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Phase field theory of surface- and size-induced microstructures

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Abstract. – New surface- and size-induced microstructures are found as analytic solutions to a phase field theory of first-order phase transformations. A recently developed exact stability criterion, based on most destabilizing fluctuations, is used to analyze the stability and physical interpretation of each microstructure. Conditions for barrierless surface nucleation, *i.e.* relationship between surface energy, driving force for the transformation and sample size, are found. If they are met, some of these microstructures are destroyed resulting in the barrierless transformation to alternative phases.

Introduction. – The phase field or Ginzburg-Landau (GL) equation (1) is used for the description of a wide class of first-order phase transformations (PTs), including polymorphic, ferroelastic, martensitic, reconstructive, ferroelectric and magnetoelastic PTs, as well as twinning and dislocations. Several types of periodic analytic solutions of the time-independent GL equation, *i.e.*, static periodic microstructures, have been obtained for neglected surface energy [1,2]. However, differences in the surface energies of different phases may induce new surface phenomena, *e.g.* surface pre-melting, ordering or disordering [3,4], and can lead to new microstructures in the bulk. The effects of surfaces are of course most pronounced in nanoscale systems [4]. Surfaces were taken into account in [5], but for semi-infinite samples only; hence, this analysis did not account for the influence of sample size. It was found in [6] that the main effect of finite sample size, l, is a change in the bulk co-existence conditions. However, none of the microstructures for finite l was obtained in closed form, a shortcoming that prevented a comprehensive analysis of the combined effects of surfaces and sample size.

In this letter, *all static surface-induced microstructures in a finite sample are obtained analytically and a simple geometric method to analyze the effects of surfaces and sample size is developed*. Some of them exist only in nanoscale samples with phase-dependent surface energies. Others can be generated by barrierless nucleation, *i.e.*, nucleation that does not require fluctuations; the conditions for barrierless nucleation are found. The stability of new phases is analyzed using the method that we recently developed [7].

In one dimension, the standard dimensionless GL energy is of the form $g_{GL} = g(\xi) + \xi'(x)^2$, where ξ is the order parameter and $g(\xi)$ is the Landau potential. The energy of a specimen

of thickness l is $e = \int_{-l/2}^{l/2} g_{GL} dx + f(\xi_-) + f(\xi_+)$, where $f(\xi)$ is the surface energy, and $\xi_\pm$ are the values of ξ at the boundaries $x = \pm l/2$. The corresponding TDGL equation reads

$$\partial\xi/\partial t = -dg/d\xi + 2\xi'', \tag{1}$$

$$\xi'_- = p(\xi_-); \qquad \xi'_+ = -p(\xi_+); \qquad p(\xi) := f'(\xi)/2. \tag{2}$$

The boundary conditions simplify to $\xi'_\pm = 0$ if the surface energy is structure independent ($f' = 0$). Solutions that satisfy boundary conditions (2) cannot be found in closed form. However, given the general solution to eq. (1) (no boundary conditions imposed) we can "cut" from it solutions that satisfy eq. (2). For $\partial\xi/\partial t = 0$, the first integral of eq. (1) is $(\xi')^2 = g - g_0$ with boundary conditions $g(\xi_\pm) = g_0 + p^2(\xi_\pm)$, where g_0 is a constant and $g \geq g_0$. In this letter we present results only for the potential $g = B\xi^2 - \xi^3 + \xi^4$ (similar results are obtained for a 2-4-6 potential). Note that the factors before ξ^3 and ξ^4, as well as the kinetic and gradient energy coefficients in eq. (1), are set equal to unity by rescaling the length, time, energy and order parameter. This potential has two minima if $0 < B < 9/32$: a high-symmetry phase, H ($\xi_H = 0$), and a low-symmetry phase, L ($\xi_L = (3 + \sqrt{9 - 32B})/8$). When $B < 1/4$ ($B > 1/4$) the stable (lower-energy) phase is L (H); H and L are in thermodynamic equilibrium for $B = 1/4$. The energy barrier between H and L is denoted g_{max}. For the surface energy we adopt $f = a + 2b|\xi|$, then $\xi'_\pm = \mp b\,\text{sign}(\xi)$ and $g_\pm = g_0 + b^2$. Thus, if ξ has the same (or opposite) signs on both ends, the derivatives $\xi'_\pm$ at the ends have opposite (or the same) signs. For $\xi_\pm = 0$ we assume $-|b| \leq \xi'_\pm \leq |b|$, *i.e.* the homogeneous phase H satisfies eqs. (1) and (2).

Stability of static microstructures: critical fluctuations. – A static solution $\xi(x)$ of the GL equation is stable under infinitesimal fluctuations if it minimizes the energy $e[\xi]$. The solution $\xi(x)$ yields a minimum of the energy if the second variation of the energy

$$\delta^2 e[h]/2 = \int_{-l/2}^{l/2} \left[C(x)h(x)^2 + h'(x)^2 \right] dx + p'_- h_-^2 + p'_+ h_+^2, \quad C(x) := \frac{1}{2}\frac{d^2 g(\xi(x))}{d\xi^2}, \tag{3}$$

is positive for all admissible fluctuations $h(x)$. On the boundaries we have $h'_\pm = \mp p'(\xi_\pm)h_\pm$ in general, and $h'_\pm = 0$ for $p = b\,\text{sign}(\xi)$ (excluding $\xi = 0$). Instead of considering all admissible fluctuations, we have developed an exact method [7] in which we find the critical, *i.e.*, most destabilizing, fluctuation h_c that minimizes $\delta^2 e$. If $\delta^2 e[h_c] > 0$ ($\delta^2 e[h_c] < 0$), then the static microstructure $\xi(x)$ is stable (unstable). However, finding h_c is not straightforward because the proper problem formulation has to be determined. Our final problem formulation is [7] $\delta^2 e \to \min$ under the constraints $\int_{-l/2}^{l/2} h(x)dx = \text{const} = N$ and $\int_{-l/2}^{l/2} C(x)h(x)dx = 0$, and it results in

$$h''(x) = C(x)[h(x) - \alpha] + \lambda, \tag{4}$$

where λ is the Lagrange multiplier. Integrating eq. (4) over $[-l/2; l/2]$, one obtains $\alpha = \lambda l/J$ with $J := \int_{-l/2}^{l/2} C dx > 0$. The first constraint limits the magnitude of $h(x)$; the second constraint ensures that $\delta^2 e[h_c] < \delta^2 e[h_c + \alpha]$ for any constant shift $\alpha \neq 0$. The solution to eq. (4) and consequently N scale with λ. The arbitrariness in λ is physically relevant: only the shape of the critical fluctuation is determined.

Static solutions I-IV of the GL equation are of the form

$$\xi(x) = \frac{\xi_2(\xi_3 - \xi_1) - \xi_1(\xi_3 - \xi_2)\,\text{sn}^2(xq/2, s/q)}{\xi_3 - \xi_1 - (\xi_3 - \xi_2)\,\text{sn}^2(xq/2, s/q)}, \tag{5}$$

where sn is the Jacobi elliptic function, $s := \sqrt{(\xi_3 - \xi_2)(\xi_4 - \xi_1)}$, $q := \sqrt{(\xi_3 - \xi_1)(\xi_4 - \xi_2)}$, and the ξ_i are the four roots of the equation $g = g_0$. Interchange of any two roots in eq. (5) yields another solution, but some are unphysical.
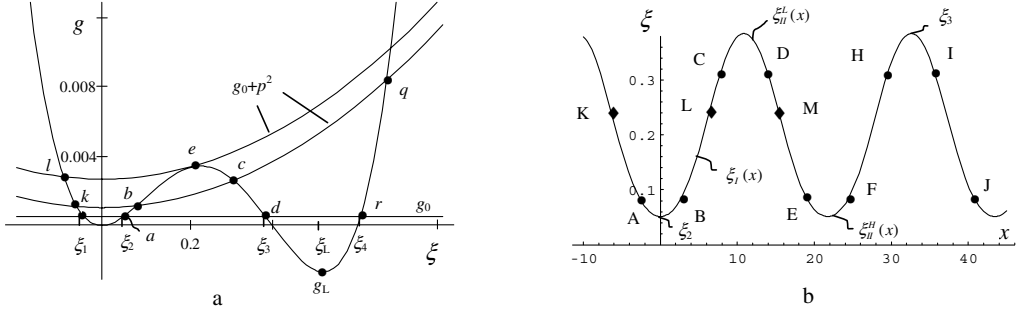
Fig. 1 – (a) Gibbs potential for $B = 0.24$ and (b) the microstructures ξ_I (periodic in general) and ξ_{II}. The ξ_I are associated with paths along the curve *abcd* that begin and end at *b* or *c* and include *a* or *d* or both. For $p < 0$: AC (*baec*), AF (*baeceab*), AH (*baeceabec*), and DF (*ceab*) (critical nuclei for $B \neq 1/4$; equilibrium H-L microstructures for $B = 1/4$; FGN for $B = 1/4$ and small sample length). For $p > 0$: CE (*cdeb*), CI (*cdeaedc*), CJ (*cdeaedceb*), and BD (*bedc*) (similar microstructures as for $p < 0$). The ξ_{II} microstructures are $\xi_{II}^{\mathsf{H}} \sim$ AB (*bab*) ($p < 0$) and $\xi_{II}^{\mathsf{L}} \sim$ CD (*cdc*) ($p > 0$). KL (*eae*) and LM (*ede*) are critical microstructures $\xi_{II}^{\mathsf{H}} = \xi_I$ and $\xi_{II}^{\mathsf{L}} = \xi_I$ (associated with tangency of the curves $g(\xi)$ and $g_0 + p^2(\xi)$) corresponding to barrierless nucleation of ξ_{IV}^{L} and metastable H.

H-L *microstructures which exist for both $p \neq 0$ and $p = 0$.* – If neither H nor L is unstable ($0 < B < 9/32$), $g_0 > 0$, and all ξ_i are real (we assume $\xi_i \leq \xi_{i+1}$), then there exist microstructures $\xi_I(x)$, in general periodic, with $n \geq 1$ interfaces (fig. 1b). The $\xi_I(x)$ oscillate between ξ_2 and ξ_3. For $p = 0$, the boundary conditions give $l = 2nK(s/q)/q$, where K is the complete elliptic integral of the first kind. For $p \neq 0$ the microstructures ξ_I are obtained geometrically (numerically) by restricting eq. (5) to closed intervals $[x_-, x_+]$ for which $\xi'(x_{\pm}) = \mp p$ and $\xi_- \neq \xi_+$ (fig. 1). The intersections of the curves $g(\xi)$ and $g_0 + p^2(\xi)$ give the boundary values $\xi_{\pm}$ (fig. 1a). For $p \neq 0$ and $B \neq 1/4$ the length $l = x_+ - x_-$ can be determined numerically only, but for $B = 1/4$, due to the symmetry of g with respect to H and L, the length is independent of p, so it is given by the $p = 0$ expression. The period of the microstructure is $2l/n$. The length l diverges as $g_0 \to 0$ or as $g_0 \to g_{\mathsf{L}}$.

For given B and g_0, l/n is a decreasing (increasing) function of p for $B < 1/4$ ($B > 1/4$). In addition, l/n decreases as $g_0 \to g_{max}$ for fixed p. It follows that l/n has a minimum value $l_{min}(p)$ corresponding to tangency of the curves $g(\xi)$ and $g_0 + p^2(\xi)$ ($\xi_- = \xi_+$, fig. 1a); for $p^2 = b^2$, l_{min} is determined by the condition $g_0 + b^2 = g_{max}$. $l_{min}(p)$ is minimized for $p = 0$, which corresponds to $\xi_2 = \xi_3$ (fig. 1a), hence $s = 0$ and $l_{min}(0) = 2K(0)/q_{max} = \pi/q_{max}$, where $q_{max} = \sqrt{(\xi_3 - \xi_1)(\xi_4 - \xi_2)}$, $\xi_2 = \xi_3 = (3 - r)/8$, $\xi_1 \approx -0.1264 + 0.0156r + 0.0009r^2$, $\xi_4 \approx 0.3764 + 0.2344r - 0.0009r^2$, and $r := \sqrt{9 - 32B}$.

Due to the gradient term, eq. (1) possesses a characteristic length $l_i \simeq 20$ which is the width of an interface between H and L for $l \gg l_i$ and $B = 1/4$. Typically, l_i is in the nanometer range. If $l_{min} \leq l/n \leq l_i$, the microstructure consists of continuously varied phases with continuously varying properties across the sample. In three dimensions, the crystal structures and symmetries of these phases may differ from those of both H and L. Such microstructures can be described as *functionally graded nanophases* (FGN) and may be observable in nanofilms or nanotubes of large radius.

If H and L are not in thermodynamic equilibrium ($B \neq 1/4$), then ξ_I is unstable for any n, b, and l. Numerical solution of the TDGL eq. (1) shows that the ξ_I are critical L nuclei if $B < 1/4$ or critical H nuclei if $B > 1/4$. Their energies minus the energies of the initial metastable phases are the activation energies for nucleation. Since the activation energies $\sim n$, it is very improbable that critical nuclei with $n > 2$–3 would be observed.

When H and L are in thermodynamic equilibrium ($B = 1/4$), an analysis of stability based on eq. (4) for the critical perturbation shows that there is a critical length $l_c^{(n)}$ for n interfaces above (below) which ξ_I is stable (unstable). Similarly, there is a critical length for the microstructures ξ_{II}, ξ_{III} and ξ_V discussed below. For $l < l_c^{(n)}$ ($\delta^2 e < 0$), the degree of stability parameter, DS (defined in [7]), for ξ_I increases with l and decreases with p. As $l \to l_c^{(n)}$ from below, $\delta^2 e \to 0^-$, resulting in a logarithmic singularity in $DS^{(1)}$. Multi-interface microstructures correspond to periodically continued $C(x)$ (period l/n) and $h_c(x)$, therefore $\delta^2 e^{(n)} = n\delta^2 e^{(1)}$. Consequently, $DS^{(n)} = DS^{(1)} = DS$ and $l_c^{(n)} = n\, l_c^{(1)}$, both of which are unexpected: since $e^{(n)} \sim n$ we expect $DS^{(n)} < DS^{(1)}$ and, therefore, $l_c^{(n)} > n\, l_c^{(1)}$. Numerical calculations for $p = 0$ give $l_c^{(1)} = 44.1$ and $DS = 0.216\, l - 2.02$ (excluding the neighborhood of $l \to l_c$).

Referring to fig. 1a, as p^2 is increased, the points b and c approach e and coincide when the conditions $g(\xi) = p^2(\xi) + g_0$ and $\mathrm{d}g/\mathrm{d}\xi = 2p\mathrm{d}g/\mathrm{d}\xi$ are both satisfied. Any further increase in p^2 destroys the ξ_I microstructure, thus new phases must be nucleated. Given an initial microstructure ξ_I satisfying the above conditions, numerical solutions of the TDGL equation for $B = 1/4$ reveal that an instantaneous increase in $|p|$ or $|B - 1/4|$ results in ξ_I transforming into ξ_{IV}^{L} (discussed below) for $p < 0$ and into pure H for $p > 0$. This nucleation (and transformation) does not require fluctuations, *i.e.* it is barrierless. Note that for $p^2 = b^2$ the conditions for barrierless nucleation reduce to $g_0 + b^2 = g_{max}$, which corresponds to minimum specimen thickness, $l_{min}(b)$. If $l_{min} > l_c^{(n)}$ ($l_{min} < l_c^{(n)}$), then ξ_I is stable (unstable) when the condition for barrierless nucleation is satisfied. Barrierless nucleation could occur from unstable ξ_I provided it is sufficiently long-lived, *i.e.* $DS \gg 0$.

Class II microstructures: surface- and size-induced transformations. – A class of non-periodic microstructures, $\xi_{II}(x)$, can be constructed from the same solution as ξ_I by restricting it to an interval that is symmetric around a maximum or a minimum. These microstructures exist only for $p \neq 0$. They are of two types, ξ_{II}^{H} and ξ_{II}^{L}, which correspond to the paths bab and cdc in fig. 1a and to the paths AB and CD in fig. 1b. Given B and g_0, l increases from zero as $|p|$ increases from zero. For $B < 1/4$ ($B > 1/4$), $l \to \infty$ as $g_0 \to 0$ ($g_0 \to g_{\mathsf{L}}$) for ξ_{II}^{H} (ξ_{II}^{L}) but l is always finite for ξ_{II}^{L} (ξ_{II}^{H}); if H and L are in equilibrium, both ξ_{II}^{H} and ξ_{II}^{L} exist for $l \to \infty$. When $g_0 + b^2 = g_{max}$, ξ_{II} coincides with ξ_I, and as for ξ_I, barrierless nucleation occurs: ξ_{II}^{H} ($p < 0$) $\to \xi_{IV}^{\mathsf{L}}$ and ξ_{II}^{L} ($p > 0$) $\to \mathsf{H}$. Remarkably, the transformation $\xi_{II}^{\mathsf{L}} \to \mathsf{H}$, which is possible in a finite sample only, is from the stable to the metastable phase.

Class III microstructures: surface-induced transformations. – We now consider another class of surface-induced phases, ξ_{III}, for which two of the roots ξ_i are real and the other two are complex conjugate (fig. 2). Like ξ_{II}, they are of two types, ξ_{III}^{L} which exists for $g_{\mathsf{L}} \leq g_0 \leq 0$ and $p \neq 0$, and ξ_{III}^{H} which exists for $0 \leq g_0 \leq g_{\mathsf{L}}$ and $p < 0$. When $p > 0$ ($p < 0$), the magnitude of the order parameter decreases (increases) on approach to the surface in order to minimize the free energy. The condition for barrierless nucleation is again $g_0 + b^2 = g_{max}$; graphically this condition is the coincidence of points b and c in fig. 2a, *i.e.* coincidence of points A and C, and B and D in figs. 2b and c. Numerical solution of the TDGL equation shows that the final microstructures are the same as for barrierless nucleation from ξ_I and ξ_{II}. Note that a barrierless transformation from the stable to the metastable phase can occur as $g_0 \to g_{\mathsf{L}}$, *i.e.* for an infinite sample (in contrast to ξ_{II}).

Microstructures AB, $A'B'$ and EC (fig. 2b) only are stable for l greater than the critical length. For $p > 0$, the microstructures CD, CB and AD are critical nuclei for transformations $\mathsf{H} \leftrightarrow \xi_{III(AB)}^{\mathsf{L}}$. For $p < 0$ and $B > 1/4$, all the microstructures ξ_{III}^{H} but $A'B'$ are critical nuclei for transformations H (or $\xi_{III(A'B')}^{\mathsf{H}}$) $\leftrightarrow \xi_{IV}^{\mathsf{L}}$. For $p > 0$ and $B < 1/4$, the microstructure $\xi_{III(EF)}^{\mathsf{L}}$ is a critical nucleus for the transformation $\xi_{IV}^{\mathsf{H}} \leftrightarrow \xi_{IV}^{\mathsf{L}}$; the microstructure $\xi_{III(EA)}^{\mathsf{L}}$
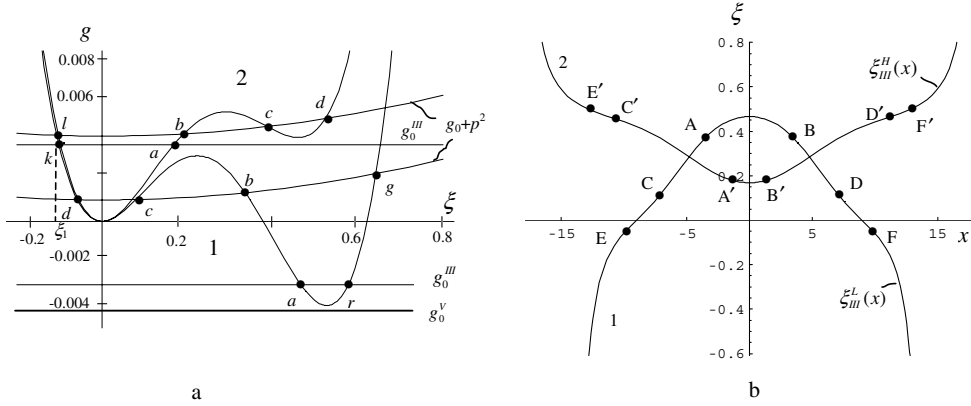
a

b

Fig. 2 – (a) Gibbs potentials for $B = 0.235$ (case 1) and $B = 0.267$ (case 2) and (b) corresponding static microstructures ξ_{III}^{L} for $p \neq 0$ and ξ_{III}^{H} for $p < 0$. All of the ξ_{III}^{L} for $p > 0$ can be obtained by following paths (panel (a)) from b or c to a and back to b or c for a total of four possible structures, and for $p < 0$ the paths are *dad*, *dc* and *db* for a total of five microstructures. The corresponding paths in panel (b) are A or C to B or D for $p > 0$, and EF, EC, EA, FD and FB for $p < 0$. The nine possible ξ_{III}^{H} for $p < 0$ are $E'B'$, $E'D'$, $E'F'$, $C'B'$, $C'D'$, $E'B'$, $C'F'$, $A'B'$, $A'D'$ and $A'F'$ and they correspond to the paths *dab*, *dac*, *dad*, *cab*, *cac*, *cad*, *bab*, *bac* and *bad*, respectively.

is a critical nucleus for the transformation $\xi_{III(EC)}^{\mathsf{L}} \leftrightarrow \xi_{IV}^{\mathsf{L}}$. When $g_0 + p^2 < 0$ for $p > 0$ or $g_0 + p^2 < g_{\mathsf{L}}$ for $p < 0$, one solution ξ_{III} only exists for each p. Note that only one of the microstructures, either ξ_{II} or ξ_{III}, exists for the same l, B and p.

For a semi-infinite sample, barrierless nucleation (termed interface delocalization) for $B \to 1/4$ was obtained in [5]. For the specific choice $f = m\xi^2$, it was continuous, *i.e.* the static solution existed for the entire process $B \to 1/4$. The nature of the barrierless nucleation, *i.e.*, continuous or discontinuous, can be ascertained for any combination of g, f, and l by means of the analysis methodology developed in this letter. If l is finite, the nucleation is discontinuous even for $f = m\xi^2$.

Class IV microstructures: stable phases for $p < 0$. – Two additional types of microstructures always exist for $p < 0$ (see fig. 3). Type ξ_{IV}^{L}, which corresponds to the path *qrq* in fig. 1a, varies in the range $\xi_L < \xi_4 < \xi_{IV}^{\mathsf{L}} < \infty$, *i.e.* the order parameter lies above that of the L phase, and it exists for $g_0 \geq g_{\mathsf{L}}$. Type ξ_{IV}^{H} corresponds to the path *fef* in fig. 1a, it varies in the
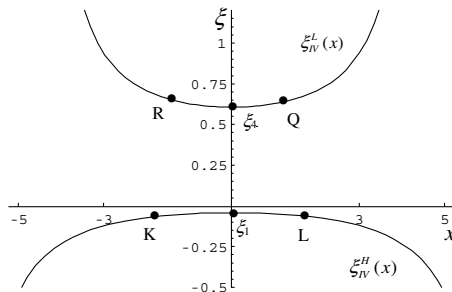
Fig. 3 – The microstructures ξ_{IV}^{L} and ξ_{IV}^{H} for $B = 0.24$ (see fig. 1a) and $p < 0$.
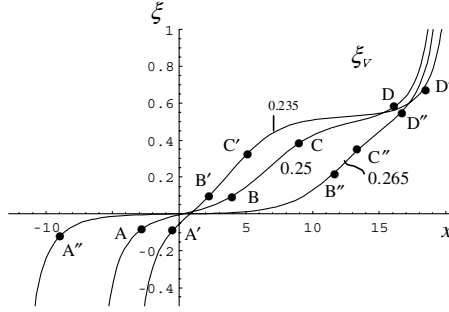
Fig. 4 – The surface-modified microstructure ξ_V^{H} (lines AB), critical nucleus ξ_V (lines AC) for the transformations $\xi_V^{\mathsf{H}} \leftrightarrow \xi_V^{\mathsf{HL}}$ and the surface-stabilized H-L microstructure ξ_V^{HL} (lines AD). Numbers near the curves are values of B.

range $-\infty < \xi_{IV}^{\mathsf{H}} < \xi_1 < 0$, *i.e.* its order parameter is below that of H, and it exists only for $g_0 \geq 0$. In contrast to ξ_I, ξ_{II}, and ξ_{III}, which are destroyed if $|p|$ is sufficiently large, the ξ_{IV} phases exist for arbitrarily large $|p|$. Since $C(x) > 0$ everywhere for the ξ_{IV}, they are stable.

Class V microstructures: surface-modified phase ξ^{H} and surface-stabilized $\xi^{\mathsf{L}} - \xi^{\mathsf{H}}$ microstructure for $p < 0$. – They correspond to $g_0 < g_{min}$ and $g_0 < 0$, *i.e.* to two pairs of complex conjugate roots ξ_i. The analytical solution is

$$\xi_V(x) = \left(b_1 + a_1 g_1 - \frac{b_1(1 + g_1^2)}{1 + g_1 \tan(am(\frac{1}{2}(c_1 + c_2)x, \frac{4c_1 c_2}{(c_1 + c_2)^2}))} \right) / g_1;$$

$$a_1 = (\xi_1 + \xi_2)/2; \quad a_2 = (\xi_3 + \xi_4)/2; \quad b_1^2 = -(\xi_1 - \xi_2)^2/4; \quad b_2^2 = -(\xi_3 - \xi_4)^2/4;$$

$$c_1^2 = (a_1 - a_2)^2 + (b_1 + b_2)^2; \quad c_2^2 = (a1 - a2)^2 + (b_1 - b_2)^2; \quad g_1^2 = \frac{4b_1^2 - (c_1 - c_2)^2}{(c_1 + c_2)^2 - 4b_1^2}, \quad (6)$$

where am gives the amplitude for Jacobi elliptic functions. There are three types of these microstructures:

1) ξ_V^{H} (AB, $A'B'$ and $A''B''$ in fig. 4, dc in fig. 2a, line 1, and lb in fig. 2a, line 2) which is similar to the microstructure ξ_{III}^{H} (EC in fig. 2b).

2) ξ_V (AC, $A'C'$ and $A''C''$ in fig. 4, db in fig. 2a, line 1, and lc in fig. 2a, line 2) which is similar to the microstructure ξ_{III}^{H} (EA in fig. 2b). It represents a critical nucleus for the transformations $\xi_V^{\mathsf{H}} \leftrightarrow \xi_V^{\mathsf{HL}}$.

3) The H-L microstructure ξ_V^{HL} (AD, $A'D'$ and $A''D''$ in fig. 4, dg in fig. 2a, line 1, and ld in fig. 2a, line 2).

With increasing $|p|$, the microstructures ξ_V^{H} and ξ_V tend toward each other and their coincidence corresponds to barrierless nucleation of the microstructure ξ_V^{HL}. With decreasing $|p|$, when the number of intersection points between g and $g_0 + p^2$ decreases from four to two, the microstructure ξ_V^{HL} transforms to ξ_{IV}^{L} for $g(0) > g(\mathsf{L})$ and to ξ_V^{H} for $g(0) < g(\mathsf{L})$. The larger $|p|$ is the more stable the microstructure ξ_V^{HL} is, since its larger part at both surfaces belongs to the region with positive $C(x)$. For the microstructure ξ_V^{H}, an increase in $|p|$ leads to stabilization of the part for $\xi < 0$ and destabilization of the part for $\xi > 0$ finally leading to barrierless transformation to the microstructure ξ_V^{HL}. When $p \to 0$, then the final microstructure is H-L microstructure (for $B = 1/4$), pure H phase (for $B > 1/4$), and pure L phase (for $B < 1/4$).

The energy depends on B, l and b. As an example, we present the results for $B = 1/4$, $l_1 = 11.28$ and $l_2 = 20.26$ and five values of $|b|$ between zero and the maximum values ($b_1^m = 0.0539$ and $b_2^m = 0.0624$) corresponding to coincidence of ξ_I and ξ_{II}^{H}. Note that ξ_{III} does not exist for $B = 1/4$. For $b > 0$, the energy grows in the following sequence: H-ξ_{II}^{L}-ξ_I for both l and all b; for $b > b^m$, the phase H exists only. For $b < 0$, the situation is more sophisticated. For $l = l_1$, $b_1 = -0.0127$, $b_1 = -0.0260$ and $b_1 = -0.0393$, as well as for $l = l_2$ and $b_2 = -0.00363$, the energy sequence is ξ_{IV}^{L}-ξ_{II}^{H}- ξ_V^{H}-ξ_{IV}^{H}-H-ξ_I-ξ_V^{HL}-ξ_V (note that for $b_1 = -0.0127$ solutions ξ_V^{HL} and ξ_V do not exist). For $l = l_2$, $b_2 = -0.0107$ and $b_2 = -0.0256$ the energy grows in the sequence ξ_{IV}^{L}-ξ_{II}^{H}- ξ_V^{H}-ξ_{IV}^{H}-H-ξ_V^{HL}-ξ_I-ξ_V. For $l = l_1$, $b_1 = -0.0498$ and $b_2 = -0.0539$, the energy sequences are ξ_{IV}^{L}-ξ_{II}^{H}- ξ_V^{H}-ξ_I-ξ_V^{HL}-ξ_{IV}^{H}-ξ_V-H and ξ_{IV}^{L}-ξ_V^{HL}-ξ_{II}^{H}- ξ_I-ξ_{IV}^{H}-ξ_V^{H}-ξ_V-H. For $l = l_2$, $b_2 = -0.0488$ and $b_2 = -0.0624$, the energy grows in the sequences ξ_{IV}^{L}-ξ_V^{HL}-ξ_{II}^{H}- ξ_V^{H}-ξ_{IV}^{H}-ξ_I-ξ_V-H and ξ_{IV}^{L}-ξ_V^{HL}-ξ_{II}^{H}- ξ_I-ξ_V^{H}-ξ_V-ξ_{IV}^{H}-H. Note that for large p and $l < l_i$, microstructures ξ_{II}-ξ_V are FGN.

It is of interest to determine the $l \to \infty$ microstructure corresponding to each of the ξ_I-ξ_{IV} for $p \neq 0$. Class I microstructures are comprised of $n \geq 1$ interfaces separating macroscopic layers of H and L plus FGN at the surfaces. The $l \to \infty$ limits of ξ_{II}, ξ_{III}, and ξ_{IV} are pure H or L (no interfaces) with surface FGN; the limits of ξ_V are H or L-H with surface FGN.

In summary, new surface- and size-induced microstructures were found analytically. The stability and physical interpretation of each microstructure was analyzed using a novel method. The conditions for barrierless surface nucleation, *i.e.* the relationship between surface energy, driving force for the transformation, and sample size, were obtained. Our results are applicable to metastable surface-induced microstructures, *e.g.* those associated with pre-melting as well as disordering and ordering [3, 5, 6]), and to PTs in nanoparticles or nanograined materials where the surface energy leads to PTs from stable to metastable phases in the bulk [4–6].

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