted using a simulation block much smaller than the one employed in the capillary wave study (the latter was too big to afford a detailed parametric study). The block contained only 8192 atoms and had a two-phase $\gamma/\gamma'$ structure shown in figure 5. The thickness of the system in the $z$-direction (normal to the page) was the same as in the simulations reported in the main text. Periodic boundary conditions were maintained in all three directions and the volume was fixed.
Monte Carlo simulations were performed at the temperature of 1000 K using the feedback method of this work as well as the VC method [34] implemented in the same simulation code. A series of simulation parameters $\alpha$ (respectively, $b$) were tested in Monte Carlo runs comprising up to 480,000 trial moves per atom. In all tests, the target composition of the system was 18 at.-% Al, which ensures approximately equal amounts of the phases. Probability distributions of the energy, chemical potential difference $\Delta \mu$, number of Al atoms $N$ and other parameters, as well as correlations moments between these parameters, were computed for each test.

The observed fluctuations of energy, $\Delta \mu$ and chemical composition accurately followed the Gaussian distribution for both algorithms. A few examples are given in figure 6 for the feedback algorithm. This figure also illustrates that with increasing $\alpha$, the algorithm effectively constrains the fluctuations of both energy and chemical composition while keeping them Gaussian.

A more detailed fluctuation behavior is illustrated in figure 7, showing plots of $(\Delta U)^2$ and $(\Delta N)^2$ as functions of $\alpha$ (respectively, $b$). Both algorithms constrain the compositional fluctuations at large $\alpha$ (respectively, $b$), gradually changing the ensemble from Gaussian to canonical as expected theoretically. At small $\alpha$ (respectively, $b$), the fluctuations in $\Delta \mu$ become small and the ensemble approaches semi-grand canonical. Theoretically, for a two-phase system $(\Delta U)^2$ and $(\Delta N)^2$ must diverge to infinity in this limit. In reality, this does not happen because the system remains constrained by the lattice misfit strains (recall that the volume is fixed and the two phases have slightly different molar volumes). As a result, the fluctuations tend to large but still finite values. It is evident that both algorithms reproduce similar fluctuation behaviors. The same trends were found for $(\Delta(\Delta \mu))^2$, $\Delta N \Delta U$, and all other covariances that were computed.

It is hoped that these tests demonstrate that both Monte Carlo algorithms are equally suitable for simulations in the Gaussian ensemble. As far as their practical implementation,
Figure 7. Mean-square fluctuations of (a), (b) energy in meV and (c), (d) number of Al atoms in the system as functions of parameters $\alpha$ and $b$ in Monte Carlo simulations of the $\gamma/\gamma'$ system at 1000 K using the present method (a), (c) and the VC method (b), (d).

a more detailed comparative study is underway to further test their computational efficiency, limits of applicability and other characteristics important for applications.

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