

The role of phase separation on Rayleigh-Plateau type instabilities in alloys

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Abstract: Classical molecular dynamics (MD) simulations are used to investigate the role of phase separation (PS) on the Rayleigh-Plateau (RP) instability. Ni-Ag bulk structures are created at temperatures 2000K and 1400K which generate different PS lengthscales, λ_{PS} , relative to the RP instability lengthscale, λ_{RP} . Rectanguloids are then cut from the bulk structures and patterned with a perturbation of certain amplitude and wavelength, λ_{RP} . It is found that when $\lambda_{PS} \ll \lambda_{RP}$ (2000K)

the patterned rectanguloids break up into nanoparticles in a manner consistent with classical RP theory, whereas when $\lambda_{PS} \approx \lambda_{RP}$ (1400K), soluto-capillarity affects the RP instability significantly. Specifically, since Ag has a lower surface energy than Ni, Ag migrates to cover neighboring Ni regions, therefore modifying the RP instability. Thus, we demonstrate that the phase separation lengthscale of an immiscible alloy can be exploited to direct the assembly of functional bi-metallic alloys.

Keywords: Molecular Dynamics Simulations; Phase Separation; Metallic Nanoparticles; Self-assembly; Rayleigh-Plateau instability

1. Introduction

This work extends recent studies that explore how hydrodynamic instabilities in two dimensional single-component thin metal films¹⁻³ and nanostructures^{4, 5} can be used to create different arrays of organized and correlated nanoparticles. The Rayleigh-Plateau (RP) instability, for instance, is a phenomenon that emerges in a liquid jet: as different modes of surface-tension-driven instabilities evolve on the surface of the liquid, the fastest-growing mode dominates and pinches the liquid jet at regular points along its length, breaking it into droplets. The spinodal and nucleation types of instability for a thin film deposited on a substrate are other examples; in such a configuration, thin films break up and may generate nanoparticles with a correlated size and lengthscale; see recent reviews^{6, 7} for more details. Other effects can compete with (or enhance) these types of instabilities. For example, thermal gradients can lead to gradients in surface energy (the thermo-capillary effect, also known as thermal Marangoni effect), which may influence the dewetting mechanism^{8, 9}. Similarly, differences in chemical concentration may lead to gradients in surface energy¹⁰, known

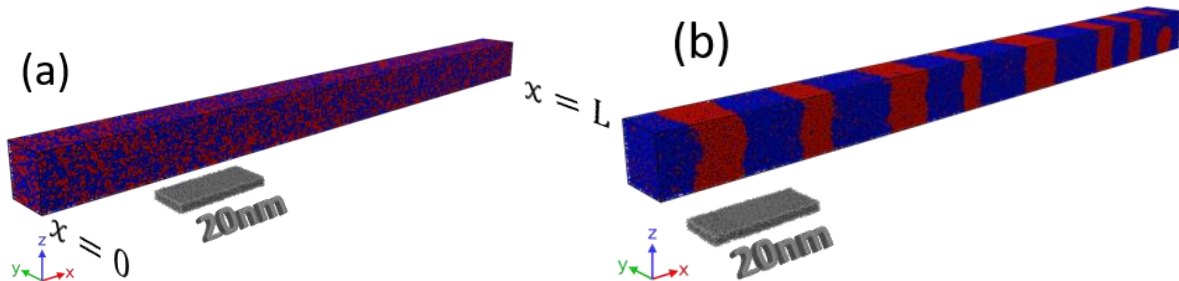
as the soluto-capillary effect (or concentration Marangoni effect). In this work we focus on how RP hydrodynamic instabilities compete with soluto-capillarity. We leverage so-called synthetic perturbations, which are lithographically patterned rectanguloids with varicose edge perturbations, to control the competition/cooperation of the RP and soluto-capillarity. Synthetic perturbations in elemental liquid metals have been demonstrated experimentally and verified via detailed simulations to direct the precise assembly of nanoparticle arrays via unstable RP instabilities^{11, 12}.

We use here classical molecular dynamics (MD) simulations to study the $\text{Ni}_{0.5}\text{Ag}_{0.5}$ chemical composition and focus on the influence of phase separation (PS) on RP-type hydrodynamic instabilities. Several previous MD studies have investigated the spinodal^{13, 14} and RP^{13, 15, 16} instabilities, as well as other dewetting phenomena¹⁷⁻²⁵ in single-component films. Additionally, several groups have studied liquid-state PS in metallic systems, such as Al-Pb²⁶ and Al-Ge-Mn²⁷; see also our recent work exploring the role that a liquid-vacuum and liquid-substrate interface has on the phase separation in Ag-Ni single drops²⁸. The Ag-Ni system is interesting in that Ag is an efficient plasmonic material and Ni is ferromagnetic, thus in principle bi-functional magnetoplasmonic nanoparticles can be generated²⁹. Recent experimental pulsed laser induced dewetting studies of various alloys for plasmonic³⁰⁻³⁴, magnetic³⁵, and magnetoplasmonic³⁶⁻³⁸ systems have been performed. For instance, control of the thin film thickness of gold and silver affects the resultant nanoparticle size distribution, which subsequently affects the surface plasmon resonance energy.

2. Materials and Methods

Bulk structures of $\text{Ni}_{0.5}\text{Ag}_{0.5}$ were equilibrated using a small sample of 256 atoms with the isothermal-isobaric (NPT), canonical (NVT), and micro-canonical (NVE) ensembles, sequentially.

Subsequently, the small samples were expanded to a large bulk of 829440 atoms and equilibrated (using the same ensembles) in decreasing 200K increments at temperatures ranging from 3000K down to 1400K. In our previous work, we found that phase separation of Ni and Ag phases in a $\text{Ni}_{0.5}\text{Ag}_{0.5}$ bulk started at temperatures below 2400K, consistent with the equilibrium phase diagram, and that larger phase separation lengthscales emerged as the temperature was lowered²⁸. When the bulk $\text{Ni}_{0.5}\text{Ag}_{0.5}$ was suspended in vacuum, such that a free surface existed, a Ag@Ni core-shell morphology emerged due to Ag's lower surface energy. Based on our previous work, here we consider temperature as a proxy to control the PS lengthscale, which we call λ_{PS} . We focus on two temperatures: 2000K, which is in the immiscible Ag-Ni liquid-liquid phase region of the phase diagram; and 1400K, which is in the Ag-Ni liquid-solid phase. To emulate pulsed laser induced dewetting experiments, where metal nano structures are lithographically patterned onto substrates, we cut thin rectanguloids (referred to as lines for simplicity) from the bulk structures with lengthwise (x) perturbations of a prescribed wavelength and amplitude. We denote the length of the respective bulk and associated line by L and impose periodic boundary conditions at $x = 0, L$. Figure 1 shows bulk structures created at 2000K (a), and at 1400K, (b), (c), as well as examples of lines cut from the bulk structures, (d). Note that both the lengths of the bulks in Fig.1(a), (b), (c), and the width of the respective lines are not constructed exactly equal (see the supporting information for more details).



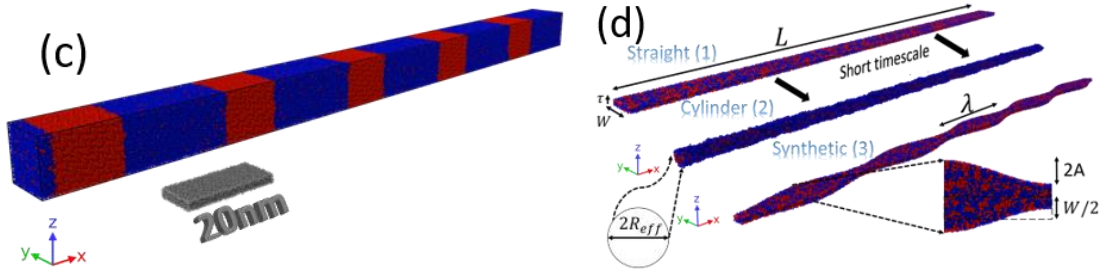


Figure 1. Equilibrated $\text{Ni}_{0.5}\text{Ag}_{0.5}$ bulk structures at (a) 2000K and (b), (c) 1400K. In (a) phase separation leads to the formation of small clusters of Ni and Ag, whereas in (b) PS results in the formation of unequally sized stripes along the x -axis. In (c) PS stripes were created to have a fixed length (the difference in size is due to the unequal atomic volumes of the two phases). (d) Straight lines (1) and lines with perturbations (referred to as synthetic lines) (3) are cut from bulks (a)-(c) (here the lines from (a) are shown). In vacuum, the lines quickly deform into cylinders (2). The cross-sections of (1) and (3) are both rectangles of thickness, τ but (1) has a fixed width, W , whereas the width in (3) varies with x . The cross-sections of (2) are circles of radius R_{eff} . For (3) the perturbations have wavelength λ and amplitude A (half the distance of peak to trough). Color code: Ni (red), Ag (blue).

As seen in Fig.1(a), at 2000K small clusters of Ni and Ag form. Using the cluster analysis tool in Ovito³⁹, the average sizes of Ni and Ag clusters (assuming clusters are all densely⁴⁰ filled spheres) are found to be 6.2 and 6.7 Å respectively, and $\lambda_{\text{PS}} = 12.9$ Å is defined to be the sum of the Ni and Ag average cluster sizes.

In Fig.1(b), at 1400K, Ni (red) and Ag (blue) stripes form along the longitudinal axis, x . There is some variation in the lengths of each of the stripes as the line was equilibrated from high temperature. The PS lengthscale is defined as a sum of the average lengths of both Ni and Ag stripes, $\lambda_{\text{PS}} = 170.7$ Å.

The bulk structure in Fig.1(c) is also created at 1400K but in a slightly different manner. In this case, 2560 atoms of Ni were joined with 2560 atoms of Ag to make a small (5120 atoms) phase-separated initial structure that was then equilibrated and expanded following the process for Fig.1(a) and (b), resulting in the large phase-separated structure of 921,600 atoms. Similar to Fig.1(b), Ni and Ag stripes form but now, by design, each Ag-Ni stripe pair has a fixed length; note also that each Ag and Ni stripe has approximately the same number of atoms, but the atoms are closer to each other for Ni (the atomic volume for Ag is roughly 1.66 times larger than that for Ni at 1400K). The PS lengthscale, defined in the same manner as in Fig.1(b), is $\lambda_{PS}=315.6 \text{ \AA}$.

Figure 1(d) shows a few examples of lines cut from the bulk structures at 2000K. Here, image (1) shows a straight line of length L and width W , and image (3) is a line of the same length L with applied perturbations of amplitude A and wavelength λ (referred to as a synthetic line). Note that, when suspended in vacuum, both straight and synthetic lines quickly form a cylinder, so as to minimize surface energy (such a cylinder is shown in Fig.1(d), image (2)); even in the case of the synthetic lines cylinders form faster than line breakup, as discussed in what follows.

2.1. The Rayleigh-Plateau Theory for Liquid Metals

Consider a perturbed liquid cylinder of radius $R(x, t)$ with axis, x and surface given by:

$$R(x, t) = R_0 + A \exp(ikx + \omega t), \quad (1)$$

where R_0 is the average radius and A, k, ω are the perturbation amplitude, wavenumber, and growth rate, respectively, with $A \ll R_0$. Classical RP theory predicts that such small perturbations to liquid cylinders in vacuum, neglecting viscosity, will grow at the rate given by

$$\omega^2 = \frac{\gamma}{\rho R_0^3} k R_0 \frac{I_1(k R_0)}{I_0(k R_0)} (1 - k^2 R_0^2), \quad (2)$$

where γ, ρ are the liquid surface tension and density, and I_0, I_1 are Bessel functions of the first kind of the zeroth and first order, respectively. In this paper, we focus on the (unstable) modes that grow ($\omega > 0$, only possible when $k R_0 < 1$). Of the unstable modes, the one that grows the fastest is that with wavenumber k_m , found by maximizing $\omega(k)$ in Eq. (2) with given values of γ, ρ (see Table 1) and R_0 (see Table 2), given by

$$k_m R_0 \approx 0.697. \quad (3)$$

The corresponding wavelength, $\lambda_m = 2\pi/k_m$, of this mode depends only on the initial radius of the cylinder, and is given by $\lambda_m = 9.01 R_0$.

	$\rho_{2000K} \text{ (kg/m}^3\text{)}$	$\gamma_{2000K} \text{ (N/m)}$	$\rho_{1400K} \text{ (kg/m}^3\text{)}$	$\gamma_{1400K} \text{ (N/m)}$
Ni	7587.2	1.7	8283.2	1.9
Ag	8652.4	0.8	9196.4	0.9
Ni_{0.5}Ag_{0.5}	8119.8	1.2	8739.8	1.4

Table 1: Material parameters for Ni, Ag, and Ni_{0.5}Ag_{0.5} alloy at both 2000K and 1400K obtained by linearly extrapolating properties from the melting temperature. Properties for the alloy are found by averaging.

Previously, we have shown that synthetic perturbations characterized by an unstable RP wavelength can be used to control the breakup of nanoscale metallic liquid lines into droplets of desired size and spacing^{11, 12}. Here we investigate whether the RP instability can be used to describe the breakup of Ni_{0.5}Ag_{0.5} lines (rather than pure element cylinders) in vacuum. Although the RP theory technically only applies to single-element liquids, we apply it to the Ni_{0.5}Ag_{0.5} alloy

by averaging densities and surface liquid tensions for the single elements (Vegard's law) as given in Table 1. As mentioned earlier, when suspended in vacuum, the lines transform into cylinders of effective radius R_{eff} perturbed along the long axis with effective amplitude A_{eff} (in the case of straight lines, $A_{\text{eff}} = 0$). For simplicity, we define the effective radius to be the radius of the cylinder that results from the straight lines, found by equating cross-sectional areas, and is given by:

$$R_{\text{eff}} = \sqrt{\frac{W\tau}{\pi}},$$

where τ is the line thickness, which we fix in all cases as $\tau = W/5$. For the synthetic perturbation cases, the effective amplitude can be found by equating the cross-sectional area of the perturbation troughs to that of the thinnest part of the perturbed cylinder. Since the width of the line at troughs is $(W - 2A)$ and the radius of the thinnest parts of the cylinder is $R_{\text{eff}} - A_{\text{eff}}$, equating cross-sectional areas, $(W - 2A)\tau = \pi(R_{\text{eff}} - A_{\text{eff}})^2$, we find the effective amplitude,

$$A_{\text{eff}} = \sqrt{\frac{W\tau}{\pi}} - \sqrt{\frac{(W - 2A)\tau}{\pi}}.$$

For each of Fig.1(a), (b), and (c), the wavelength is chosen so that $L = 5\lambda$, where L is the (fixed) length of the respective bulk. With the values of the widths W given in Table 2, the chosen wavelengths correspond to unstable perturbations (stability curves will be shown shortly). By removing atoms from the bulk structures, $\text{Ni}_{0.5}\text{Ag}_{0.5}$ lines of certain width, wavelength, amplitude and thickness (values are given in Table 2) are extracted at 2000K and 1400K. We use **A**, **B** and **C** to denote the straight and synthetic lines cut from Fig.1(a), (b) and (c), respectively.

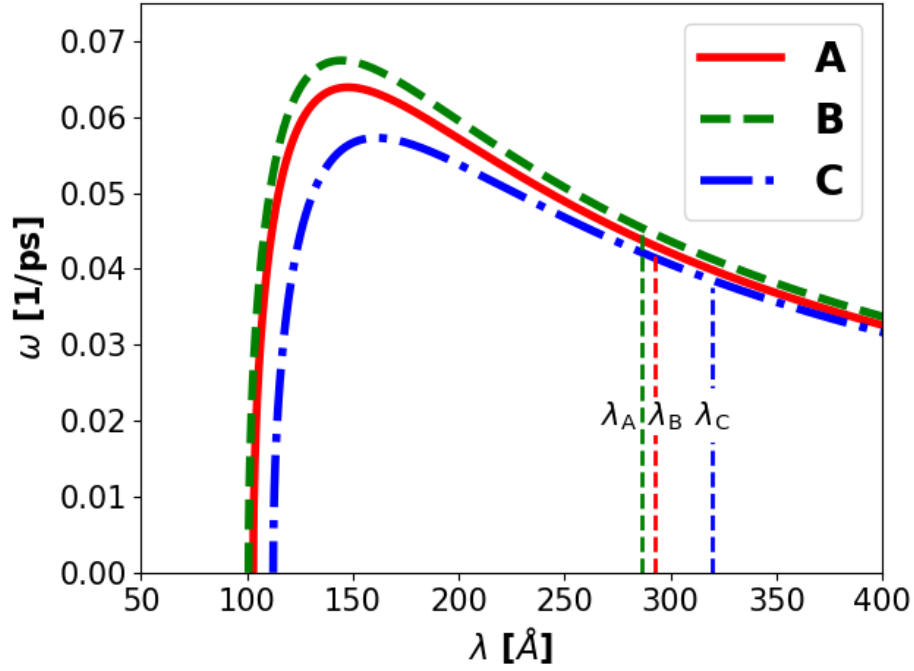


Figure 2. RP dispersion curves, using Eq. (2) with effective cylinder radius R_{eff} , where the growth rate is calculated using the geometric parameters from lines **A** (red solid line), **B** (green dashed line) and **C** (blue dot-dashed line) (Table 2), and the material parameters given in Table 1. The vertical dashed lines correspond to the wavelengths used in the corresponding simulations.

Figure 2 displays the theoretical dispersion curves for the material parameters given in Table 1 and using $R_0 = R_{\text{eff}}$ in Eq. 2 for **A**, **B** and **C**. The values of the chosen wavelengths for **A**, **B** and **C** are given by vertical dashed lines and are denoted here by λ_A , λ_B and λ_C , respectively. Except for the differences in maximum growth rate, ω_m at $\lambda_m = 9.01R_{\text{eff}}$, these curves are very similar. Note that we have used a non-maximum wavelength, $\lambda > \lambda_m$, in each case so that the RP dynamics occur on a longer timescale (see the supporting information, Fig.S.4, for a case where λ_m is used). The numerical values of λ and $\omega(\lambda)$ are given in Table 2 along with the widths, effective radii, lengths, temperatures and PS lengthscales. The values of A_{eff} will be discussed further at the end

of section 3. The question now is, how do the values for ω and λ obtained from the RP analysis differ from those obtained via MD simulations? Specifically, we are interested in studying how phase separation interacts with the RP instability and affects the breakup of the lines.

Line	Temperature (K)	W (Å)	R_{eff} (Å)	λ (Å)	λ_{PS} (Å)	L (Å)	ω (1/ps)
A	2000	65.0	16.4	292.6	13.0	1463.2	4.3×10^{-2}
B	1400	63.6	16.1	286.7	170.7	1433.7	4.5×10^{-2}
C	1400	71.0	17.9	319.8	315.6	1598.9	3.8×10^{-2}

Table 2: Temperature, width W , wavelength λ , phase separation lengthscale λ_{PS} , and length L , for lines **A**, **B** and **C**, as well as transformed cylinder effective radius R_{eff} , and associated RP growth-rate prediction ω , via Eq. 2.

3. Results

In what follows we show how temperature and the phase separation lengthscale affect the breakup of straight and synthetic lines into nanoparticles, producing results that differ from those predicted by the RP theory. Unless otherwise stated we set the RP lengthscales to the wavelengths provided in Table 2 and denote them λ_{RP} to differentiate from λ_{PS} .

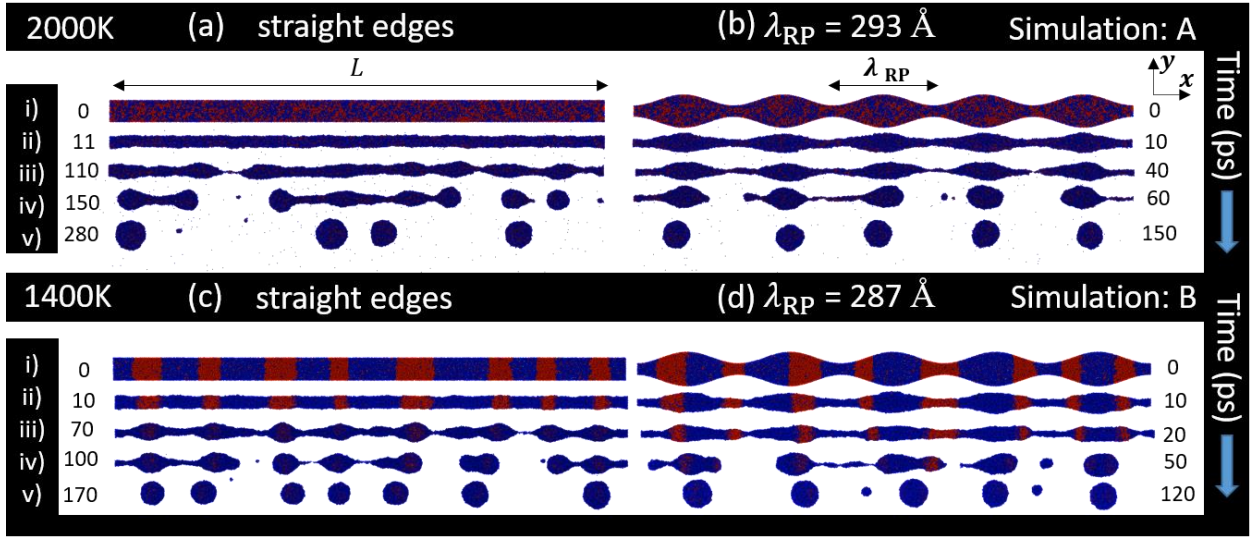


Figure 3. Time evolution of straight (left) and synthetic (right) lines at 2000K ((a) and (b)) and 1400K ((c) and (d)). The parameters for 2000K and 1400K are given in Table 2 under **A** and **B**, respectively. Time labels in ps (see text below) are placed next to the corresponding lines.

Figure 3 shows the temporal evolution of $\text{Ni}_{0.5}\text{Ag}_{0.5}$ lines in vacuum. Straight and synthetic lines are shown in the left and right columns of Fig. 3, respectively. Labels i)-v) indicate the time stamps at which the lines undergo significant changes during the simulation: i) indicates the initial configuration; ii) the time at which surface perturbations develop; iii) the time immediately prior to the breakup of the line; iv) the intermediate time between the breakup and the formation of nanoparticles; and v) the time of nanoparticle formation. On panel (b), the wavelength of the imposed perturbation is also indicated. In Figure 3 a key difference between the initial structures (row i)) is in the relative sizes of the PS and RP lengthscales. At 2000K, the PS lengthscale is a stable RP wavelength (surface perturbations due to PS would decay: $\omega(\lambda_{\text{PS}}) < 0$ in Fig. 2), whereas at 1400K surface perturbations of wavelength λ_{PS} are RP-unstable ($\omega(\lambda_{\text{PS}}) > 0$). For

what follows we refer to a small PS lengthscale as one where PS-induced perturbations decay, and a large PS lengthscale as one where they grow.

At 2000K, the PS lengthscale is small and the straight line (Fig.3(a)) develops surface perturbations at 11ps (row ii)) due to small fluctuations in the initial configuration rather than perturbations induced by PS. By comparison, in the synthetic lines (Fig.3(b)), at 10ps (row ii)) the perturbation is already well developed, as expected since the perturbation of wavelength λ_{RP} was already prescribed in the initial configuration. Nanoparticles are formed in the synthetic lines 90ps faster than in the straight lines. Five nanoparticles are formed in the synthetic lines, which corresponds well to the five patterned wavelengths, whereas in the straight lines the asymmetry of line breakup results in shortening of the resulting line parts via material transport, leading to (in this case) four nanoparticles only. For instance, note that, following line breakup the central part of Fig.3(a), row iv) at 150 ps has 3 varicose perturbations (and thus one would expect 4 droplets), but the breakup only occurs near the middle of this region (the surrounding instabilities are suppressed) resulting in just two particles. The two droplets in the rightmost region of Fig.3(a), row iv), on the other hand, coalesce into one droplet by row v). The locations of the nanoparticles differ in the straight and synthetic lines. For the latter, as expected, nanoparticles form at the peaks of the perturbation and are well spaced; for the straight lines, the nanoparticles are not equidistant/periodic. For both types of lines, the resultant nanoparticles are homogenous and contain Ni and Ag in a liquid-like configuration with a small phase separation lengthscale.

At 1400K (Fig. 3(c) and (d)), the PS lengthscale is large. As the simulations proceed, the troughs of the perturbation develop primarily in Ag-rich regions or at the interface between adjacent Ag-

rich/Ni-rich regions. Both lines break up faster than their 2000K counterparts, 110ps and 30ps faster for the straight and synthetic lines, respectively. This is somewhat counterintuitive: 1400K is below the melting point of Ni (1728K) and less than 200K above the melting point of Ag (1235K). Therefore, at 1400K one would expect the atom mobility to be less than at 2000K and thus breakup to take longer. The reason behind a faster breakup at 1400K is due to the thinning of the line in Ag-rich locations (Ag “migrates” to neighboring regions faster than does Ni due to the lower melting temperature). The straight line, for instance, forms seven nanoparticles, whereas the synthetic line forms five. Interestingly, these nanoparticles are not uniform but have a core-shell like structure, with Ag in the shell and Ni in the core (see particle slices in supplemental information).

From the results above, it appears that at 1400K for lines where the PS lengthscale is on the order of the RP instability length scale, the soluto-capillary Ag migration induces unstable perturbations that modify the existing RP instability and affect breakup. To investigate this effect more carefully, we created synthetic lines and prescribed perturbations (cut from bulk Fig.1(c)) where troughs are located in the Ag-rich or Ni-rich regions, or close to the interface between these two regions, see Fig. 4(a), (b), and (c), respectively. (See supporting information for a detailed explanation of how these lines were created.) In all these lines, the lengths of Ni and neighboring Ag regions sum to the RP wavelength, λ_{RP} . As stated earlier, the length of the Ag phase-separated regions (average length of blue regions in Fig.3(c)) is slightly larger than that of the Ni regions. This difference is small, however, thus the structures seen for the lines in Fig.4 correspond to the regime where the PS lengthscales of Ni and Ag are approximately half the RP lengthscale. Two

different perturbation amplitudes were considered, 3.2 Å and 16 Å, which we refer to as small and large amplitudes.

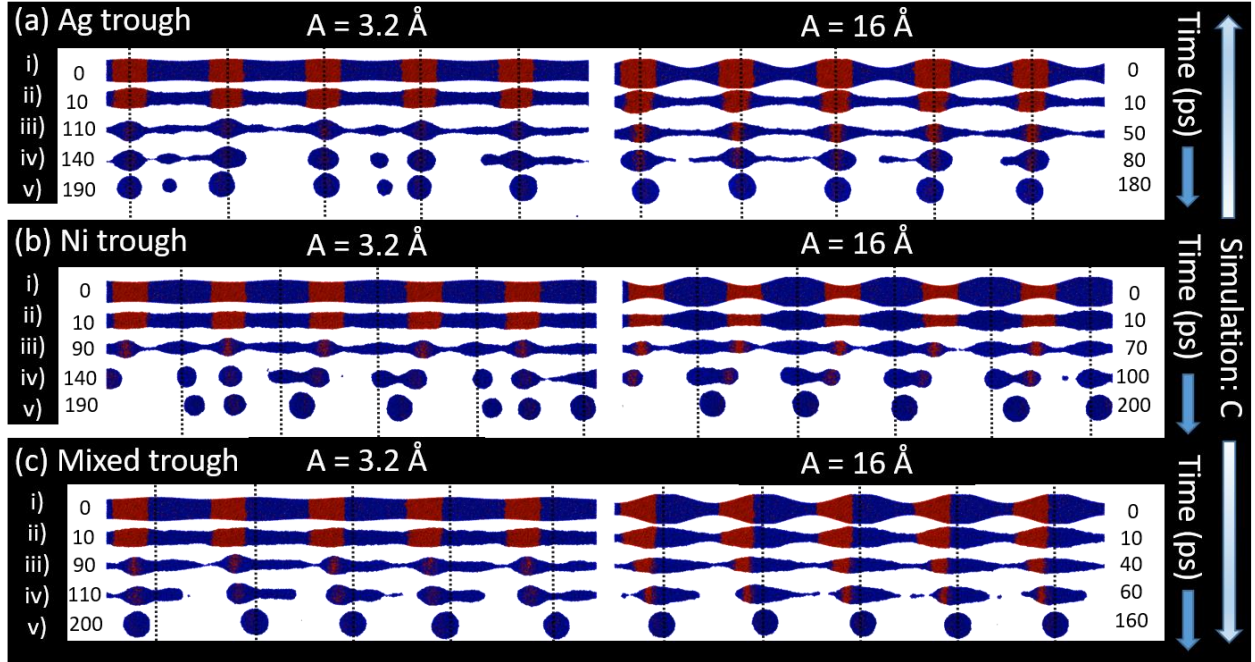


Figure 4. Time evolution of synthetic lines for Ag-rich troughs (a), Ni-rich troughs (b), and mixed Ni and Ag troughs (c) for perturbations of amplitudes $A=3.2\text{Å}$ (left) and $A=16.0\text{Å}$ (right). The labels i)-v) correspond to different time intervals in ps with description as in Fig.3. Guides (dotted lines) are placed at the location of the original synthetic peak position in i). The geometric details for the lines are given in Table 2 under simulation C.

Figure 4 shows the temporal evolution of $\text{Ni}_{0.5}\text{Ag}_{0.5}$ lines at 1400K. The troughs of the perturbations are either located at (a) Ag-rich regions (referred to as Ag trough), (b) Ni-rich regions (Ni trough) or (c) mixed Ni/Ag regions (Mixed trough). The main finding is that the location of the resultant nanoparticles differs between (a), (b) and (c).

The primary difference between the small (Fig.4, left column) and large amplitude (Fig.4, right column) is the time it takes the lines to reach the first pinch. In general, the large amplitude lines

pinch faster than their small amplitude counterparts since there is less material in the trough of the perturbation. The large amplitude case can be thought of as further along in the destabilization process that is inherited from the RP instability. The largest difference in the pinch time (60ps) occurs in case (a). Further, the small amplitude case generates small secondary or satellite particles near two of the perturbation peak regions in Fig.4(b), left column.

Figures 4(a), (b), and (c) collectively highlight the importance of the initial trough composition. Consider, in the large amplitude cases (right panel of Fig.4), the position of the resultant nanoparticles in v relative to the trough guides (the dashed vertical lines). In (a) the nanoparticles are primarily located at the peak of the perturbation (the dashed lines), which is consistent with the typical RP instability where the material thins at the troughs and accumulates at the peaks. In comparison, the resultant nanoparticles in (b) are slightly misaligned relative to the prescribed peaks. This difference can be explained as follows. The RP instability tends to thin and pinch the lines at the trough of the perturbation. If the trough is Ag-rich, the Ag migration and the RP instability cooperate in breaking the line. However, if the trough is Ni-rich, Ag migration and the RP instability compete. Cooperation and competition should be more apparent in the small amplitude case, since in this case breakup occurs later. Indeed, the left panel of Fig. 4 shows that for a Ag-rich trough (a), the primary particle positions are aligned with the peak regions. For the Ni-rich trough (b), the trough coarsens slightly as the Ag soluto-capillary effect opposes the RP instability. The initially Ag-rich regions eventually act as the pinch points and the primary particles end slightly off-center from the original synthetic perturbation peak; secondary particles also emerge due to the inter-Ag filament thinning. Notably, all secondary satellite particles are

nearly pure Ag and thus, while most of the core-shell nanoparticles are $\sim \text{Ni}_{0.5}\text{Ag}_{0.5}$, primary particles that neighbor a secondary satellite are Ag-deficient.

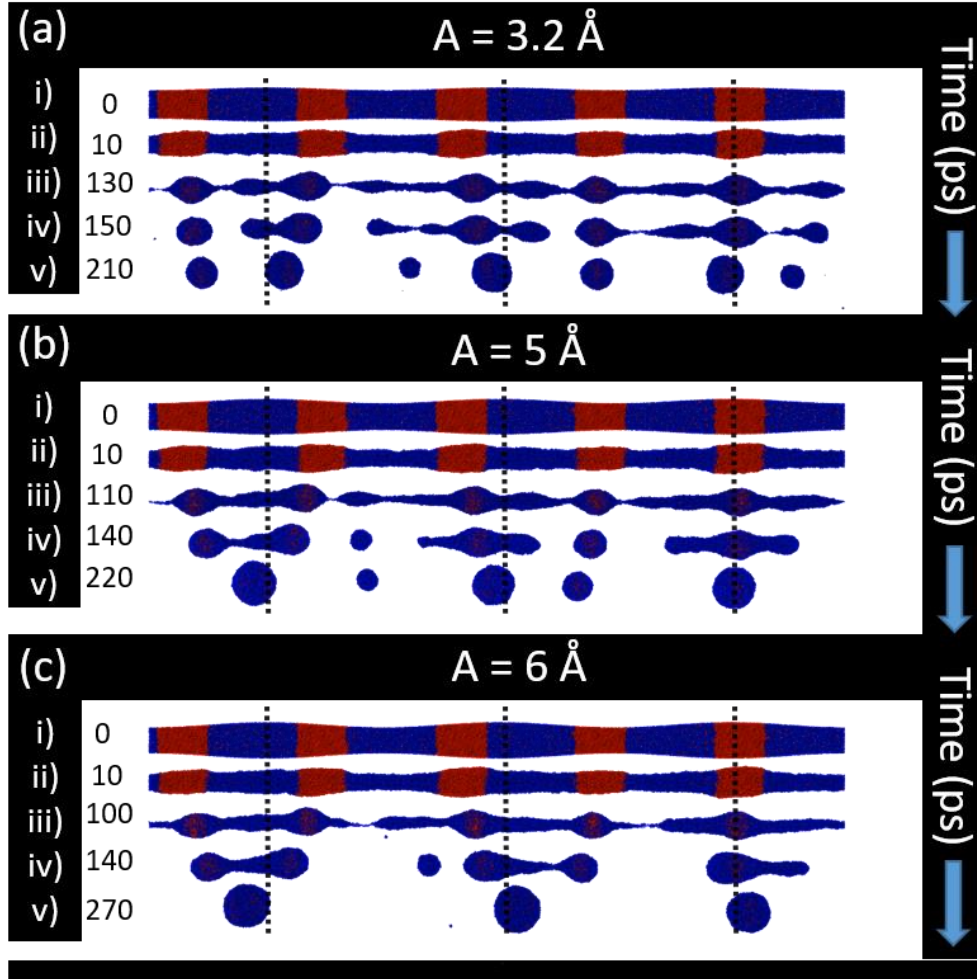


Figure 5. Time evolution of synthetic lines patterned with wavelength $\lambda_{\text{RP}}=533.0\text{\AA}$ and amplitudes $A=3.2 \text{ \AA}$ (a), $A=5 \text{ \AA}$ (b), and $A=6 \text{ \AA}$ (c). Time labels (in ps) are placed next to the corresponding lines. The labels i)-v) correspond to those of in Fig. 4. Guides (dotted lines) are placed at the location of the original peak in i). Except for the wavelength, the geometric details for the lines are as given in Table 2 under simulation C.

To test the competition between the soluto-capillary effect and the RP, we use the PS lengthscale, λ_{PS} , from Fig. 4 (see C from Table 2 for the parameters); and in addition we pattern the synthetic perturbations at longer (slower growth rate) unstable wavelengths ($\lambda_{RP} = 533.0 \text{ \AA}$; see Fig. 2, simulation C) and variable amplitudes. Figure 5 illustrates the time evolution of these structures with the following initial amplitudes in i): (a) 3.2 \AA , (b) 5 \AA , and (c) 6 \AA (larger amplitudes were also simulated, and the outcomes are similar to (c)). The times i)-iv) are similar to those described for Fig.3 and Fig.4. Time v) represents the earliest time stamp of full droplet coalescence. The main finding is that the number of resultant primary droplets depends on the amplitude of the prescribed perturbation. At low amplitude ($A < 5 \text{ \AA}$; (a)), the soluto-capillary driven instability clearly dominates as 5 primary nanoparticles (droplets roughly comparable in size) result and are positioned near the original Ni-rich regions (the Ag migration offsets the resultant droplet positioning slightly and leads to formation of 2 smaller satellite droplets). At intermediate amplitudes ($5 \text{ \AA} < A < 6 \text{ \AA}$; (b)), there is a transition: 4 primary nanoparticles result (also one satellite droplet), and the coalescence of two Ni regions occurs adjacent to the peak located in the Ag region (left-most droplet). Finally, at higher amplitudes ($A > 6 \text{ \AA}$; (c)), the RP driven instability dominates as 3 primary nanoparticles result and are located at the peaks of the synthetic perturbations.

Temperature (K)	Reference	Amplitude (\AA)	Eff. Amplitude (\AA)	MD Pinch Time (ps)	RP Theory Pinch Time (ps)
2000	Fig.3 (2000K)	16	4.7	40	29
1400	Fig.3 (1400K)	16	4.7	30	27
1400	Fig.4 (Ni Trough)	3.2	0.8	100	80

1400	Fig.4 (Ni Trough)	16	4.6	70	35
1400	Fig.4 (Ag Trough)	3.2	0.8	120	80
1400	Fig.4 (Ag Trough)	16	4.6	60	35
1400	Fig.4 (Mixed Trough)	3.2	0.8	100	80
1400	Fig.4 (Mixed Trough)	16	4.6	50	35

Table 3: Comparison of simulated breakup (pinch) times and predicted pinch times according to RP theory for the simulations **A**, **B**, and **C**, as well as others not described in the text.

Finally, we compare MD pinch times of the nanoscale alloys to RP theory pinch times. Table 3 lists the MD simulated breakup times for the simulations reported here (where data was recorded every 10ps), and the prediction made via RP theory. The theoretical breakup times are based on the linear growth rate ω , amplitude, A , and effective radius, R_{eff} , via:

$$t_{\text{pinch}} = \frac{-\ln (A_{\text{eff}}/R_{\text{eff}})}{\omega}. \quad (4)$$

Though detailed statistics and higher time resolution output would enhance the accuracy of the MD pinch time, the simulated breakup times agree well with the theoretical predictions even though, in some instances, PS competes with or enhances RP. Thus, it appears that the soluto-capillary dynamics occur on timescales similar¹ to those of traditional RP.

4. Conclusions

¹ Although the MD pinch times are comparable in size to the RP predictions, they are consistently longer, possibly due to nonlinear effects which slow down the exponential growth predicted by linear stability analysis.

Molecular dynamics (MD) simulations are used to investigate the effect of phase separation on the breakup mechanism of thin liquid lines of $\text{Ni}_{0.5}\text{Ag}_{0.5}$ alloy in vacuum. At 2000K, the NiAg structures are mostly homogeneous and the defining phase separation (PS) lengthscale, λ_{PS} , is much smaller than the Rayleigh-Plateau (RP) lengthscale, λ_{RP} . Here, breakup occurs in the classical manner, as if the structure were homogeneous with material parameters averaged over those of the constituents, and resultant nanoparticles are aligned with the peak of the underlying synthetic perturbations. At 1400K, the PS lengthscale is comparable to the RP lengthscale and the long axis migration of Ag onto Ni influences the resultant droplet location relative to the initial perturbation. The positioning of the final droplets is found to be influenced by the composition of the trough of the undulations and the strength of the RP instability (controlled by the amplitude). For small amplitudes PS competes with RP when lines contain Ni-rich troughs, resulting in some primary nanoparticles of Ag@Ni core-shell morphology aligned with the initially Ni-rich regions as well as some pure Ag satellite drops. When the troughs contain either Ag-rich or mixed NiAg troughs the RP instability is complemented by the PS structure resulting in primary nanoparticles aligned with the peaks of the initial perturbation. In general, these resultant nanoparticles are of Ag@Ni core-shell morphology, but for the low amplitude, Ag-rich trough, some pure Ag satellite droplets form.

The soluto-capillary/RP competition is further interrogated by simulating lines with PS lengthscales shorter than λ_{RP} , so that growth of the RP instability is slow relative to PS-induced perturbations. We demonstrate that tuning the synthetic perturbation amplitude dictates whether soluto-capillarity or RP drives the instability. Keeping in mind the average line radius of 35.5 Å, when the amplitude is sufficiently small (here, $A < 5$ Å), soluto-capillarity dominates. Increasing

the amplitude increases the “strength” of the RP instability and for $A > 6 \text{ \AA}$ the RP mechanism dominates. The MD breakup times of the nanoscale alloys are found to be in good agreement with the predictions of RP theory.

Supporting Information Description: Section S.1: discussion of the construction and equilibration of the bulk structures. Section S.2: details of the creation of the lines and slices of the final nanoparticles (Fig.S.1, S.2, and S.3). Section S.3: time evolution of lines at maximum RP wavelength (Fig.S.4.) and discussion.

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