# Coexistence of twisted and untwisted crystals: An impurity/structural order model with implications for agate patterns

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## Abstract

Coexistence of twisted and untwisted crystals is explained via a model that accounts for the coupling of the entropic and energetic effects of impurities and a supra-lattice-scale structural order parameter. It is shown that twisted impure crystals can be in equilibrium with untwisted purer ones. The model explains how coexistence can occur in agates and other systems under hydrostatic stress. The model implies that untwisted crystals grown under one set of conditions could undergo a phase separation that, when accompanied by an imposed compositional gradient, leads to commonly observed, alternating bands of twisted and untwisted crystals and, when occurring in the absence of an external gradient, mossy patterns of crystal texture can emerge. This phenomenon is not related to anisotropic applied stress. Rather coexistence is a consequence of a compositional segregation/twist phase transition. Since twist coexistence is a compositional equilibrium, it arises from the exchange between bulk phases; hence, the detailed nature of the atomic structure within an interface between twisted and untwisted zones is not relevant. The approach places crystal-twist phenomena within the theory of order/disorder phase transitions.

**Keywords:** Agate, agate banding, free energy model, phase separation, quartz fibers, self-organization, twisted crystals, twisted/untwisted crystal equilibria

## Introduction

Crystals that exhibit a twisted habit have long been recognized and many examples have been described in a variety of minerals (Frondel 1936; Spencer 1921). In large crystals, progressive changes in orientation of the crystal lattice are represented by obvious curvature of crystal faces and may result in a pronounced helical twisting of elongated crystals (Frondel 1936; Spencer 1921). In small crystallites or fibers, twisting is generally not obvious upon megascopic examination, but is easily identified by the sweeping extinction in thin section when viewed with polarized light under crossed polars (Frondel 1978; Milliken 1979) (Fig. 1). Sweeping extinction documents the changing orientation of a crystal lattice along the length of the fibers.

While the phenomenon of twisting has long been known, the causes are less well understood. Explanations for crystal twisting include twinning (Kozlova and Belov 1981; Xu et al. 1998), point and edge defects (Radke and Mathis 1980; Searl 1989), lattice dislocations (Frondel 1978; White and Wilson 1978), and ionic substitutions and interstitial defects (Heaney and Davis 1995; Wang and Merino 1990).

Spencer (1921) stated that twinning is a common cause of twisted crystal habits. Kozlova and Belov (1981) concluded that Brazil twinning accounted for curved prism faces in α-quartz, and observed that the intergrowth of twinned crystals produces a fine mosaic structure that imparts an apparently continuous curvature to prism faces. Xu et al. (1998) showed that Brazil twinning accounted for most of the atomic-scale defects in fibrous chalcedony, and a high density of twin boundaries, sometimes forming discrete domains of the silica polymorph moganite, has been documented at the unit-cell scale (Heaney and Davis 1995; Xu et al. 1998). Zebraic chalcedony (Fig. 1) is a classic example of twisting of crystalline fibers along the axis of elongation (Milliken 1979).

Saddle structure in dolomite has been explained as due to curvature caused by substitution of Ca for Mg or the introduction of extra Ca-depleted layers as edge defects in the dolomite lattice (Barber et al. 1985; Radke and Mathis 1980; Searl 1989). Following this notion, Wang and Merino (1990) attributed twisting of chalcedony fibers in agate to the substitution of Al for Si in tetrahedral lattice sites. Heaney and Davis (1995) confirmed the coupled substitution of $Al^{3+}$ and $Na^{1+}$ for $Si^{4+}$ in agate chalcedony using secondary ion mass spectrometry.

Twisting of crystals during periods of deformational strain is also well known (Williams and Urai 1989), and curved fibers have been used to quantify the strain associated with different deformational phases (Carminati 2001; Durney and Ramsay 1973). Crystal fibers may twist as they grow in response to syn-tectonic deformation (Durney and Ramsay 1973) or they may bend during subsequent deformational strain (Williams and Urai 1989) or both (White and Wilson 1978). The twisting is caused by multiple lattice defects that include voids (bubbles), lattice
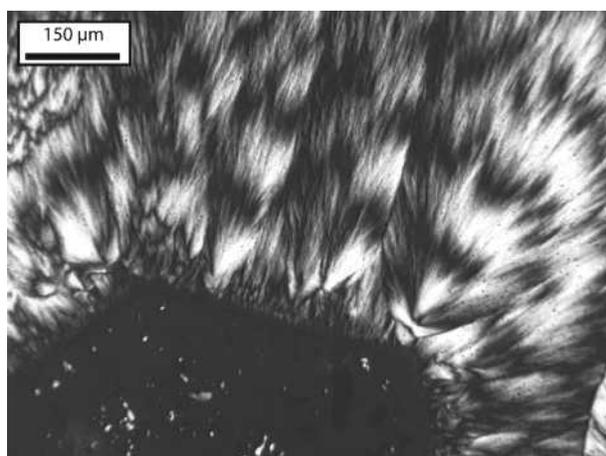
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**FIGURE 1.** Twisted fibers of chalcedony growing on a quartz crystal showing that twist can emerge in hydrostatic environments. Courtesy of K.L. Milliken.



**FIGURE 2.** Growth bands of untwisted (right and center) and twisted (left) quartz. Courtesy of K.L. Milliken.

dislocations that may be healed fractures, and planar dislocations (twin boundaries) (White and Wilson 1978).

These observations suggest there are several distinct types of twisting. Thus, while in many of the examples shear stress plays a role in the formation of bending and twisting, in other cases the medium from which twisted crystals grow is aqueous fluid or gel-like in character. Certainly the alternating zones of twisted and untwisted crystals, as in agates, are not compatible with an overall applied shear. Hence, hydrostatic stress conditions can accompany twisted crystal growth. In this study, we focus on these hydrostatic cases and, thereby, do not address the issues of the energetics of crystals under nonhydrostatic stress regimes. As we show for these hydrostatic systems, twisting becomes a characteristic of the lattice order and need not be a direct reflection of shear stress.

While natural crystals are often observed to have twisted habits (Fig. 1), a central question in resolving the physical origins of twisting is to discriminate between equilibrium and self-organized kinetic patterns in the spatial distribution of twisted crystals, as addressed in the wider context of geochemistry, geomechanics, and hydrology (Ortoleva 1994). Twisting is observed in agates where concentric orbs of twisted crystals alternate with orbs of untwisted ones (Fig. 2), whereas mossy agate patterns reflect more complex patterns of twisted and untwisted crystals (Ortoleva et al. 1994). Considering the stiffness of crystals and that twisting can emerge under apparently hydrostatic conditions and in the proximity of untwisted ones, it is at first puzzling how this twisting and its supracrystalline banding and mossy patterns are created and maintained over geological time. The objective of this study is to develop a free energy model, which shows how the twisted state can be at equilibrium with the untwisted state for crystals such as quartz when the impurity content in the former is greater than a critical value.

Our approach closely parallels the thermodynamic theory of compositional phase transitions. In that approach, one develops an expression for the free energy as a function of composition. One then seeks conditions under which the system can support states wherein there are two compositionally distinct spatial
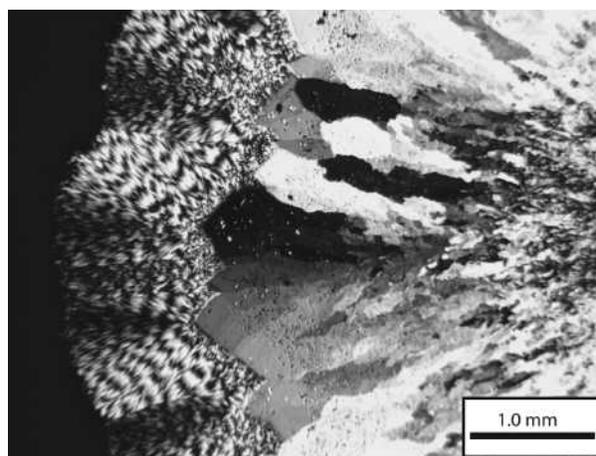
zones and that the process of transferring molecules from one domain to the other is at equilibrium. Clearly, the latter condition depends on temperature (i.e., there are temperature ranges where a melt can phase separate and others wherein it cannot). This does not imply that the existence of compositionally distinct phases should be built into a model. For example, in a gas/liquid equilibrium, a rare gas formula for the chemical potential is used for the vapor, while a liquid state formula is used for the condensed phase. The two phases are built in from the beginning. Rather, the objective is to determine if there are conditions wherein two compositionally distinct phases can be at equilibrium. For the twisted/untwisted crystal problem, the analogous two distinct domains differ in both composition (i.e., of an impurity) and in a crystal structural order parameter that characterizes the twist.

Quartz can accommodate small impurity concentrations in its untwisted crystal structure. A $Si^{4+}$ site in quartz could be filled by an impurity (e.g., $Al^{3+}$). For small impurity content, the free energy is lowered due to entropy of mixing, and the untwisted, impure state is stable. However, as impurity concentration increases, atomic-scale strains in the solid solution raise free energy and the untwisted crystal structure becomes higher in free energy than the twisted state. Thus, it is plausible to suggest that there is an impurity concentration at which a twisted crystal is in equilibrium (with respect to Si and impurity exchange) with a purer untwisted crystal. Consequently, crystal twist can occur through free energy minimization such that the state of a closed system with a single untwisted impure phase is of higher free energy than the "phase separated" state wherein an impurity and the $SiO_2$ are redistributed between a twisted impure crystal and a purer untwisted crystal. This phenomenon is now examined for impure quartz systems via a model wherein twist and composition are coupled via a free-energy ansatz. The phase-separated state is, thus, to be revealed via the classic free energy minimization approach.

The hypothesis that twisted and untwisted crystals can be in equilibrium is based on the assumption that the exchange of mass between crystals is allowed kinetically. To assess this possibility,

assume that diffusion along a fiber/fiber boundary is fast relative to impurity migration out of the fiber in a direction perpendicular to the long fiber axis. Thus, the exchange of impurity would be limited by the time needed for intracrystal diffusion across the width $w$ of a fiber. If $D$ is the diffusion coefficient for the impurity in a quartz matrix, then the axial diffusion time $\tau_d$ is of order $w^2/16D$, where $w/2$ is the diffusion distance. In systems where twisted and untwisted crystals reside in close proximity (notably agates), twisted fibers are observed to have $w$ in the range 5 to 10 nm, while untwisted ones have $w$ in the range 100 to 1000 nm (Heaney and Davis 1995). Diffusion coefficients for Na range from $1.0 \times 10^1$ to $3.6 \times 10^{-7}$ m²/s (Frischat 1970; Freer 1981), while diffusion coefficients for Al range from $10^{-24}$ to $10^{-27}$ m²/s (Pankrath and Florke 1994). The smallest diffusion coefficient applied to the largest quartz fibers gives a diffusion time of two million years. Agates from host rocks ranging in age from 38 Ma to 3.48 Ga are known and oscillatory banding of twisted and untwisted fibers is best developed in agates that are less than 400 Ma (Moxon and Rios 2004; Moxon et al. 2006). Because these ages are commonly much older than $\tau_d$, we conclude that twist coexistence can readily be attained in agates.

Phase transitions in macroscopic systems are commonly understood in terms of "order parameters." For example, melting is attributed to a breakdown in long-range lattice coherence, boiling is a loss in local structural organization in the liquid state, and the loss of magnetization is due to the randomization of atomic-scale magnetic moments. The existence of two-phase equilibrium implies that total system mass is organized in two distinct ways and that the net rate of atoms or other subunits passing from a region in one state of organization to that in the other is zero.

Phase equilibria are common in mixtures. For example, an oil/water system can often support only one phase at high temperature, while at lower temperatures the mass tends to be in either an oil-rich/water-poor state, the reverse, or there may be a gap in composition that corresponds to unstable states. We claim that this provides an analog for the twisted/untwisted crystal phenomenon.

Our hypothesis is that $SiO_2$/impurity systems can exist in two distinct states that can be in equilibrium, namely a twisted state of higher impurity and an untwisted, purer state. At equilibrium in a closed system, $SiO_2$ and impurity Y are distributed among the twisted and untwisted domains just like oil and water are distributed among the oil-rich and water-rich domains. As suggested in Figure 3, $SiO_2$ and Y freely exchange between the two phases. If the system is closed, then this exchange is constrained by mass conservation, i.e., loss of $SiO_2$ from one phase results in gain by the other.

Net exchange is ultimately halted when either one of the phases disappears or an equilibrium criterion is met; for example, at isobaric, isothermal conditions, equilibrium occurs when the Gibbs free energy is a minimum. Again, this equilibrium is established between two bulk phases. Thus, the nature of the zone separating two phases might be interesting for nanomaterials, but it is not relevant to the overall equilibrium between bulk phases.

In the twisted crystal problem, we suggest there are two parameters needed to characterize the state of a given phase (i.e., content of the impurity Y and the twist). These two "order parameters" are of distinctly different character. In particular, the impurity and $SiO_2$ content are conserved within a closed system, while the degree of twisting is not. With these notions, we develop a theory of twisted/untwisted, purer/impure, dual order parameter phase transition phenomena. In the following sections, a general free energy formulation of twist coexistence is presented. Next, we establish the general free energy-minimization framework along with demonstrating and analyzing a minimal model to show that twist coexistence can be attained even when simple phenomenological thermodynamical laws are adopted. Finally, we demonstrate twist coexistence in more detail by making a detailed free energy ansatz.

## Free energy formulation

We now develop a general approach based on the Gibbs free energy of a solid solution that accounts for twist and composition. As with other thermodynamic approaches to multiphase systems, we then seek conditions under which the free energy minimum occurs: (1) when the system "phase separates" into twisted and untwisted phases in equilibrium, and (2) alternatively, when either the untwisted phase or the twisted phase is stable. We focus on the case of a single impurity structural unit Y and a majority unit (e.g., $SiO_2$).

First, we examine the Gibbs free energy of a single uniform bulk phase. Let $y$ be the mole fraction of Y units in the crystal and hence $(1 - y)$ is that of $SiO_2$. Define a twist order parameter $\varepsilon$ to be the angle of rotation of the lattice (times a fiber radius and divided by the fiber length). Let $n_{SiO_2}$ and $n_Y$ be the number of moles of $SiO_2$ and Y units, respectively, while $G(n_{SiO_2}, n_Y, \varepsilon)$ denotes the Gibbs free energy of a single uniform crystal. We omit the pressure and temperature dependence in all expressions since they are assumed to be constant. By definition, $y = n_Y/(n_Y + n_{SiO_2})$ is the mole fraction of Y units in the crystal.

The chemical potentials $\mu_{SiO_2}$ and $\mu_Y$, and the conjugate shear stress-like quantity $\sigma$ are defined via

$$\mu_{SiO_2}(y,\varepsilon) = \left( \frac{\partial G}{\partial n_{SiO_2}} \right)_{n_Y, \varepsilon} \tag{1}$$

$$\mu_Y(y,\varepsilon) = \left( \frac{\partial G}{\partial n_Y} \right)_{n_{SiO_2}, \varepsilon} \tag{2}$$

$$\sigma(y,\varepsilon) = \left( \frac{\partial G}{\partial \varepsilon} \right)_{n_{SiO_2}, n_Y} \tag{3}$$

This completes the description of a single bulk phase.

The total free energy $G$ of a two-crystal system (one with $y$, $\varepsilon$, and the other with $y'$, $\varepsilon'$) takes the form:

$$G = G(n_{SiO_2}, n_Y, \varepsilon) + G(n'_{SiO_2}, n'_Y, \varepsilon'). \tag{4}$$

At equilibrium in a closed system, $G$ is a minimum with respect to the $n$ and $\varepsilon$ subject to the total mass constraint

$$n_{SiO_2} + n'_{SiO_2} = n_{SiO_2}^{tot} \tag{5a}$$

and similarly for Y. Within this framework, we seek conditions (if any) under which $G$ attains a minimum at coexistence, i.e.,
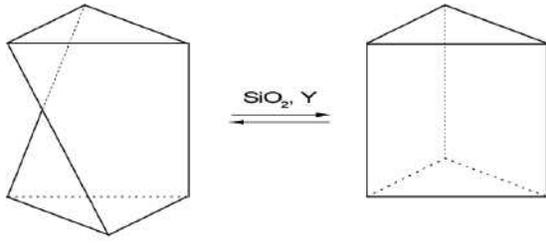
**FIGURE 3.** At equilibrium the twisted impure crystal exchanges $SiO_2$ and the impurity Y with the untwisted, purer one. In a closed system, free-energy minimization determines the fractions of $SiO_2$ and of Y in the twisted and untwisted phases. Under conditions of high impurity content, all crystals are twisted. At very low total impurity, no crystals are twisted. In intermediate average impurity content, there is a mixture of coexisting twisted and untwisted crystals.

for which y ≠ y', $\varepsilon \neq \varepsilon'$. Under other conditions we expect that only single-phase states exist, i.e., all crystals are either twisted or untwisted in a multi-crystal system like agate. The key parameter is

$$y^{tot} = n_y^{tot} / \left( n_{SiO_2}^{tot} + n_y^{tot} \right). \tag{5b}$$

As suggested in Figure 4 we expect that the system exhibits the classic phase diagram such that below a critical temperature there is a gap in $y^{tot}$ within which there is twist coexistence. At high temperatures the quartz-like lattice is impurity accommodating so that $SiO_2$/Y solutions exist across a broad range of $y^{tot}$. However, this may not be observable as such a temperature may exceed the melting point, or a new mineral might emerge (for example, a clay mineral when Y is an aluminum species).

Equilibrium of the system is obtained when G is a minimum for constant total mass of $SiO_2$ and of Y; this yields

$$\mu_{SiO_2}(y,\varepsilon) = \mu_{SiO_2}(y',\varepsilon') \tag{6}$$
$$\mu_Y(y,\varepsilon) = \mu_Y(y',\varepsilon') \tag{7}$$
$$\sigma(y,\varepsilon) = 0, \; \sigma(y',\varepsilon') = 0 \tag{8}$$

In arriving at Equations 6 and 7, we have used Lagrange multipliers to impose the conservation of mass conditions, shown in Equation 5, for the closed system. The two equations in Equation 8 are consistent with our assumption that twist can develop in a hydrostatically stressed environment.

From this point, the conceptual flow is that we first set forth an explicit form for G and then use it to make the equilibrium relations 6 to 8 more explicit. These four equations do not imply that the theory is restructured to the coexistence situation. As suggested in Figure 4, there can be conditions in which Equations 6 to 8 only have the trivial solution y = y', $\varepsilon = \varepsilon'$ corresponding to a single crystal state, not the coexistence of multiple crystals of two distinct compositions and twist. Finally, these four equations determine the four unknowns y, $\varepsilon$, y', and $\varepsilon'$.

## AN EXTENDED DILUTE MODEL

To further explore the twist coexistence theory, more explicit formulas for the chemical potentials and stress-like factor σ must
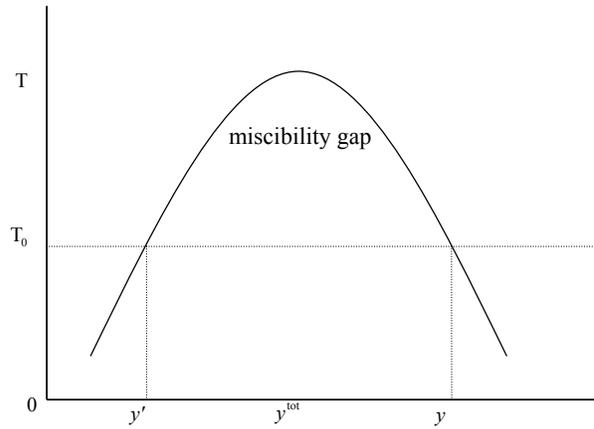


**FIGURE 4.** Phase diagram showing temperature on the vertical axis and impurity mole fraction $y^{tot}$ on the horizontal axis; $y^{tot}$ varies over the full range of allowed compositions. At a given temperature $T_0$ there are only untwisted states ($y^{tot} < y'$) or twisted states ($y^{tot} > y$), while a system starting with $y^{tot}$ in the miscibility gap will decompose into crystals with composition y and y' in twist coexistence. Effects such as melting or strong departures from ideality in the free energy can yield deviations from this schematic phase diagram.

be developed. The dilute limit (small mole fraction y) is an appropriate starting point for the impurity-intolerant quartz-like lattice. Symmetry requires that if $\varepsilon$ is an equilibrium state (i.e., solution to Eq. 8), then the opposite twist $-\varepsilon$ also must be a state with the same energy for a given value of y (i.e., extremum of the free energy). This symmetry implies that the untwisted (stable or unstable) state $\varepsilon = 0$ is an omnipresent solution of Equation 8. Furthermore, if σ is the stress for $\varepsilon$, then $-\sigma$ is the value for $-\varepsilon$. Thus, σ has the form

$$\sigma = A\varepsilon + B\varepsilon^3 \tag{9}$$

for functions A and B of y. Higher order terms in odd powers could also play a role but are not needed in a minimal model that captures the present phenomenon, as shown below. The untwisted solution of Equation 8 is $\varepsilon = 0$. One might suggest that $\varepsilon^2 = -A/B$ corresponds to the twisted states. However, the stiffness of crystals implies that $\varepsilon$ should be small, and hence the $\varepsilon^3$ (nonlinear elastic) term in σ is not likely to be the origin of twisted energy-minimizing states. This suggests that the twisted state must correspond to $A(y) = 0$, as follows.

Equilibrium between an untwisted ($\varepsilon' = 0$), low-impurity crystal and a twisted ($\varepsilon \neq 0$), more impure one implies

$$\mu_{SiO_2}(\varepsilon,y) = \mu_{SiO_2}(0, y') \tag{10}$$
$$\mu_Y(\varepsilon,y) = \mu_Y(0, y') \tag{11}$$
$$\sigma(\varepsilon,y) = 0. \tag{12}$$

These three equations determine the three unknowns y, y', and $\varepsilon$. To explore twist coexistence in more detail, assume for simplicity the free energy takes an extended dilute form because the impurity content is small:

$$G = n_{SiO_2}\left[\overline{G}_S + RT\ln(1 - y)\right] + n_Y\left[\mu_Y^* + RT\ln y\right] + \left[\alpha y + \beta y^2\right]\left(n_{SiO_2} + n_Y\right) \tag{13}$$

Here $\overline{G}_S(\varepsilon)$ is the molar free energy of pure $SiO_2$ crystal and $\mu_Y^*(\varepsilon)$ is the limiting law reference potential for Y substituted in an $SiO_2$ lattice; $\alpha$ and $\beta$ are parameters that could, in principle, depend on $\varepsilon$ but are taken to be constant for simplicity. The $\varepsilon$ dependence of $\overline{G}_S$ and $\mu_Y^*$ is assumed to be linear elastic in character and, hence, quadratic in $\varepsilon$:

$$\overline{G}_S = \overline{G}_S^0 + C\varepsilon^2 \tag{14}$$

$$\mu_Y^* = \mu_Y^{*0} + C^*\varepsilon^2 \tag{15}$$

These forms preserve the aforementioned symmetry. We assume that with increasing $\varepsilon$, $\overline{G}_S$ increases; thus, $C$ is positive. While individual elements of the fourth-rank elasticity coefficient matrix can be positive or negative, the combination of these coefficients constituting $C$ is assumed to be positive. Assuming the contrary implies that impurity-free crystals spontaneously twist, which is contrary to the observation that the purest crystals in agate are untwisted. Combining Equations 3, 13, 14, and 15 yields

$$\sigma = 2n_{SiO_2}(C + C^*y)\varepsilon. \tag{16}$$

In writing this expression, we made the approximation that $n_Y = (n_Y + n_{SiO_2})y \approx n_{SiO_2}y$ since $n_Y \ll n_{SiO_2}$. From the Equation 5, both $\sigma$ and $G$ are extensive variables (i.e., scale with the size of the crystal). This implies the $n_{SiO_2}$ factor in $\sigma$. Also, $\sigma$ has units of energy, since it is the derivative of free energy with respect to the dimensionless order parameter $\varepsilon$.

For nontrivial solutions to the equilibrium problem ($\varepsilon \neq 0$),

$$y = -C/C^*. \tag{17}$$

The elastic coefficient $C$ is positive. If twist makes the crystal lattice more accommodating to Y, then $C^* < 0$. Hence, Equation 17 is physically consistent, i.e., $y > 0$. With this, Equation 17 yields the composition $y$ at which the energy penalty from twist is balanced by the reduction in energy the twist allows for accommodating the impurity.

The determination of $y$, $\varepsilon$ for the twisted crystal, and $y'$ for the untwisted one with which it is in equilibrium, follows from Equations 6 and 7. For the present model, keeping only leading terms for small $y$, we find the equilibrium is attained when the following combinations are satisfied:

$$C\varepsilon^2 + RT\ln(1 - y) - \beta y^2 = RT\ln(1 - y') - \beta y'^2 \tag{18}$$

$$C^*\varepsilon^2 + RT\ln y + \beta(2y - y^2) = RT\ln y' + \beta(2y' - y'^2). \tag{19}$$

As $y = -C/C^*$, this yields two equations for $\varepsilon$ and $y'$. Physical solutions are found when $\varepsilon^2$ and $y'$ are positive, implying conditions on $C$, $C^*$, and $\beta$ for which twist coexistence is possible. Measurements of $y$, $y'$, $\varepsilon$, and the elastic coefficient $C$ can be used to calibrate $C^*$ and $\beta$. With these calibrated values one can create a phase diagram of the type suggested in Figure 4.

## Concluding remarks

Twisted crystals grown in hydrostatic environments are shown to arise from the balance of twist-induced accommodation of impurities, and the entropics and energetics of dilute solid solutions. This conclusion follows from our assumptions on the form of the Gibbs free energy as a function of crystal composition and a twist "order parameter." The coexistence of twisted impure $SiO_2$ crystals with purer untwisted ones, such as observed in agates, is shown to be a natural implication of our thermodynamic model. If impure untwisted crystals grow under one condition, the model implies that the system could undergo a phase separation into a state with twisted and untwisted crystals in equilibrium when conditions change.

If agates started as an amorphous silica glass or gel mass, then transition to a more crystalline state could place the system in any of the three domains shown in Figure 4: (1) the extremely high or low impurity content regimes of only twisted or untwisted crystals, or (2) the miscibility gap leading to twist coexistence. In the twist coexistence case, an imposed radial compositional gradient can initiate the inward or outward propagation of a wave of twisted/untwisted phase separation leading to the commonly observed concentric orbicular patterns in agates. If there is no imposed gradient, then the tendency to phase separate leads to mossy or other complex patterns that are also observed in agates (Hurlbut and Switzer 1979)—see Ortoleva (1994) and Ortoleva et al. (1994) for further discussion. While twist phase equilibria can explain the coexistence of twisted and untwisted crystals, it is the kinetics of crystal growth/dissolution and mass transport that determine agate pattern geometry and scale.

Our theory assumed that impurity content is constant along a fiber. However, measurements suggest variations might be present in some cases. This could be due to complications from multiple impurity types, dislocations, or a reflection of measurement errors. Longitudinal variations might also suggest a phase transition wherein a fiber is evolving toward domains of purer, untwisted state altering with more impure twisted zones. We suggest that more accurate and higher spatially resolved measurements of agate patterns would reveal such phenomena.

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