Droplet Fluctuations in the Morphology and Kinetics of Martensites

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We derive a coarse grained, free-energy functional which describes droplet configurations arising on nucleation of a product crystal within a parent. This involves a new ‘slow’ vacancy mode that lives at the parent-product interface. A mode-coupling 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 ‘lens-shaped’ strips having alternating twin domains, with well-defined front velocities. Several empirically known structural and kinetic relations drop out naturally from our theory.

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In modern metallurgical parlance, a martensitic transformation \cite{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 (\( \sim 10^5 \text{cm s}^{-1} \)) \cite{2}: fast compared to typical atomic diffusion speeds. The plates consist of an alternating array of twin BCC crystals along the equatorial plane. Despite the considerable amount of empirical and theoretical work \cite{3,4}, 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” modes that change over time scales corresponding to the propagation of the nucleation front. The slow modes of a solid undergoing a first-order structural transformation are the displacement field \( \mathbf{u}(r,t) \), and the momentum density \( \mathbf{g}(r,t) \). 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 \( \Delta \mathbf{u} \cdot \hat{n} \equiv \phi \), 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, \( \phi(r,t) \) appears as a new slow mode (vacancy field), which relaxes diffusively over a time scale \( \tau_\phi \).

A Langevin description of the dynamics of the transformation, requires a free-energy functional \textit{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 behaviour, though their effect on dynamics is significant.

Nucleation of a droplet of the product of size \( L \) and interfacial thickness \( \xi \), results in a strained crystal. The free-energy functional \( \mathcal{F} \) of this strained crystal is given by,

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

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 \( \rho \) of the liquid at freezing. The above expression is exact at \( T = 0 \); corrections are of the order of the r.m.s. fluctuations of the atoms about their perfect lattice positions, which are small in the solid phase \( \rho \).

Since the range of \( c \) is of order \( \xi \), 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 $u(R')$ about $R$ in the first part, leads to the usual bulk elastic free-energy functional $F_{el} [3]$. 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 $\Gamma (r) = 0$, with $R$ and $R'$ lying infinitesimally close to $\Gamma = 0$. Across this interface, the normal component of $u$ is discontinuous; $\lim_{\Gamma - R \rightarrow 0} (u(R) - u(R')) \cdot \hat{n} \equiv (u_+ - u_-) \cdot \hat{n} \equiv \phi$, where $\hat{n}$ is the unit normal to the interface. The discontinuity $\phi(r)$, which is simply $\xi (\rho(r) | r = 0 - \rho)/\rho$, is the local vacancy field ($\rho$ 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),

$$F = F_{el} + \frac{\gamma}{2 \xi^2} \int \frac{d\tau}{\Omega_0} \left[ (u_+ - u_-) \cdot \hat{n} \right]^2 \xi \delta(\Gamma), \quad (2)$$

where $\Omega_0$ is the unit cell volume of the parent. The coefficient $\gamma \equiv \Omega_0^{-1} \sum e \xi^2 \partial_3 c(r)$, 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 $e_{ij} \equiv \left( \partial_i u_j + \partial_j u_i \right)/2$ are continuous across the interface, we replace the delta function in Eq. (1) by a regulator $\xi^{-1} [1 - \exp(-\xi \partial_3 e_{ij})^2]$, so that the final regulated free-energy functional which incorporates all the slow modes in the problem is,

$$F = F_{el} + \frac{\gamma}{2 \Omega_0} \int d\tau \phi^2 \left( \partial_3 e_{ij} \right)^2 \quad (3)$$

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 $\phi$ (Fig. 1(b)). Having created this discontinuity $\phi$ at the parent-product interface, it will diffuse over a time $\tau_\phi$. The Langevin equation describing the linearised dynamics of the slow modes $u_i$ and $\phi$ can be written as,

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

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

where $e_{ij}$ is the time derivative of the strain tensor $e_{ij}$. The inertial term $\dot{u}_i$ (propagation of sound waves) and solid viscosity tensor $\nu_{ijkl}$ (damping of sound waves) are obtained from the coupling of $u$ with the momentum density $g$ [10].

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 extended to the tetragonal to orthorhombic transition (essentially a 2-dim square to rectangular [3]), are of relevance to structural transformations in alloys like In-Pb, In-Tl, Mn-Fe. This transformation involves a shear+volume deformation, and so the strain order parameter $e_{ij}$ has only one nontrivial component $e_{33} = (u_{xy} + u_{yx})/2$.

We construct a bulk elastic free energy with three minima — one corresponding to the undeformed square cell ($e_{33} = 0$) and the other two corresponding to the two variants of the rhombic cell ($e_{33} = \pm e_0$). The free-energy functional, in dimensionless variables, is

$$F = \int_{x,y} a(c_3^2 - c_3^4 + c_3^6 + (\nabla c_3)^2) + \gamma (\phi \partial_3 c_3)^2 \quad (6)$$

The three minima of the homogeneous part of $F$ at $c_3 = 0$ (austenite) and $c_3 = \pm e_0 = \pm [(1 + \sqrt{1 - 3a})/3]^{1/2}$ (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 $\gamma$ for an interface between the square ($c_3 = 0$) and the rhombus ($c_3 = e_0$) positioned along the $y$-axis is given by $\gamma \equiv (\epsilon''(l + \epsilon''(l + e_0l))/2$, where $\epsilon''(r)$ 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 neighbours of the parent square lattice of spacing $l$.

There are two time scales relevant to our kinetics — the quench rate $\tau^{-1} = (dF/dt)/T$ and the vacancy relaxation time $\tau_\phi$. Accordingly two extreme dynamical limits suggest themselves. When $\tau \gg \tau_\phi$, the $\phi$ fields relax instantaneously (fast mode) to $\phi = 0$, its equilibrium value. The only surviving slow modes are $u_i$, which obey Eq. (3), with the free-energy functional $F = F_{el}$. Since we are interested in the growth of the product nucleus in the parent matrix, it is appropriate to rewrite Eq. (3) in terms of the broken symmetry mode $c_3(r, t)$, which takes the form $c_3(r - R(t))$, when the interface is sharp ($R(t)$ is the position of the interface). The equation for $c_3$ is purely dissipative, $\dot{c}_3 = -\delta F_{el}/\delta c_3$. Minimising $F_{el}$ with respect to $c_3$, subject to boundary conditions $c_3 = 0$ at $|r| \rightarrow \infty$ and $c_3 = \pm e_0$ at $|r| = 0$, obtains a ferrite nucleus, growing as $R \sim t^{1/2}$ at late times [4].

On the other hand, when $\tau \ll \tau_\phi$, the $\phi$ fields are frozen in the frame of reference of the nucleating front. In this limit, $\phi$ is nonzero only at the parent-product interface, and so $v$ in Eq. (3) can be interpreted as the local front velocity. In the frame front, $\phi$ obeys a diffusion equation with the diffusion coefficient $D_\phi = \sqrt{\tau_\phi}$. Recasting Eq. (1), in terms of $c_3$, leads again to a purely dissipative equation with the free-energy functional $F$ given by Eq. (3). To determine the structure of the product nucleus, we use a variational ansatz for $c_3$, consistent with boundary conditions mentioned above. Consider a rectangular nucleus of length $L$ (along $x$) and width $W$ (along $y$) divided into $N$ twins (Fig. 2 (inset)). The $N - 1$ twin interfaces, all of thickness $\eta$, can be parametrized.
by $e_4(x)$, 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 interface 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,

$$E(L, W) = [\Delta FLW + (2I - \Delta F)(L\xi + W\zeta) + \eta/2 < x < iL/N - \eta/2]$$

$$+ (N - 1)(I - \Delta F)W\eta + 2e_0^2I\xi + W\zeta + 4e_0^2(N - 1)/\eta + (\gamma e_0^2/\xi)(2L^3N^{-2}/3 + L^2\eta(N^{-2} - N^{-1}) + \Delta\eta^2(1/2 - 3N^{-1}/4) - L\zetaN^{-1}(LN^{-2} - \zeta/4 - \eta/2)] + \gamma e_0^4\zeta^{-1}$$

$$[2W^3/3 - W\xi + W\xi^2/2].$$

In Eq. (3), $\Delta F \equiv ae_0^2 - e_0^4 + e_0^6$ 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 minimising $E(L, W)$ with respect to the order parameter profile $e_4$ (both the amplitude and phase). Within our variational scheme, this amounts to minimising $E(L, W)$ with respect to the interfacial widths $\eta$, $\xi$, and $\zeta$ and the phase of the order parameter, $N$. Minimisation yields the structural relation (Fig. 2),

$$L / N \sim W^{\sigma}.$$  

The exponent, $\sigma \sim 1/2$, with tiny deviations for large $W$. The exponent $\sigma$ is empirically known to lie between 0.4 and 0.5. Note that our theory suggests that Eq. (6) 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 TEM studies of growing martensite fronts.

Twinning is a consequence of the $f$ term which is confined to the parent-product interface. When $\tau < \tau_0$, 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 $u$. The growing nucleus, gets around this by creating a twin. Though this costs interface energy due to $(\nabla e_3)^2$ (which is small), the contribution from $\phi$ is identically zero at the twin interface, due to symmetry.

From the contour plots of the optimised free energy plotted in Figs. 3(a) and 3(b), one observes a minimum in $W$ for large $\gamma \sim O(1)$ (Fig. 3(b)). Since we find that, $W_{\text{min}} < L$, the free energy is minimised by thin rectangular strips reminiscent of ‘hard’ acicular martensites seen in Fe-Ni or Fe-C systems. For small $\gamma \sim O(10^{-3})$, 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.

![Plot of $L/N$ vs $W^{1/2}$ for a twinned rectangular strip of length $L$ and width $W$](image)

The time derivative of $e_3$, can be easily computed from our ansatz, and leads to the following form for the energy dissipation, $\nu e_0^2(L^2W/\xi + W^2L/\xi)$. It is easy to determine the asymptotic solutions for $L$ and $W$, from the resulting first-order, nonlinear ODE. Assuming $L(t) = vtL^\alpha$ and $W(t) = vtL^\beta$ as $t \to \infty$ ($\alpha, \beta > 0$), and equating the dominant singular contributions on either side of Eq. (8), we obtain $\alpha = \beta = 1/2$. The nonlinear ODE also gives the velocity $v_L \sim \sqrt{\gamma/\nu}$. Since $\gamma$ 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.
Thus the martensite nucleus grows in $L$ with velocity $v_L$, till it collides with other growing nuclei, whereupon the high elastic energy barriers prevent coalescence $^{[1]}$. Growth in $W$ proceeds slowly, up to a point where $W = W_{\text{min}}$ (for large $\gamma$). When $\gamma$ is small, growth in $W$ proceeds unimpeded, unless pinned by other nuclei or impurities. The solid has now got 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 (say, by raising $T$), leading to thermal arrest of martensites $^{[3]}$. In addition, growth can terminate, if $\phi$ is made to relax (say, by raising $T$), leading to thermal arrest of martensites $^{[3]}$.

A more detailed account will explore a ‘morphology phase-diagram’ as a function of kinetic and structural parameters. In this paper, we have confined ourselves to a simple variational ansatz for the shape. Indeed, hard martensites like Fe-Ni are ‘lens shaped’ plates. We see however, that the interfacial energy at either end of our rectangular strip can be further reduced by decreasing $W(x = L)$ and $W(x = 0)$, thus forming a ‘lens’. In three dimensions, the possibility of several twin variants would lead to interesting stacking patterns. Moreover, the fascinating phenomenon of shape memory $^{[2]}$ can be studied by coupling $\epsilon_{ij}$ to an external stress field.

Conventional analysis of the kinetics of martensites $^{[1]}$, minimises the elastic energy, subject to the condition that $u$ is continuous across the parent-product interface. This ad-hoc boundary constraint gives rise to long-range stress fields. The analysis of the dynamics is complicated by the fact that the boundary constraints are moving, allowing for analytic solutions only in 1-dim $^{[3]}$. Our approach does not suffer from this handicap, since the $\phi$ field, which lives at the interface, naturally leads to the boundary constraint at late times.

Before we close, we would like to point out some important features not included in our theory. When the surface compressibility $\gamma$ is large, the product might prefer to generate dislocations at the parent-product interface, producing instead internal slip bands $^{[6]}$. 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.

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