Predicting the patterns in lamellar growth

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The removal of the degeneracy in the steady-state diffusion-capillarity relation for the undercooling of lamellar eutectics as a function of forced growth velocity and spacing requires the statement of a global principle. The consequences of Langer's conjecture that "each lamella must grow in a direction which is perpendicular to the solidification front" have been explored. In the first instance it is demonstrated that the principle is equivalent on the isotherm to a conditional minimum in the frontal-surface free energy. Secondly, it is deduced for forced-velocity eutectics that the stable spacing is $\sqrt{2}\lambda_m$, where λ_m is given by a minimum in the undercooling. Langer and co-workers have been led to favor the value λ_m on the basis of an unjustified approximation. In contradistinction to Langer's identification of a "diffusive mode" for relaxation of lamellar spacing, we find that the mechanism of stabilization is best described as a damped oscillation in the spacing. The present stable coordinate is identical with that obtained for isothermal structures via Langer's conjecture and by a number of earlier related perturbation arguments. It corresponds to an isothermal state of the spacing which coincides with a maximum in the entropy-production rate. The thermodynamic validation of this principle is briefly discussed.

INTRODUCTION

Lamellar growth of eutectics or eutectoids is now recognized by physicists and others as a paradigm for pattern-forming or "self-organizing systems."[1–3] The remarkable spacial ordering which occurs spontaneously under both controlled and uncontrolled experimentation identifies the reaction with the large class of "dissipative structures" which are now under intensive study.[4–7] Because the steady-state transport analysis of this three-phase chemical reaction for certain ideal models has been rigorously expressed and is generally tractable, workers are confident that accurate prediction of the observed steady patterns will ultimately be achieved. However, the limitations of these ideals have often been overlooked so the conclusions have not always been valid. We begin, therefore, with a discussion of the experiments wherein some of the pitfalls lie.

The reaction is formally expressed by

$$\gamma \rightarrow \alpha + \beta , \tag{1}$$

where a supersaturated homogeneous binary γ alloy at the eutectic (liquid→solid) or eutectoid (solid→solid) composition transforms via the collective action of diffusion segregation into the ordered lamellar (or sometimes rod) bicrystal products shown in Figs. 1 and 2.[8,9] The isothermal (Fig. 1) and forced velocity (Fig. 2) experiments each have their advantages and disadvantages from the point of view of the theoretician. In the isothermal case, usually carried out in a quenched solid, the reaction originates by nucleation at grain boundaries, producing many competing three-dimensional cells of random orientation and extent and imperfect structure (Fig. 3).[10] While this multiplicity and the attendant imperfections present serious experimental problems, they automatically suggest a fluctuating statistical ensemble whereupon a thermokinetic optimal principle can be based (see below).[11] Tedious micrography on sectioned samples followed by statistical analysis is required to obtain measurements on cell-front velocity, v, and spacing, λ, as a function of the undercooling, ΔT.[12] It is necessarily assumed that the latent heat evolved is small enough and the thermal conductivity is great enough to transmit the temperature of the quench bath uniformly. Notwithstanding the difficulties, some highly reliable average data have become available for testing the theory.[12–14] These are to be compared with consequences through stability theory of the degenerate

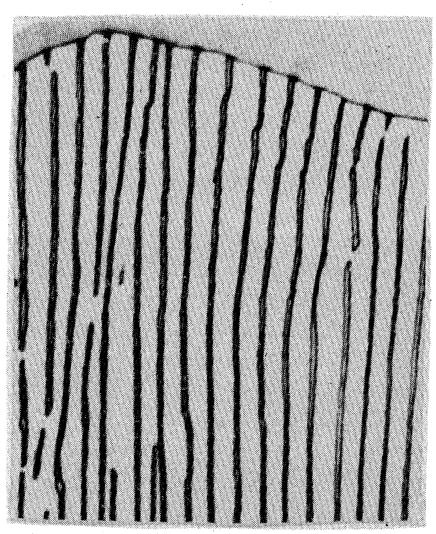

FIG. 1. Quench-interrupted spontaneous growth of the isothermal solid-state bicrystal eutectoid or "pearlite" in 0.8% carbon steel. The order parameter in this degenerate binary diffusion problem may be identified as the growth velocity or the lamellar spacing ($\sim$2 μm). They are functionally related. (After Vilella.[8])

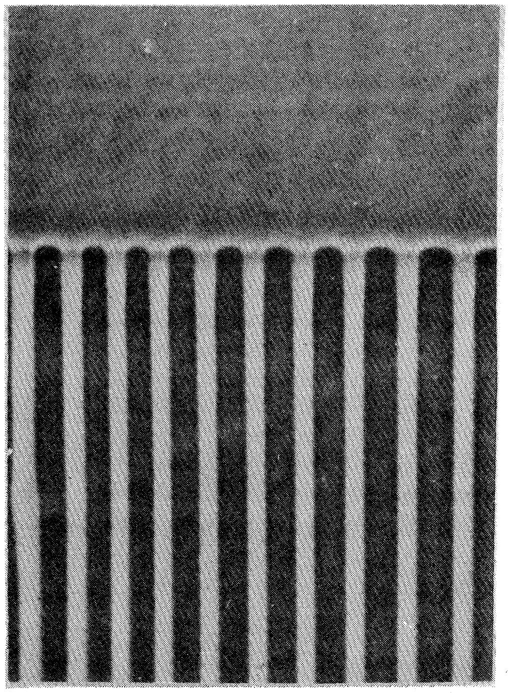

FIG. 2. A lamellar carbon tetrabromide-hexachlorethane eutectic or "pearlite" grown in a forced-velocity temperature gradient.[9] The order parameter in this degenerate mass-heat diffusion problem may be identified as the undercooling at the interface or the lamellar spacing.

steady-state velocity relation (α,β constant)[15,16]

$$v=\frac{\Delta T}{\alpha\lambda^n}\left[1-\frac{\beta}{\lambda\,\Delta T}\right] \tag{2}$$

(or more rigorous versions[17]) where the critical spacing for nucleation $\lambda_c=\beta/\Delta T$ varies as the inverse of fixed ΔT and the power n is determined by the diffusion model ($n=1$ for volume diffusion and $n=2$ for phase boundary diffusion). This relation is singly degenerate in the sense that one further constraint on v and λ is required to specify a unique solution. The degree of freedom arises through the fact that neither of the internal order parameters, v and λ, are constrained by the boundary conditions. The removal of such characteristic degeneracies is the main source of our theoretical interest in such dissipative structures.

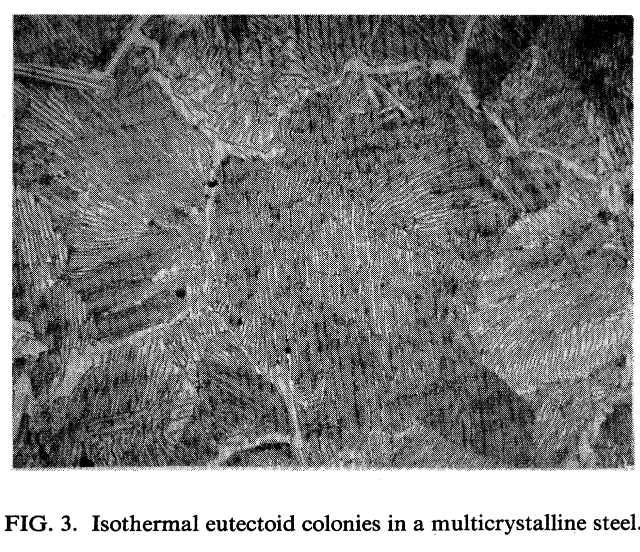

FIG. 3. Isothermal eutectoid colonies in a multicrystalline steel.[10]

By contrast, the forced-velocity structure is generated in a temperature gradient (Fig. 2), and this in at least two distinct ways. In the most common experimental arrangement a radiatively or electron beam heated molten zone is passed at a fixed velocity v along a bar of the appropriate binary eutectic alloy composition.[18] At the trailing edge of the molten zone steady-state solidification occurs. This experiment, despite its wall defects and thermal homogeneities, produces lamellar microstructural arrays which are remarkably uniform and reproducible as to spacing. In experiments of this kind the thermal gradients are rather uncertain, although in principle measurable. To earlier analysts this presented no problem for it has been argued that (2) is still accurately applicable since with typical gradients the very narrow diffusion zone is to all intents and purposes isothermal. Thus one can solve (2) for the undercooling

$$\Delta T=\alpha v\lambda^n+\beta/\lambda\ , \tag{3}$$

where α and β are weak functions of ΔT through the diffusion coefficient and surface tension, respectively. Thus analogously to (2) we have two related internal order parameters, ΔT and λ, with v constant. Most of the data on forced-velocity eutectics has been adequately if not accurately analyzed on the basis of the "*ad hoc*" constraint defined by a minimum in $\Delta T(\lambda=\sqrt{\beta/\alpha v}\,)$.[19] Since the free variable ΔT has not usually been measured simultaneously, the closure with experiment is by-and-large incomplete (see however, Ref. 20). Note that since the boundary conditions are constantly moving points of fixed temperature, variations in ΔT must lead to variations in the liquid and solid gradients. Current theorists have not distinguished between this classical experiment and the "thin-film" experiment which was devised by Jackson and Hunt for studying transparent organic eutectics.[21,22] Here the experimental structure can be observed and analyzed "*in situ*" (Fig. 2). The boundary condition is, however, different because the thin eutectic bicrystal is grown between two thick glass plates which rigidly determine the value and constancy of the sample temperature gradient through their end contact with a moving heat source and sink. It is natural from the theoretical point-of-view to favor the thin-film experiment[3] since the gradient is in principle constant and defined and the structures observed usually have great perfection. There are, however, as yet no reliable experiments for this configuration. Furthermore, it may be difficult to generate them, for the thin-film configuration is strongly subject to hysteresis effects. In the three-dimensional free-boundary transformation experiments described above there are always sufficient wall, grain boundary, and growth-generated defects to provide prompt mechanisms for spacing change and thus the rapid attainment of a unique steady structure which has lost all correlation with the initial condition. Unfortunately, there is a strong tendency in the two-dimensional thin-film experiment for a "memory" of initial conditions and thus for a broad set of metastable structures of different spacings [in accord with (2)] to appear and persist for the order of experimental times.[9,23] For this situation, a unique stable spacing does not exist nor can a meaningful stability calculation be proposed. All of this emphasizes a key point which has been overlooked by the theorists: that the only theoretically interesting lamellar arrays are those which are sufficiently defective and fluctuation prone that a stochastic phase space which is independent of initial conditions has emerged. They must not, of course, be too defective (chaotic or turbulent) or they would not be recognized as pattern forming. It is for structures within the aforementioned phase space that an appropriate stability theory must be found. To the extent that such a statistical ensemble can be experimentally recognized it will be demonstrated that the same stability principles apply to all of the aforementioned boundary conditions and therefore that a statistically unique configurational state is in fact defineable.

LANGER'S CONJECTURE

If with many hydrodynamicists[23] and other workers one forsakes the idea that perturbation theory is appropriate to the removal of the steady-state degeneracies in the search for unique stability conditions for dissipative structures there is no recourse but to seek global principles which may remove the degree(s) of freedom. In recent papers Langer and co-workers[2,3] have proceeded in this way, expressing in a mathematical form a qualitative global principle which materials scientists had applied with varying success to the eutectic and eutectoid problem for over two decades.[24–27] They have thus been able to claim a confirmation of the stability regimes for forced velocity eutectics which had been crudely argued in the past. This writer, realizing that the Langer conjecture had not been worked through to its full conclusion, was able to identify the stability point for isothermal structures at the inflection point of the $v(\lambda)$ curve [Eq. (2)] (see Ref. 28). It recently occurred to us that a similar argument applies to the forced velocity case, and accordingly that its stability point might also be inferred from Langer's condition. In the following we recapitulate the entire argument with modifications and with critical asides pertaining to the physical meaning of the conjecture and experimental interpretation.

Figure 4, reproduced from Langer, defines the significant parameters. The eminently plausible proposition is that "each lamella must grow in a direction which is locally perpendicular to the solidification front"[2] (dashed line) and takes the discrete form in Ref. 3, relation 3.10, or the continuous form[2]

$$\frac{\partial y}{\partial t} = -v_0 \frac{\partial \zeta}{\partial x} . \quad (4)$$

This summarizes our intuition that the collective action of the analytic diffusion fields and capillarity [which has been invoked in the derivation of (2)] are such that the

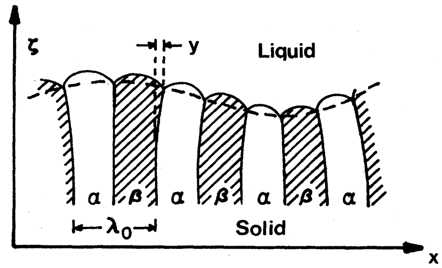

FIG. 4. Schematic illustration of a lamellar eutectic growing up the page with a deformed solidification front. The lamellae may be visualized as semi-infinite plates perpendicular to the plane of the paper. (After Langer[2]).

discrete triple point parameters y and ζ reside as an array of points in a differentiable manifold. It may also be interpreted as a conditional minimum surface free energy principle.[27,28] This latter will be explicitly demonstrated in a later section.

Since we require a theoretical connection with Eq. (2) we further, with Langer, extend the differentiability principle by expressing the local lamellar spacing according to Fig. 4 (and Ref. 3, relation 3.1) as[2]

$$\lambda(x,t) = \lambda_0(1+\partial y/\partial x) , \quad (5)$$

where λ_0 is an unperturbed trial spacing, and assume that this is differentiable to the second order. In the following treatment we will restrict attention to long wavelength perturbations with vanishing amplitudes in both λ and ζ for then the linkage of (2), (4), and (5) may be perceived as approaching precision. This apparent limitation of the stability analysis is to be comprehended within the "*a posteriori*" nature of the science of pattern formation. We do not try to predict the occurrence of patterns; we only try to explain those which are observed. As with the stability of equilibrium states in classical thermodynamics, the kinetic stability of a particular system is given by observation. It is therefore sufficient to test a model's stability via a single class of perturbations. If the model and procedure are rigorous and every accessible state but one is unstable to this class of perturbations then the single stable state defines the true stability point.

Langer has understood (4) and (5) as strictly applying only to a perfect system such as in Figs. 2 and 4 but conjectures that lamellae can be gained or lost via noise or stochastic processes. We fully agree with this conception of the mechanism of spacing change and have argued in the preamble that the only interesting systems are those which possess a low density of defects which are capable of effecting spacing changes. Lamellar faults, which have been observed in both the isothermal and forced velocity cases are generally assigned this function.[29,21,27] These, like edge dislocations, are terminated lamellae which upon moving into the array decrease the spacing or on moving out of the array increase the spacing. Also, like dislocations they can be created at the sample walls or upon bicrystal defects like grain boundaries. Appearing only rarely at a cross section like Fig. 4 they do not deny the validity of (4) and (5) as differentiable system averages.

Yet by negating the conservation of lamellae, they allow for the quasisteady drift whereby the system in an arbitrary initial condition can ultimately reach a unique stable state. The point will become clearer within the completed mathematical structure.

EVALUATION OF THE STABILITY POINT FOR FORCED-VELOCITY EUTECTICS

Differentiating (4) with respect to t and (5) with respect to x and combining yields

$$\frac{\partial \lambda}{\partial t} = -v_0 \lambda_0 \frac{\partial^2 \zeta}{\partial x^2} . \tag{6}$$

Differentiating once more we obtain

$$-v_0 \frac{\partial^2}{\partial x^2}\left[\frac{\partial \zeta}{\partial t}\right] = \frac{\partial^2(\lambda/\lambda_0)}{\partial t^2} . \tag{7}$$

Since the local velocity v can be written as

$$v = v_0 + \frac{\partial \zeta}{\partial t} \tag{8}$$

(7) can be written as[28]

$$-v_0 \frac{\partial^2 v}{\partial x^2} = \frac{\partial^2(\lambda/\lambda_0)}{\partial t^2} . \tag{9}$$

Now in the thin-film experiment or the hypothetical case where the latent heat is negligible and the thermal conductivity is constant the temperature gradient can be taken as a strict constant G^3. In reference to Fig. 4 with $\zeta = 0$ at temperature $T = T_E$ Langer, and Datye and Langer suggest that it is therefore valid to write[2,3]

$$G\zeta(x,t) = -\Delta T(x,t) , \tag{10}$$

where ΔT is the mean local undercooling at the interface. With such a strong constraint over space and time the calculation is thereby committed to a quasistationary or parametric approach. Combining (10) and (6) yields[2]

$$\frac{\partial \lambda}{\partial t} = \frac{v_0 \lambda_0}{G} \frac{\partial^2}{\partial x^2}(\Delta T) . \tag{11}$$

Now keeping in mind our vanishing amplitude, long wavelength caveat we will seek a solution which is parametric in v and λ according to (2) or (3), viz.,

$$\Delta T = \Delta T(v(x,t), \lambda(x,t)) \tag{12}$$

which approaches precision in the perturbation limit defined. We thus evaluate via (3) for $n = 1$

$$\frac{\partial}{\partial x}\Delta T = \alpha\lambda \frac{\partial v}{\partial x} + \left[\alpha v - \frac{\beta}{\lambda^2}\right]\frac{\partial \lambda}{\partial x} \tag{13}$$

and from this, (11) and (9) obtain

$$\frac{\partial \lambda}{\partial t} = \frac{v_0 \lambda_0}{G}\left[2\alpha \frac{\partial \lambda}{\partial x}\frac{\partial v}{\partial x} - \frac{\alpha \lambda}{v_0 \lambda_0}\frac{\partial^2 \lambda}{\partial t^2} + \left[\alpha v - \frac{\beta}{\lambda^2}\right]\frac{\partial^2 \lambda}{\partial x^2} + \frac{2\beta}{\lambda^3}\left[\frac{\partial \lambda}{\partial x}\right]^2\right] . \tag{14}$$

It can be argued that in the second-order expansion of (12) $(\partial\lambda/\partial x)^2$ should be replaced by $1/2\partial^2(\lambda-\lambda_0)^2/\partial x^2$.[29] However, this only produces an additional term $(\lambda-\lambda_0)\partial^2\lambda/\partial x^2$ which vanishes relatively to other terms in the low amplitude limit of interest here. The same considerations apply to $\partial^2 v/\partial x^2$. Now in testing for stability in accord with the quasistationary approach it is convenient to investigate the first-order stationary state $(\partial v/\partial t = \partial\lambda/\partial t = 0)$ which implies a planar interface $(\partial^2\zeta/\partial x^2 = 0)$ via (6) and $\partial^2\zeta/\partial t^2 = 0$ via (8). Furthermore, consider an initial condition with a constant undercooling, $\partial\Delta T/\partial x = 0$, whereby from (13) and (14) we can deduce

$$\lambda^2 \frac{\partial^2 \lambda}{\partial t^2} = 2\frac{v_0\lambda_0}{\alpha}\left[\frac{2\beta}{\lambda^2} - \alpha v\right]\left[\frac{\partial \lambda}{\partial x}\right]^2 + \frac{v_0 \lambda_0}{\alpha\lambda}\left[\alpha v - \frac{\beta}{\lambda^2}\right]\frac{\partial^2 \lambda}{\partial x^2} \tag{15}$$

with v and λ, and therefore ΔT and the coefficients stationary to the first order in t. First consider a linear perturbation in λ, i.e., $\partial^2\lambda/\partial x^2 = 0$. Stability, defined by stationarity of λ to the first and second order at $t = 0$, is thus specified exactly by the sign change of the first term on the right, viz.,

$$\lambda = (2\beta/\alpha v)^{1/2} . \tag{16}$$

This applies to the volume diffusion case (which is normal for a liquid parent phase). Relation (16) differs from the result for the minimum undercooling criterion by the factor of $\sqrt{2}$ (see above). Generalizing to arbitrary n yields a stability point at

$$\lambda = (2\beta/n\alpha v)^{1/n+1} . \tag{17}$$

If in accord with experiment (see below) the frontal temperature and curvature remains constant then (15) describes λ oscillations which are perfectly damped only at the stability point (16). Langer has reached a weaker conclusion closely related to the minimum undercooling criterion via the unjustified approximation of setting $\partial v/\partial x = 0$ in (13),[2] differentiating once more, and combining with (11) (see the Appendix).

While our new result based on relation (4) is elegant and plausible, it bears further scrutiny in relation to the stabilization of three-dimensional structures. Generally speaking for the usual range of experimentation the latent heat evolved is not negligible nor are the thermal conductivities of liquid and solid κ_L and κ_S equal. Indeed the latter usually lie in the relation

$$\kappa_S \sim 2\kappa_L . \tag{18}$$

Thus (10) is invalidated since G (or better, average G) becomes a function of v. Furthermore, since the thermal diffusion length ($\sim$5 cm) is much greater than typical perturbation wavelengths (say 100 μm) interface perturbations according to (10), or its modification for G nonconstant, will be completely damped by thermal relaxation, solid protuberances short-circuiting heat to the trailing interfaces. This is not only expected for the three-dimensional experiment, but appears also to be the case for the thin-film experiment. As Fig. 5 for such an experiment demonstrates,[30] the average interface is perfectly planar despite the strong perturbing effects of a grain boundary and a spacing differential of a factor of 2. This variation should have produced a surface deviation greater than a lamellar spacing (~ 20 μm) if Langer's relation (10) were to have any bearing on the problem. A review of Jackson's film impressed us with the effectiveness of the constraint provided by thermal relaxation. This damping provides an experimental reason for considering only ΔT=constant perturbations in the theory and suggests a procedure which bypasses the imperfect relation (10).

If we suppose that the region of phase space defined by (10) is not accessible we must seek another degree of freedom for perturbation testing. This is placed in evidence by exploring the direct consequences of Eq. (9). Proceeding as before in the quasistationary approximation, substituting

$$v = v(\lambda(x,t), \Delta T(x,t)) \tag{19}$$

and relaxing to the usual limit, noting that $[d^2 v/(\Delta T)^2]_\lambda = 0$, one obtains the nonlinear equation

$$-\frac{1}{\lambda_0 v_0}\frac{\partial^2 \lambda}{\partial t^2} = \left[\frac{dv}{d\lambda}\right]_{\Delta T}\frac{\partial^2 \lambda}{\partial x^2} + \left[\frac{d^2 v}{d\lambda^2}\right]_{\Delta T}\left[\frac{\partial \lambda}{\partial x}\right]^2 + \left[\frac{dv}{d\Delta T}\right]_{\lambda}\frac{\partial^2 \Delta T}{\partial x^2} + 2\left[\frac{d^2 V}{d\lambda\, d\Delta T}\right]\frac{\partial \Delta T}{\partial x}\frac{\partial \lambda}{\partial x} \tag{20}$$

which is the replacement for (14). Let us again examine the stationary, zero curvature states defined by $\partial\lambda/\partial t \sim \partial^2\zeta/\partial x^2 = 0$ [Eq. (6)] and consider a low amplitude linear initial condition in the spacing ($\partial^2\lambda/\partial x^2 = 0$; $\partial\lambda/\partial x$ = constant; ΔT=constant) centered in turn on each (v_0, λ_0). One now recognizes that (20) has become identical with (15) whereby the stability point is defined by

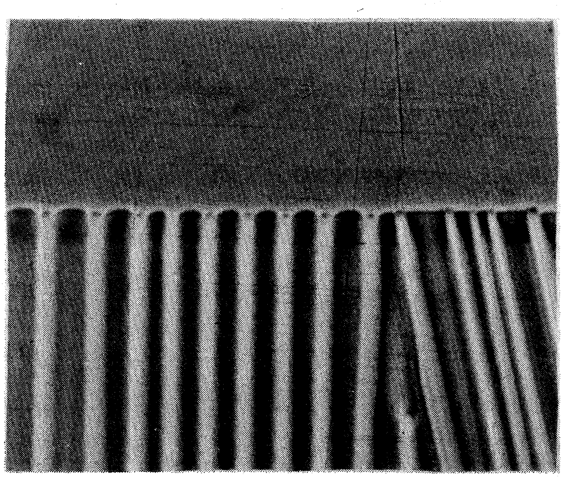

FIG. 5. Frame from Bell Telephone System film demonstrating a planar interface despite a strong spacing change. See also Fig. 2.

$$\left[\frac{d^2 v}{d\lambda^2}\right]_{\Delta T} = 0 \tag{21}$$

or from (2)

$$\lambda = \frac{n+2}{n}\frac{\beta}{\Delta T}\,. \tag{22}$$

This result is also obtained by combining (3) and (17). Accordingly, the two procedures prove to be equivalent despite the limitations of Eq. (10), and the stability point is identical with that obtained earlier for the isothermal case.[28] The equivalence arises in part because the initial condition for (15), $\partial\Delta T/\partial x = 0$, nullifies constraint (10). This identity of the two forced-velocity and isothermal cases has been argued on qualitative grounds a number of times.[13,25,27] Relation (4), however, offers for the first time a basis for a mathematical conclusion. One should now appreciate that the Langer nonplanar structure of Fig. 4 experimentally exists only on the isotherm, a fact not recognized by that author. Accordingly, all deductions from (4) and (5) relative to forced-velocity structures are arrived at by analytic continuation from a virtual isotherm to the planar isothermal interface. It is for this reason that the predicted stability point is the same for the isothermal and forced-velocity cases. This equivalence has been confirmed in at least two independent experiments.[13,31]

There is a further important inference to be drawn from relation (6), viz., the ultimate steady state must satisfy $\partial\lambda/\partial t = 0$, which defines a state of zero curvature on the isotherm, independent of the kind of constraint which one imposes via the boundary conditions. The result accordingly expresses an isothermal tendency towards a conditional minimum global surface free energy state. This is undoubtedly the reason why the conjecture and relation (4) appear intuitively plausible. This writer, using a different argument, demonstrated some years ago for the isothermal case that the inflection point stability criterion was equivalent to this conditional free energy optimum. Indeed, we have noted from a more detailed analysis of interface shapes that the local interface configurations tend in the same direction (flat interfaces) at this particular point.[27] We would not like to leave the impression, however, that such a conditional minimum is generally to be expected in solidification structures. In fact, the resolution of two-phase instabilities such as cells and dendrites tends towards maximum surface energy.

ENTROPY EVOLUTION AND OPTIMALITY

However disguised, it does not appear to the writer that a conditional minimum free energy principle can be regarded as fundamental in solving stability problems of this kind. For other reasons, Datye and Langer have expressed their reservations.[3] Consider again the perturbation program leading to (21) and note that for the linear initial condition we are free to choose (v_0, λ_0) at any position along the interface. This allows us to infer via (20) that the relaxation rate as indexed by $\partial^2\lambda/\partial t^2$ will be larger (via $d^2v/d\lambda^2$) the further is the local spacing from the stable value. It implies for arbitrary (v_0, λ_0) that if the number of lamellae are not conserved, the relaxation must be to a uniform spacing which tends closer to but possibly different than the stable value. A spectrum of uniform metastable or hysteretic states may thus be defined by (20). Yet, as indicated in the preamble, if nature arranges that the lamellar density can change via slow nucleation or annihilation processes or injection or rejection to or from external or internal surfaces, then a stochastic approach to stability with increments in accord with equations (13) and (14) or (20) can be envisaged.[2] Alternatively, one can conceive in relation to Fig. 4 of a fluctuating phase space consisting of metastable states and mathematicized as usual via a virtual ensemble,[32] and then seek an entropylike function which optimizes at the stable steady state. For the systems of present interest, this is easy to identify if we locate our small test system within a diaphragm separating two very large energy-mass reservoirs, the entire assembly placed in an adiabatic enclosure.[11] Following any fluctuation which successfully changes the pattern there is a pulse of heat to or from the reservoirs corresponding to the change in the subsystem entropy production rate. If such states survive for a time τ on the average then the entropy change of the composite or discontinuous system relative to some base $S(t)$ is represented to sufficient precision by

$$\Delta S = \int \Delta \dot{S}_i \, dt = \tau \Delta \dot{S}_i \ , \tag{23}$$

where $\dot{S}_i$ is the integral entropy production over the test system. In general, the continuation and summation of ΔS over many transitions leads to an entropy function in isolation which is not everywhere differentiable. Now one can insist in accord with classical thermodynamics that the second derivative of the enclosure entropy be everywhere defined (macroscopic smoothness of the entropy function) or equivalently that an appropriately defined path probability be maximized in isolation.[11] In either case the optimal path is one for which deviations due to pattern changes are subject at the steady state to

$$d^2S = \Delta S = \tau \Delta \dot{S}_i = 0 \tag{24}$$

which specifies a maximum or a minimum in the entropy production rate and minimal space and time correlation between the subsystem and the reservoirs. This is an eminently reasonable generalization of equilibrium concepts to the stochastic patterned steady state.[6] For isothermal eutectics ($\lambda_c = \beta/\Delta T$)

$$\dot{S}_i \sim v \left[1 - \frac{\lambda_c}{\lambda} \right] \sim \frac{1}{\lambda^n} \left[1 - \frac{\lambda_c}{\lambda} \right]^2 \tag{25}$$

which possesses a maximum at

$$\lambda = \frac{n+2}{n} \lambda_c \tag{26}$$

a result which is identical to the consequences of relation (4). We emphasize that this minimax principle is only indirectly related to the principle of minimum entropy production. Indeed, because the signature of the optimum is not "*a priori*" specified it is a weaker principle than that derived within the linear theory of irreversible thermodynamics.

This particular dissipation model identifies only one internal order parameter, λ, which optimizes to a univariate maximum in the dissipation. The minimal part of possible pattern fluctuation excursions is accordingly missing.[11] There remains, however, a minimal part corresponding to the microscopic fluctuation spectrum in the dissipation which is an alternative to that expressed by the regression equations (15) and (20). This is to say, all of the hysteretic states (including the stable one) lie at a trivial minimum in the dissipation with respect to spacing changes with the total number conserved. We emphasize the approximate character of the microscopic principle since it is the Prigogine-Glansdorff general evolution criterion[33] which strictly applies in this case. The connection between the two principles, which agree at the stability point, lies in the fact that the entropy fluctuation spectrum is common. The distinction lies only in the time scale of observation. The regression time for the minimal part is $< \tau$ while that for the maximal part is $> \tau$ (see also Ref. 34).

The optimal states of forced-velocity structures are not as transparent as in the isothermal case for the thermal gradients greatly complicate the evaluation of the dissipation. The writer has dealt with this problem with some success in an earlier publication.[35] The simplest conception is of a displacement of the chemical zone of the interface at fixed mean v and ΔT into virtual transient states of slightly varying λ for which the dissipation is given by an integral over dx on the right-hand side (rhs) of (25). Then the optimum evaluated via the variational calculus, which involves chemical dissipation only, is identical with that specified in the isothermal case. However justified in theory, this optimum provides good predictions of the experimental results for all of the arrangements considered.[17,27,36]

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APPENDIX

In Langer's treatment,[2] also based on Eqs. (11) and (12), there is a departure at Eq. (13). In particular, $\partial v/\partial x$ is set equal to zero in (13). Thus (11) yields

$$\frac{\partial \lambda}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial \lambda}{\partial x} \right] , \tag{A1}$$

where

$$D = \frac{v_0 \lambda_0}{G} \left[\alpha v - \frac{\beta}{\lambda^2} \right] . \tag{A2}$$

Langer recognizes this as a diffusion equation in which the λ variable is conserved, and argues that the change in sign of D from positive to negative signals the onset of absolute instability as in spinodal decomposition. Actually, the quantity which is conserved in the model of Fig. 4 is $1/\lambda$ which is proportional to the trailing surface energy. If one rephrases A1 in terms of $1/\lambda$ it is no longer a diffusion equation to full precision.

Datye and Langer have rephrased Langer's treatment in discrete terms [Eqs. (4) and (5), in particular] and carried out an elaborate linear perturbation analysis, the central conclusions of which are identical to the above. Since we can find no *a priori* justification for setting $\partial v/\partial x=0$ we are forced to conclude that the "diffusive" modes of transformation do not in fact exist. In contradistinction, our result in Eqs. (14) and (15) is free of ambiguity and definitive in its inferences. There is no doubt in our minds that stability of lamellar structures is defined in the theoretical ideal by a damped oscillatory rather than a diffusive mechanism.

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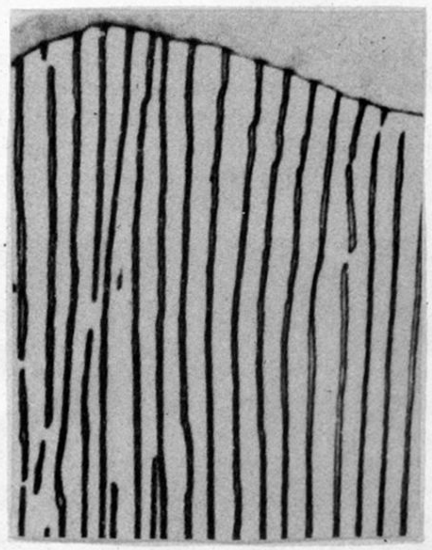

FIG. 1. Quench-interrupted spontaneous growth of the isothermal solid-state bicrystal eutectoid or "pearlite" in 0.8% carbon steel. The order parameter in this degenerate binary diffusion problem may be identified as the growth velocity or the lamellar spacing ($\sim 2\ \mu m$). They are functionally related. (After Vilella.[8])

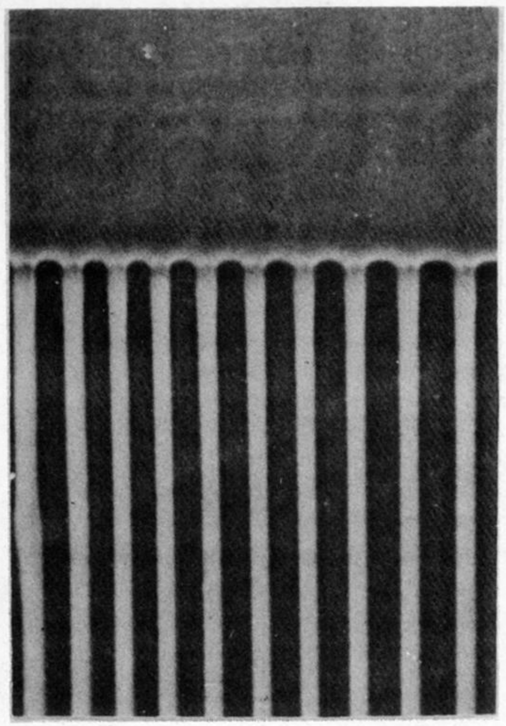

FIG. 2. A lamellar carbon tetrabromide-hexachlorethane eutectic or "pearlite" grown in a forced-velocity temperature gradient.[9] The order parameter in this degenerate mass-heat diffusion problem may be identified as the undercooling at the interface or the lamellar spacing.

FIG. 3. Isothermal eutectoid colonies in a multicrystalline steel.[10]

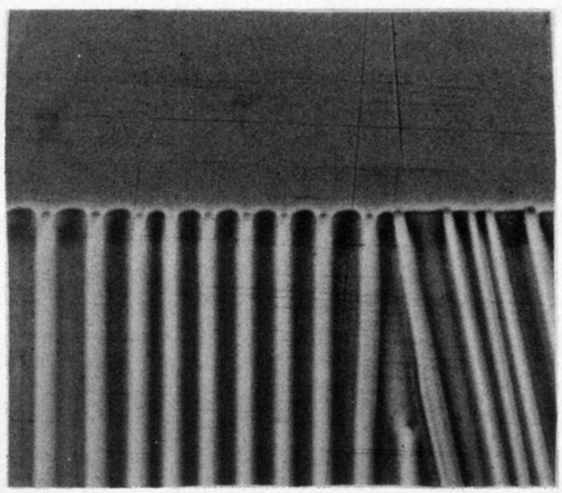

FIG. 5. Frame from Bell Telephone System film demonstrating a planar interface despite a strong spacing change. See also Fig. 2.