Martensites are metastable phases, possessing a characteristic morphology, usually formed during a fast quench across a structural transition. We attempt to understand these morphological features using a coarsegrained free energy functional $F[\epsilon; \Phi]$ which contains, in addition to the usual strain fields $\epsilon_{ij}$ (the “order parameter” for the transition), the “vacancy” field $\phi$ which arises due to the geometric mismatch at a parent-product interface. The relaxation of this mismatch is slow compared to typical front propagation times and hence $\phi$ is essentially frozen in the reference frame of the growing martensite front. Minimisation of $F$ then automatically yields typical martensite morphologies. We demonstrate this in two dimensions for the square to rhombus transformation and obtain internally twinned martensites, which grow as thin strips, for “hard” martensites (e.g., Fe-based alloys) or with a ‘single-interface’, for “soft” martensites (e.g., In-Tl alloys).

I. INTRODUCTION AND PHENOMENOLOGY

Martensites, a generic term applied to diffusionless structural transformations producing long-lived metastable phases with characteristic morphologies, are observed in a wide variety of systems ranging from metals, alloys and ceramics to organic crystals and crystalline membranes. Although a substantial amount of empirical knowledge has been acquired over the years, a systematic theoretical study of the morphology and kinetics of martensites is lacking. Analysis is made difficult by the fact that the formation of martensite is necessarily a non-equilibrium process. A theory of the martensitic transformation should, therefore, be able to describe the system for all times, $t$, and strictly equilibrium ($t \to \infty$) descriptions are invalid. In this paper, we derive from microscopics a free energy functional capable of describing a droplet of growing martensite at intermediate times. We obtain several, empirically observed, morphological features of Martensites by minimising the free energy functional subject to appropriate constraints. In the rest of this section we review relevant aspects of Martensite phenomenology. We derive the droplet free energy functional in Section 2. In Section 3 we use it to investigate the morphology of two-dimensional martensites. Lastly, in Section 4 we discuss our results and conclusions.

As a typical example of a Martensitic transformation consider the case of steel (an alloy of iron, Fe and carbon, C). Pure Fe at atmospheric pressures undergoes an equilibrium structural phase transition from the austenite ($\gamma$) phase, which has an FCC structure to a BCC, ferrite ($\alpha$) phase, at a temperature $T_c = 910^\circ$C. A fast quench from $T > T_c$ to $T \leq T_m$ (martensite—start temperature) $< T_c$, produces, however, a rapidly transformed metastable phase called the martensite. On nucleation, martensite “plates” grow with a constant front velocity ($v \sim 10^5$ cm s$^{-1}$ in Fe) which is comparable to typical acoustic speeds in solids. The plates consist of an array of twinned or slipped BCC crystals, having well defined orientational relations with each other and with the parent matrix. The Miller indices of the habit plane (the equatorial plane of the plates), are fixed relative to the parent. The morphology of the plates depends on the elastic moduli of the solid, ranging from “lens-shaped” discs (typically $\sim 1\, \mu m$) with a high aspect ratio in the case of hard Fe-based alloys to a region bounded by a single interface in the case of the softer In-Tl alloys. If the elastic energy barriers are large, the plates stop on colliding with other plates. The resulting pattern displays a scale invariant size distribution of the plates.

Several empirical facts suggest that martensites are always metastable with respect to the ferrite. Firstly, the detailed morphology of the plates is a sensitive function of the quench history. Secondly, mechanical properties of martensites are dependent on aging and tempering — metallurgical processes which consist of holding steel at elevated temperatures for specific periods of time to obtain required properties. Lastly, martensites are never formed when

*To appear in Defects in Condensed Media, eds. K. Krishan, C. S. Sundar and V. Kumar (SciTech Publ. Ltd., Switzerland, 1996).
steel is cooled sufficiently slowly, thus there is an intimate relation between the kinetics of cooling and the morphology — slow cooling nucleates a spherical droplet of the ferrite, while rapid quenching produces a martensite with a well-defined morphology. Any theory of the Martensitic transformation should therefore include variables that change slowly over time scales corresponding to the nucleation front propagation. Such typical “slow modes” of a solid undergoing a first-order structural transformation are the displacement field $u(r, t)$ (goldstone mode), the mass and momentum densities $\rho(r, t)$ and $g(r, t)$ (conservation laws) and the strain tensor $\epsilon_{ij}(r, t)$ (the symmetry breaking order parameter). Imagine, however, a grain of the product nucleating within a parent matrix at time $t = 0$.

It is clear (Fig. 1), 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 [12] (a consequence of the fact that the $\gamma \rightarrow \alpha$ structural transformation involves a spontaneous breaking of a discrete symmetry), $\Delta u \cdot \hat{n} \equiv \phi$, and leads to a local compression or dilation of the atomic environment at the interface. Since in martensites, the transformation front velocity, $v$, is large compared to atomic diffusion times, $\phi(r, t)$ appears as a new slow mode (vacancy field). Once formed, this new field, relaxes diffusively over a time scale $\tau_\phi >> L/v$, where $L$ is the typical size of the grains. A Langevin description of the dynamics of the front, requires a free-energy functional which describes all intermediate configurations between an austenite and a ferrite. Thus the free-energy functional should include configurations corresponding to crystalline inclusions of the $\alpha$ phase in the $\gamma$ phase, where the vacancy field $\phi$ appears explicitly. The usual elastic free-energy functional of a solid, $F_{el}$, has to be augmented by an interfacial term $F_{int}$, describing the parent-product interface. It must be stressed that these droplet configurations do not affect equilibrium behaviour. Thus the equilibrium ferrite will be obtained by minimising $F_{el}$. The dynamics, however, is crucially altered by the inclusion of such fluctuations. In the next section we derive, starting from a microscopic density functional theory, a free energy functional which includes such droplet fluctuations.

II. THE DROPLET FREE ENERGY FUNCTIONAL

Consider a droplet of the product phase of size $L$ within a parent matrix bounded by an interface of thickness $\xi$. The presence of the droplet results in a strained parent crystal such that the strain varies from zero far away from the droplet to a limiting value at its center. The free-energy functional of this strained parent is given by,

$$\frac{F}{k_B T} = \sum_{\{R, R'\}} c \left( |R - R' + u(R) - u(R')| \right),$$

(1)
where \( \{ \mathbf{R} \} \) represent the lattice vectors of the parent crystal, \( \mathbf{u}(\mathbf{R}) \) are the displacement fields (degradation of each atom from the (perfect) lattice positions of the parent), and \( c(r - r') \) is the direct correlation function 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.

Since the range of \( c \) is of order \( \xi \), the sum over \( \{ \mathbf{R}, \mathbf{R}' \} \) in Eq. (3) can be split into three parts — (i) \( \mathbf{R} \land \mathbf{R}' \in \text{parent} \), (ii) \( \mathbf{R} \land \mathbf{R}' \in \text{product} \) and (iii) \( \mathbf{R} \in \text{parent} \) and \( \mathbf{R}' \in \text{product} \). Expanding \( \mathbf{u}(\mathbf{R}') \) about \( \mathbf{R} \) in the first two parts, leads to the usual bulk elastic free-energy functional \( F_{\text{el}} \). However, as argued above, the assumption of continuity breaks down in (iii), 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: \( \lim_{\mathbf{R} \in \text{R} \Gamma(\mathbf{r}) \to 0} (u(\mathbf{R}) - u(\mathbf{R}')) = \hat{n} \equiv (u_+ - u_-) \cdot \hat{n} = \phi \delta(\Gamma) \), where \( \hat{n} \) is the unit normal to the interface. The discontinuity \( \phi(\mathbf{r}) = (\rho(\mathbf{r})|_{\Gamma=0} - \rho_{\text{vac}})/\rho_{\text{av}} \) is the local vacancy field, while \( \rho \) is the local density and \( \rho_{\text{av}} \) is the density averaged over a unit cell of the parent. In the continuum limit, the contribution to \( \mathcal{F} \) from (iii), to leading order in the discontinuity, reduces to

\[
\frac{\gamma}{2\xi^2} \int d\mathbf{r} [(u_+ - u_-) \cdot \hat{n}]^2 \delta(\Gamma). \tag{2}
\]

The coefficient \( \gamma \equiv \int d\mathbf{r} \delta(\zeta) \xi^2 c''(r) \) is clearly the inverse surface compressibility modulus of vacancies, \( \phi \). This is expected to be of the same order of magnitude as the other elastic moduli, and thus ranges from \( \mathcal{O}(10^{-3}) \) for soft materials (e.g., In-Tl) to \( \mathcal{O}(1) \) for hard materials (e.g., Fe-Ni). 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 \([1 - \exp(-\xi \partial_n \epsilon_{ij})]^2\), so that the final regulated free-energy functional which incorporates all the slow modes in the problem is

\[
\mathcal{F} = F_{\text{el}} + F_{\text{int}} = F_{\text{el}} + \frac{\gamma}{2} \int d\mathbf{r} \phi^2 (\partial_n \epsilon_{ij})^2. \tag{3}
\]

At the initial time \( t = 0 \), the transformed region (product) is simply obtained as a geometrical deformation of the parent, Fig. 1, which fixes the initial value of \( \phi \). Having created this discontinuity \( \phi \) at the parent-product interface, it will diffuse over a time \( \tau_\phi \). Note the two time scales relevant to our kinetics — the quench rate \( \tau^{-1} = (dT/dt)/T \) and the vacancy relaxation time \( \tau_\phi \). Accordingly, two extreme dynamical limits, suggest themselves — a “slow quench”, \( \tau \gg \tau_\phi \), where the \( \phi \) field relaxes instantaneously; and a “fast quench”, \( \tau \ll \tau_\phi \), where the \( \phi \) field is “frozen” in the frame of reference of the moving nucleation front and \( \phi \) relaxes only once the growth of the front stops [3]. Consequences of an infinitely slow quench is well known from standard classical nucleation theory [4] since the \( \phi \) field relaxes to zero instantaneously and hence does not contribute. In the next section we study infinitely fast quenches which produce martensitic morphologies in the simple setting of a two-dimensional first order structural transformation.

### III. MORPHOLOGY OF 2D MARTENSITES

We study the first-order structural transformation from a square (austenite) to a rhombus (ferrite) unit cell in two dimensions [15]. Our results, which can be easily extended to the tetragonal to orthorhombic transition (essentially a 2-dim square to rectangular [4]), 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 \( \epsilon_{ij} \) has only one nontrivial component \( \mathbf{e}_3 = (u_{xy} + u_{yx})/2 \).

The bulk elastic free energy has three minima — one corresponding to the undeformed square cell (\( \mathbf{e}_3 = 0 \)) and the other two corresponding to the two variants of the rhombic cell (\( \mathbf{e}_3 = \pm \mathbf{e}_0 \)). This immediately leads to the free-energy functional \( F \equiv F_{\text{el}} + F_{\text{int}} \) (in dimensionless variables),

\[
F_{\text{el}} + F_{\text{int}} = \int dx \, dy \left[ a \, \mathbf{e}_3^2 - \mathbf{e}_3^4 + \mathbf{e}_3^6 + \{ (\partial_x \mathbf{e}_3)^2 + (\partial_y \mathbf{e}_3)^2 \} + \gamma (\phi \partial_\mathbf{n} \mathbf{e}_3)^2 \right]. \tag{4}
\]

The three minima of the homogeneous part of \( F \) at \( \mathbf{e}_3 = 0 \) (austenite) and \( \mathbf{e}_3 \equiv \pm \mathbf{e}_0 = \pm[(1 + \sqrt{1 - 3a})/3]^{1/2} \) (ferrite), are obtained in the parameter range \( 0 < a < 1/3 \). The parameter \( a \) is the degree of undercooling and plays the role of temperature. An infinitely fast quench implies that the \( \phi \) field is “frozen” in the frame of reference travelling with the front, \( \mathbf{r} \to \mathbf{r} - \mathbf{v} t \) and \( \phi \to -\mathbf{v} \cdot \nabla \phi \), where \( \phi \) denotes the derivative with respect to time. Quenching the solid across the structural transition, nucleates an inclusion which initially grows as a ferrite. Further growth as a single-domain ferrite is discouraged by \( F_{\text{int}} \). The growing nucleus, gets around this problem by creating a twin. This costs interfacial energy which is however small. We use a variational strain profile to include specifically such twinned domains. For a start,
let us consider a rectangular nucleus of length $L$ (along the $x$-axis) and width $W$ (along the $y$-axis). The nucleus is divided into $N$ twins (Fig. 2) with $e_3$ alternating between $e_0$ and $-e_0$. The $N - 1$ twin interfaces, all of thickness $\eta$, can be parametrized by $e_3(x)$, which for the $i$-th interface takes values $-e_0$ (ferrite) at $(i-1)L/N + \eta/2 < x < iL/N - \eta/2$ and $e_0$ (twin ferrite) at $iL/N + \eta/2 < x < (i+1)L/N - \eta/2$, with a linear interpolation in between. The thickness of the austenite-ferrite interface along the $x$-axis is $\xi$ within which $e_3(x)$ interpolates linearly between 0 and $e_0$ (or $-e_0$). The free-energy of a nucleus with $N$ twins is

$$F(L, W) = [\Delta F L W + (2I - \Delta F)(L \xi + W \xi) + (N - 1)(I - \Delta F) W \eta + 2e_0^2(L \eta + W \eta) + 4e_0^2(N - 1) \frac{W \eta}{\xi}]$$

$$+ \frac{\gamma e_0^4}{\xi} \left[ \frac{2L^3}{3N^2} + L^2 \eta \left( \frac{1}{N^2} - \frac{1}{N} \right) + L \eta \left( \frac{1}{2} - \frac{3}{4N^2} \right) - \frac{L \eta}{N} \left( \frac{L \xi}{N} - \frac{\xi}{4} - \frac{\eta}{2} \right) \right] + \frac{\gamma e_0^4}{\xi} \left[ \frac{2W^2}{3} - W^2 \xi + \frac{W \xi^2}{2} \right]. \quad (5)$$

The interfacial widths are taken as variational parameters. The minimised widths $\xi$ and $\eta$ are independent of the number of domains $N$, while the width $\xi$ scales as $L/N$. The free energy, once minimized with respect to the widths, is a function of $L$, $W$ and $N$. As is apparent from Eq. 5, $F$ goes through a minimum as $N$ is varied, for every value of $L$ and $W$. This is a consequence of the competition between the interfacial energy at the twin interface (which disfavours twinning) and the interfacial energy at the parent-product interface which favours twinning since it reduces $\phi$. Minimising the free energy with respect to the number of twins $N$ immediately gives us, $L/N = W^\sigma$ (Fig. 3). The exponent $\sigma$ is empirically known to lie between .4 and .5. A relation similar to ours has been obtained (with $\sigma = \frac{1}{3}$) from equilibrium continuum elastic theory [4]. It should be noted here, however, that the statement we make is stronger — we imply that $L/N = W^\sigma$ for all times during the growth of a martensite plate as a consequence of demanding local equilibrium. Our prediction for $L/N$ can be verified from in situ transmission electron microscopic studies of growing martensite fronts.

The free energy minimised with respect to all the “fast” variables (viz. the interfacial widths and $N$) is plotted in Fig. 4. One observes that for $\gamma = 1.0$ (Fig 4), the free energy, for all choices of $L$, shows a minimum in $W$ for $W < L$, so that the system will always prefer to have thin rectangular strips reminiscent of acicular martensites seen in Fe-Ni or Fe-C systems. For $\gamma = .001$ there is no such minimum and the martensitic region would like to grow in both directions.

![Fig. 3](image1)

Fig. 3 $L/N$ plotted against $W^{1/2}$ for $L = 20000$ and $\gamma = .001$.

![Fig. 4](image2)

Fig. 4 Contour plots of the droplet free energy minimized with respect to the interfacial widths and $N$ in the $L - W$ plane for $\gamma = 1.0$. Note that there is a minimum in $W$ for all choices of $L$ (for large $L$ and $W$) in this case.

Once growth in one of the directions traverses the entire extent of the sample, growth will proceed thereafter only along a single interface. Such single interface growth is seen in “soft” In-Tl systems. The critical nucleus is obtained by locating the saddle point in each of these free energy surfaces. Using the quantity $\kappa = (\xi \eta / LW)^{1/2}$ as a measure of the sharpness of the interface (indeed one can talk of a definite droplet shape only if the size of the droplet is larger
than this measure), we find that the critical nucleus is diffuse for both $\gamma = 1.0$ ($\kappa = .4$) and $\gamma = .001$ ($\kappa = 1.43$). However, as the size of the droplet increases $\kappa$ rapidly reduces to zero in both cases.

IV. SUMMARY AND DISCUSSION

In summary, we have derived from microscopics a free energy functional $F[\epsilon_{ij}, \phi]$ capable of describing droplets of a martensitic product enclosed within a parent austenitic matrix. Essential to this description is a new field $\phi(r, t)$ viz. the geometric mismatch between the parent and the product at the austenite-martensite interface. This mismatch relaxes diffusively. For martensites, the typical front velocities are empirically known to be very high so that $\phi(r, t)$ fails to relax within the timescale of front motion. We have therefore minimised our droplet free energy functional, using a variational strain profile, subject to the constraint $\phi(r, t) = \phi(r, t = 0)$. We show that typical martensite morphologies drop out naturally from such a procedure. The condition of local equilibrium yields experimentally verifiable quantitative morphological features. In this context, it is worth noting that in practice, real martensites in “hard” systems (e.g. Fe-Ni) do not occur as rectangular strips but as lens shaped objects. The following argument will show that a droplet in the form of “convex-lens” has, in fact, lower energy. The interfacial energy at either end of the rectangular strip (where the interface is along the $\hat{y}$ direction) is $O(\zeta W(L)) = O(W^2)$, where $W(L)$ is the width of the strip at $x = L$. This can be reduced further by making $W(L)$ (and $W(0)$, the width of the strip at $x = 0$) as small as possible. The “lens” shaped structure thus obtained is consistent with structures seen in acicular martensites, like Fe-Ni and Fe-C.

We would like to thank S. G. Mishra and V. S. Raghunathan for useful discussions.

[1] Z. Nishiyama, *Martensitic Transformation*, (Academic Press, New York, 1978).
[2] A. Roitburd, in *Solid State Physics*, ed. Seitz and Turnbull (Academic Press, New York, 1958).
[3] G. B. Olson and H. Hartman, J. Physique, Colloq. 43, C4-855 (1982).
[4] G. R. Barsch and J. A. Krumhansl, Phys. Rev. Lett. 37, 9328 (1974); G. R. Barsch, B. Horovitz and J. A. Krumhansl, Phys. Rev. Lett. 59, 1251 (1987).
[5] P. Kartha, J. Sethna, J. Shore, Phys. Rev. Lett. 60, 9328 (1990).
[6] A. G. Kachaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).
[7] M. Rao, S. Sengupta and H. K. Sahu, Phys. Rev. Lett. 75, 2164 (1995).
[8] The high thermal conductivity of metallic martensites, transports heat rapidly across the transformation front and is therefore not a ‘slow’ mode.
[9] W. S. Owen and F. J. Shoen, in *Structural Characteristics of Materials*, ed. H. M. Finniston (Elsevier, Amsterdam, 1971).
[10] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B42, 2386 (1974). The elastic free-energy has an additional entropic contribution which can be incorporated through the dependence of the density profile on the strain (for large strains). This contribution is small and leads only to a renormalization of the elastic moduli.
[11] J. P. Hansen and I. R. MacDonald, in *Theory of Simple Liquids*, (Academic Press, NY, 1976).
[12] L. Landau and E. M. Lifshitz, *Theory of Elasticity*, (Pergamon Press, NY, 1988).
[13] Long range stress fields are generated when $\phi$ relaxes after the martensite has formed (since the austenite will close any gaps generated at the parent-product interface). No such stress fields are generated when $\phi$ relaxes much faster than the formation of a critical nucleus (and so the ferrite formation is not accompanied by long range stress fields).
[14] E. Becker and W. Döring, Ann. Physik 24, 719 (1935).
[15] Two dimensional examples include martensitic transformations in crystalline membranes as in the tail sheaths of the tobacco mosaic virus (G. B. Olson and H. Hartman, J. Physique, Colloq. 43, C4-855 (1982)).