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SYMMETRY ANALYSIS OF EXTREME AREAL POISSON'S RATIO IN ANISOTROPIC CRYSTALS

LEWIS WHEELER AND CLIFF YI GUO

Poisson's ratio is defined as the negative of the ratio of the transverse strain to the longitudinal strain in response to a longitudinal uniaxial stress. In the presence of anisotropy, this means that the ratio depends on two directions. With a view to assessing crystals that exhibit directions for which the ratio is negative, we resort to a transverse average to eliminate one directional variable and at the same time to arrive at a measure that poses a challenge to achieving significant negative values. The areal Poisson ratio coincides with the Poisson ratio for an isotropic material. We determine the stationary directions of the areal Poisson ratio for all crystal symmetry classes. The directions represented by invariant stationary points—those that hold independently of the material—we identify and explain class-by-class in terms of the axes of symmetry for the class. It is shown that for cubic crystals, positive definiteness of the strain energy requires that the areal Poisson ratio lie between -1 and $1/2$, as it does for isotropy. We conclude that the areal Poisson ratio for the classes of lower symmetry are not restricted.

1. Introduction

Over the last two decades there has been increasing interest in finding, creating, and understanding material structures that exhibit a negative Poisson's ratio describing materials that are referred to as *auxetic*, a term attributed to Evans et al. [1991]. While much of the work has focused on microstructures, there is an abundance of crystal structures that possess a negative ratio values for specific directions due to their anisotropic nature. The knowledge that a crystal may possess a negative Poisson's ratio is by no means recent. Love [1927] mentions a pyrite that yields a value near $-1/7$. Moreover, auxeticity in crystals is not uncommon, since nearly 69 of cubic elemental metals have a negative Poisson's ratio when the stressed axis lies along the [110] direction [Baughman et al. 1998]. Ting and Barnett [2005] derived simple necessary and sufficient conditions on elastic compliances to identify if any given material of cubic or hexagonal symmetry is completely auxetic or nonauxetic. Further examples of auxetic behavior in crystals of cubic, hexagonal, and monoclinic symmetry are discussed in [Tokmakova 2005] with the aid of stereographic projections.

The meaning of the Poisson's ratio in the presence of anisotropy raises questions that are not apparent in the isotropic case. Not only does the ratio depend upon the choice of a direction for the longitudinal strain, but all directions at right angles to it for the transverse strain component. This transverse variation is apt to yield offsetting ratios [Baughman et al. 1998], a negative value for one transverse direction and a positive value for another, that diminish or negate the auxetic effect. Guo and Wheeler [2006]

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introduced an *areal* Poisson's ratio that is relatively simple in form and serves to measure the offsetting effects. The search for auxetic directions leads naturally to the search for the direction of the minimum areal Poisson's ratio, and more broadly to an examination of directions that yield stationary values. Of special interest, as we demonstrate, are stationary directions that are related only to the symmetry of the material and bear a simple relation to the crystallographic directions. For each crystal class, we find the stationary directions of the areal Poisson's ratio, examine their extremal nature, and graphically illustrate them for a particular crystal within the class.

The effect of crystal symmetry on the elastic constants of crystals is covered thoroughly in [Nye 1957; Ting 1996]. Cazzani and Rovati [2003; 2005] examine the directionality and extrema of Young's modulus in crystals of cubic, transversely isotropic and tetragonal symmetry. Ting and Chen [2005] proved that for all of the seven crystal classes, the Poisson's ratio can have an arbitrarily large positive or negative value under the constraint of positive definiteness of the strain energy density. In contrast, for the cubic crystal class we conclude here that the areal Poisson's ratio must lie within bounds. For the remaining crystal classes, there are no bounds on the areal Poisson's ratio.

In this paper, we investigate the directional variation of the areal Poisson's ratio for all nine crystal classes. Stationary directions that are independent of the material are called *invariant* stationary points. The directions represented by invariant stationary points are related to the axes of symmetry belonging to the particular crystal class. Where sensible, both the invariant and material dependent stationary directions are found, and their extremal nature is discussed. Based on the values of the areal Poisson's ratio at stationary directions and positive definiteness of the compliance tensor, we analyze the boundedness of the areal Poisson's ratio for each crystal class.

2. Preliminaries

We denote by $\mathbb{C}$ the linear operator on the linear space of all symmetric 2-tensors that accounts for the elastic properties in the linear theory of anisotropic elastic solids. The elasticity operator $\mathbb{C}$ and its adjoint $\mathbb{C}^*$, are related by

$$\langle \boldsymbol{A}, \mathbb{C}[\boldsymbol{B}]\rangle = \left\langle \mathbb{C}^*[\boldsymbol{A}], \boldsymbol{B}\right\rangle,$$

under the inner product

$$\langle \boldsymbol{A}, \boldsymbol{B}\rangle = \operatorname{tr} \boldsymbol{A}\boldsymbol{B}^T.$$

Here, the elasticity operator $\mathbb{C}$ is required to be self adjoint, $\mathbb{C} = \mathbb{C}^*$, in other words to possess the major symmetry, so that

$$\langle \boldsymbol{A}, \mathbb{C}[\boldsymbol{B}]\rangle = \langle \boldsymbol{B}, \mathbb{C}[\boldsymbol{A}]\rangle.$$

Let $\{\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3\}$ denote a right-handed orthonormal frame, for short a *cartesian* frame. Define $\boldsymbol{E}_{ij}$ as

$$\boldsymbol{E}_{ij} = \operatorname{sym}\left(\boldsymbol{e}_i \otimes \boldsymbol{e}_j\right).$$

The set $\left\{\boldsymbol{E}_{ij}\right\}$ is an orthogonal basis for the linear space of 2-tensors. These basis elements $\boldsymbol{E}_{ij}$ though orthogonal are not normalized, but rather obey

$$\left\langle \boldsymbol{E}_{ij}, \boldsymbol{E}_{kl}\right\rangle = \frac{1}{2}\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right), \tag{1}$$

which implies

$$\left|\boldsymbol{E}_{ij}\right|^2 = \begin{cases} 1, & i = j, \\ \frac{1}{2}, & i \neq j. \end{cases}$$

The components of $\mathbb{C}$ in the frame $\{\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3\}$ are given by Gurtin [1972]:

$$C_{ijkl} = \left\langle \boldsymbol{E}_{ij}, \mathbb{C}\left[\boldsymbol{E}_{kl}\right]\right\rangle. \tag{2}$$

These components are simultaneously the components of the operator $\mathbb{C}$ and the fourth-order tensor associated with $\mathbb{C}$.

The components I_{ijkl} of the identity $\mathbb{I}$ are given by the right side of Equation (1),

$$I_{ijkl} = \frac{1}{2}\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right). \tag{3}$$

We assume for the remainder of this presentation that $\mathbb{C}$ is positive definite. Thus, $\mathbb{C}$ has an inverse, the compliance operator, denoted by $\mathbb{S}$, that, like $\mathbb{C}$, is self-adjoint and positive definite.

The reduced forms of the matrix of elastic constants that appear in [Nye 1957] and [Gurtin 1972] represent these constants in a preferred frame, which we denote by $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$ to distinguish it from the generic frame $\{\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3\}$. Remarkably, this frame may be taken as orthonormal. Here, we frequently refer to the frame $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$ as a *crystallographic* frame. The crystallographic counterparts of the basis elements $\boldsymbol{E}_{ij}$ are denoted by $\boldsymbol{A}_{ij}$.

The Voigt compliances s_{ij} and the corresponding crystallographic tensor components S_{ijkl} are related through [Nye 1957],

$$\left(s_{ij}\right) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} & s_{16} \\ & s_{22} & s_{23} & s_{24} & s_{25} & s_{26} \\ & & s_{33} & s_{34} & s_{35} & s_{36} \\ & & & s_{44} & s_{45} & s_{46} \\ & & & & s_{55} & s_{56} \\ & & & & & s_{66} \end{pmatrix} = \begin{pmatrix} S_{1111} & S_{1122} & S_{1133} & 2S_{1123} & 2S_{1131} & 2S_{1112} \\ & S_{2222} & S_{2233} & 2S_{2223} & 2S_{2231} & 2S_{2212} \\ & & S_{3333} & 2S_{3323} & 2S_{3331} & 2S_{3312} \\ & & & 4S_{2323} & 4S_{2331} & 4S_{2312} \\ & & & & 4S_{3131} & 4S_{3112} \\ & & & & & 4S_{1212} \end{pmatrix}. \tag{4}$$

3. Definition of the Poisson's ratio and areal Poisson's ratio for an anisotropic crystal

Consider a unit uniaxial stress

$$\tau = \boldsymbol{l} \otimes \boldsymbol{l}, \ \ |\boldsymbol{l}| = 1$$

in the direction $\boldsymbol{l}$. The longitudinal strain $\varepsilon(\boldsymbol{l})$ is given by

$$\varepsilon(\boldsymbol{l}) = \boldsymbol{l} \bullet \varepsilon \boldsymbol{l} = \boldsymbol{l} \bullet \mathbb{S}[\boldsymbol{l} \otimes \boldsymbol{l}]\,\boldsymbol{l} = \langle \boldsymbol{l} \otimes \boldsymbol{l}, \mathbb{S}[\boldsymbol{l} \otimes \boldsymbol{l}]\rangle. \tag{5}$$

Let $\boldsymbol{t}$ be a given direction perpendicular to $\boldsymbol{l}$, that is, $\boldsymbol{l} \bullet \boldsymbol{t} = \boldsymbol{0}$, $|\boldsymbol{t}| = 1$. The strain $\varepsilon(\boldsymbol{t})$ in the transverse direction $\boldsymbol{t}$ is given by

$$\varepsilon(\boldsymbol{t}) = \boldsymbol{t} \bullet \varepsilon \boldsymbol{t} = \boldsymbol{t} \bullet \mathbb{S}[\boldsymbol{l} \otimes \boldsymbol{l}]\,\boldsymbol{t} = \langle \boldsymbol{t} \otimes \boldsymbol{t}, \mathbb{S}[\boldsymbol{l} \otimes \boldsymbol{l}]\rangle. \tag{6}$$

The Poisson's ratio corresponding to the longitudinal direction $\boldsymbol{l}$ and the transverse direction $\boldsymbol{t}$ is defined as

$$\nu(\boldsymbol{l},\boldsymbol{t}) = -\frac{\varepsilon(\boldsymbol{t})}{\varepsilon(\boldsymbol{l})},$$

and in view of Equations (5) and (6) is expressed in terms of the compliance in the form

$$\nu(\boldsymbol{l},\boldsymbol{t}) = -\frac{\langle \boldsymbol{t}\otimes\boldsymbol{t}, \mathbb{S}[\boldsymbol{l}\otimes\boldsymbol{l}]\rangle}{\langle \boldsymbol{l}\otimes\boldsymbol{l}, \mathbb{S}[\boldsymbol{l}\otimes\boldsymbol{l}]\rangle}. \tag{7}$$

For given orthogonal unit vectors $\boldsymbol{l}$ and $\boldsymbol{t}$, the ratio is determined by the elastic properties of the crystal. We note that for $\mathbb{S}$ positive definite, the denominator is positive, so the sign of ν is determined by the numerator. The areal Poisson's ratio is defined by

$$\widehat{\nu}(\boldsymbol{l}) = \frac{1}{2\pi}\int_0^{2\pi} \nu(\boldsymbol{l},\boldsymbol{t}(\alpha))\, d\alpha.$$

It is readily seen that this averaging reduces to finding the average of $\boldsymbol{t}\otimes\boldsymbol{t}$, with the result

$$\widehat{\nu}(\boldsymbol{l}) = -\frac{\langle\langle \boldsymbol{t}\otimes\boldsymbol{t}\rangle, \mathbb{S}[\boldsymbol{l}\otimes\boldsymbol{l}]\rangle}{\langle \boldsymbol{l}\otimes\boldsymbol{l}, \mathbb{S}[\boldsymbol{l}\otimes\boldsymbol{l}]\rangle}$$

where

$$\langle \boldsymbol{t}\otimes\boldsymbol{t}\rangle = \frac{1}{2}(\boldsymbol{I}-\boldsymbol{l}\otimes\boldsymbol{l}). \tag{8}$$

Therefore,

$$\widehat{\nu}(\boldsymbol{l}) = \frac{1}{2}\left(1 - \frac{\operatorname{tr}\mathbb{S}[\boldsymbol{l}\otimes\boldsymbol{l}]}{\langle \boldsymbol{l}\otimes\boldsymbol{l}, \mathbb{S}[\boldsymbol{l}\otimes\boldsymbol{l}]\rangle}\right). \tag{9}$$

Of course, $\widehat{\nu}$ reduces to the Poisson's ratio if $\mathbb{S}$ is isotropic.

The direction $\boldsymbol{l}$ of the stressed axis can be expressed in spherical coordinates,

$$\boldsymbol{l} = \cos\theta\,\sin\phi\,\boldsymbol{a}_1 + \sin\theta\,\sin\phi\,\boldsymbol{a}_2 + \cos\phi\,\boldsymbol{a}_3,$$

where $0 \le \phi \le \pi$, $0 \le \theta < 2\pi$. Thus, the areal Poisson's ratio can be expressed in terms of the polar angles ϕ and θ through

$$\widehat{\nu}(\boldsymbol{l}) = \widehat{\nu}(\phi,\theta) = \frac{1}{2}(1 - \frac{\operatorname{tr}\mathbb{S}[\boldsymbol{l}(\phi,\theta)\otimes\boldsymbol{l}(\phi,\theta)]}{\langle \boldsymbol{l}(\phi,\theta)\otimes\boldsymbol{l}(\phi,\theta), \mathbb{S}[\boldsymbol{l}(\phi,\theta)\otimes\boldsymbol{l}(\phi,\theta)]\rangle}).$$

To identify the directions $\boldsymbol{l}$ for which the areal Poisson's ratio attains extreme values, we begin by examining stationary directions, those for which

$$\begin{cases} \widehat{\nu}_\phi = \dfrac{\partial\widehat{\nu}(\phi,\theta)}{\partial\phi} = 0, \\ \widehat{\nu}_\theta = \dfrac{\partial\widehat{\nu}(\phi,\theta)}{\partial\theta} = 0, \end{cases} \tag{10}$$

which we also at times refer to as stationary "points". With the aid of the matrix

$$J = \begin{pmatrix} \widehat{\nu}_{\phi\phi} & \widehat{\nu}_{\phi\theta} \\ \widehat{\nu}_{\phi\theta} & \widehat{\nu}_{\theta\theta} \end{pmatrix}, \tag{11}$$

we are able to further analyze the stationary points. If J is nonsingular, we can determine the extremal nature of a stationary point. If the matrix is sign definite, there is an extreme point—a minimum if positive definite, a maximum if negative definite. For J nonsingular but indefinite, there is a saddle point. If J is singular, additional analysis is required.

4. Poisson's ratio for the isotropic case

For an isotropic medium, the elasticity tensor may be expressed in spectral form as

$$\mathbb{C} = 3k\,\frac{1}{3}\,\boldsymbol{I}\otimes\boldsymbol{I} + 2\mu(\mathbb{I} - \frac{1}{3}\,\boldsymbol{I}\otimes\boldsymbol{I}), \tag{12}$$

where k denotes the bulk modulus and μ stands for the shear modulus. The principal values of $\mathbb{C}$ are $3k$ and 2μ. They are coefficients of orthogonal projections of rank 1 and rank 5, respectively. Hence, $\mathbb{S} = \mathbb{C}^{-1}$ is given by

$$\mathbb{S} = \frac{1}{3k}\,\frac{1}{3}\,\boldsymbol{I}\otimes\boldsymbol{I} + \frac{1}{2\mu}\,(\mathbb{I} - \frac{1}{3}\,\boldsymbol{I}\otimes\boldsymbol{I}).$$

Therefore, and by Equation (7), one finds

$$\nu = \frac{1}{2}\left(\frac{3k - 2\mu}{3k + \mu}\right). \tag{13}$$

Similarly, Equation (9) furnishes

$$\widehat{\nu} = \frac{1}{2}\left(\frac{3k - 2\mu}{3k + \mu}\right),$$

and we see that *the Poisson's ratio and its areal counterpart reduce to the same elastic constant if the material is isotropic*. In passing, we mention that in view of Equation (12), positive definiteness is equivalent to

$$k > 0, \;\; \mu > 0, \tag{14}$$

and by Equation (13), furnish the well-known restriction on the Poisson's ratio for isotropic materials,

$$-1 < \nu < \frac{1}{2}.$$

Such bounds do not hold for the Poisson's ratio for the crystal classes, as demonstrated in [Ting and Chen 2005]. We examine the corresponding question for the areal Poisson's ratio in what follows.

4.1. *Cubic materials.* For a crystal of cubic symmetry, the Voigt compliance matrix takes the form

$$(s_{ij}) = \begin{pmatrix} s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\ & s_{11} & s_{12} & 0 & 0 & 0 \\ & & s_{11} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & & & & s_{44} & 0 \\ & & & & & s_{44} \end{pmatrix}. \tag{15}$$

In terms of the Voigt compliances, positive definiteness is equivalent to (see [Nye 1957])

$$s_{11} > 0,\ s_{44} > 0,\ -\frac{1}{2}s_{11} < s_{12} < s_{11}. \tag{16}$$

The areal Poisson's ratio can be expressed in spherical coordinates as:

$$2\widehat{\nu}(\phi,\theta) = 1 - \frac{(S_{1111} + 2S_{1122})}{S_{1122} + 2S_{1212} + (S_{1111} - S_{1122} - 2S_{1212})\left[\left(\sin^4\theta + \cos^4\theta\right)\sin^4\phi + \cos^4\phi\right]}. \tag{17}$$

From this expression, we find

$$\widehat{\nu}(\phi,\theta) = \widehat{\nu}(\pi-\phi,\theta) = \widehat{\nu}\left(\phi, \frac{\pi}{2}+\theta\right) = \widehat{\nu}\left(\phi, \frac{\pi}{2}-\theta\right),$$

a manifestation of the symmetry associated with the class of crystals of cubic symmetry.

So we can limit the scope to $0 \le \phi \le \pi/2$, $0 \le \theta \le \pi/4$ without loss of generality. A contour plot of the areal Poisson's ratio for the cubic material *pyrite* is shown in Figure 1. At room temperature, the independent elastic compliance components are $s_{11} = 2.652\ (\text{TPa})^{-1}$, $s_{12} = -0.199\ (\text{TPa})^{-1}$, $s_{44} = 9.141\ (\text{TPa})^{-1}$ [Simmons and Wang 1971]. By Equation (17), the angles (θ, ϕ) for the stationary directions of cubic

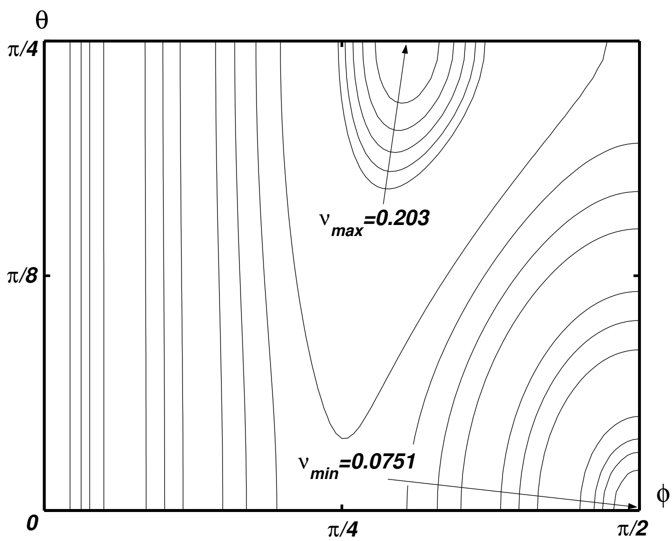

Figure 1. Contours for the areal Poisson's ratio for a pyrite of cubic symmetry.

materials obey

$$\begin{cases} 0 = \dfrac{2\sin 2\phi\left[\sin^2\phi\left(\sin^4\theta+\cos^4\theta\right)-\cos^2\phi\right]\left(S_{1111}+2S_{1122}\right)\beta}{\left\{S_{1122}+2S_{1212}+\beta\left[\left(\sin^4\theta+\cos^4\theta\right)\sin^4\phi+\cos^4\phi\right]\right\}^2}, \\ 0 = \dfrac{-\sin^4\phi\sin 4\theta\left(S_{1111}+2S_{1122}\right)\beta}{\left\{S_{1122}+2S_{1212}+\beta\left[\left(\sin^4\theta+\cos^4\theta\right)\sin^4\phi+\cos^4\phi\right]\right\}^2}. \end{cases} \tag{18}$$

The factor

$$\beta \stackrel{\text{def}}{=} S_{1111} - S_{1122} - 2S_{1212} \tag{19}$$

does not vanish unless the material is isotropic and the factor $S_{1111} + 2S_{1122}$ is positive owing to positive definiteness. Hence, the stationary points of the areal Poisson's ratio are given by

$$\begin{cases} \phi = 0, \ \text{and}\ \phi = \frac{\pi}{2}, \theta = 0, \\ \phi = \frac{\pi}{2}, \theta = \frac{\pi}{4}, \text{and}\ \phi = \frac{\pi}{4}, \theta = 0, \\ \theta = \frac{\pi}{4}, \ (\cos\phi)^2 = \frac{1}{3}. \end{cases} \tag{20}$$

The stationary points in the first line of Equation (20) lie along the [100] direction, those in the second line lie along the [110] direction, and the last line describes stationary points along the [111] direction. The directions represented by these stationary points thus lie respectively on a four-fold axis, a two-fold axis and a three-fold axis of symmetry for cubic crystals. One important fact is that these directions do not depend upon the compliances. For a crystal of cubic symmetry, the directions of the extreme areal Poisson's ratio must coincide with the direction of a lattice vector, face diagonal, or body diagonal.

To determine the nature of a stationary point, whether it is a local extremum or a saddle point, we examine the value of the areal Poisson's ratio and its second derivatives at these points. For a stationary point lying along the [100] direction,

$$\begin{cases} \widehat{\nu} = -S_{1122}/S_{1111}, \\ \widehat{\nu}_{\phi\phi} = \widehat{\nu}_{\theta\theta} = -2\left(S_{1111} + 2S_{1122}\right)\beta/S_{1111}^2, \\ \widehat{\nu}_{\phi\theta} = 0. \end{cases}$$

Assuming that the material is not isotropic, so that $\beta \neq 0$, the matrix J defined by Equation (11) assumes diagonal form. The eigenvalues, $\widehat{\nu}_{\phi\phi}$ and $\widehat{\nu}_{\theta\theta}$, are positive or negative accordingly as β is negative or positive. In conclusion for the [100] direction, a stationary point is a minimum or maximum accordingly as $\beta \lessgtr 0$. For a stationary point on the [110] direction,

$$\begin{cases} \widehat{\nu} = \frac{1}{2}\left[1 - \dfrac{2\left(S_{1111}+2S_{1122}\right)}{\left(S_{1111}+S_{1122}+2S_{1212}\right)}\right], \\ \widehat{\nu}_{\phi\phi} = -\dfrac{4\left(S_{1111}+2S_{1122}\right)\beta}{\left(S_{1111}+S_{1122}+2S_{1212}\right)^2}, \\ \widehat{\nu}_{\theta\theta} = \dfrac{8\left(S_{1111}+2S_{1122}\right)\beta}{\left(S_{1111}+S_{1122}+2S_{1212}\right)^2}, \\ \widehat{\nu}_{\phi\theta} = 0. \end{cases}$$

The matrix Equation (11) is again diagonal, but the eigenvalues are of opposite sign for $\beta \neq 0$, indicative of a saddle point. The stationary values of the areal Poisson's ratio associated with a face diagonal direction are neither a local minimum nor a local maximum. If a stationary point lies along the [111] direction,

$$\begin{cases} \widehat{\nu} = \frac{1}{2}\left[1 - \frac{3(S_{1111}+2S_{1122})}{(S_{1111}+2S_{1122}+4S_{1212})}\right], \\ \widehat{\nu}_{\phi\phi} = \frac{12(S_{1111}+2S_{1122})\beta}{(S_{1111}+2S_{1122}+4S_{1212})^2}, \\ \widehat{\nu}_{\theta\theta} = \frac{8(S_{1111}+2S_{1122})\beta}{(S_{1111}+2S_{1122}+4S_{1212})^2}, \\ \widehat{\nu}_{\phi\theta} = 0. \end{cases}$$

Hence, the matrix Equation (11) is once again in diagonal form. Its eigenvalues are positive if $\beta > 0$, yielding a relative minimum, whereas a relative maximum is present if $\beta < 0$.

The global minimum and maximum are obtained by comparing the values of the areal Poisson's ratio at the stationary points. For the pyrite described earlier, $\beta = -4.372$. Thus the [111] direction locates the maximum value, $\widehat{\nu}_{\max} = 0.203$, whereas the [100] direction is associated with the minimum value, $\widehat{\nu}_{\min} = 0.075$. In Figure 1, the extreme points are easily identified by the closed contours.

In summary, for a cubic crystal that is *not* isotropic, we find

$$\beta > 0, \begin{cases} \widehat{\nu}_{\max} = -\frac{S_{1122}}{S_{1111}} < \frac{1}{2}, & \text{along } \boldsymbol{a}_1, \\ \widehat{\nu}_{\min} = \frac{1}{2}[1 - \frac{3(S_{1111}+2S_{1122})}{S_{1111}+2S_{1122}+4S_{1212}}] > -1, & \text{along } \boldsymbol{q}, \end{cases}$$

$$\beta < 0, \begin{cases} \widehat{\nu}_{\max} = \frac{1}{2}[1 - \frac{3(S_{1111}+2S_{1122})}{S_{1111}+2S_{1122}+4S_{1212}}] < \frac{1}{2}, & \text{along } \boldsymbol{q}, \\ \widehat{\nu}_{\min} = -\frac{S_{1122}}{S_{1111}} > -1, & \text{along } \boldsymbol{a}_1, \end{cases}$$

where

$$\boldsymbol{q} = \frac{1}{\sqrt{3}}(\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3).$$

With the aid of these results, and by means of definiteness conditions (16), we conclude that for the case of cubic symmetry,

$$-1 < \widehat{\nu} < \frac{1}{2},$$

the same as for an isotropic medium. If $s_{11} + 2s_{12} \to 0^+$, both $\widehat{\nu}_{\min}$ and $\widehat{\nu}_{\max}$ approach the upper bound 1/2 and the material behaves like an isotropic medium. There are many cubic materials for which s_{12}/s_{11} is near $-1/2$, for example, gold (-0.462), $\gamma - \text{Fe}$ (-0.440), lead (-0.459), $Cu_{2.7}AlMn_{0.3}$ (-0.475). When the shear compliance s_{44} is much larger than s_{11} and s_{12}, β is negative, and the areal Poisson's ratio assumes its maximum value ($1/2$) along the $\boldsymbol{q}$ direction. But if s_{44} is much smaller than s_{11} and $|s_{12}|$, then the areal Poisson's ratio can assume either the maximum or the minimum value along $\boldsymbol{q}$, depending on the relative values of s_{12} and s_{11}, and approach the limits -1 for $s_{11} \gg -2s_{12}$ or $1/2$ for $s_{11} \simeq -2s_{12}$. Moreover, we see that positive s_{12} yields a negative areal ratio. Measured values of this constant are recorded for many cubic materials, including the ones just mentioned, in [Landolt and Bornstein 1992], and the scarcity of cubic materials possessing a positive s_{12} is readily apparent.

4.2. *Hexagonal crystal.* The Voigt compliance matrix for the hexagonal class assumes the form [Nye 1957]

$$(s_{ij}) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ & s_{11} & s_{13} & 0 & 0 & 0 \\ & & s_{33} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & & & & s_{44} & 0 \\ & & & & & 2(s_{11}-s_{12}) \end{pmatrix}$$

in an orientation frame $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$ There are thus five independent elastic compliance constants for material possessing hexagonal symmetry. Positive definiteness is equivalent to [Nye 1957]

$$\begin{cases} s_{11} > 0,\, s_{33} > 0,\, s_{44} > 0, \;\; s_{11} + |s_{12}| > 0, \\ s_{33}s_{11} > s_{13}^2, \;\; s_{33}(s_{11}+s_{12}) > 2s_{13}^2. \end{cases} \tag{21}$$

In terms of spherical angles, the areal ratio takes the form

$$\begin{aligned} \widehat{\nu}(\phi,\theta) = [(\cos 4\phi - 1)(S_{1111} - 4S_{1313} + S_{3333}) - 8(\sin\phi)^2 S_{1122} \\ -2(5 + 2\cos 2\phi + \cos 4\phi) S_{1133}]/\{16[(\sin\phi)^4 S_{1111} \\ + (\cos\phi)^4 S_{3333} + 2(\sin\phi)^2(\cos\phi)^2(S_{1133} + 2S_{1313})]\}, \end{aligned}$$

from which we conclude that the areal Poisson's ratio is independent of θ. We further conclude that

$$\widehat{\nu}(\phi,\theta) = \widehat{\nu}(\phi) = \widehat{\nu}(\pi - \phi),$$

so we can limit the range of ϕ to $0 \le \phi \le \pi/2$. A plot of the areal Poisson's ratio for hexagonal crystalline *graphite* is shown in Figure 2. The room temperature compliances are [Landolt and Bornstein 1992]:

$$s_{11} = 0.98\,(\text{TPa})^{-1}, \qquad s_{12} = -0.16\,(\text{TPa})^{-1},$$
$$s_{13} = -0.33\,(\text{TPa})^{-1}, \qquad s_{33} = 27.5\,(\text{TPa})^{-1},$$
$$s_{44} = 250\,(\text{TPa})^{-1}$$

The stationary condition for a hexagonal crystal is

$$\begin{aligned} 0 = \sin 2\phi\{16(\sin\phi)^4 S_{1111}^2 - 16(\cos\phi)^4 S_{3333}^2 - 2[16(\sin\phi)^4 S_{1122} \\ -(6 + 24\cos 2\phi + 2\cos 4\phi) S_{1133}]\left(S_{1133} + 2S_{1313}\right) + 4(\cos\phi)^2[(2\cos 2\phi - 6)\left(S_{1122} + S_{1133}\right) \\ + 16(\cos\phi)^2 S_{1313}]S_{3333} + 4S_{1111}[4(\sin\phi)^4 S_{1122} + (10 + 6\cos 2\phi)(\sin\phi)^2 S_{1133} - 16(\sin\phi)^4 S_{1313} \\ -4\cos 2\phi S_{3333}]\}/\{32[(\sin\phi)^4 S_{1111} + (\cos\phi)^4 S_{3333} + 2(\sin\phi)^2(\cos\phi)^2\left(S_{1133} + 2S_{1313}\right)]^2\}, \end{aligned} \tag{22}$$

from which we conclude that the stationary points of $\widehat{\nu}$ are given by

$$\begin{cases} \phi = 0, \text{ and } \phi = \frac{\pi}{2}, \\ \phi_S = \arcsin\left(\sqrt{\frac{-b\pm\sqrt{b^2-4ac}}{2a}}\right), \end{cases} \tag{23}$$

where the subscript S indicates that ϕ depends upon the compliance constants, and a, b, c are given by

$$a = \left[S_{1111}^2 + S_{1111}S_{1122} - 3S_{1111}S_{1133} - 2S_{1122}S_{1133} + 2S_{1133}^2 + S_{1122}S_{3333} + S_{1133}S_{3333} - S_{3333}^2 + 4S_{1313}\left(-S_{1111} - S_{1122} + S_{1133} + S_{3333}\right)\right],$$

$$b = 2(2S_{1111}S_{1133} - 4S_{1133}^2 - 8S_{1133}S_{1313} + S_{1111}S_{3333} - 4S_{1313}S_{3333} + S_{3333}^2),$$

$$c = (4S_{1133}^2 + 8S_{1133}S_{1313} - S_{1111}S_{3333} - S_{1122}S_{3333} - S_{1133}S_{3333} + 4S_{1313}S_{3333} - S_{3333}^2).$$

The stationary points $\phi = 0$ and $\phi = \pi/2$ are *invariant stationary points*. The direction represented by the stationary point $\phi = 0$ coincides with the unique six-fold rotation symmetry axis, and the direction represented by stationary point $\phi = \pi/2$ lies in the reflection symmetry plane along an axis of two-fold symmetry. The stationary point $\phi = \phi_S$, which depends on the elastic compliance constants, lies between $\phi = 0$ and $\phi = \pi/2$. The three stationary points for the hexagonal material graphite, indicated in Figure 2, have the values $\widehat{\nu}_{\max} = 0.433$ at $\phi = \phi_S$, $\widehat{\nu}_{\min} = 0.012$ at $\phi = 0$ and $\widehat{\nu} = 0.254$ at $\phi = \pi/2$.

Consider $\widehat{\nu}$ at the stationary points

$$\widehat{\nu}(0) = -S_{1133}/S_{3333}, \tag{24}$$

$$\widehat{\nu}\left(\frac{\pi}{2}\right) = -\left(S_{1122} + S_{1133}\right)/\left(2S_{1111}\right), \tag{25}$$

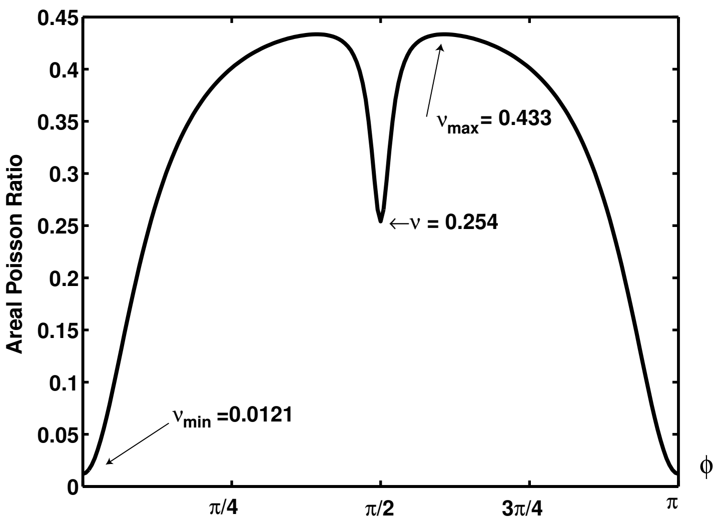

Figure 2. Areal Poisson's ratio for graphite (hexagonal).

$$\widehat{\nu}(\phi_S) = \frac{-[\sin^4\phi_S(S_{1111}-2S_{1133}-4S_{1313}+S_{3333})+2S_{1133}-\sin^2\phi_S(S_{1111}-S_{1122}-S_{1133}-4S_{1313}+S_{3333})]}{2[\sin^4\phi_S(S_{1111}+S_{3333}-2S_{1133}-4S_{1313})+2\sin^2\phi_S(S_{1133}+2S_{1313}-S_{3333})+S_{3333}]}.$$

Whether the areal Poisson's ratio is a local minimum or maximum at $\phi = 0,\ \pi/2,\ \phi_S$ depends on the elastic compliance constants. The global extreme values of the areal Poisson's ratio can be found by comparing the values at the stationary points. Without violating the positive definite conditions (21), S_{1122}, S_{1133} can be expressed in terms of S_{1111}, S_{3333}.

$$S_{1122} = pS_{1111}, \quad -1 < p < 1,$$
$$S_{1133} = q\sqrt{S_{1111}S_{3333}}, \quad -1 < q < 1.$$

The formulae (24) and (25) can be rewritten as

$$\begin{cases} \widehat{\nu}(0) = -q\sqrt{\frac{S_{1111}}{S_{3333}}}, \\ \widehat{\nu}\left(\frac{\pi}{2}\right) = -\frac{1}{2}\left(p + q\sqrt{\frac{S_{3333}}{S_{1111}}}\right). \end{cases}$$

The parameters p, q are bounded by ±1,. The ratio $\chi = S_{3333}/\ S_{1111}$ can take on any positive value without violating the positive definite conditions (21). For $q < 0$, the limits as $\chi \longrightarrow \pm\infty$ are

$$\begin{cases} \chi \to \infty, & \widehat{\nu}(0) \to 0^+, & \widehat{\nu}\left(\frac{\pi}{2}\right) \to \infty, \\ \chi \to 0, & \widehat{\nu}(0) \to \infty, & \widehat{\nu}\left(\frac{\pi}{2}\right) \to -\frac{1}{2}p. \end{cases}$$

and for $q > 0$,

$$\begin{cases} \chi \to \infty, & \widehat{\nu}(0) \to 0^-, & \widehat{\nu}\left(\frac{\pi}{2}\right) \to -\infty, \\ \chi \to 0, & \widehat{\nu}(0) \to -\infty, & \widehat{\nu}\left(\frac{\pi}{2}\right) \to -\frac{1}{2}p. \end{cases}$$

This means that there is neither an upper bound nor a lower bound for the areal Poisson's ratio of a hexagonal crystal. As the case of s_{12} for cubic material, s_{13} is negative for all hexagonal materials in [Landolt and Bornstein 1992]. This interesting fact can be investigated in future research.

4.3. ***Tetragonal (six constants).*** For tetragonal crystal material with symmetry $4mm$, $\bar{4}2$, 422, $4/mmm$, the Voigt compliance matrix s_{ij} takes the form

$$(s_{ij}) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ & s_{11} & s_{13} & 0 & 0 & 0 \\ & & s_{33} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & & & & s_{44} & 0 \\ & & & & & s_{66} \end{pmatrix}.$$

indicating six independent elastic compliance constants. Positive definiteness is equivalent to [Nye 1957]

$$\begin{cases} s_{11} > 0, \quad s_{33} > 0, \quad s_{44} > 0, \quad s_{66} > 0, \\ s_{11} > \pm s_{12}, \quad s_{33}s_{11} > s_{13}^2, \quad s_{33}(s_{11} + s_{12}) > 2s_{13}^2. \end{cases} \tag{26}$$

In terms of spherical angles, the areal Poisson's ratio takes the form

$$\widehat{\nu}(\phi,\theta)=$$
$$\frac{1}{2}-\frac{2\sin^2\phi\left(S_{1111}+S_{1122}\right)+(3+\cos 2\phi)\,S_{1133}+2\cos^2\phi S_{3333}}{\sin^4\phi\left[(3+\cos 4\theta)\,S_{1111}+2\sin^2 2\theta\left(S_{1122}+2S_{1212}\right)\right]+2\sin^2 2\phi\left(S_{1133}+2S_{1313}\right)+4\cos^4\phi S_{3333}}.$$

From this expression, we find that the restrictions imposed by the symmetry are

$$\widehat{\nu}(\phi,\theta)=\widehat{\nu}(\pi-\phi,\theta)=\widehat{\nu}\left(\phi,\frac{\pi}{2}+\theta\right)=\widehat{\nu}\left(\phi,\frac{\pi}{2}-\theta\right),$$

so we can limit the scope to $0\le\phi\le\frac{\pi}{2}$, $0\le\theta\le\frac{\pi}{4}$ without loss of generality. A contour plot for α-cristobalite is shown in Figure 3. The room temperature compliances are [Yeganeh-Heari et al. 1992]:

$$s_{11}=17.0\,(\text{TPa})^{-1},\quad s_{12}=-0.965\,(\text{TPa})^{-1},$$
$$s_{13}=1.67\,(\text{TPa})^{-1},\quad s_{33}=23.9\,(\text{TPa})^{-1},$$
$$s_{44}=14.9\,(\text{TPa})^{-1},\quad s_{66}=38.9\,(\text{TPa})^{-1}.$$

From the stationary conditions (10), the invariant stationary points of the areal Poisson's ratio are

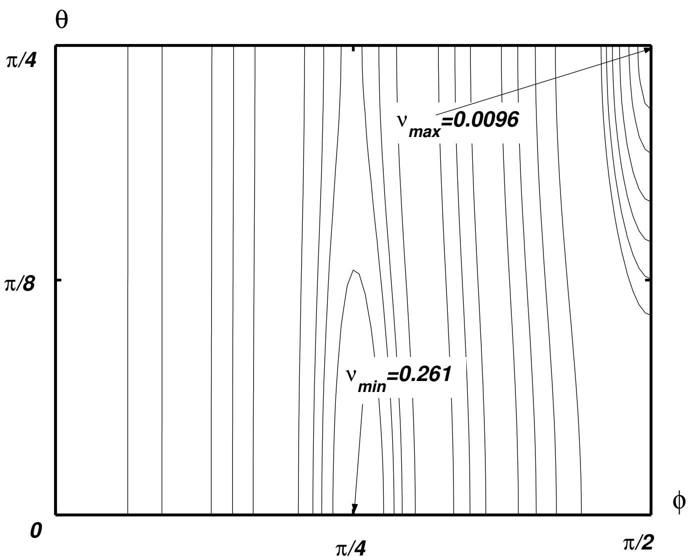

Figure 3. Areal Poisson's ratio for tetragonal material: α-cristobalite.

$$\begin{cases} \phi = 0, \text{ and } \phi = \frac{\pi}{2}, \theta = 0, \\ \phi = \frac{\pi}{2}, \theta = \frac{\pi}{4}, \\ \phi_{S1} = \arcsin(\sqrt{\frac{-b_1 \pm \sqrt{b_1^2 - 4a_1c_1}}{2a_1}}), \theta = 0, \\ \phi_{S2} = \arcsin(\sqrt{\frac{-b_2 \pm \sqrt{b_2^2 - 4a_2c_2}}{2a_2}}), \theta = \frac{\pi}{4}, \end{cases}$$

where

$$\begin{aligned} a_1 = &\left[S_{1111}^2 + S_{1111}S_{1122} - 3S_{1111}S_{1133} - 2S_{1122}S_{1133} + 2S_{1133}^2 + S_{1122}S_{3333} + S_{1133}S_{3333} - S_{3333}^2 \right. \\ &\left. + 4S_{1313}\left(-S_{1111} - S_{1122} + S_{1133} + S_{3333}\right)\right], \\ b_1 = &\ 2(2S_{1111}S_{1133} - 4S_{1133}^2 - 8S_{1133}S_{1313} + S_{1111}S_{3333} - 4S_{1313}S_{3333} + S_{3333}^2), \\ c_1 = &\ (4S_{1133}^2 + 8S_{1133}S_{1313} - S_{1111}S_{3333} - S_{1122}S_{3333} - S_{1133}S_{3333} + 4S_{1313}S_{3333} - S_{3333}^2), \end{aligned}$$

and

$$\begin{aligned} a_2 = &\ 2\left[S_{1111}^2 + 2S_{1111}S_{1122} + S_{1122}^2 - 5S_{1111}S_{1133} - 5S_{1122}S_{1133} + 4S_{1133}^2 + 2S_{1212}\left(S_{1111} + S_{1122} - S_{1133} - S_{3333}\right). \right. \\ &\left. + 8S_{1313}\left(-S_{1111} - S_{1122} + S_{1133} + S_{3333}\right) + S_{3333}\left(S_{1111} + S_{1122} + 2S_{1133} - 2S_{3333}\right)\right], \\ b_2 = &\ 4\left[2S_{1133}\left(S_{1111} + S_{1122} - 4S_{1133} + 2S_{1212} - 8S_{1313}\right) + S_{3333}\left(S_{1111} + S_{1122} + 2S_{1212} - 8S_{1313} + 2S_{3333}\right)\right], \\ c_2 = &\ 4(4S_{1133}^2 + 8S_{1133}S_{1313} - S_{1111}S_{3333} - S_{1122}S_{3333} - S_{1133}S_{3333} + 4S_{1313}S_{3333} - S_{3333}^2). \end{aligned}$$

The stationary points $(\phi, \theta) = (0, \theta)$, $(\pi/2, 0)$, $(\pi/2, \pi/4)$ are invariant stationary points. The directions represented by invariant stationary points are thus respectively on a unique four-fold axis, a two-fold axis and another two-fold axis of rotation symmetry for tetragonal crystals. The stationary points $(\phi_{S1}, 0)$, $(\phi_{S2}, \pi/4)$ depend on the elastic compliances. The global extreme values of the areal Poisson's ratio can be obtained by comparing the values at above stationary points. Consider the values of the areal Poisson's ratio at the stationary points:

$$\begin{cases} \widehat{\nu}(0, \theta) = -S_{1133}/S_{3333}, \\ \widehat{\nu}\left(\frac{\pi}{2}, 0\right) = -\left(S_{1122} + S_{1133}\right)/2S_{1111}, \\ \widehat{\nu}\left(\frac{\pi}{2}, \frac{\pi}{4}\right) = \left(-\beta - 2S_{1122} - 2S_{1133}\right)/2(S_{1111} + S_{1122} + 2S_{1212}); \end{cases}$$

$$\begin{cases} \widehat{\nu}(\phi_{S1}, 0) = \frac{1}{2} - [\sin^2\phi_{S1}\left(S_{1111} + S_{1122} - S_{1133} - S_{3333}\right) \\ \qquad + 2S_{1133} + S_{3333}]/\{2[\sin^4\phi_{S1}\left(S_{1111} + S_{3333} - 2S_{1133} - 4S_{1313}\right) \\ \qquad + 2\sin^2\phi_{S1}\left(S_{1133} + 2S_{1313} - S_{3333}\right) + S_{3333}]\}, \\ \widehat{\nu}\left(\phi_{S2}, \frac{\pi}{4}\right) = \frac{1}{2} - [2\sin^2\phi_{S2}\left(S_{1111} + S_{1122} - S_{1133} - S_{3333}\right) \\ \qquad + 4S_{1133} + 2S_{3333}]/\{\sin^4\phi_{S2}[2S_{1111} + 2\left(S_{1122} + 2S_{1212}\right) - 8\left(S_{1133} + 2S_{1313}\right) + 4S_{3333}] \\ \qquad + 8\sin^2\phi_{S2}\left(S_{1133} + 2S_{1313} - S_{3333}\right) + 4S_{3333}\}. \end{cases}$$

For the tetragonal material α-cristobalite, the $(\pi/2, \pi/4)$ direction locates the maximum value, $\widehat{\nu}_{\max} = 9.6\times 10^{-4}$ and the $(\phi_{S1}, 0)$ direction is associated with the minimum value, $\widehat{\nu}_{\min} = -0.261$. In Figure 3, the extreme points are easily identified by the closed contours. While many crystal materials can have a negative Poisson's ratio in a particular direction, α-cristobalite is one of the few materials that also yield a negative areal Poisson's ratio.

Proceeding as we did in the hexagonal case, from positive definiteness (26), we obtain

$$\begin{cases} \widehat{\nu}(0) = -q\sqrt{\frac{S_{1111}}{S_{3333}}}, \\ \widehat{\nu}\left(\frac{\pi}{2}\right) = -\frac{1}{2}\left(p+q\sqrt{\frac{S_{3333}}{S_{1111}}}\right). \end{cases}$$

The ratio $\chi = S_{3333}/S_{1111}$ can be any positive value. If we set $q \neq 0$, the areal Poisson's ratio is not bounded for tetragonal crystal material with symmetry $4mm$, $\overline{4}2m$, 422, $4/mmm$ either.

4.4. *Tetragonal (seven constants).* For crystal material with tetragonal symmetry 4, $\overline{4}$, $4/m$, the Voigt compliance matrix s_{ij} takes the form

$$(s_{ij}) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & s_{16} \\ & s_{11} & s_{13} & 0 & 0 & -s_{16} \\ & & s_{33} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & & & & s_{44} & 0 \\ & & & & & s_{66} \end{pmatrix},$$

which shows six independent elastic compliance constants. In addition to the inequalities in Equation (26) the positive definite of strain energy requires

$$2s_{16}^2 - (s_{11} - s_{12})\, s_{66} > 0.$$

In terms of spherical angles, the areal Poisson's ratio takes the form

$$\widehat{\nu}(\phi,\theta) = \frac{1}{2} - \frac{2\sin^2\phi\left(S_{1111}+S_{1122}\right)+(3+\cos 2\phi)\, S_{1133}+2\cos^2\phi S_{3333}}{\sin^4\phi\left[(3+\cos 4\theta)\, S_{1111}+4\sin 4\theta\, S_{1112}+2\sin^2 2\theta\left(S_{1122}+2S_{1212}\right)\right]\sin^2 2\phi\left(S_{1133}+2S_{1313}\right)+4\cos^4\phi S_{3333}}.$$

From this expression, we can find that the relationships imposed by tetragonal 4, $\overline{4}$, $4/m$ symmetry are

$$\widehat{\nu}(\phi,\theta) = \widehat{\nu}(\pi-\phi,\theta) = \widehat{\nu}\left(\phi, \frac{\pi}{2}+\theta\right),$$

so we can limit the scope to $0 \le \phi \le \frac{\pi}{2}$, $0 \le \theta \le \frac{\pi}{2}$ without loss of generality. Contours of the areal Poisson's ratio are plotted for the tetragonal material calcium molybdate (+Z = −Z) in Figure 4. At

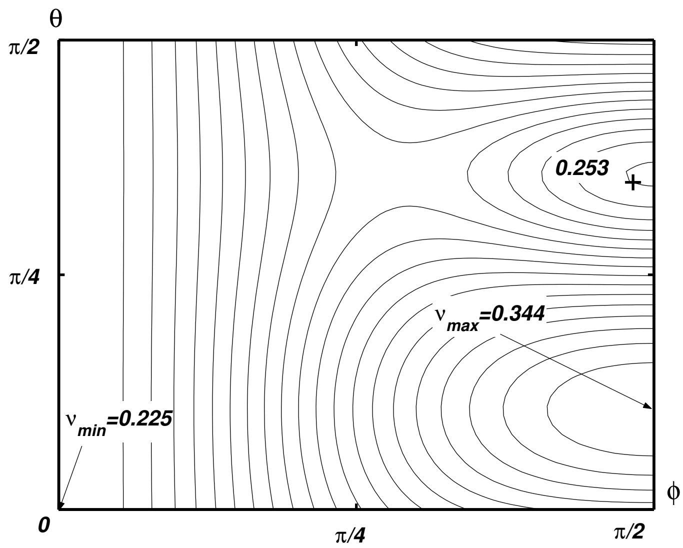

Figure 4. Areal Poisson ratio for calcium molybdate ($+Z = -Z$).

room temperature, the compliances are [Landolt and Bornstein 1992]:

$$s_{11} = 9.90\,(\text{TPa})^{-1}, \qquad s_{12} = -4.2\,(\text{TPa})^{-1},$$
$$s_{13} = -2.1\,(\text{TPa})^{-1}, \qquad s_{16} = 4.2\,(\text{TPa})^{-1},$$
$$s_{33} = 9.48\,(\text{TPa})^{-1}, \qquad s_{44} = 27.1\,(\text{TPa})^{-1},$$
$$s_{66} = 24.4\,(\text{TPa})^{-1}.$$

From the stationary conditions (10), the stationary points of the areal Poisson's ratio are

$$\begin{cases} \phi = 0, \\ \phi = \frac{\pi}{2}, \theta_{S1} = \frac{1}{4}\arctan\left(4S_{1112}/\beta\right), \\ \phi = \frac{\pi}{2}, \theta_{S2} = \theta_{S1} + \frac{\pi}{4}. \end{cases}$$

The stationary point $\phi = 0$ is the only invariant stationary point. The direction represented by this stationary point is the unique four-fold (C_4) rotation symmetry axis. The stationary points $\left(\frac{\pi}{2}, \theta_{S1}\right)$, $\left(\frac{\pi}{2}, \theta_{S2}\right)$ depend on the elastic compliance constants. The global extreme values of the areal Poisson's ratio can be obtained by comparing values at the stationary points. We find

$$\widehat{\nu}\,(0,\theta) = -S_{1133}/S_{3333},$$

$$\widehat{\nu}\left(\frac{\pi}{2}, \theta_{S1}\right) = \frac{1}{2} - \frac{2\left(S_{1111} + S_{1122}\right) + 2S_{1133}}{3S_{1111} + S_{1122} + 2S_{1212} + 4\sin 4\theta_{S1} S_{1112} + \cos 4\theta_{S1}\left(S_{1111} - S_{1122} - 2S_{1212}\right)},$$

$$\widehat{\nu}\left(\frac{\pi}{2}, \theta_{S2}\right) = \frac{1}{2} - \frac{2\left(S_{1111} + S_{1122}\right) + 2S_{1133}}{3S_{1111} + S_{1122} + 2S_{1212} - 4\sin 4\theta_{S2} S_{1112} - \cos 4\theta_{S2}\left(S_{1111} - S_{1122} - 2S_{1212}\right)}.$$

For tetragonal material Calcium Molybdate (+Z $= -$Z), the $\left(\frac{\pi}{2}, \theta_{S1}\right)$ direction locates the maximum value, $\widehat{\nu}_{\max} = 0.344$ and the $(0, \theta)$ direction is associated with the minimum value, $\widehat{\nu}_{\min} = 0.225$ as illustrated in Figure 4. The stationary point $\left(\frac{\pi}{2}, \theta_{S2}\right)$ is also a local extreme point since it is circumscribed by contours.

Similar to the hexagonal case, from the positive-definiteness conditions (26), we obtain

$$\widehat{\nu}(0) = -q\sqrt{\frac{S_{1111}}{S_{3333}}}.$$

The ratio $\chi = S_{3333}/\,S_{1111}$ may assume any positive value. For $q \neq 0$, the areal Poisson's ratio for tetragonal crystal material with symmetry $4, \bar{4}, 4/m$, like those before and those to follow, is unbounded.

4.5. *Trigonal crystal (six constants).* For crystal material with trigonal symmetry $32, \bar{3}m, 3m$, the Voigt compliance matrix s_{ij} appears as

$$\left(s_{ij}\right) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & s_{14} & 0 & 0 \\ & s_{11} & s_{13} & -s_{14} & 0 & 0 \\ & & s_{33} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & & & & s_{44} & s_{14} \\ & & & & & 2\left(s_{11} - s_{12}\right) \end{pmatrix},$$

indicating six independent elastic compliance constants. In addition to (21), positive definiteness requires

$$s_{44}s_{11} > s_{14}^2,\ \left(s_{11} - s_{12}\right)s_{44} > 2s_{14}^2,\ \left(s_{11} - s_{12}\right) > \frac{s_{14}}{2}. \tag{27}$$

In terms of spherical angles, the areal ratio takes the form

$$\widehat{\nu}(\phi, \theta) = \frac{\frac{1}{2} - [2\sin^2\phi\left(S_{1111} + S_{1122}\right) + 2\cos^2\phi S_{3333} + (3 + \cos 2\phi)\, S_{1133}]}{\{2[2\sin^4\phi S_{1111} + 8\sin^3\phi\cos\phi\sin 3\theta S_{1123} + \sin^2 2\phi\left(S_{1133} + 2S_{1313}\right) + 2\cos^4\phi S_{3333}]\}}.$$

Hence, the relationships imposed by trigonal symmetry are

$$\widehat{\nu}(\phi, \theta) = \widehat{\nu}\left(\phi, \theta + \frac{2\pi}{3}\right) = \widehat{\nu}\left(\pi - \phi, \theta + \frac{\pi}{3}\right).$$

Thus, we may limit the ranges to $0 \le \phi \le \pi$, $0 \le \theta \le \frac{\pi}{3}$ without loss of generality. Contours of the areal Poisson's ratio for the trigonal material aluminum oxide are plotted in Figure 5. The room temperature

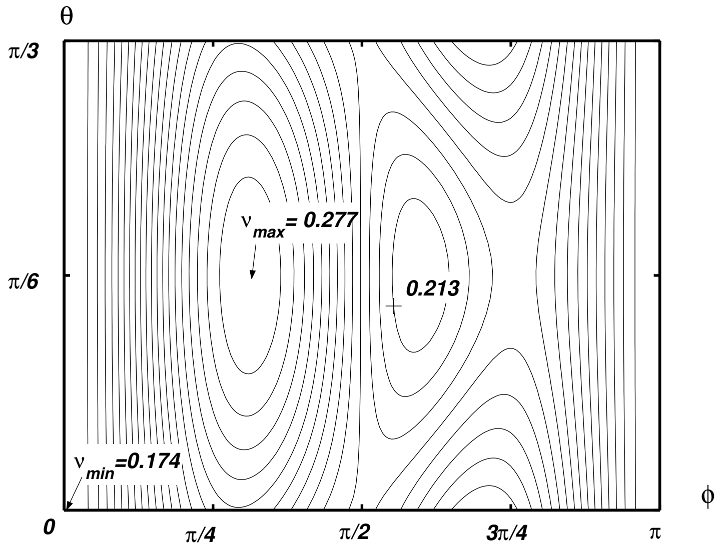

Figure 5. Areal Poisson's ratio for trigonal material: aluminum oxide.

elastic compliance constants are [Landolt and Bornstein 1992]:

$$s_{11} = 2.35\,(\text{TPa})^{-1}, \qquad s_{12} = -0.69\,(\text{TPa})^{-1},$$
$$s_{13} = -0.38\,(\text{TPa})^{-1}, \quad s_{14} = 0.47\,(\text{TPa})^{-1},$$
$$s_{33} = 2.18\,(\text{TPa})^{-1}, \qquad s_{44} = 7.0\,(\text{TPa})^{-1}.$$

By Equation (10), the stationary points of the areal Poisson's ratio are:

$$\begin{cases} \phi = 0, \\ \phi = \frac{\pi}{2}, \theta = 0, \frac{\pi}{3}, \\ \theta = \frac{\pi}{6}, \phi = \phi_{S1}, \phi_{S2}, \end{cases}$$

where ϕ_{S1}, ϕ_{S2} satisfy the condition:

$$\begin{aligned} 0 = \Big\{ \left(S_{1111} + S_{1122} - S_{1133} - S_{3333}\right) \left[2\sin^4\phi S_{1111} + 8\cos\phi \sin^3\phi S_{1123} \right. \\ \left. + \sin^2 2\phi \left(S_{1133} + 2S_{1313}\right) + 2\cos^4\phi S_{3333}\right] - 2\left[2\sin^2\phi \left(S_{1111} + S_{1122}\right) \right. \\ \left. + (3 + \cos 2\phi)\, S_{1133} + 2\cos^2\phi S_{3333}\right] \times \left[\sin 4\phi \left(S_{1133} + 2S_{1313}\right) \right. \\ \left. + 2\sin 2\phi \sin^2\phi S_{1111} + \sin 3\phi S_{1123} - \cos^3\phi S_{3333}\right] \Big\}. \end{aligned}$$

The stationary points $(\phi, \theta) = (0, \theta)\,, (\pi/2, 0)\,, (\pi/2, \pi/3)$ are invariant stationary points. The direction for the stationary point $\phi = 0$ is the unique three-fold (C_3) rotation symmetry axes, and the directions corresponding to the stationary points $\left(\frac{\pi}{2}, 0\right), (\pi/2, \pi/3)$ are two-fold (C_2) rotation symmetry axes, while the stationary points $(\phi_{S1}, \pi/6)\,, (\phi_{S2}, \pi/6)$ depend on the elastic compliance constants. The global extrema may be analyzed by comparing the values at the stationary points. For $\phi = 0$,

$$\begin{cases} \widehat{\nu}(0,\theta) = -\frac{S_{1133}}{S_{3333}}, \\ \widehat{\nu}_{\phi\phi}(0,\theta) = \frac{4S_{1133}(S_{1133}+2S_{1313})-S_{3333}(S_{1111}+S_{3333}+S_{1122}+S_{1133}-4S_{1313})}{S_{3333}^2}, \\ \widehat{\nu}_{\theta\theta}(0,\theta) = \widehat{\nu}_{\phi\theta}(0,\theta) = 0. \end{cases}$$

The values represent, at $\phi = 0$, a local minimum for $\widehat{\nu}_{\phi\phi} > 0$, and a local maximum for $\widehat{\nu}_{\phi\phi} < 0$. For $(\phi,\theta) = (\pi/2, 0)\,,\,(\pi/2, \pi/3)\,,$ we have

$$\begin{cases} \widehat{\nu}\left(\frac{\pi}{2},0\right) = \widehat{\nu}\left(\frac{\pi}{2},\frac{\pi}{3}\right) = -\frac{S_{1122}+S_{1133}}{2S_{1111}}, \\ \widehat{\nu}_{\phi\phi}\left(\frac{\pi}{2},0\right) = \frac{2(S_{1122}+S_{1133})(S_{1133}+2S_{1313})-S_{1111}(S_{1111}+S_{3333}+S_{1122}+S_{1133}-4S_{1313})}{S_{1111}^2}, \\ \widehat{\nu}_{\phi\phi}\left(\frac{\pi}{2},\frac{\pi}{3}\right) = \widehat{\nu}_{\phi\phi}\left(\frac{\pi}{2},0\right), \\ \widehat{\nu}_{\theta\theta}\left(\frac{\pi}{2},0\right) = \widehat{\nu}_{\theta\theta}\left(\frac{\pi}{2},\frac{\pi}{3}\right) = 0, \\ \widehat{\nu}_{\phi\theta}\left(\frac{\pi}{2},0\right) = -6S_{1123}\left(S_{1111}+S_{1122}+S_{1133}\right)/S_{1111}^2, \\ \widehat{\nu}_{\phi\theta}\left(\frac{\pi}{2},\frac{\pi}{3}\right) = -\widehat{\nu}_{\phi\theta}\left(\frac{\pi}{2},0\right). \end{cases}$$

Hence, at $(\pi/2, 0)\,,\,(\pi/2, \pi/3)$,

$$\det(J) = -\frac{36S_{1123}^2\left(S_{1111}+S_{1122}+S_{1133}\right)^2}{S_{1111}^4} < 0.$$

Thus the values of the areal Poisson's ratio at $(\pi/2, 0)\,,\,(\pi/2, \pi/3)$ furnish neither a local minimum nor a local maximum. The global extreme values are achieved at $\phi = 0$ and the material dependent stationary points $(\phi_{S1}, \pi/6)\,,\,(\phi_{S2}, \pi/6)$. This is illustrated in Figure 5 for the trigonal material aluminum oxide, where the $(\phi_{S1}, \pi/6)$ direction locates the maximum value, $\widehat{\nu}_{\max} = 0.277$ and the $(0,\theta)$ direction is associated with the minimum value, $\widehat{\nu}_{\min} = 0.174$. The stationary point $(\phi_{S2}, \pi/6)$ is also a local extreme point.

Without violating the definiteness conditions (27), we may write

$$\widehat{\nu}(0) = -q\sqrt{\frac{S_{1111}}{S_{3333}}}.$$

The ratio $\chi = S_{3333}/\,S_{1111}$ is free to assume any positive value. If we take $q \neq 0$, we see that the areal Poisson's ratio is not bounded for trigonal crystal material with symmetry 32, $\overline{3}m$, $3m$.

4.6. ***Trigonal crystal (seven constants).*** For a crystal with trigonal 3, $\overline{3}$ symmetry, the Voigt compliance matrix takes the form

$$(s_{ij}) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} & 0 \\ & s_{11} & s_{13} & -s_{14} & -s_{15} & 0 \\ & & s_{33} & 0 & 0 & 0 \\ & & & s_{44} & 0 & -s_{15} \\ & & & & s_{44} & s_{14} \\ & & & & & 2\,(s_{11}-s_{12}) \end{pmatrix},$$

which indicates the presence of seven independent elastic compliance constants.

In addition to the constraints in Equation (21), positive definiteness requires

$$\begin{cases} s_{44}s_{11} > s_{14}^2, \ \ s_{44}s_{11} > s_{15}^2, \ \ (s_{11}-s_{12})\,s_{44} > 2s_{14}^2, \\ (s_{11}-s_{12})\,s_{44} > \frac{s_{14}^2}{2}, \ \ (s_{11}-s_{12})\,s_{44} > \frac{s_{15}^2}{2}. \end{cases} \tag{28}$$

In terms of spherical angles, the areal Poisson's ratio reads as

$$\widehat{\nu}\,(\phi,\theta) = \frac{1}{2} - \frac{2\sin^2\phi\left[\left(S_{1111}+S_{1122}\right)+(3+\cos 2\phi)\,S_{1133}+2\cos^2\phi S_{3333}\right]}{2[2\sin^4\phi S_{1111}+8\sin^3\phi\cos\phi\left(\cos 3\theta S_{1113}+\sin 3\theta S_{1123}\right)+\sin^2 2\phi\left(S_{1133}+2S_{1313}\right)+2\cos^4\phi S_{3333}]}.$$

From this expression, we see that the relationships imposed by trigonal symmetry are:

$$\widehat{\nu}\,(\phi,\theta) = \widehat{\nu}\left(\phi,\theta+\frac{2\pi}{3}\right) = \widehat{\nu}\left(\pi-\phi,\theta+\frac{\pi}{3}\right).$$

Thus, we may limit the ranges to $0 \le \phi \le \pi$, $0 \le \theta \le \pi/3$ without loss of generality.

Contours for the trigonal material $MgSiO_3$ ilmenite are shown in Figure 6. At room temperature, the independent elastic compliance constants are reported to be [Weidner and Ito 1985]:

$$\begin{aligned} s_{11} &= 2.604\,(\mathrm{TPa})^{-1}, & s_{12} &= -0.976\,(\mathrm{TPa})^{-1}, \\ s_{13} &= -0.298\,(\mathrm{TPa})^{-1}, & s_{14} &= 0.911\,(\mathrm{TPa})^{-1}, \\ s_{15} &= -0.810\,(\mathrm{TPa})^{-1}, & s_{33} &= 2.727\,(\mathrm{TPa})^{-1}, \end{aligned}$$
$$s_{44} = 10.265\,(\mathrm{TPa})^{-1}.$$

The first derivatives of the areal Poisson's ratio are:

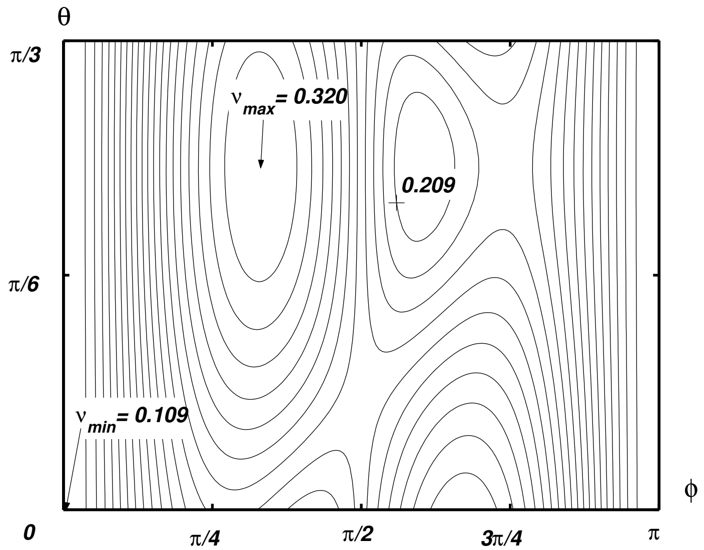

Figure 6. Areal Poisson's ratio for $MgSiO_3$ ilmenite.

$$\begin{aligned}\widehat{\nu}_\phi = -\{&2\sin\phi[2\sin^2\phi\left(S_{1111}+S_{1122}\right)+(3+\cos 2\phi)\,S_{1133}+2\cos^2\phi S_{3333}]\\ &\times[\cos\phi\sin^2\phi S_{1111}-\cos^3\phi S_{3333}+\sin 3\phi\left(\cos 3\theta S_{1113}+\sin 3\theta S_{1123}\right)\\ &+\cos\phi\cos 2\phi\left(S_{1133}+2S_{1313}\right)]-\sin 2\phi\left(S_{1111}+S_{1122}-S_{1133}-S_{3333}\right)\\ &\times[\sin^4\phi S_{1111}+\cos^4\phi S_{3333}+4\sin^3\phi\cos\phi\left(\cos 3\theta S_{1113}+\sin 3\theta S_{1123}\right)\\ &+2\sin^2\phi\cos^2\phi\left(S_{1133}+2S_{1313}\right)]\}/\{2[\sin^4\phi S_{1111}+\cos^4\phi S_{3333}\\ &+4\sin^3\phi\cos\phi\left(\cos 3\theta S_{1113}+\sin 3\theta S_{1123}\right)\\ &+2\sin^2\phi\cos^2\phi\left(S_{1133}+2S_{1313}\right)]^2\},\end{aligned}$$

$$\begin{aligned}\widehat{\nu}_\theta = -\{&3\sin^3\phi\cos\phi\left(\sin 3\theta S_{1113}-\cos 3\theta S_{1123}\right)[2\sin^2\phi\left(S_{1111}+S_{1122}\right)\\ &+(3+\cos 2\phi)\,S_{1133}+2\cos^2\phi S_{3333}]\}/[\sin^4\phi S_{1111}\\ &+4\sin^3\phi\cos\phi\left(\cos 3\theta S_{1113}+\sin 3\theta S_{1123}\right)\\ &+2\sin^2\phi\cos^2\phi\left(S_{1133}+2S_{1313}\right)+\cos^4\phi S_{3333}]^2.\end{aligned}$$

Thus, the stationary points are:

$$\begin{cases}\phi = 0,\\ \phi = \frac{\pi}{2},\, \theta = \theta_{S1},\\ \theta = \theta_{S2},\, \phi = \phi_{S1},\, \phi_{S2},\end{cases}$$

where θ_{S1} obeys $\cos 3\theta S_{1113} + \sin 3\theta S_{1123} = 0$, θ_{S2} satisfies $\sin 3\theta S_{1113} - \cos 3\theta S_{1123} = 0$, ϕ_{S1} is governed by

$$\begin{aligned} 0 = {} & [2\sin^2\phi\left(S_{1111}+S_{1122}\right) + (3+\cos 2\phi)\, S_{1133} + 2\cos^2\phi S_{3333}] \\ & \times [\cos\phi \sin^2\phi S_{1111} + \sin 3\phi\sqrt{\left(S_{1113}^2+S_{1123}^2\right)} + \cos\phi\cos 2\phi\left(S_{1133}+2S_{1313}\right) - \cos^3\phi S_{3333}] \\ & - \cos\phi\left(S_{1111}+S_{1122}-S_{1133}-S_{3333}\right) \times [\sin^4\phi S_{1111} + 4\sin^3\phi\cos\phi\sqrt{\left(S_{1113}^2+S_{1123}^2\right)} \\ & + 2\sin^2\phi\cos^2\phi\left(S_{1133}+2S_{1313}\right) + \cos^4\phi S_{3333}], \end{aligned}$$

and ϕ_{S2} satisfies

$$\begin{aligned} 0 = {} & \left[2\sin^2\phi\left(S_{1111}+S_{1122}\right) + (3+\cos 2\phi)\, S_{1133} + 2\cos^2\phi S_{3333}\right] \\ & \times [\cos\phi \sin^2\phi S_{1111} - \sin 3\phi\sqrt{\left(S_{1113}^2+S_{1123}^2\right)} + \cos\phi\cos 2\phi\left(S_{1133}+2S_{1313}\right) - \cos^3\phi S_{3333}] \\ & - \cos\phi(S_{1111}+S_{1122}-S_{1133}-S_{3333}) \times [\sin^4\phi S_{1111} - 4\sin^3\phi\cos\phi\sqrt{\left(S_{1113}^2+S_{1123}^2\right)} \\ & + 2\sin^2\phi\cos^2\phi\left(S_{1133}+2S_{1313}\right) + \cos^4\phi S_{3333}]. \end{aligned}$$

The values $(\phi, \theta) = (0, \theta)$ furnish the only invariant stationary points. The direction represented by stationary point $\phi = 0$ is the unique three-fold (C_3) rotation symmetry axes, while $(\pi/2, \theta_{S1})$, (ϕ_{S1}, θ_{S2}), (ϕ_{S2}, θ_{S2}) depend on the elastic compliance constants. The global extreme values of the areal Poisson's ratio are obtained by comparing the values at above stationary points. Thus

$$\begin{cases} \widehat{\nu}(0,\theta) = -\frac{S_{1133}}{S_{3333}}, \\ \widehat{\nu}_{\phi\phi}(0,\theta) = \frac{4S_{1133}(S_{1133}+2S_{1313})-S_{3333}(S_{1111}+S_{3333}+S_{1122}+S_{1133}-4S_{1313})}{S_{3333}^2}, \\ \widehat{\nu}_{\theta\theta}(0,\theta) = \widehat{\nu}_{\phi\theta}(0,\theta) = 0. \end{cases}$$

The areal Poisson's ratio has a local minimum if $\widehat{\nu}_{\phi\phi} > 0$, a local maximum if $\widehat{\nu}_{\phi\phi} < 0$. Further,

$$\begin{cases} \widehat{\nu}\left(\frac{\pi}{2},\theta_{S1}\right) = -\frac{S_{1122}+S_{1133}}{2S_{1111}}, \\ \widehat{\nu}_{\phi\phi}\left(\frac{\pi}{2},\theta_{S1}\right) = \frac{2(S_{1122}+S_{1133})(S_{1133}+2S_{1313})-S_{1111}(S_{1111}+S_{3333}+S_{1122}+S_{1133}-4S_{1313})}{S_{1111}^2}, \\ \widehat{\nu}_{\theta\theta}\left(\frac{\pi}{2},\theta_{S1}\right) = 0, \\ \widehat{\nu}_{\phi\theta}\left(\frac{\pi}{2},\theta_{S1}\right) = -\frac{6\sqrt{S_{1123}^2+S_{1113}^2}\,(S_{1111}+S_{1122}+S_{1133})}{S_{1111}^2}. \end{cases}$$

This yields

$$\det(J) = -\frac{36\left(S_{1123}^2+S_{1113}^2\right)\left(S_{1111}+S_{1122}+S_{1133}\right)^2}{S_{1111}^4} < 0.$$

Thus the value of the areal Poisson's ratio at the invariant stationary point $(\pi/2, \theta_{S1})$ is neither a local minimum nor a local maximum. The global extreme values are achieved at $\phi = 0$ and the material dependent stationary points. These conclusions are demonstrated in Figure 6 for trigonal material $MgSiO_3$

ilmenite, where the (ϕ_{S1}, θ_{S1}) direction locates the maximum value $\widehat{\nu}_{\max} = 0.320$ and the $(0, \theta)$ direction is associated with the minimum value, $\widehat{\nu}_{\min} = 0.109$.

Without violating (28), we may write

$$\widehat{\nu}(0) = -q\sqrt{\frac{S_{1111}}{S_{3333}}}.$$

The ratio $\chi = S_{3333}/\,S_{1111}$ is free to assume arbitrary positive values. For $q \neq 0$, positive definiteness fails to impose bounds on $\widehat{\nu}$ for trigonal crystals with symmetry $3, \overline{3}$.

4.7. *Orthorhombic.* For an orthorhombic crystal, the Voigt compliance matrix s_{ij} takes the form

$$(s_{ij}) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ & s_{22} & s_{23} & 0 & 0 & 0 \\ & & s_{33} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & & & & s_{55} & 0 \\ & & & & & s_{66} \end{pmatrix}.$$

There are nine independent elastic compliance constants. Positive definiteness imposes the requirements

$$\begin{cases} s_{11} > 0, \; s_{22} > 0, \; s_{33} > 0, \;\; s_{44} > 0, \; s_{55} > 0, \; s_{66} > 0, \\ s_{11}s_{22} > s_{12}^2, \; s_{33}s_{11} > s_{13}^2, \;\; s_{33}s_{22} > s_{23}^2, \\ s_{11}\left(s_{33}s_{22} - s_{23}^2\right) - s_{12}^2 s_{33} + 2s_{12}s_{13}s_{23} - s_{13}^2 s_{22} > 0. \end{cases} \tag{29}$$

The areal Poisson's ratio can be expressed in spherical coordinates as

$$\begin{aligned} \widehat{\nu}(\phi,\theta) = \frac{1}{2} - \frac{1}{2}\Big\{ &\sin^2\phi\left[S_{1122} + \cos^2\theta\left(S_{1111} + S_{1133}\right) + \sin^2\theta\left(S_{2222} + S_{2233}\right)\right] \\ &+ \cos^2\phi\left(S_{1133} + S_{2233} + S_{3333}\right)\Big\} \Big/ \Big\{\sin^4\phi(\cos^4\theta S_{1111} + \sin^4\theta S_{2222} + 2\sin^2\theta\cos^2\theta S_{1122}) \\ &+ \cos^4\phi S_{3333} + \sin^2\phi\left[2\cos^2\phi\cos^2\theta S_{1133} + 4\sin^2\theta\cos^2\theta\sin^2\phi S_{1212}\right. \\ &\left.+2\cos^2\phi\left(2\cos^2\theta S_{1313} + \sin^2\theta(S_{2233} + 2S_{2323})\right)\right]\Big\}. \end{aligned}$$

From this expression, we find that orthorhombic symmetry requires

$$\widehat{\nu}(\phi,\theta) = \widehat{\nu}(\pi - \phi, \theta) = \widehat{\nu}(\phi, \pi + \theta) = \widehat{\nu}(\phi, \pi - \theta).$$

Therefore, we may limit the ranges to $0 \le \phi \le \pi/2$, $0 \le \theta \le \pi/2$ without loss of generality. Contours for the orthorhombic material acenaphthene are shown in Figure 7. The elastic compliance matrix (at room

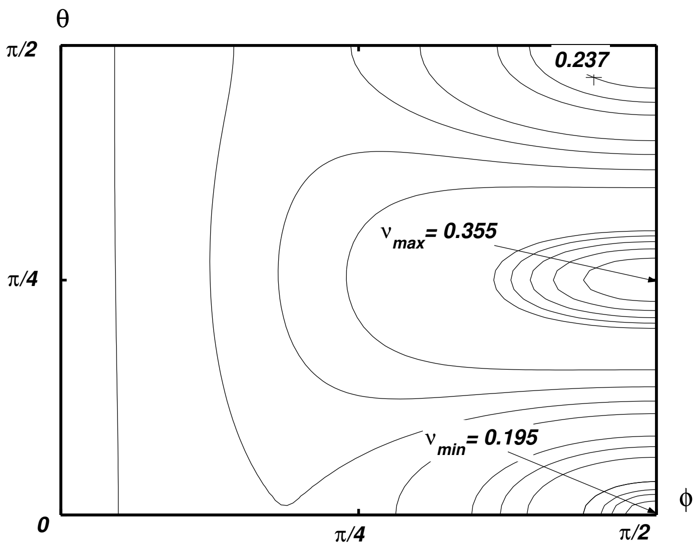

Figure 7. Areal Poisson's ratio for acenaphthene.

temperature), expressed in term of $(\mathrm{TPa})^{-1}$ is [Simmons and Wang 1971]

$$(s_{ij}) = \begin{pmatrix} 81.438 & -3.125 & -28.605 & 0 & 0 & 0 \\ & 93.354 & -37.298 & 0 & 0 & 0 \\ & & 115.385 & 0 & 0 & 0 \\ & & & 377.358 & 0 & 0 \\ & & & & 344.828 & 0 \\ & & & & & 540.540 \end{pmatrix}.$$

By (10), the stationary points of the areal Poisson's ratio are

$$\begin{cases} \phi = 0, \\ \phi = \frac{\pi}{2}, \theta = 0, \frac{\pi}{2}, \\ \phi = \frac{\pi}{2}, \theta = \theta_S, \end{cases}$$

where θ_S satisfes the condition

$$\begin{aligned} 0 = \sin 2\theta \left[\cos^4\theta S_{1111} + 2\sin^2\theta\cos^2\theta\left(S_{1122} + 2S_{1212}\right) + \sin^4\theta S_{2222}\right] \times \left(S_{1111} + S_{1133} - S_{2222} - S_{2233}\right) \\ - \sin 2\theta\left[2\cos^2\theta S_{1111} - 2\cos 2\theta\left(S_{1122} + 2S_{1212}\right) - 2\sin^2\theta S_{2222}\right] \\ \times \left[S_{1122} + \cos^2\theta\left(S_{1111} + S_{1133}\right) + \sin^2\theta\left(S_{2222} + S_{2233}\right)\right]. \end{aligned}$$

The stationary points $(\phi, \theta) = (0, \theta)$, $(\pi/2, 0)$, $(\pi/2, \pi/2)$ are invariant with respect to the elastic constants. The directions represented by these stationary points are the two-fold (C_2) rotation symmetry axes. The stationary point $(\pi/2, \theta_S)$ depends on the elastic compliance constants. The global extreme values of areal Poisson's ratio can be obtained by comparing the values at above stationary points,

$$\begin{cases} \widehat{\nu}(0,\theta) = -\frac{S_{1133}+S_{2233}}{2S_{3333}}, \\ \widehat{\nu}\left(\frac{\pi}{2},0\right) = -\frac{S_{1122}+S_{1133}}{2S_{1111}}, \\ \widehat{\nu}\left(\frac{\pi}{2},\frac{\pi}{2}\right) = -\frac{S_{1122}+S_{2233}}{2S_{2222}}, \end{cases} \tag{30}$$

$$\widehat{\nu}(\frac{\pi}{2},\theta_S) = \frac{1}{2} - \frac{1}{2}\frac{S_{1122}+\cos^2\theta_S\left(S_{1111}+S_{1133}\right)+\sin^2\theta_S\left(S_{2222}+S_{2233}\right)}{\left[\cos^4\theta_S S_{1111}+2\sin^2\theta_S\cos^2\theta_S\left(S_{1122}+2S_{1212}\right)+\sin^4\theta_S S_{2222}\right]}.$$

For the orthorhombic material acenaphthene, the $(\pi/2,\theta_S)$ direction locates the maximum value $\widehat{\nu}_{\max} = 0.355$ and the $(\pi/2, 0)$ direction is associated with the minimum value, $\widehat{\nu}_{\min} = 0.195$ as indicated in Figure 7. From the definiteness conditions Equation (29), S_{1122}, S_{1133}, S_{2233} can be expressed in terms of S_{1111}, S_{2222}, S_{3333}:

$$\begin{aligned} S_{1122} &= r\sqrt{S_{1111}S_{2222}}, \quad -1 < r < 1, \\ S_{1133} &= q\sqrt{S_{1111}S_{3333}}, \quad -1 < q < 1, \\ S_{2233} &= w\sqrt{S_{2222}S_{3333}}, \quad -1 < w < 1. \end{aligned}$$

The expressions in Equation (30) give way to

$$\begin{cases} \widehat{\nu}(0,\theta) = -\frac{1}{2}\left(q\sqrt{\frac{S_{1111}}{S_{3333}}}+w\sqrt{\frac{S_{2222}}{S_{3333}}}\right), \\ \widehat{\nu}\left(\frac{\pi}{2},0\right) = -\frac{1}{2}\left(r\sqrt{\frac{S_{2222}}{S_{1111}}}+q\sqrt{\frac{S_{3333}}{S_{1111}}}\right), \\ \widehat{\nu}\left(\frac{\pi}{2},\frac{\pi}{2}\right) = -\frac{1}{2}\left(r\sqrt{\frac{S_{1111}}{S_{2222}}}+w\sqrt{\frac{S_{3333}}{S_{2222}}}\right). \end{cases}$$

Consider $\widehat{\nu}(0,\theta)$. Since the ratios S_{3333}/S_{1111} and S_{3333}/S_{2222} may take on any positive value without violating the definiteness conditions (29), it is not bounded. A similar argument can be made for $\widehat{\nu}(\pi/2, 0)$ and $\widehat{\nu}(\pi/2, \pi/2)$. Thus the areal Poisson's ratio is not bounded for an orthorhombic crystal.

4.8. ***Monoclinic.*** The Voigt compliance matrix s_{ij} for monoclinic materials takes the form

$$(s_{ij}) = \begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & s_{16} \\ & s_{22} & s_{23} & 0 & 0 & s_{26} \\ & & s_{33} & 0 & 0 & s_{36} \\ & & & s_{44} & s_{45} & 0 \\ & & & & s_{55} & 0 \\ & & & & & s_{66} \end{pmatrix},$$

involving thirteen independent elastic constants. In addition to the conditions in Equation (29), definiteness of the strain energy requires

$$\begin{cases} s_{44}s_{55} > s_{45}^2, \ s_{33}s_{66} > s_{36}^2, \\ s_{22}s_{66} > s_{26}^2, \ s_{11}s_{66} > s_{16}^2. \end{cases} \tag{31}$$

The areal Poisson's ratio can be expressed in spherical coordinates as

$$\begin{aligned}\widehat{\nu}(\phi,\theta) = \frac{1}{2} - \frac{1}{2}&\left\{\sin^2\phi[S_{1122} + \cos^2\theta\left(S_{1111} + S_{1133}\right) + \sin^2\theta\left(S_{2222} + S_{2233}\right)]\right.\\ &\left.+ \cos^2\phi\left(S_{1133} + S_{2233} + S_{3333}\right)\right\} / \left\{\sin^4\phi(\cos^4\theta S_{1111} + \sin^4\theta S_{2222} + 2\sin^2\theta\cos^2\theta S_{1122})\right.\\ &+ \cos^4\phi S_{3333} + \sin^2\phi\left[2\cos^2\phi\cos^2\theta S_{1133} + 4\sin^2\theta\cos^2\theta\sin^2\phi S_{1212}\right.\\ &\left.\left. + 2\cos^2\phi(2\cos^2\theta S_{1313} + \sin^2\theta S_{2233} + 2\sin^2\theta S_{2323})\right]\right\}.\end{aligned}$$

From this expression, we see that the relationships imposed by monoclinic symmetry are

$$\widehat{\nu}(\phi,\theta) = \widehat{\nu}(\pi-\phi,\theta) = \widehat{\nu}(\phi,\pi+\theta).$$

Accordingly, we may limit the ranges of the spherical angles to $0 \le \phi \le \frac{\pi}{2}$, $0 \le \theta \le \pi$. A contour plot of the areal Poisson's ratio for the monoclinic material feldspar (plagioclase — 29 AN) is shown in Figure 8. The room temperature elastic compliance matrix $(\mathrm{TPa})^{-1}$ is [Simmons and Wang 1971]:

$$(s_{ij}) = \begin{pmatrix} 15.460 & -3.403 & -3.739 & 0 & 0 & 1.333 \\ & 7.786 & -0.852 & 0 & 0 & 0.266 \\ & & 9.526 & 0 & 0 & 4.390 \\ & & & 54.157 & 1.737 & 0 \\ & & & & 29.210 & 0 \\ & & & & & 34.861 \end{pmatrix}$$

By Equation (10), the stationary points are

$$\begin{cases} \phi = 0, \\ \phi = \frac{\pi}{2}, \theta = \theta_{S1}, \\ \phi = \phi_S, \theta = \theta_{S2}, \end{cases}$$

where θ_{S1} satisfy

$$\begin{aligned}0 = -&\left\{\cos^4\theta S_{1111} + \sin\theta[4\cos^3\theta S_{1112} + \sin^3\theta S_{2222} + \sin 2\theta(\cos\theta\left(S_{1122} + 2S_{1212}\right) + 2\sin 2\theta S_{2212})]\right\}\\ &\times\left[\sin 2\theta\left(-S_{1111} - S_{1133} + S_{2222} + S_{2233}\right) + 2\cos 2\theta(S_{1112} + S_{2212} + S_{3312})\right] + \frac{1}{2}\left[4\left(\cos 2\theta + \cos 4\theta\right)S_{1112}\right.\\ &\left. + 2\sin 4\theta\left(S_{1122} + 2S_{1212}\right) + 8\sin\theta\left(-\cos^3\theta S_{1111} + \sin 3\theta S_{2212} + \cos\theta\sin^2\theta S_{2222}\right)\right]\\ &\times\left\{\cos^2\theta S_{1111} + \sin 2\theta S_{1112} + S_{1122} + \cos^2\theta S_{1133} + \sin\theta\left[\sin\theta\left(S_{2222} + S_{2233}\right) + 2\cos 2\theta\left(S_{2212} + S_{3312}\right)\right]\right\}.\end{aligned}$$

The point $\phi = 0$ is the only invariant stationary point. The direction represented by this stationary point is the two-fold (C_2) rotation symmetry axis. The stationary points $(\pi/2, \theta_{S1})$, (ϕ_S, θ_{S2}) depend on the elastic compliance constants. The global extreme values of the areal Poisson's ratio may be obtained by comparing the values at the above stationary points.

Let us consider the values of the areal Poisson's ratio at stationary points

$$\begin{cases} \widehat{\nu}(0,\theta) = -\frac{S_{1133}+S_{2233}}{2S_{3333}}, \\ \widehat{\nu}\left(\frac{\pi}{2},\theta\right) = \frac{1}{2} - \frac{1}{2}\frac{\cos^2\theta(S_{1111}+S_{1133})+\sin^2\theta(S_{2222}+S_{2233})+S_{1122}+2\sin\theta\cos\theta(S_{1112}+S_{2212}+S_{3312})}{\cos^4\theta S_{1111}+\sin^4\theta S_{2222}+2\sin^2\theta\cos^2\theta(S_{1122}+2S_{1212})+4\sin\theta\cos^3\theta S_{1112}+4\sin^3\theta\cos\theta S_{2212}}. \end{cases}$$

For the monoclinic material feldspar (plagioclase — 29 AN), the $(\pi/2, \theta_{S1})$ direction locates the maximum value, $\widehat{\nu}_{\max} = 0.399$ and the (ϕ_S, θ_{S2}) direction is associated with the minimum value, $\widehat{\nu}_{\min} = 0.168$ in Figure 8.

Similar to the orthorhombic case, we obtain

$$\widehat{\nu}(0,\theta) = -\frac{1}{2}\left(q\sqrt{\frac{S_{1111}}{S_{3333}}} + w\sqrt{\frac{S_{2222}}{S_{3333}}}\right).$$

Since the ratios S_{3333}/S_{1111} and S_{3333}/S_{2222} may be arbitrarily small or large while remaining positive, the areal Poisson's ratio is thus not bounded for monoclinic crystal materials.

4.9. *Triclinic.* The Voigt compliance matrix s_{ij} is shown in Equation (4). There are twenty one independent elastic constants. The elastic compliance matrix must obey the positive definiteness conditions (29) and (31).

The areal Poisson's ratio are restricted only by inversion center symmetry

$$\widehat{\nu}(\phi,\theta) = \widehat{\nu}(\pi-\phi,\pi+\theta),$$

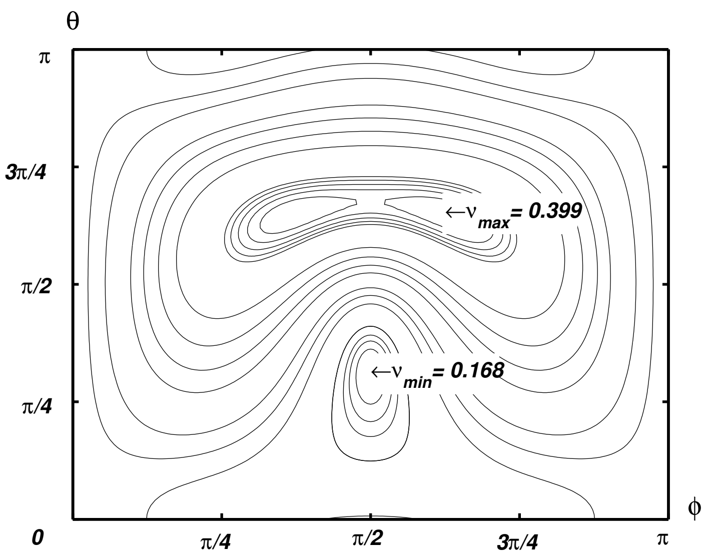

Figure 8. Areal Poisson's ratio for monoclinic material: feldspar.

so we can limit the scope to $0 \le \phi \le \pi$, $0 \le \theta \le \pi$ without loss of generality. Contours are shown for the triclinic material copper sulfate pentahydrate in Figure 9. At room temperature, the elastic compliance matrix in term of $(\mathrm{TPa})^{-1}$ is [Krishnan et al. 1971]

$$(s_{ij}) = \begin{pmatrix} 28.61 & -9.67 & -9.77 & 2.39 & 0.45 & 9.83 \\ & 49.26 & -25.21 & -6.24 & 2.26 & -8.01 \\ & & 39.16 & 6.92 & 1.94 & 3.26 \\ & & & 60.0 & -4.32 & -0.76 \\ & & & & 88.04 & 23.46 \\ & & & & & 110.64 \end{pmatrix}.$$

By investigating the stationary conditions (10), we find no invariant stationary point for triclinic materials. All stationary points depend on the elastic compliance constants. For the triclinic material copper sulfate pentahydrate, the maximum value, $\widehat{\nu}_{\max} = 0.456$ and minimum value $\widehat{\nu}_{\min} = 0.250$ are shown in Figure 9.

Let's look at the values of the areal Poisson's ratio at $\phi = 0$.

$$\widehat{\nu}(0, \theta) = -\left(S_{1133} + S_{2233}\right)/2S_{3333}$$

Similar to the orthorhombic case, we obtain

$$\widehat{\nu}(0, \theta) = -\frac{1}{2}\left(q\sqrt{\frac{S_{1111}}{S_{3333}}} + w\sqrt{\frac{S_{2222}}{S_{3333}}}\right).$$

Since the ratios S_{3333}/S_{1111} and S_{3333}/S_{2222} can be arbitrary small or large positive value, the areal Poisson's ratio is not bounded for triclinic crystal material.

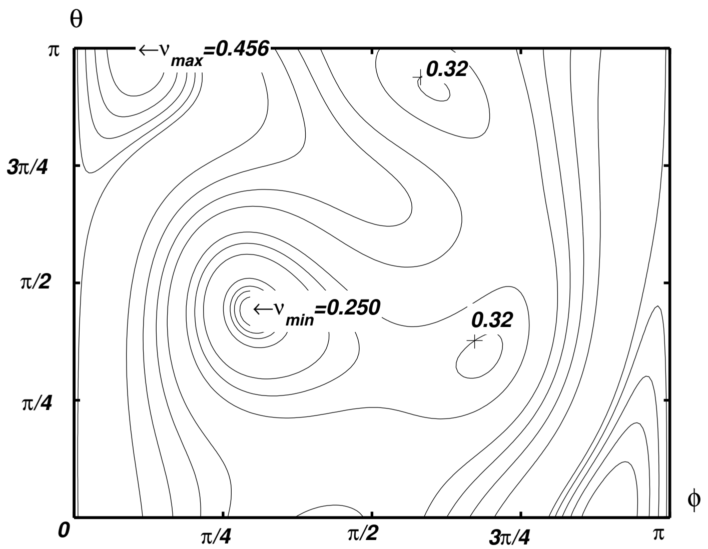

Figure 9. Areal Poisson's ratio for copper sulphate pentahydrate.

Symmetry Class	1	2	3
Cubic	$(0, \theta)$, $(\pi/2, 0)$	$(\pi/2, \pi/4)$, $(\pi/4, 0)$	$\left(\arctan\sqrt{3}/3, \pi/4\right)$
Hexagonal	$(0, \theta)$	$(\pi/2, \theta)$	none
Tetragonal $(4mm, \underline{\bar{4}}2m, 422, 4/mmm)$	$(0, \theta)$	$(\pi/2, 0)$	$(\pi/2, \pi/4)$
Tetragonal $\left(4, \bar{4}, 4/m\right)$	$(0, \theta)$	none	none
Trigonal $\left(32, \bar{3}m, 3m\right)$	$(0, \theta)$	$(\pi/2, 0)$	$(\pi/2, \pi/3)$
Trigonal $\left(3, \bar{3}\right)$	$(0, \theta)$	none	none
Orthorhombic	$(0, \theta)$	$(\pi/2, 0)$	$(\pi/2, \pi/2)$
Monoclinic	$(0, \theta)$	none	none
Triclinic	none	none	none

Table 1. Invariant stationary points (ϕ, θ) of all crystal symmetry classes.

5. Summary

We determine the stationary points of the areal Poisson's ratio for all crystal classes, and illustrate them graphically. The directions of *invariant* stationary points are related directly to the symmetry of the crystal class, but do not depend upon the elastic constants of the particular material at hand. The invariant stationary directions are summarized in Table 1, apart from points that are trivially related to these by symmetry.

For crystals of low symmetry, at least one of the global extreme values occurs on the direction of an invariant stationary point. To find the remaining global extreme, we have to consider both invariant and material dependent stationary points. It is also shown that the areal Poisson's ratio for cubic crystal is bounded between -1 and 1/2, just as the case for isotropic material. But the areal Poisson's ratio the remaining eight lower symmetry crystal classes can have arbitrarily large positive or negative values without violating the positive definiteness of strain energy density.

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