

Droplet Fluctuations in the Morphology and Kinetics of Martensites

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(Received 8 July 1996)

We present a mode-coupling theory which describes the morphology and kinetics of the nucleation of twinned martensite droplets within a parent crystal. This involves a “slow” vacancy field that lives at the parent-product interface. Our theory suggests that a *slow* quench from the parent phase produces an equilibrium product, while a *fast* quench produces a metastable martensite. In two dimensions, the martensite nuclei grow as strips having alternating twin domains, with well-defined front velocities. Several empirically known structural and kinetic relations drop out naturally from our theory. [S0031-9007(97)02674-4]

PACS numbers: 81.30.Kf, 63.70.th, 64.60.Qb, 64.70.Kb

In modern metallurgical parlance, a *martensitic transformation* [1] has come to denote any diffusionless, structural transformation resulting in a long-lived metastable phase with a high degree of short-range order. For instance, when adiabatically cooled below $T_c = 910^\circ\text{C}$, Fe undergoes a first-order structural transition from an fcc solid (*austenite*) to an equilibrium bcc solid (*ferrite*). A faster quench produces, instead, a rapidly transformed metastable phase called the *martensite*. On nucleation, martensite “plates” ($\sim 1\ \mu\text{m}$) grow with a constant front velocity ($\sim 10^5\ \text{cm s}^{-1}$) [2]; fast compared to typical atomic diffusion speeds. The plates consist of an alternating array of twin bcc crystals along the equatorial plane. A significant amount of empirical [2] and theoretical work [3–5] accrued over the years has added to our understanding of this complex phenomenon. However, as far as we know, a unified theoretical approach addressing both kinetics and morphology, and capable of describing the metastable martensite *as well as* the equilibrium ferrite, has not emerged. In this Letter, we present a mode-coupling theory for the nucleation and growth of a product crystalline droplet within a parent crystal. We show that for slow quenches, the droplet grows diffusively as an equilibrium ferrite inclusion, while for fast quenches, the droplet grows ballistically, as a martensite having twinned internal substructure, with a speed comparable to the sound velocity.

Our mode-coupling dynamics involves “slow” variables that change over time scales corresponding to the propagation of the nucleation front. The slow variables of a solid undergoing a first-order structural transformation are the displacement field $\mathbf{u}(\mathbf{r}, t)$ and the momentum density $\mathbf{g}(\mathbf{r}, t)$. Imagine, however, a droplet of the product nucleating within a parent crystal at time $t = 0$. It is clear [Fig. 1(a)] that an atomic mismatch is generated at the parent-product interface [2] as soon as the nucleus is formed. This mismatch appears as a discontinuity in the normal component of the displacement field across the parent-product interface [6] $\Delta\mathbf{u} \cdot \hat{\mathbf{n}} \equiv \phi$ and leads to a compression or dilation of the local atomic environment, Fig. 1(b). Since the martensite front velocity is large

compared to atomic diffusion times, the vacancy field $\phi(\mathbf{r}, t)$ [7] appears as a *slow variable*, which relaxes diffusively over a microscopic time scale τ_ϕ .

A Langevin description of the dynamics of the transformation requires a free-energy functional *which describes all intermediate configurations between an austenite and a ferrite*. Thus the usual elastic free-energy functional of a solid, F_{el} , has to be augmented by an interfacial term, describing the parent-product interface. As we see below, such droplet configurations do not affect equilibrium behavior, though their effect on dynamics is significant.

Nucleation of a droplet of the product of size L and interfacial thickness ξ results in a strained crystal. The free-energy functional [8] of this strained crystal is given by

$$\mathcal{F} = \sum_{\{\mathbf{R}, \mathbf{R}'\}} c(|\mathbf{R} - \mathbf{R}' + \mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')|), \quad (1)$$

where $\{\mathbf{R}\}$ represent the lattice vectors of the parent crystal, $\mathbf{u}(\mathbf{R})$ are the displacement fields, and $c(|\mathbf{r} - \mathbf{r}'|)$ is the direct correlation function [9] of the liquid at freezing. The above expression is exact at $T = 0$; corrections are of the order of the rms fluctuations of the atoms about their perfect lattice positions, which are small in the solid phase [10].

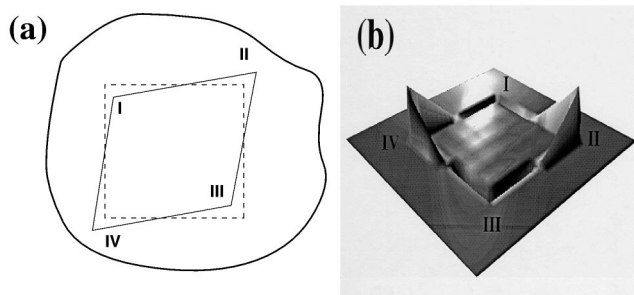


FIG. 1. (a) Inclusion of a product (rhombus) in a parent crystal, showing the discontinuity in \mathbf{u} across the parent-product interface at $t = 0$. (b) A 3D plot of the initial value of $\phi(x, y)$ for the inclusion shown in (a). The four corners in (a) and (b) are clearly marked.

Since the range of c is of order ξ , the sum over $\{\mathbf{R}, \mathbf{R}'\}$ in Eq. (1) can be split into two parts, with $\{\mathbf{R}, \mathbf{R}'\}$ being on the *same or on either side* of the interface. Expanding $\mathbf{u}(\mathbf{R}')$ about \mathbf{R} in the first part leads to the usual bulk elastic free-energy functional F_{e1} [10]. However, as argued above, the assumption of continuity breaks down for the second part, and so *such an expansion cannot be carried out*. In the limit $\xi/L \ll 1$, the interface can be parametrized by a sharp surface $\Gamma(\mathbf{r}) = 0$, with \mathbf{R} and \mathbf{R}' lying infinitesimally close to $\Gamma = 0$. Across this interface, the normal component of \mathbf{u} is discontinuous; $\lim_{|\mathbf{R}-\mathbf{R}'| \rightarrow 0} [\mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')] \cdot \hat{\mathbf{n}} \equiv (\mathbf{u}_+ - \mathbf{u}_-) \cdot \hat{\mathbf{n}} \equiv \phi$, where $\hat{\mathbf{n}}$ is the unit normal to the interface. The discontinuity $\phi(\mathbf{r})$, which is simply $\xi(\rho(\mathbf{r})|_{\Gamma=0} - \bar{\rho})/\bar{\rho}$, is the local vacancy field (ρ and $\bar{\rho}$ are the local and the average densities, respectively). In the continuum limit, this leads to the free-energy functional (to leading order in the discontinuity)

$$\mathcal{F} = F_{e1} + \frac{\gamma}{2\xi^2} \int \frac{d\mathbf{r}}{\Omega_0} [(\mathbf{u}_+ - \mathbf{u}_-) \cdot \hat{\mathbf{n}}]^2 \xi \delta(\Gamma), \quad (2)$$

where Ω_0 is the unit cell volume of the parent. The coefficient $\gamma \equiv \Omega_0^{-1} \sum' \xi^2 \partial_n \partial_n c(r)$, where the prime denotes a sum across the interface, is clearly the *surface compressibility modulus* of vacancies, whose magnitude is of the order of the bulk elastic moduli; it is, however, dependent on the local orientation of the parent-product interface. Since the strains $\epsilon_{ij} \equiv (\partial_i u_j + \partial_j u_i)/2$ are continuous across the interface, we replace the delta function in Eq. (2) by a regulator $\xi^{-1} [1 - \exp(-\xi \partial_n \epsilon_{ij})^2]$, so that the final regulated free-energy functional which incorporates *all the slow variables* in the problem is

$$\mathcal{F} = F_{e1} + \frac{\gamma}{2\Omega_0} \int d\mathbf{r} \phi^2 (\partial_n \epsilon_{ij})^2. \quad (3)$$

At the initial time ($t = 0$), the transformed region (product) is simply obtained as a geometrical deformation of the parent, Fig. 1(a), which fixes the initial value of ϕ [Fig. 1(b)]. Having created this discontinuity ϕ at the parent-product interface, it will diffuse over a microscopic time τ_ϕ . The equations of motion describing the linearized dynamics of the slow variables u_i (nonconserved) and ϕ (conserved) can be written as

$$\frac{\rho}{2} \ddot{u}_i - \frac{\delta \mathcal{F}}{\delta u_i} = \phi \nabla_i \frac{\delta \mathcal{F}}{\delta \phi} - \nu_{ijkl} \nabla_j \dot{\epsilon}_{kl}, \quad (4)$$

$$\dot{\phi} + \frac{\mathbf{g}}{\rho} \cdot \nabla \phi = \frac{1}{\tau_\phi} \nabla^2 \frac{\delta \mathcal{F}}{\delta \phi}, \quad (5)$$

where $\dot{\epsilon}_{ij}$ is the time derivative of the strain tensor ϵ_{ij} . The inertial term \ddot{u}_i (propagation of sound waves) and solid viscosity tensor ν_{ijkl} (damping of sound waves [6]) are obtained from the coupling of \mathbf{u} with the total momentum density \mathbf{g} [11,12]. The second term in Eq. (5) is the Poisson bracket of ϕ and \mathbf{g} .

We study the consequences of this dynamical theory, in the simple setting of a first-order structural transformation from a square (austenite) to a rhombic (ferrite) crystal in two dimensions. Our results, which can be easily ex-

tended to the tetragonal to orthorhombic transition (essentially a 2D square to rectangular [3]), are of relevance to structural transformations in alloys like In-Pb, In-Tl, and Mn-Fe. This transformation involves a shear + volume deformation, and so the strain order parameter ϵ_{ij} has only one nontrivial component $e_3 = (u_{xy} + u_{yx})/2$.

We construct a bulk elastic free energy with three minima—one corresponding to the undeformed square cell ($e_3 = 0$) and the other two corresponding to the two variants of the rhombic cell ($e_3 = \pm e_0$). The free-energy functional, in dimensionless variables, is

$$\mathcal{F} = \int_{x,y} a e_3^2 - e_3^4 + e_3^6 + (\nabla e_3)^2 + \gamma (\phi \partial_n e_3)^2. \quad (6)$$

The three minima of the homogeneous part of F at $e_3 = 0$ (austenite) and $e_3 \equiv \pm e_0 = \pm[(1 + \sqrt{1 - 3a})/3]^{1/2}$ (ferrite) are obtained in the parameter range $0 < a < 1/3$. The parameter a is the degree of undercooling $T - T_c$. The surface compressibility γ for an interface between the square ($e_3 = 0$) and the rhombus ($e_3 = e_0$) positioned along the y axis is given by $\gamma = [c''(l) + c''(l + e_0 l) + c''(|l - e_0 l|)]/2$, where $c''(r)$ is the second derivative of a typical direct correlation function for a two-dimensional fluid whose range is taken to be of the order of the distance between next-nearest neighbors of the parent square lattice of spacing l .

There are two time scales relevant to our kinetics—the quench rate $\tau^{-1} = (dT/dt)/T$ and the vacancy relaxation time τ_ϕ . Accordingly, two extreme dynamical limits suggest themselves. When $\tau \gg \tau_\phi$, the ϕ fields relax instantaneously to $\phi = 0$, its equilibrium value. The only surviving slow fields are u_i , which obey Eq. (4), with the free-energy functional $\mathcal{F} = F_{e1}$. Since we are interested in the growth of the product nucleus in the parent matrix, it is appropriate to rewrite Eq. (4) in terms of the broken symmetry variable $e_3(\mathbf{r}, t)$, which takes the form $e_3(\mathbf{r} - \mathbf{R}(t))$, when the interface is sharp [$\mathbf{R}(t)$ is the position of the interface]. The equation for e_3 is purely dissipative, $\dot{e}_3 = -\delta F_{e1}/\delta e_3$. Minimizing F_{e1} with respect to e_3 , subject to boundary conditions $e_3 = 0$ at $|\mathbf{r}| \rightarrow \infty$ and $e_3 = \pm e_0$ at $|\mathbf{r}| = 0$, obtains a ferrite nucleus, growing as $R \sim t^{1/2}$ at late times [12].

On the other hand, when $\tau \ll \tau_\phi$, the ϕ fields are frozen in the frame of reference of the nucleating front. In this limit, ϕ is nonzero only at the parent-product interface, and so $\mathbf{g}/\bar{\rho}$ in Eq. (5) can be interpreted as the local front velocity. In the front frame, ϕ obeys a diffusion equation with the diffusion coefficient $D_\phi = \sqrt{\gamma/\tau_\phi}$. Recasting Eq. (4), in terms of e_3 , leads again to a purely dissipative equation with the free-energy functional \mathcal{F} given by Eq. (6). To determine the structure of the product nucleus, we use a variational ansatz for e_3 , consistent with boundary conditions mentioned above. Consider a rectangular nucleus of length L (along \hat{x}) and width W (along \hat{y}) divided into N twins [Fig. 2(inset)]. The $N - 1$ twin interfaces, all of thickness η , can be parametrized by $e_3(x)$, which for the i th interface takes

values $-e_0$ at $(i-1)L/N + \eta/2 < x < iL/N - \eta/2$ and e_0 at $iL/N + \eta/2 < x < (i+1)L/N - \eta/2$, connected by a linear interpolation. The strain at the austenite-ferrite in-

terface varies linearly between 0 at $x < -\xi/2$ and $\pm e_0$ at $x > \xi/2$. The free energy $E(L, W)$ for the nucleus reads

$$E(L, W) = [\Delta FLW + (2I - \Delta F)(L\xi + W\zeta) + (N-1)(I - \Delta F)W\eta + 2e_0^2(L/\xi + W/\zeta) + 4e_0^2(N-1)W/\eta] \\ + (\gamma e_0^4/\xi) [2L^3N^{-2}/3 + L^2\eta(N^{-2} - N^{-1}) + L\eta^2(1/2 - 3N^{-1}/4) - L\zeta N^{-1}(LN^{-1} - \zeta/4 - \eta/2)] \\ + \gamma e_0^4 \zeta^{-1} (2W^3/3 - W^2\xi + W\xi^2/2). \quad (7)$$

In Eq. (7), $\Delta F \equiv ae_0^2 - e_0^4 + e_0^6$ is the difference between the *bulk* free energies of the austenite and the ferrite, while $I \equiv ae_0^2/3 - e_0^4/5 + e_0^6/7$. The structure of the growing nucleus is obtained by minimizing $E(L, W)$ with respect to the order parameter profile e_3 (both the amplitude and phase). Within our variational scheme, this amounts to minimizing $E(L, W)$ with respect to the interfacial widths η , ξ , and ζ and the phase of the order parameter N .

Minimization yields the structural relation (see Fig. 2)

$$\frac{L}{N} \sim W^\sigma. \quad (8)$$

The exponent $\sigma \sim 1/2$ with tiny deviations for large W . The exponent σ is empirically known [3] to lie between 0.4 and 0.5. Note that our theory suggests that Eq. (8) *holds at all times* during the growth of a martensite as a consequence of *local equilibrium*. Our prediction for L/N can be verified from *in situ* high resolution transmission electron microscopy studies of growing martensite fronts.

Twinning is a consequence of the ϕ term which is confined to the parent-product interface. When $\tau \ll \tau_\phi$, the quench nucleates an inclusion which initially grows

as a ferrite. Further growth as a single-domain ferrite is discouraged since the energy cost at the interface is proportional to the square of the discontinuity in \mathbf{u} . The growing nucleus gets around this by creating a twin. Though this costs interfacial energy due to $(\nabla e_3)^2$ (which is small), the contribution from ϕ is identically zero at the twin interface, due to symmetry.

From the contour plots of the optimized free energy plotted in Figs. 3(a) and 3(b), one observes a minimum in W for large $\gamma \sim \mathcal{O}(1)$ [Fig. 3(b)]. Since we find that $W_{\min} < L$, the free energy is minimized by thin rectangular strips reminiscent of “hard” acicular martensites seen in Fe-Ni or Fe-C systems. For small $\gamma \sim \mathcal{O}(10^{-3})$, there is no such minimum in W . As we shall see below, growth along L is much faster than along W , and so the martensite traverses the entire extent of the sample along L , whereupon growth proceeds along W . Such single interface growth is indeed seen in soft solids, like In-Tl and Au-Cd alloys [13]. The critical nucleus is obtained by locating the saddle point in each of these free energy surfaces. Taking the curvature at the corners $\kappa = \sqrt{\xi\zeta}/LW$ as a measure of the sharpness of the growing nucleus, we find the critical nucleus to be diffuse for both $\gamma = 1$ ($\kappa = 0.4$) and $\gamma = 10^{-3}$ ($\kappa = 1.43$). Once past the critical size, the martensite droplet grows. As growth proceeds the interfacial widths shrink and κ rapidly reduces to a microscopic value. A well-defined front velocity now emerges. We can determine the late time growth behavior of the martensite droplet by requiring that the rate of energy change, computed from the time derivative of $E(L, W, N \sim L/W^\sigma)$, equals the energy dissipation from

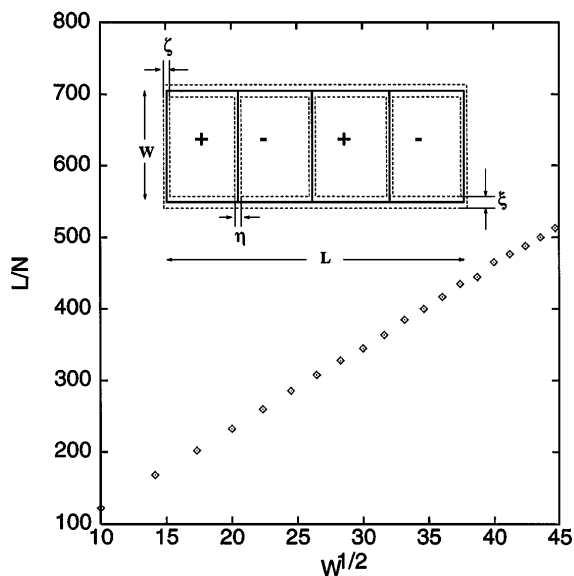


FIG. 2. Plot of L/N vs $W^{1/2}$ for a twinned rectangular strip of length L and width W having N twins, obtained by minimizing $E(L, W)$, for $a = 0.01$, $\gamma = 0.001$. The inset shows the variational profile for e_3 , with interfacial widths ξ , ζ , and η . The + and - denote regions where $e_3 = \pm e_0$, respectively.

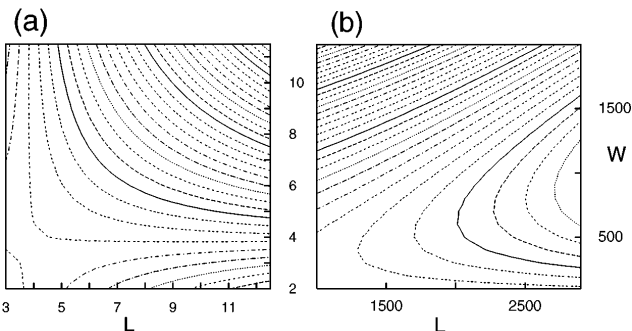


FIG. 3. Contour plots of the minimized $E(L, W)$ in the $L - W$ plane for $a = 0.01$ and (a) $\gamma = 0.001$ and (b) $\gamma = 1$. A comparison of our value for η with typical experimental values yields a unit of length of 1–2 Å.

the local evolution of the order parameter e_3 [14]. Since e_3 follows a purely dissipative dynamics,

$$\dot{E}(L, W, N \sim L/W^\sigma) = \nu \int \dot{e}_3^2 dx dy. \quad (9)$$

The time derivative of e_3 can be easily computed from our ansatz and leads to the following form for the energy dissipation, $\nu e_0^2(\dot{L}^2 W/\xi + \dot{W}^2 L/\xi)$. It is easy to determine the asymptotic solutions for L and W from the resulting first-order, nonlinear, ordinary differential equation (ODE). Assuming $L(t) = \nu_L t^\alpha$ and $W(t) = \nu_W t^\beta$ as $t \rightarrow \infty$ ($\alpha, \beta > 0$), and equating the dominant singular contributions on either side of Eq. (9), we obtain $\alpha = 1$ and $\beta = 1/2$. The nonlinear ODE also gives the velocity $\nu_L \sim \sqrt{\gamma}$. Since γ is of the order of typical elastic moduli, the martensite grows with a constant velocity close to the velocity of sound, in the direction perpendicular to the twinning plane. Parallel to the twinning planes, the front moves diffusively [15].

Thus the martensite nucleus grows in L with velocity ν_L , until it collides with other growing nuclei, whereupon the high elastic energy barriers prevent coalescence [16]. Growth in W proceeds slowly, up to a point where $W = W_{\min}$ (for large γ). When γ is small, growth in W proceeds unimpeded, unless pinned by other nuclei or impurities. The solid is now trapped as a metastable martensite and requires large thermal activation to transform to the equilibrium ferrite. The martensite can thereafter reduce interfacial energy by deforming the crystal such that the discontinuity in \mathbf{u} (and hence ϕ) vanishes. In addition, growth can terminate, if ϕ is made to relax (say, by raising T), leading to thermal arrest of martensites [2].

A more detailed account will explore a ‘‘morphology phase diagram’’ as a function of kinetic and structural parameters. In three dimensions, the possibility of several twin variants would lead to interesting stacking patterns. Indeed, hard martensites like Fe-Ni are ‘‘lens shaped’’ plates. From our 2D ansatz, we see that the interfacial energy at either end of the rectangular strip can be further reduced by decreasing $W(x=L)$ and $W(x=0)$, thus forming a ‘‘lens.’’

Conventional analysis of the structure and kinetics of martensites [3,5] forces the condition that \mathbf{u} be continuous across the parent-product interface. This boundary constraint, once imposed, gives rise to long-range stress fields. Minimization of the total elastic energy leads to a twinned product. Demanding this boundary constraint at all times generates a dynamics which is complicated by the fact that it involves moving boundary conditions, allowing for analytic solutions only in 1D [5]. Moreover, conventional analysis [3,5] does not explain why a ferrite rather than a martensite nucleates for slower rates of cooling. On the other hand, our nonequilibrium statistical mechanics approach can describe, in principle, the ferrite, martensite, as well as all intermediate scenarios resulting from different quench rates. Further, our dynamics does not require imposition of the moving boundary constraint,

since the ϕ field, which lives at the interface, naturally leads to this boundary condition at late times.

Before we close, we would like to point out some important features not included in our theory. When the surface compressibility γ is large, the product might prefer to generate dislocations at the parent-product interface, producing instead internal slip bands [2]. Moreover, for solids with low thermal conductivity, transport of heat across the interface might significantly alter the shape of grains. We are currently working on these refinements to the theory.

We thank S.G. Mishra, T.V. Ramakrishnan, and S. Banerjee for discussions and encouragement.

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