Morphological instability of stressed spherical particles growing by diffusion in a matrix

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The morphological stability of a growing spherical particle epitaxially stressed in a supersaturated matrix has been investigated with respect to shape deviation of the particle from sphericity expanded on a basis of spherical harmonics $Y_l^0(\theta)$. A dispersion law has been determined for the growth rate of each harmonic, and a critical radius of the particle above which the sphere is unstable has been determined as a function of the different parameters of the problem such as the lattice mismatch between the matrix and the particle or the ratio of shear modulus. The influence of stress on the instability threshold already studied [Mullins and Sekerka, J. Appl. Phys. **34**, 323 (1963)] in the case of a stress-free particle has been finally investigated.

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I. INTRODUCTION

The diffusional evolution of microstructures consisting of matrix and particle phases in metals is of great technological importance since the shape of the particles strongly influences the mechanical characteristics of materials, among which are stiffness, strength, or toughness. The evolution of the size and shape of particles has been widely investigated for a number of materials ranging from nickel-based superalloys and aluminum to steel from both experimental and theoretical points of view. For example, experimental observations of nickel-based superalloys have demonstrated that the kinetic of the precipitate evolution by diffusion is influenced by the elastic effects of epitaxy in the general case of anisotropic and nonhomogeneous elastic media as well as by the surface energy and nucleation density effects.[1,2] It has also been observed in Ni-Al alloys that spherical precipitates may evolve toward cuboid, platelike, or rodlike shaped particles depending on the values of the elastic and interface energy or the magnitude and symmetry of stress.[1] Using diffusion[3–5] or sharp interface models (see Ref. 6 and references therein), the microstructure evolution of multicomponent materials has also been widely investigated. The diffusion interface model where the evolution of materials is mimicked through the evolution of a smooth field (e.g., composition or phase field) has been used to characterize, for example, martensitic transformation and diffusional microstructures in three dimensions.[7–9] Recently, sharp interface models have been used to study the coarsening and Ostwald ripening.[10,11] Simulations in two and three dimensions have been carried out and the development of microstructures, i.e., precipitate alignment, translation, merging, and coarsening, has been characterized as a function of elastic inhomogeneity, misfit strain, and applied fields (see Refs. 13–15 and references therein).

Analytical analysis of the linear stability of the shape of precipitates undergoing diffusion-controlled growth in a supersaturated matrix has been first performed by Mullins and Sekerka[16,17] and co-workers.[18] These authors have demonstrated that above a critical radius equal to seven times the nucleation radius, the spherical particles are unstable with respect to shape perturbations decomposed on a basis of spherical harmonics. In their papers, two terms have been considered in the expression of the growth rate of each harmonic: the gradient of concentration in the matrix favoring the growth of the perturbation and the surface energy favoring the decay. A similar study has been performed by Coriell *et al.*[19] in the case of a cylindrical precipitate embedded in an infinite size matrix. Considering radial and axial sinusoidal perturbations of the interface of the precipitate, a critical radius has also been determined above which the particles are unstable. In the present paper, the stress effect on the instability threshold of spherical particles has been investigated.

The problem of the stability of the surface of stressed planar solids has been first studied by Asaro and Tiller, Grinfeld, and others.[20–25] Considering sinusoidal fluctuations of the surface, a critical wave number has been determined below which the solid undergoes morphological changes. The stability of cylindrical stressed structures such as pores in a matrix, whiskers, or tubules has also been investigated assuming that the mass transport mechanism is surface diffusion.[26–29] It has been demonstrated that an applied stress along the axis of the cylinder strongly influences the instability threshold when sinusoidal fluctuations of the radius are considered. The more general case of nonaxisymmetric instability has been investigated by Kirill *et al.*[28] It has been demonstrated by these authors that a corkscrew-shaped instability can appear for a particular spectrum of applied stress, and for a cylindrical tubule, two distinct eigenmodes develop for any wave number, applied stress, or geometry.

In this paper, the problem of the morphological change of a spherical particle growing in a supersatured matrix has been reexamined in the case where the precipitate is epitaxially stressed in its infinite size matrix. The interaction of the elastic deformation and the composition fields has been considered through the generalized Gibbs-Thomson boundary condition for the composition in the matrix at the matrix-precipitate interface. It is then assumed that the atomic volumes of the two chemical species are of the same order of magnitude so that stress generated by nonuniform concentration is negligible.[10–12,14,15] The effect of this stress due to compositional inhomogeneity has already been studied but in the case of a precipitate growing from a supersatured melt.[30] The elastic deformation of the spherical precipitate and the-matrix has been first calculated in the case where the epitaxy reduces to an eigenstrain located in the precipitate. Consid-

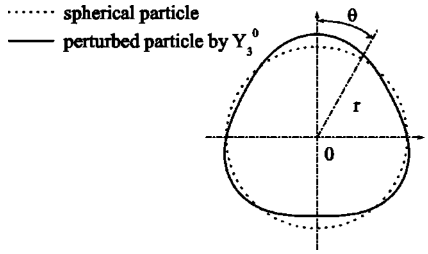

FIG. 1. An initially spherical surface of radius r_0 is perturbed by a spherical harmonic $Y^0_{l=3}$.

ering shape deviation of the particle from sphericity decomposed on a basis of spherical harmonics $Y_l^0(\theta)$, a critical radius has been determined above which the particle is unstable. The effect of lattice mismatch on instability threshold has been finally characterized.

II. LINEAR STABILITY ANALYSIS OF THE SHAPE OF SPHERICAL PARTICLES

A. Determination of the epitaxial stress

An initially spherical particle of radius r_0, shear modulus μ_p, and Poisson's ratio ν_p is embedded in an infinite-size matrix of shear modulus μ_m and Poisson's ratio ν_m (see Fig. 1). The two lattice parameters of the matrix a_m and the precipitate a_p are assumed to be independent of the concentration fields. The calculations presented in this paper have been performed using spherical coordinates (r,θ,φ). Since the two lattice networks of the matrix and particle are different and the interface is assumed to be coherent, an eigenstrain $\epsilon_{rr}^{p,*}=\delta a/a_p$ can be defined in the particle where $\delta a=(a_p-a_m)$ is the lattice mismatch. Without loss of generality, it is assumed that $a_p>a_m$. The first step of this work has been to determine the elastic deformation of both phases when the interface is flat. This has been carried out in the framework of linear elasticity theory solving in both phases $(k=m,p)$ the Navier's equation,

$$\mu_k \nabla^2 \mathbf{u}^{k,0} + (\lambda_k+\mu_k)\,\nabla\ \nabla\, \mathbf{u}^{k,0} = \mathbf{0}, \tag{1}$$

with $\mathbf{u}^{k,0}$ the elastic displacement field and λ_k and μ_k Lame's constants of both phases.

Considering a displacement field of the form

$$u_i^{k,0} = f^{k,0}(r)x_i, \tag{2}$$

it has been found that Navier's Eq. (1) is satisfied if $f^{k,0}(r)=A^{k,0}/r^3+B^{k,0}$, where $A^{k,0}$ and $B^{k,0}$ are two constants. Once the elastic displacement is determined, the strain tensor $\epsilon_{ij}^{k,0}=\frac{1}{2}(u_{i,j}^{k,0}+u_{j,i}^{k,0})$ can be derived as well as the stress tensor with the help of Hooke's law written in the particle phase,

$$\sigma_{ij}^{p,0} = C_{ijkl}^{p}\{\epsilon_{kl}^{p,0}-\epsilon_{kl}^{p,*}\}, \tag{3}$$

and in the matrix,

$$\sigma_{ij}^{m,0} = C_{ijkl}^{m}\epsilon_{kl}^{m,0}, \tag{4}$$

with C_{ijkl}^r the elastic constants of the two phases $(r=m,p)$.

Considering that the interface must be traction-free and the deformation continuous at $r=r_0$,

$$(\sigma_{ij}^{p,0}-\sigma_{ij}^{m,0})n_j=0, \tag{5}$$

$$\epsilon_{rr}^{p,0}+\frac{\delta a}{a_p}=\epsilon_{rr}^{m,0}, \tag{6}$$

with $(i,j)=(r,\theta,\varphi)$ and $\mathbf{n}=(1,0,0)$ the normal to the sphere, the elastic state can be easily determined to the first order in $\delta a/a_p$. For example, the σ_{rr} component of stress in the particle has been found to be

$$\sigma_{rr}^{p,0}(r,\theta,\varphi) = -\frac{2\mu_p\mu_*}{\mu_*\dfrac{1-2\nu_p}{1+\nu_p}-1}\frac{\delta a}{a_p} \tag{7}$$

and

$$\sigma_{rr}^{m,0}(r,\theta,\varphi) = -\frac{2\mu_m}{\mu_*\dfrac{1-2\nu_p}{1+\nu_p}-1}\frac{r_0^3}{r^3}\frac{\delta a}{a_p} \tag{8}$$

in the matrix, with $\mu_*=\mu_m/\mu_p$. At this point, it can be underlined that even if the nonhomogeneous strain is localized in the precipitate, the resulting elastic strains and stresses extend over the sphere in the matrix.

B. Morphological change by diffusion

The diffusion-controlled growth of a spherical particle has been investigated from a supersaturated matrix of initial concentration c_∞. The concentration in the particle c_p is assumed to be constant; the position-dependent concentration in the matrix is labeled c_m. The equilibrium value of c_m when the matrix-particle interface is flat is denoted by c_0. The velocity v of the growing interface by diffusion is then defined as

$$v = \frac{D}{c_p-c_s}\frac{\partial c_m}{\partial n}, \tag{9}$$

where c_s is the concentration in the matrix near the curved interface, D is the diffusion coefficient, and $(\partial c_m/\partial n)$ is the normal derivative of the concentration field at the interface. The evolution of the stressed precipitate is investigated in the rest of this paper with the hypothesis[16]

$$\left|\frac{c_\infty-c_s}{c_p-c_s}\right| \leqslant \left|\frac{c_\infty-c_0}{c_p-c_0}\right| \ll 1, \tag{10}$$

where the concentration field near the interface can be obtained solving Laplace's Eq. (11) while holding constant the shape of the precipitate. Assuming also local equilibrium at the interface, the concentration field c_m and the radius of the distorded sphere ρ satisfy the following set of equations:[3–5,31,32]

$$\Delta^2 c_m = 0, \tag{11}$$

$$c_m(\infty,t)=c_\infty, \tag{12}$$

in the matrix and

$$D\frac{\partial c_m}{\partial n}\bigg)_{r=\rho} = (c_p-c_s)\frac{d\rho}{dt}, \tag{13}$$

$$c_m(\rho,t)=c_s=c_0+c_0\Gamma_D\left(\kappa+\frac{G^{elas}}{\gamma}\right), \quad (14)$$

at the interface, where t is time and Γ_D is the capillarity term defined by $\Gamma_D=\gamma\Omega/RT$ with γ the interfacial energy, Ω the increment of particle volume per mole of added solute, R the gas constant, and T the absolute temperature. Since the shape of the sphere is modified, the initially traction-free particle is assumed to undergo elastic deformation to satisfy the mechanical equilibrium at the interface. Relaxation stresses and strains labeled $\sigma_{ij}^{k,rel}$ and $\epsilon_{ij}^{k,rel}$, respectively, are then appearing in both phases leading to an elasticity term G^{elas} in the modified Gibbs-Thompson Eq. (14). Since it is assumed that the lattice parameter does not depend on concentration fields in the matrix and in the precipitate, the coupling effect between elasticity and diffusion occurs through this Gibbs-Thomson Eq. (14) which is a good approximation for systems where stress generated by composition gradients is much smaller than misfit stress. During the diffusion-controlled growth of the precipitate, the total stress and strain tensors are defined by

$$\sigma_{ij}^{k,tot}=\sigma_{ij}^{k,0}+\sigma_{ij}^{k,rel}, \quad \epsilon_{ij}^{k,tot}=\epsilon_{ij}^{k,*}+\epsilon_{ij}^{k,0}+\epsilon_{ij}^{k,rel}, \quad (15)$$

with $\sigma_{ij}^{k,rel}=C_{ijop}^{k}\epsilon_{op}^{k,rel}$ and $k=m,p$. Following Leo and Sekerka,[31] the elasticity term G^{elas} can be then written as

$$G^{elas}=\frac{1}{2}\sigma_{ij}^{p,tot}(\epsilon_{ij}^{p,tot}-\epsilon_{ij}^{p,*})-\frac{1}{2}\sigma_{ij}^{m,tot}\epsilon_{ij}^{m,tot}+\sigma_{ij}^{m,tot}(\epsilon_{ij}^{m,tot}-\epsilon_{ij}^{p,tot}). \quad (16)$$

The key point in solving this boundary value problem is to determine for each profile ρ of the moving interface the elastic deformation in the precipitate and the matrix. This has been achieved considering a radius of the sphere ρ of the form (see Fig. 1)

$$\rho(\theta,t)=r_o(t)+\delta(t)Y_l^0(\theta), \quad (17)$$

where r_0 is the radius of the growing spherical particle and δ is the amplitude of the shape perturbation Y_l^0, l assuming integral values $(l=0,1,2,\ldots)$. At this point it has to be noticed that the linear stability analysis of the sphere has been carried out to the first order in amplitude δ with respect to Legendre's function $P_l^0(\cos\theta)$ corresponding to a spherical harmonic $Y_l^0(\theta)$ that does not depend on φ angle, i.e., for $m=0$. Since the epitaxial strain determined in the first subsection is independent of φ, the elasticity problem has been carried out in the hypothesis of a symmetrically loaded sphere where the displacement components u_r and u_θ are independent of φ. It can also be emphasized that the evolution of any infinitesimal distortion of the sphere independent of φ can be obtained by developing the fluctuation on the basis of orthogonal functions Y_l^0 and considering the set of linear equations of evolution used in this work. Writing the mechanical equilibrium equations on the perturbed interface of the precipitate yields

$$(\sigma_{ij}^{p,0}+\sigma_{ij}^{p,rel})n_j^{rel}=(\sigma_{ij}^{m,0}+\sigma_{ij}^{m,rel})n_j^{rel}, \quad (18)$$

$$u_i^{p,tot}=u_i^{m,tot} \quad (19)$$

with $u_i^{k,tot}$ the total displacement, $(i,j)=(r,\theta,\varphi)$, and $\mathbf{n}^{rel}=(1,-(\delta/r_0)(dY_l^0 d\theta),0)$ the normal to the perturbed sphere. Navier's Eq. (1) has been solved representing the elastic displacement of relaxation $\mathbf{u}^{k,rel}$ in terms of Papkovich-Neuber potentials $\psi^{k,rel}$ and $\phi^{k,rel}$ as follows:

$$\mathbf{u}^{k,rel}=\frac{1}{\mu_k}\left[\psi^{k,rel}+\frac{1}{4(1-\nu_k)}\nabla(\phi^{k,rel}-\mathbf{r}\cdot\psi^{k,rel})\right], \quad (20)$$

with $k=m,p$ and

$$\nabla^2\psi^{k,rel}=\mathbf{0}, \quad (21)$$

$$\nabla^2\phi^{k,rel}=0. \quad (22)$$

Following Lur'e,[33] the general potentials $\psi^{p,rel}$ and $\phi^{p,rel}$ in the precipitate can be taken as

$$\psi_r^{p,rel}(r,\theta)=-\alpha_0^p l r^l Y_{l-1}^0(\theta),$$

$$\psi_\theta^{p,rel}(r,\theta)=\alpha_0^p r^l\frac{Y_{l-1}^0}{d\theta}(\theta),$$

$$\psi_\varphi^{p,rel}(r,\theta)=0, \quad \phi^{p,rel}(r,\theta)=-\alpha_1^p r^{l-1}Y_{l-1}^0(\theta), \quad (23)$$

and the displacement field yields in this case

$$u_r^{p,rel}(r,\theta)=[\alpha_0^p r^{l+1}(l+1)(l-2+4\nu_p)+\alpha_1^p r^{l-1}l]Y_l^0(\theta), \quad (24)$$

$$u_\theta^{p,rel}(r,\theta)=[\alpha_0^p(5-4\nu_p+l)r^{l+1}+\alpha_1^p r^{l-1}]\frac{dY_l^0}{d\theta}(\theta). \quad (25)$$

Changing l by $-(l+1)$ in the potentials defined in Eq. (23) yields the following displacements in the matrix:

$$u_r^{m,rel}(r,\theta)=\left[\frac{\alpha_0^m}{r^l}l(l+3-4\nu_m)-\frac{\alpha_1^m(l+1)}{r^{l+2}}\right]Y_l^0(\theta), \quad (26)$$

$$u_\theta^{m,rel}(r,\theta)=\left[\frac{\alpha_0^m}{r^l}(4-4\nu_m-l)+\frac{\alpha_1^m}{r^{l+2}}\right]\frac{dY_l^0}{d\theta}(\theta). \quad (27)$$

The stress and strain tensors in the precipitate and the matrix can then be easily derived in the framework of linear and isotropic elasticity theory.[33] The constants α_0^k and α_1^k have been determined with the help of Eqs. (18) and (19), and the elasticity term G^{elas} defined in the modified Gibbs-Thompson Eq. (14) has been found to be to the first order in the fluctuation amplitude δ

$$G^{elas}=G^0+\delta G^{rel}+\Theta(\delta^2), \quad (28)$$

with

$$G^0 = \mu_p\left(\frac{\delta a}{a_p}\right)^2 g^0 = \mu_p\left(\frac{\delta a}{a_p}\right)^2 \frac{\mu_*(1+\nu_p)[10\mu_*(1-2\nu_p)-(1+\nu_p)]}{2[1+\nu_p-\mu_*(1-2\nu_p)]^2},$$

and

$$G^{rel} = \frac{\mu_p}{r_0}\left(\frac{\delta a}{a_p}\right)^2 g^{rel} = \frac{\mu_p}{r_0}\left(\frac{\delta a}{a_p}\right)^2 \frac{f(\mu_*,\nu_p,\nu_m)}{g(\mu_*,\nu_p,\nu_m)}. \tag{29}$$

The two dimensionless functions f and g are defined by

$$\begin{aligned} f(\mu_*,\nu_p,\nu_m) = {} & 3l(1+l)\mu_*^2(1+\nu_p)((-2+3l+2l^2)\mu_*^2(1+\nu_m)(1-2\nu_p)[1-2\nu_p+l(3-4\nu_p)] \\ & -(1+\nu_p)\{-6+7\nu_m+6\nu_p-5\nu_m\nu_p+l(-7+9\nu_m+7\nu_p-10\nu_m\nu_p) \\ & +l^2[7-7\nu_p+\nu_m(-9+4\nu_p)]+2l^3[3-3\nu_p+\nu_m(-5+4\nu_p)]\} \\ & -2\mu_*\{2(1-2\nu_p)[1-(2-3\nu_m)\nu_p]+l[2-11\nu_p+8\nu_p^2-3\nu_m(1-6\nu_p+4\nu_p^2)] \\ & +2l^3[(4-5\nu_p)\nu_p+\nu_m(-2-3\nu_p+8\nu_p^2)]+l^2[2+8\nu_p-15\nu_p^2+\nu_m(-8-9\nu_p+32\nu_p^2)]\}) \end{aligned} \tag{30}$$

and

$$\begin{aligned} g(\mu_*,\nu_p,\nu_m) = {} & [l^2(3+\mu_*-4\nu_m)-(2-\mu_*)(1-\nu_m) \\ & +l(-1+\mu_*+2\nu_m-2\mu_*\nu_m)] \\ & \times[1+\nu_p-\mu_*(1-2\nu_p)]^2\{1+l+l^2+\nu_p+2l\nu_p \\ & -(2+l)\nu_*[-1+2\nu_p-l(3-4\nu_p)]\}. \end{aligned} \tag{31}$$

The concentration of solute c_m has also been determined to the first order in δ. Following Mullins and Sekerka,[16] the general solution of Laplace's Eq. (11) has been written as

$$c_m(r,\theta,\varphi) = c_\infty + \frac{A_m}{r} + B_m\frac{\delta}{r^{l+1}}Y_l^0(\theta) + \Theta(\delta^2). \tag{32}$$

The constants A_m and B_m have been determined with the help of Eqs. (12)–(14) considering that the first-order development in δ of the curvature κ in Eq. (14) can be expressed as[16]

$$\kappa(\theta,\varphi) = \frac{2}{\rho} - \nabla^2\rho + \Theta(\delta^2) = \frac{2}{r_0}\left(1-\frac{\delta}{r_0}Y_l^0(\theta)\right) + \delta\frac{l(l+1)}{r_0^2}Y_l^0(\theta) + \Theta(\delta^2). \tag{33}$$

Finally, the concentration field in the matrix yields

$$\begin{aligned} c_m(r,\theta,\varphi) & = c_\infty + (c_0-c_\infty)\frac{r_0}{r} + \frac{\Gamma_D c_0}{r}\left(2+\frac{r_0}{\gamma}G^0\right) \\ & + \frac{(c_0-c_\infty)r_0^l + c_0\Gamma_D l(l+1)r_0^{l-1} + \frac{\Gamma_D c_0}{\gamma}\left(\frac{G^0}{r_0}+G^{rel}\right)}{r^{l+1}} \\ & \times \delta Y_l^0(\theta) + \Theta(\delta^2). \end{aligned} \tag{34}$$

With the help of Eqs. (9), (13), and (34), the velocity v of the interface satisfies the following relation:

$$\begin{aligned} v & = \frac{dr_0}{dt} + \frac{d\delta}{dt}Y_l^0(\theta) \\ & = \frac{D}{c_p-c_s}\left(\frac{\partial c_m}{\partial n}\right)_{r=\rho} \\ & = \frac{D}{c_p-c_s}\left[\frac{c_\infty-c_R}{r_0} - \frac{c_0\Gamma_D}{r_0^2}\frac{r_0G^0}{\gamma} + \delta\left\{(l-1)\frac{c_\infty-c_0}{r_0^2} - \frac{c_0\Gamma_D}{r_0^3}\right.\right. \\ & \quad \times\{l(l+1)^2-4\} - \frac{c_0\Gamma_D}{\gamma}\left((l-1)\frac{G^0}{r_0^2}+(l\right. \\ & \quad \left.\left.\left.+1)\frac{G^{rel}}{r_0}\right)\right\}Y_l^0(\theta)\right], \end{aligned} \tag{35}$$

with $c_R = c_0 + (2c_0\Gamma_D/r_0)$ the concentration on the undistorded sphere. Equating coefficients of Y_l^0, the growth rate $\dot{\delta} = d\delta/dt$ of the amplitude of the spherical harmonic has been finally found to be

$$\frac{\dot{\delta}}{\delta} = \frac{D}{c_p-c_s}\frac{l-1}{r_0}\left[\frac{c_\infty-c_0}{r_0} - \frac{c_0\Gamma_D}{r_0^2}\{2+(l+1)(l+2)\} - \frac{c_0\Gamma_D}{\gamma}\left(\frac{G^0}{r_0}+\frac{l+1}{l-1}G^{rel}\right)\right]. \tag{36}$$

All harmonics such that $l > 1$ and satisfying the inequality

$$\frac{c_\infty-c_0}{r_0} - \frac{c_0\Gamma_D}{r_0^2}\{2+(l+1)(l+2)\} - \frac{c_0\Gamma_D}{\gamma}\left(\frac{G^0}{r_0}+\frac{l+1}{l-1}G^{rel}\right) \geqslant 0 \tag{37}$$

are assumed to grow. The problem of a stress-free precipitate already investigated by Mullins and Sekerka[16] have been first reexamined here since the instability threshold defined by the above-cited authors can be derived from Eq. (37) assuming there is not epitaxy between the precipitate and the matrix ($\delta a = 0$). In that case, a critical radius of the sphere $r_0^c(l)$ can be defined above which the harmonics develop,

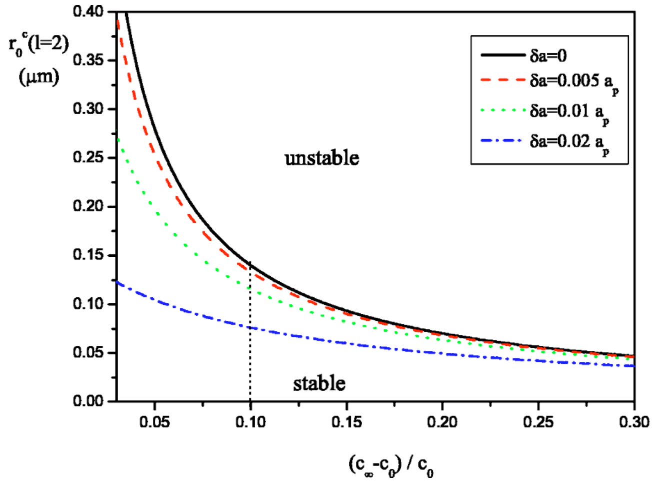

FIG. 2. (Color online) Critical radius r_0^c of the harmonic Y_2^0 as a function of supersaturation $(c_\infty - c_0)/c_0$ for different values of the lattice mismatch $\delta a/a_p$.

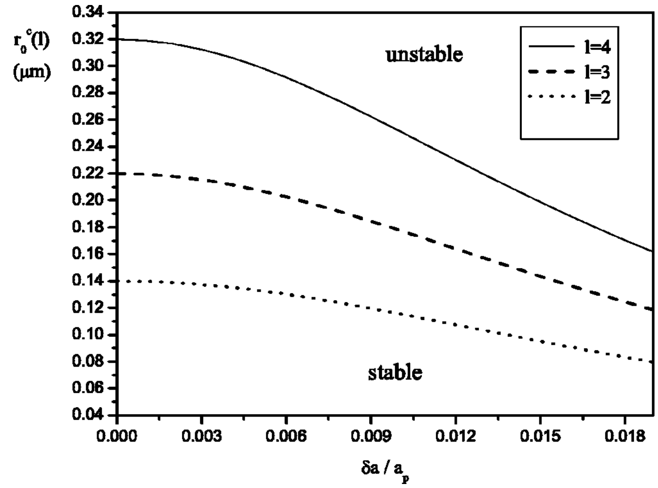

FIG. 3. Critical radius $r_0^c(l)$ for different values of l vs the lattice mismatch $\delta a/a_p$.

$$r_0^c(l) = \left[\tfrac{1}{2}(l+1)(l+2) + 1\right] r^*, \tag{38}$$

where r^* is the critical nucleation radius defined by

$$r^* = \frac{2\Gamma_D c_0}{c_\infty - c_0}. \tag{39}$$

The critical radius for which at least the second harmonic Y_2^0 develops is

$$r_0^c(2) = 7r^* = \frac{14\Gamma_D c_0}{c_\infty - c_0}. \tag{40}$$

When the precipitate is epitaxially stressed in the matrix, the critical radius is modified as follows:

$$r_0^c(l) = \frac{\tfrac{1}{2}(l+1)(l+2)+1}{1 - K\left(g^0 + \dfrac{l+1}{l-1} g^{rel}\right)} r^*, \tag{41}$$

where $K = \sigma^2 r^* / 2\mu_p \gamma$ is a dimensionless constant and $\sigma = \mu_p(\delta a/a_p)$ is the epitaxial stress. The sphere is then assumed to be unstable when at least the second harmonic Y_2^0 appears that is for radii $r_0 > r_0^c(l=2)$. This minimum critical radius $r_0^c(2)$ has been plotted in Fig. 2 as a function of supersaturation $(c_\infty - c_0)/c_0$ for different values of the lattice mismatch δa and for the following average values of the physical parameters: $\Gamma_D \approx 10^{-9}$ m, $\gamma \approx 1$ J/m^2, $\mu_p \approx 100$ GPa, $\mu_* = 0.5$, and $\nu_p = \nu_m = 0.3$ corresponding to binary alloys. It can be observed that the critical radius $r_0^c(2)$ strongly decreases as the lattice mismatch increases, demonstrating the destabilizing effect of epitaxy on the sphere. For a supersaturation $(c_\infty - c_0)/c_0$ of 10%, the critical radius $r_0^c(l=2)$ for particles free of any stress has been found to be 0.14 μm.[16] The evolution of $r_0^c(l)$ has been plotted in Fig. 3 as a function of the lattice mismatch $\delta a/a_p$ for a 10% supersaturation and for $l = 2, 3, 4$. From this curve, it can be emphasized that the effect of epitaxy already observed on the development of the harmonic $l=2$, i.e., diminution of the critical radius, still applies for the harmonics of higher orders. For a lattice mismatch $\delta a = 0.01 a_p$, the radius $r_0^c(2)$ is reduced by 20% compared to the radius determined in the case of unstressed particle. The growth of perturbation amplitude δ can also be compared to the growth of the radius r_0. Using Eqs. (35) and (36), the relation already determined by Mullins and Sekerka[16] in the case of an unstressed particle embedded in a matrix is modified as follows when the precipitate is epitaxially stressed:

$$\frac{\dot{\delta}/\delta}{\dot{r}_0/r_0} = (l-1)\left[1 - \frac{r_0^c(l)}{r_0}\right]\left[1 - K\left(g^0 + \frac{l+1}{l-1} g^{rel}\right)\right] \times \left[1 - \frac{r^*}{r_0} - K g^0\right]^{-1}. \tag{42}$$

Since the term

$$-K\left(g^0 + \frac{l+1}{l-1} g^{rel}\right)$$

is always positive when $\mu_* \leqslant 1$ and increases with l, the epitaxy is assumed to accelerate the growth of spherical harmonic perturbation Y_l^0 compared to the growth of the radius r_0. This accelerating effect can be observed in Fig. 4, where the ratio $\tau(l) = \dot{\delta}/\delta/\dot{r}_0/r_0$ has been plotted as a function of the lattice mismatch $\delta a/a_p$ for a particular radius $r_0 = 10 r_0^c(l=4)$ and for $l = 2, 3, 4$ and $(c_\infty - c_0)/c_0 = 0.1$. For the harmonic $l = 2$, the ratio $\tau(2)$, always smaller than 1 in the case of a stress-free particle, has been found to be greater than 1 above a critical lattice mismatch $\delta a/a_p \geqslant 0.0028$. This shows that under stress, even the Y_2^0 harmonic may develop faster than the sphere radius. As the lattice mismatch increases, the growth rate difference between high-order harmonics and the sphere becomes more and more important. It can finally be emphasized that one particular harmonic $Y_{l_M}^0$ for which the growth rate is maximum can be determined differentiating the growth rate $\dot{\delta}/\delta$ defined in Eq. (36) with respect to l. An average wavelength of the harmonic can then be defined as $\lambda_M = 2\pi r_0 / l_M$. The variation of this wavelength λ_M as a function of the lattice mismatch $\delta a/a_p$ has been drawn in Fig. 5 for $(c_\infty - c_0)/c_0 = 0.1$, $r_0 = 50 r^*$, and $\mu_* = 0.5$. It can be ob-

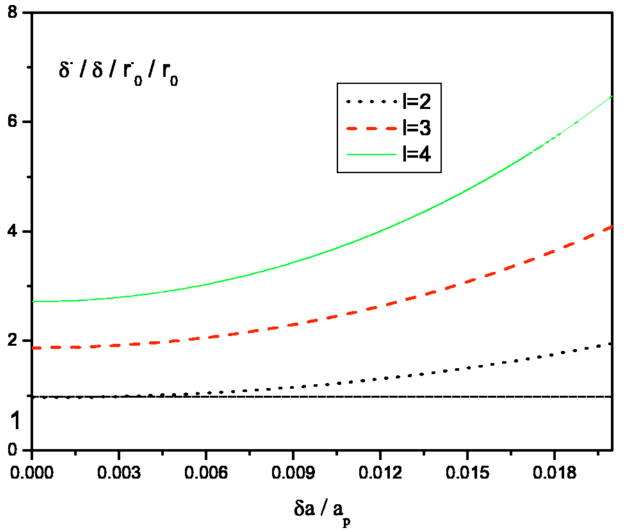

FIG. 4. (Color online) $\dot{\delta}/\delta/\dot{r}_0/r_0$ vs the lattice mismatch $\delta a/a_p$ for harmonics of different orders and for $r_0=10r_0^c(l=4)$.

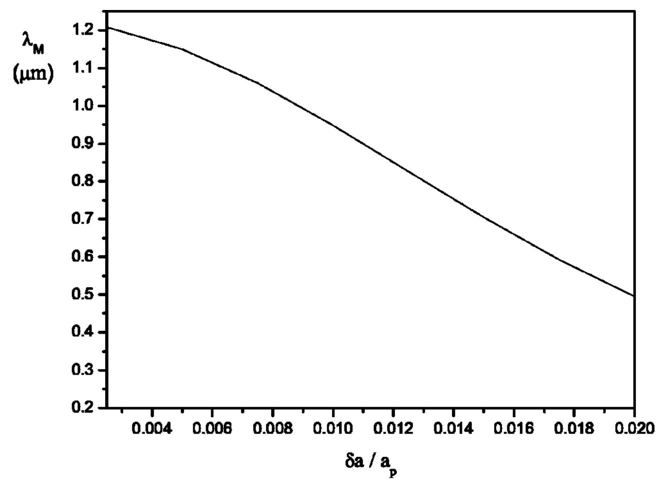

FIG. 5. The most probable wavelength λ_M vs $\delta a/a_p$ and for $r_0=50r^*$.

served that the epitaxy reduces the length scale λ_M of roughness developing onto the spherical surface.

III. CONCLUSION

In this paper, the linear stability analysis of a growing spherical particle epitaxially stressed in an infinite size matrix has demonstrated that when $\mu_* \leqslant 1$, the critical radius of the sphere above which spherical harmonic fluctuations can develop is strongly reduced as the lattice mismatch increases. The growth rate difference between the fluctuations and the radius of the sphere has been also observed to increase with the epitaxy and with the order of the considered spherical harmonic of the shape development of the sphere. The most probable harmonic to appear has been finally observed to be strongly stress-dependent.

The further step of this work would be the numerical study of the time evolution by diffusion of the different harmonic coefficients of the development of the surface profile including the nonlinear effect, φ dependence of stress, as well as stress due to composition inhomogeneity.

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[1] A. J. Ardell and R. B. Nicholson, Acta Metall. **14**, 1295 (1966).
[2] A. Maheshwari and A. J. Ardell, Phys. Rev. Lett. **70**, 2305 (1993).
[3] P. H. Leo, J. S. Lowengrub, and H. J. Jou, Acta Mater. **46**, 2113 (1998).
[4] Y. Wang and A. G. Khachaturyan, Acta Mater. **43**, 1837 (1995).
[5] W. C. Johnson and P. W. Voorhees, Solid State Phenom. **23**, 87 (1992).
[6] K. Thornton, J. Agren, and P. W. Voorhees, Acta Mater. **51**, 5675 (2003).
[7] Y. Yang and A. Kahachaturyan, Acta Mater. **45**, 759 (1997).
[8] D. Orlikowski, C. Sagui, A. Somoza, and C. Roland, Phys. Rev. B **59**, 8646 (1999).
[9] L.-Q. Chen, Annu. Rev. Mater. Sci. **32**, 113 (2002).
[10] N. Akaiwa, K. Thornton, and P. W. Voorhees, J. Comput. Phys. **173**, 61 (2001).
[11] K. Thornton, N. Akaiwa, and P. W. Voorhees, Acta Mater. **52**, 1365 (2004).
[12] K. Thornton, N. Akaiwa, and P. W. Voorhees, Phys. Rev. Lett. **86**, 1259 (2001).
[13] X. Li, J. Lowengrub, V. Cristini, and P. H. Leo, Metall. Mater. Trans. A **34**, 1421 (2003).
[14] H. J. Jou, P. H. Leo, and J. S. Lowengrub, J. Comput. Phys. **131**, 109 (1997).
[15] P. H. Leo, J. S. Lowengrub, and Q. Nie, J. Comput. Phys. **157**, 44 (2000).
[16] W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **34**, 323 (1963).
[17] W. W. Mullins, J. Appl. Phys. **28**, 333 (1975).
[18] F. A. Nichols and W. W. Mullins, J. Appl. Phys. **36**, 1826 (1965).
[19] S. R. Coriell and R. L. Parker, J. Appl. Phys. **36**, 632 (1965).
[20] R. J. Asaro and W. A. Tiller, Metall. Trans. **3**, 1789 (1972).
[21] M. A. Grinfeld, Dokl. Akad. Nauk SSSR **290**, 1358 (1986).
[22] D. J. Srolovitz, Acta Metall. **37**, 621 (1991).
[23] H. Gao, J. Mech. Phys. Solids **42**, 741 (1994).
[24] B. J. Spencer, P. W. Voorhees, and S. H. Davis, Phys. Rev. Lett. **67**, 3696 (1991).
[25] F. Jonsdottir, Modell. Simul. Mater. Sci. Eng. **3**, 503 (1995).
[26] J. Colin, Acta Mater. **46**, 4985 (2004).
[27] N. Sridhar, J. M. Rickman, and D. J. Srolovitz, Acta Metall. **45**, 2715 (1997).
[28] D. J. Kirill, S. H. Davis, M. J. Mikisis, and P. W. Voorhees, Interfaces Free Boundaries **4**, 371 (2002).
[29] F. Yang, Scr. Mater. **49**, 571 (2003).
[30] B. Caroli, C. Caroli, B. Roulet, and P. W. Voorhees, Acta Mater. **37**, 257 (1989).
[31] P. H. Leo and R. F. Sekerka, Acta Metall. **37**, 3119 (1989).
[32] F. Larche and J. W. Cahn, Acta Metall. **26**, 1579 (1978).
[33] A. I. Lur'e, *Three-Dimensional Problems of the Theory of Elasticity* (Wiley -Interscience, New York, 1964).