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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 \(\xi\) 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 \( \xi \) at the boundaries \( x = \pm l/2 \). The corresponding TDGL equation reads

\[
\begin{align*}
\partial \xi / \partial t &= -d g / d \xi + 2 \delta'' \xi, \\
\xi_-' &= p(\xi_-), \quad \xi_+' = -p(\xi_+); \quad p(\xi) := f'(\xi) / 2.
\end{align*}
\]

The boundary conditions simplify to \( \xi_+' = 0 \) 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 \((\delta^2)^2 = g - g_0\) 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 \( g = B \xi^2 - \xi^4 + \xi^6 \) (similar results are obtained for a 2-4-6 potential). Note that the factors before \( \xi^3 \) and \( \xi^4 \), 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 \( L \) \((H)\) and \( \xi \) 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 \( \xi \) has the same (or opposite) signs on both ends, the derivatives \( \xi_{\pm}' \) at the ends have opposite (or the same) signs. For \( \xi = 0 \) 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

\[
\delta^2 e [h] / 2 = \int_{-l/2}^{l/2} \left[ \frac{d^2}{dx^2} [C(x)h(x)^2 + h'(x)^2] \right] dx + p(C_{\xi}) h_x^2 + p(C_{\xi}) h_x^2,
\]

is positive for all admissible fluctuations \( h(x) \). On the boundaries we have \( h_x' = \mp b \text{sign}(\xi) h_{\pm} \) in general, and \( h_x' = 0 \) 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

\[
h''(x) = C(x)[h(x) - \alpha] + \lambda,
\]

where \( \lambda \) 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 \( \lambda \). The arbitrariness in \( \lambda \) is physically relevant: only the shape of the critical fluctuation is determined.

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

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

where \( \text{sn} \) is the Jacobi elliptic function, \( s := \sqrt{((\xi_3 - \xi_2)(\xi_4 - \xi_1))}, \quad q := \sqrt{((\xi_3 - \xi_1)(\xi_4 - \xi_2))}, \) and the \( \xi_i \) 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.
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 $\xi_i$ are real (we assume $\xi_i \leq \xi_{i+1}$), then there exist microstructures $\xi_f(x)$, in general periodic, with $n \geq 1$ interfaces (fig. 1b). The $\xi_f(x)$ oscillate between $\xi_2$ and $\xi_3$. 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 $\xi_f(x)$ 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 $g_0 \rightarrow 0$ or as $g_0 \rightarrow g_0$.

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 $g_0 \rightarrow g_{max}$ 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 $g_{max} = \sqrt{(\xi_4 - \xi_1)(\xi_4 - \xi_2)}$, $\xi_2 = \xi_3 = (3 - r)/8$, $\xi_1 \approx -0.1264 + 0.0156r + 0.00099r^2$, $\xi_4 \approx 0.3764 + 0.2344r - 0.00099r^2$.

Due to the gradient term, eq. (1) possesses a characteristic length $l_i \approx 20$ 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 $\xi_f$ is unstable for any $n, b$, and $l$. Numerical solution of the TDGL eq. (1) shows that the $\xi_f$ are critical $\xi$ nuclei if $B < 1/4$ or critical $\xi$ 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 $\xi_I$ is stable (unstable). Similarly, there is a critical length for the microstructures $\xi_{I\!I\!I}$, $\xi_{I\!I\!I}$ and $\xi_V$ discussed below. For $l < l_c^{(n)}$ ($\delta^2 e < 0$), the degree of stability parameter, $DS$ (defined in [7]), for $\xi_I$ increases with $l$ and decreases with $p$. As $l \rightarrow l_c^{(n)}$ from below, $\delta^2 e \rightarrow 0^-$, resulting in a logarithmic singularity in $DS^{(1)}$. Multi-interface microstructures correspond to periodically continued $C(x)$ (period $l/n$) and $h_n(x)$, 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 $l \rightarrow l_c$).

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 $dg/d\xi = 2pdg/d\xi$ are both satisfied. Any further increase in $p^2$ destroys the $\xi_I$ microstructure, thus new phases must be nucleated. Given an initial microstructure $\xi_I$ 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 $\xi_I$ transforming into $\xi_{IV}$ (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 $\xi_I$ is stable (unstable) when the condition for barrierless nucleation is satisfied. Barrierless nucleation could occur from unstable $\xi_I$ 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 $\xi_I$ 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, $\xi_{II}^L$ and $\xi_{II}^R$, which correspond to the paths $bab$ and $cde$ 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 $B < 1/4$ ($B > 1/4$), $l \rightarrow \infty$ as $g_0 \rightarrow 0$ ($g_0 \rightarrow g_\ast$) for $\xi_{II}^L$ ($\xi_{II}^R$) but $l$ is always finite for $\xi_{II}^H$ ($\xi_{II}^A$); if $H$ and $L$ are in equilibrium, both $\xi_{II}^H$ and $\xi_{II}^A$ exist for $l \rightarrow \infty$. When $g_0 + b^2 = g_{\max}$, $\xi_{II}^H$ coincides with $\xi_I$, and as for $\xi_I$, barrierless nucleation occurs: $\xi_{II}^H (p < 0) \rightarrow \xi_{IV}$ and $\xi_{II}^H (p > 0) \rightarrow H$. Remarkably, the transformation $\xi_{II}^H \rightarrow H$, 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, $\xi_{III}(x)$, for which two of the roots $\xi_I$ are real and the other two are complex conjugate (fig. 2). Like $\xi_I$, they are of two types, $\xi_{III}^H$ which exists for $g_L \leq g_0 \leq 0$ and $p \neq 0$, and $\xi_{III}^H$ which exists for $0 \leq g_0 \leq g_\ast$ 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 $\xi_I$ and $\xi_{II}$. Note that a barrierless transformation from the stable to the metastable phase can occur as $g_0 \rightarrow g_\ast$, i.e. for an infinite sample (in contrast to $\xi_{II}$).

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 $H \leftrightarrow \xi_{III}(AB)$. For $p < 0$ and $B = 1/4$, all the microstructures $\xi_{III}^H$ but $A'B'$ are critical nuclei for transformations $H$ (or $\xi_{III}(A'B')$) $\leftrightarrow \xi_{IV}$. For $p > 0$ and $B < 1/4$, the microstructure $\xi_{III}(EF)$ is a critical nucleus for the transformation $\xi_{IV} \leftrightarrow \xi_{IV}$; the microstructure $\xi_{III}(EA)$
is a critical nucleus for the transformation $\xi^L_{III}$ (case 1) and $\xi^H_{III}$ (case 2) and (b) corresponding static microstructures $\xi^L_{III}$ for $p \neq 0$ and $\xi^H_{III}$ for $p < 0$. All of the $\xi^L_{III}$ 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 $dab$, $dac$ and $db$ for a total of five microstructures. The corresponding paths in panel (b) are $A$ or $B$ to $D$ for $p > 0$, and $EF$, $EC$, $EA$, $FD$ and $FB$ for $p < 0$. The nine possible $\xi^L_{III}$ 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 $dab$, $dac$, $dad$, $cab$, $cad$, $bab$ and $bac$ respectively.

Class IV microstructures: stable phases for $p < 0$. Two additional types of microstructures always exist for $p < 0$ (see fig. 3). Type $\xi^V_{IV}$, which corresponds to the path $qrg$ in fig. 1a, varies in the range $\xi_L < \xi_4 < \xi^V_{IV} < \infty$, i.e. the order parameter lies above that of the L phase, and it exists for $g_0 \geq g_L$. Type $\xi^H_{IV}$ corresponds to the path $lrf$ in fig. 1a, it varies in the

![Figure 2](image1.png)

![Figure 3](image2.png)
range \(-\infty < \xi_V^H < \xi_1 < 0\), i.e. its order parameter is below that of H, and it exists only for \(g_0 > 0\). In contrast to \(\xi_I\), \(\xi_{II}\), and \(\xi_{III}\), which are destroyed if \(|p|\) is sufficiently large, the \(\xi_{IV}\) phases exist for arbitrarily large \(|p|\). Since \(C(x) > 0\) everywhere for the \(\xi_{IV}\), they are stable.

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

\[
\xi_V(x) = \frac{b_1 + a_1 g_1 - \frac{b_1 (1 + g_1^2)}{1 + g_1 \text{tan}(am(\frac{1}{2}(c_1 + c_2) x, \frac{4(c_1 + c_2)}{(c_1 - c_2)^2})))}}{g_1};
\]

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

\[
c_1^2 = (a_1 - a_2)^2 + (b_1 + b_2)^2; \quad c_2^2 = (a_1 - a_2)^2 + (b_1 - b_2)^2; \quad g_1^2 = \frac{4b_1^2 - (c_1 - c_2)^2}{(c_1 + c_2)^2 - 4b_1^2};
\]

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

1. \(\xi^H_V (AB, A'B' \text{ and } A''B'') \text{ in fig. } 4, \text{ de in fig. } 2a, \text{ line } 1, \text{ and } \text{lb in fig. } 2a, \text{ line } 2\) which is similar to the microstructure \(\xi_{III}^H (EC \text{ in fig. } 2b)\).

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

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

With increasing \(|p|\), the microstructures \(\xi^H_V\) and \(\xi_V\) tend towards each other and their coincidence corresponds to barrierless nucleation of the microstructure \(\xi^{HL}_V\). With decreasing \(|p|\), when the number of intersection points between \(g\) and \(g_0 + p^2\) decreases from four to two, the microstructure \(\xi^H_V\) transforms to \(\xi_V\) for \(g(0) > g(L)\) and to \(\xi^H_V\) for \(g(0) \leq g(L)\). The larger \(|p|\) is the more stable the microstructure \(\xi^{HL}_V\) is, since its larger part at both surfaces belongs to the region with positive \(C(x)\). For the microstructure \(\xi^H_V\), 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 \(\xi^{HL}_V\). 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 $\xi_I$ and $\xi_{III}$. Note that $\xi_{III}$ does not exist for $B = 1/4$. For $b > 0$, the energy grows in the following sequence: $\xi_{II}^{\xi_{II}} - \xi_{I}^{\xi_{I}} - \xi_{IV}^{\xi_{IV}} - \xi_{V}^{\xi_{V}}$ 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 $\xi_{II}^{\xi_{II}} - \xi_{I}^{\xi_{I}} - \xi_{IV}^{\xi_{IV}} - \xi_{V}^{\xi_{V}}$ (note that for $b_1 = -0.0127$ solutions $\xi_{II}^{\xi_{II}}$ and $\xi_{V}^{\xi_{V}}$ do not exist). For $l = l_2$, $b_2 = -0.0107$ and $b_2 = -0.0256$ the energy grows in the sequence $\xi_{II}^{\xi_{II}} - \xi_{I}^{\xi_{I}} - \xi_{IV}^{\xi_{IV}} - \xi_{V}^{\xi_{V}}$. For $l = l_1$, $b_1 = -0.0498$ and $b_2 = -0.0539$, the energy sequences are $\xi_{II}^{\xi_{II}} - \xi_{I}^{\xi_{I}} - \xi_{IV}^{\xi_{IV}} - \xi_{V}^{\xi_{V}}$ and $\xi_{II}^{\xi_{II}} - \xi_{I}^{\xi_{I}} - \xi_{IV}^{\xi_{IV}} - \xi_{V}^{\xi_{V}}$. For $l = l_2$, $b_2 = -0.0488$ and $b_2 = -0.0624$, the energy grows in the sequences $\xi_{II}^{\xi_{II}} - \xi_{I}^{\xi_{I}} - \xi_{IV}^{\xi_{IV}} - \xi_{V}^{\xi_{V}}$ and $\xi_{II}^{\xi_{II}} - \xi_{I}^{\xi_{I}} - \xi_{IV}^{\xi_{IV}} - \xi_{V}^{\xi_{V}}$. Note that for large $p$ and $l < l_1$, microstructures $\xi_{II} - \xi_{IV}$ are FGN.

It is of interest to determine the $l \to \infty$ microstructure corresponding to each of the $\xi_{II} - \xi_{IV}$ 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 $\xi_{II}$, $\xi_{III}$, and $\xi_{IV}$ are pure $H$ or $L$ (no interfaces) with surface FGN; the limits of $\xi_{V}$ 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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