Research News

Advances in Negative Poisson’s Ratio Materials**

By Roderic Lakes*

1. Introduction

Poisson’s ratio is defined as the lateral contraction strain in a solid divided by the longitudinal extension strain measured in a simple tension experiment. In almost all materials Poisson’s ratio, usually denoted by $v$, is positive. For isotropic materials (those in which the properties are independent of direction), energy arguments in the theory of elasticity may be used to show that $-1 \leq v \leq 1/2$. The relationship between shear modulus $G$, bulk modulus $K$, and Poisson’s ratio $v$ for isotropic materials is given by Equation (1).

$$G = \frac{3K(1-2v)}{2(1+v)}$$

In most common materials Poisson’s ratio is close to 1/3, however, rubbery materials have values approaching 1/2; they readily undergo shear deformations but resist volumetric (bulk) deformation, so $G \ll K$. Although textbooks can still be found which categorically state that values of Poisson’s ratio less than zero are unknown, there are in fact a number of examples of negative Poisson’s ratio solids. Such solids become fatter in cross-section when stretched. A solid with $v \approx -1$ would be the opposite of rubber: difficult to shear but easy to deform volumetrically, $G \gg K$. In several cases negative Poisson’s ratio has been observed in an existing material; in several it has been deliberately introduced by design. This article deals with materials with negative Poisson’s ratio, how they can be created with specified properties, implications of these unusual physical properties, and recent advances.

2. Negative Poisson’s Ratio Cellular Solids

We consider first cellular solids with negative Poisson’s ratio, since the physical causes of the behavior of these solids are most readily appreciated. Two-dimensional honeycombs with inverted cells (Fig. 1; compare with the conventional honeycomb in Fig. 2) have been reported with negative Poisson’s ratio in the honeycomb plane,[12–15] and these honeycombs have recently been analyzed.[16, 17] Honeycombs are sufficiently simple that the Poisson effect can be easily visualized. Macroscopic structures in two or three dimensions consisting of rods, springs, and sliders have been devised to give negative Poisson’s ratio;[18] these structures have an inverted characteristic similar to the honeycombs. Structures of the above type require some form of individual assembly. Foam materials with negative Poisson’s ratio as small as $-0.7$ have been developed[19] in which an inverted or re-entrant cell structure was achieved by isotropic permanent volumetric compression of a conventional foam, resulting in microbuckling of the cell ribs. Polymer foams which exhibit a softening point[8, 9] ductile metallic foams[8, 9] and thermosetting polymer foams[9] can be prepared with negative Poisson’s ratio; $v \approx -0.8$ can be attained in copper foam (Fig. 3). Negative Poisson’s ratio occurs over a range of strain[16, 17] and that range is larger in the polymer foams.

[*] Prof. R. S. Lakes

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than in the metal foams. In the above structures and materials, negative Poisson’s ratio arises from the unfolding of the re-entrant cells, and isotropy can be achieved along with negative Poisson’s ratio. Anisotropic microcellular foams were recently reported to exhibit an unintentional negative value of Poisson’s ratio in some directions.\[^{12,13}\] Since these are anisotropic materials, the bounds on Poisson’s ratio are wider ($-\infty < v < \infty$) than in the isotropic case. Indeed, values smaller than $-1$ have been reported. The physical mechanism appears to be associated with tilting of particulates linked by microfilaments.

Microcracks in a material can be viewed as flattened pores with minimal volume. Several types of rocks with microcracks have been reported to exhibit negative Poisson’s ratio\[^{14,15}\] of about $-0.1$; the effect is abolished under water saturation or hydrostatic pressure.

A recent advance is the synthesis of microporous polyethylene that exhibits negative Poisson’s ratio in a preferred direction;\[^{16}\] some implications were discussed in a recent review.\[^{17}\] The material was created by compacting powdered polymer, sintering and extrusion, leading to a final microstructure consisting of particles connected by fibrils. The polyethylene was mechanically anisotropic following the extrusion, with Poisson’s ratio as small as $-1.24$ for compression in the radial direction, and zero for compression in the axial direction.

### 3. Negative Poisson’s Ratio Composites

Several cases of negative Poisson’s ratio have been discovered in the analysis of anisotropic fibrous composites. In some laminates composed of fibrous layers it is theoretically possible to achieve values as small as $-0.21$ in the direction perpendicular to the layers by control of the stacking sequence.\[^{18}\] In other laminates, one can achieve negative Poisson’s ratio in some directions in the plane of the laminate, again by control of the stacking sequence.\[^{19,20}\] In these composites there is a high degree of anisotropy and Poisson’s ratio is negative only in some directions and, in some cases, only over a narrow range of orientation angles between the applied load and the fibers.

In a recent advance, laminate structures have been prepared that give rise to intentionally negative Poisson’s ratio combined with mechanical isotropy in two dimensions (Fig. 4) or in three dimensions.\[^{21}\] These laminates have structure on several levels of scale, i.e., they are hierarchical. Appropriate choice of constituent properties makes feasible laminates in which Poisson’s ratio approaches the lower limit of $-1$. This rigorous lower bound is independent of the microstructure, and therefore it will not be possible to find microstructures with much lower Poisson’s ratio for given constituent stiffnesses.

### 4. Crystalline and Amorphous Negative Poisson’s Ratio Materials

A large compilation of elastic constants for single crystals and calculated elastic constants for polycrystalline aggregates made from them has been prepared.\[^{22}\] In most polycrystalline materials Poisson’s ratio is in the vicinity of 1/3, although beryllium has a value of about 0.1 and ammonium chloride is said to assume a negative value over a narrow temperature range.

An early report suggested that Poisson’s ratio ($v \approx -1/7$) is negative in single-crystal iron pyrites;\[^{23}\] however, a recent study contradicts that claim.\[^{24}\] A negative value as small as $-0.4$ in certain directions was calculated\[^{25}\] from published data on single-crystal cadmium. Arsenic, antimony, and bismuth are highly anisotropic in single-crystal form, and arsenic is the most anisotropic of these,\[^{26}\] with a factor of 11.3 variation in Young’s modulus with direction. Poisson’s ratio calculated for these materials is negative in some directions. Arsenic is so anisotropic that Poisson’s ratio can exceed 0.5 or be less than $-1$, depending on the direction of stress. The crystals contain a layered structure with weak binding between pairs of layers. A crystalline form of silica ($\text{SiO}_2$), $\alpha$-cristobalite, exhibits values of Poisson’s ratio of $+0.08$ to $-0.5$, depending on direction.\[^{27}\] Moreover, the Voigt and Reuss bounds for Poisson’s ratio in polycrystalline $\alpha$-cristobalite are $-0.13$ and $-0.19$, with an average value of $-0.16$. Compared with the quartz form of silica, $\alpha$-cristobalite is
described as being more compliant, and with a more open crystal structure (Fig. 5). Pyrolytic graphite\cite{28} intended for thermal protection in aerospace uses was found to have negative Poisson’s ratio \((-0.21\)\) in one crystallographic direction.

![Fig. 5. Structure of α-cristobalite (27).](image)

Certain ferromagnetic films\cite{29} exhibited negative values of Poisson’s ratio which decayed with time. Several rare earth alloys \((\text{Sm}_{1-x}, Y, S)\) exhibit negative Poisson’s ratio in the vicinity of a valence transition, for certain concentration values\cite{30} experiments disclose values as small as \(-0.7\). The effect is attributed to a longitudinal mode softening, which causes the bulk modulus to tend to zero at a critical concentration. The root cause of this is thought to be a high compliance of the rare earth ion\cite{31}. A different type of phase transition was reported in certain types of polymer gels in which Poisson’s ratio becomes negative (to about \(-0.4\)) over a narrow temperature range\cite{32}.

Common aspects of the unusual crystalline materials include a high degree of anisotropy. In the case of α-cristobalite, an isotropic solid made of randomly oriented crystals would exhibit negative Poisson’s ratio.

5. Causal Mechanisms

Negative values of Poisson’s ratio are unusual and counterintuitive; it is natural to inquire what is the cause of such an unusual physical property. Causes must be sought in the microstructure, since the continuum theories of elasticity do not specify particular values of Poisson’s ratio. If the solid is made of atoms interacting by central forces, and the atoms move in an affine manner (locally equivalent to a strain combined with a rotation) under deformation, then Poisson’s ratio is \(1/4\)\cite{33,34}—a result originally deduced by S. D. Poisson. Clearly, these assumptions are not satisfied even for most ordinary materials, since Poisson’s ratio is typically close to \(1/3\). In the case of negative Poisson’s ratio foams, it had been suggested that the effect is due to bending of the cell ribs\cite{35} which can be subsumed into a Cosserat continuum model, which has more freedom than classical elasticity (a possible role of Cosserat elasticity has also been considered in a study of mechanical models for materials with negative Poisson’s ratio\cite{36}). Although foams can indeed have this extra freedom,\cite{37} it is not a likely cause of negative Poisson’s ratio\cite{38}. Negative Poisson’s ratio cannot be achieved via the bending or twisting rigidity of the cell ribs alone.\cite{39} Non-affine (locally inhomogeneous) deformation by itself can give rise to negative Poisson’s ratio effects.\cite{40} Other possible causes are prestrain in the lattice structure\cite{39} or a chiral structure.\cite{39,40} Several illustrative models involving truss elements with sliders, and hypothetical granular structures, have been presented\cite{41,42}.

In the reentrant foams and honeycombs, inhomogeneous, non-affine deformation is manifested as an unfolding of the cells as the entire structure is extended; such deformation has been experimentally observed in foams.\cite{43} The effect of microcracks would also appear to have a non-affine character. Simple analysis shows that cracks reduce Poisson’s ratio; negative values are not accounted for.\cite{44} The structure of some of the crystalline materials, notably α-cristobalite and arsenic, suggests that non-affine deformation occurs.

6. Future Possibilities

6.1. Applications

Applications of negative Poisson’s ratio materials may be envisaged based on either the value of Poisson’s ratio itself or another unusual physical property that results from the underlying structural causal mechanism. The value of Poisson’s ratio of a material influences the transmission and reflection of stress waves\cite{45,46} the decay of stress with distance according to Saint Venant’s principle\cite{47} and the distribution of stress around holes and cracks\cite{48,49}. The lateral deformation of negative Poisson’s ratio materials may be of use in new kinds of fasteners.\cite{49} Such materials may also find use in sandwich panels. When a plate or bar is bent, it assumes a saddle shape if Poisson’s ratio is positive, and a convex shape if Poisson’s ratio is negative.\cite{48,50–52} The convex shapes are more appropriate than saddle shapes for sandwich panels for aircraft or automobiles. Stress distribution in a flexible pad such as a wrestling mat is more favorable to reducing impact forces upon both small objects such as an elbow and large objects such as a leg or back if Poisson’s ratio is as small as possible.\cite{48} Among other physical properties, resilience\cite{48,9,11} and sound absorbing capacity\cite{53} are characteristic of the reentrant foams. It is hoped that some of these suggested applications will come to fruition.

6.2. New Materials

In some applications it is essential to have a material that is stiff and strong. This is difficult to achieve in a foam. It is natural to ask, following consideration of causal mechanisms, if there must be empty space in the structure in order
to make Poisson’s ratio negative. Single crystals may contain relatively close-packed atoms, but they are highly anisotropic. In any case the crystalline materials with negative Poisson’s ratio described above are not well suited to structural applications. The composites of Milton offer the intriguing possibility of stiff materials with negative Poisson’s ratio. However, the stiffness of one of the two constituents must be at least 25 times greater than that of the other in order to obtain a value of Poisson’s ratio less than zero. For Poisson’s ratio to approach −1 requires constituents with an even greater difference in stiffness, so that one phase is very soft, tending to “empty space” in its properties. Another intriguing possibility is that of creating stiffer negative Poisson’s ratio materials by design on the molecular scale. It might be possible to make use of the existing free volume which exists in polymeric materials to achieve this goal. Inspiration for future designs of new materials could be drawn from some of the material microstructures described in this article.