Negative linear compressibility of hexagonal honeycombs
and related systems

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Received 17 February 2011; revised 1 June 2011; accepted 7 June 2011
Available online 15 June 2011

Materials exhibiting negative linear compressibility display the very unusual and unexpected property of expanding in at least one direction when placed under compressive hydrostatic stress. Here, it is shown that this property may be manifested by systems having high positive Poisson’s ratios (non-auxetic), including non re-entrant hexagonal honeycombs and wine-rack models where deformation primarily involves changes in the angles between the ribs of the structures.

When a material is subjected to a hydrostatic stress it usually contracts in all directions. However, there are occasional reports of materials and structures that behave in a different fashion [1–14], i.e. exhibit negative compressibility, meaning that they possess the unusual property of expanding in one or more directions when hydrostatically compressed. Such materials are predicted to have a number of applications ranging from extremely sensitive pressure detectors, telecommunication line systems, to optical materials with very high refractive index [1].

So far, very few materials have been reported to exhibit negative linear compressibility (i.e. expand in one direction when compressed hydrostatically). The ones identified so far include methanol monohydrate [2], a hypothetical carbon-based system [1] caesium dihydrogen phosphate [4], lanthanum niobate [5], Ag₃[Co(CN)₆] [6] and orthorhombic high-pressure paratellurite (TeO₂) phase [7]. Structures which exhibit negative linear, area and volume compressibility on a macrolevel have also been reported [8–10]. These include structures assembled from triangular building blocks [8] or chiral units constructed from bimaterial strips [9]. In the case of triangular units, in the idealized scenario, the mechanism requires triangles constructed from three pin-jointed rods where the base rod is made from a different and softer material than the other two. When such a triangle is placed in an atmosphere of positive (tensile) hydrostatic stress, the base rod expands to a larger extent than the other two, pulling them apart so that overall, the triangle gets shorter, i.e. exhibits negative linear compressibility in the direction perpendicular to the base. In the case of the chiral units, the mechanism requires the use of bimaterial ligaments made up of two materials having dissimilar mechanical properties, bonded together, which can curve when placed under pressure [11]. These ligaments must be connected together in such a way that the cooperative curving of the ligaments will result in an overall expansion of the system when this is placed in a medium of negative (compressive) hydrostatic stress. As shown elsewhere [8,9], such mechanisms can be employed to exhibit not only negative linear compressibility, but also an overall area or volumetric compressibility. However, for these two mechanisms to operate, the material must be porous so as to ensure that the fluid which is exerting the hydrostatic stress on the system can freely penetrate inside the system so as to permit the uneven contraction or expansions of the different components in the system. In addition to these systems, other structures which have also been reported to exhibit negative compressibility include systems operating through a wine-rack-type mechanism which can be used to explain the experimentally measured or predicted negative linear compressibility at the molecular level [1]. In this respect, it should be noted that although it is now obvious that such mechanisms have a very important role in generating negative linear compressibility,
no rigorous treatment of such systems has been presented so far to explain the necessary conditions for achieving negative linear compressibility. In view of this, here we will examine in detail through analytical modelling the possibility of achieving negative linear compressibility by non re-entrant hexagonal (when \( \theta \) in Fig. 1 is positive) and wine-rack-type honeycombs; we will show that, under the right conditions, both systems may exhibit negative linear compressibility.

The on-axis linear and area compressibility of a two-dimensional (planar) system can be related to the compliance coefficients \( s_{ij} \), more specifically to its on-axis Poisson’s ratios \( v_{ij} \) and Young’s moduli \( E_i \) since:

\[
\beta_{11} = s_{11} + s_{12} = \frac{1}{E_1} - \frac{v_{21}}{E_2}, \\
\beta_{22} = s_{21} + s_{22} = \frac{1}{E_2} - \frac{v_{12}}{E_1}
\]

These expressions clearly suggest that the on-axis linear compressibilities may assume negative values in cases when the Poisson’s ratio is high and positive so that \( v_{ij} > E_i/E_j \). Such conditions are not impossible to achieve, and as shown below they are indeed possible for hexagonal honeycombs deforming through changes in the angle between the ribs of the honeycomb (idealized hinging model). Hexagonal honeycombs have been extensively studied [15–18] in view of the ability of their re-entrant versions to achieve negative Poisson’s ratios (auxetic behaviour). In particular, it has been shown that they can deform through three non-mutually exclusive deformation mechanisms, including flexure [15,16], stretching of the ribs and/or hinging of the ribs [17,18], where the on-axis Poisson’s ratios \( v_{ij} \) in the \( OX_1 - OX_2 \) and Young’s moduli \( E_i \) for loading in the \( OX_1 \) direction for the idealized hinging model are given by:

\[
v'_{12} = (v_{21})^{-1} = \frac{\cos^2(\theta)}{(h/l + \sin(\theta)) \sin(\theta)} \\
E'_1 = \frac{K_s \cos(\theta)}{b \sin^2(\theta)(h/l + \sin(\theta))}, \\
E'_2 = \frac{K_s(h/l + \sin(\theta))}{b \cos^3(\theta)}
\]

where, as shown in Figure 1a, \( h \) and \( l \) are the lengths of the vertical and inclined ribs, respectively; \( \theta \) is the angle that the inclined ribs make with the horizontal (negative for re-entrant honeycombs and positive for non re-entrant honeycombs); \( b \) is the out-of-plane thickness of the honeycomb; and \( K_s \) is the hinging force constant.

It has also been shown that if such honeycombs deform solely through stretching of the ribs (idealized stretching model), the corresponding Poisson’s ratios \( v'_{ij} \) and Young’s moduli \( E'_i \) are given by:

\[
v'_{12} = -\frac{\sin(\theta)}{h/l + \sin(\theta)}, \\
v'_{21} = -\frac{\sin(\theta)(h/l + \sin(\theta))}{2h/l + \sin^2(\theta)}
\]

\[
E'_1 = \frac{K_s}{b \cos(\theta)(h/l + \sin(\theta))}, \\
E'_2 = \frac{K_s(h/l + \sin(\theta))}{b \cos(\theta)(2h/l + \sin^2(\theta))}
\]

where \( K_s \) is the stretching force constant, whilst for a honeycomb which deforms through concurrent hinging and stretching, the two single-mode models can be combined to obtain the resulting Poisson’s ratios \( v''_{ij} \) and Young’s moduli \( E''_i \) since:

\[
v''_{12} = \left( \frac{1}{E''_1} + \frac{1}{E''_2} \right)^{-1}, \\
v''_{21} = E''_2 \left( \frac{v''_{12}}{E''_1} + \frac{v''_{11}}{E''_2} \right)
\]

Using these equations, the on-axis linear compressibilities \( \beta_{11} \) and \( \beta_{22} \) in the \( OX_1 \) and \( OX_2 \) directions for the idealized hinging model become:

\[
\beta_{11}^h = \frac{(h \sin(\theta) - l \cos(2\theta))b \tan(\theta)}{K_h l}, \\
\beta_{22}^h = \frac{b \cos(\theta)(l \cos(2\theta) - h \sin(\theta))}{K_h (l \sin(\theta) + h)}
\]

where in the range \(-90^\circ < \theta < 90^\circ\), \( \beta_{11}^h \) is negative if \( h/l < \cos(2\theta)/\sin(\theta) \), \( \beta_{22}^h \) is negative if \( h/l > \cos(2\theta)/\sin(\theta) \) with \( \beta_{11}^h = \beta_{22}^h = 0 \) when \( h/l = \cos(2\theta)/\sin(\theta) \). Note that the special case when \( h = 0 \), the system becomes equivalent to a wine-rack-type structure (Fig. 1b) and the compressibility expressions simplify to:

\[
\beta_{11}^h = \frac{b \cos(\theta) \tan(\theta)}{K_h}, \\
\beta_{22}^h = \frac{b \cos(\theta) \cot(\theta)}{K_h}
\]

where the sign of the compressibility is now simply dependent on \( \theta \) where \( \beta_{11}^h \) is negative if \( 0 < \theta < 45^\circ \), \( \beta_{22}^h \) is negative if \( 45^\circ < \theta < 90^\circ \) with \( \beta_{11}^h = \beta_{22}^h = 0 \) when \( \theta = 45^\circ \).

In the case of the idealized stretching model, the on-axis compressibilities are always positive and in the case of hexagonal honeycombs are given by:

\[
\beta_{11}^s = \frac{b \cos(\theta)(2l \sin(\theta) + h)}{IK_s}, \\
\beta_{22}^s = \frac{b \cos(\theta)(2l \sin^2(\theta) + h \sin(\theta) + 2h)}{K_s(l \sin(\theta) + h)}
\]

whilst in case of the concurrent hinging and stretching models, the on-axis compressibilities may assume both positive or negative values and are given by:

\[
\beta_{11}^{hs} = \frac{b}{l} \left\{ \left( h \sin(\theta) - l \cos(2\theta) \right) \tan(\theta) \right\} \\
\frac{K_s}{K_s} + \left( 2l \sin(\theta) + h \right) \cos(\theta) \right\}
\]

(11)
Figure 2. Plots of $\beta_{11}$ and $\beta_{22}$ against $\theta$ for systems where (a) $K_x \gg K_h$, (b) $K_x \ll K_h$, and (c) $K_x = 10K_h$. Note that systems with $h = 0$ correspond to a wine-rack structures. Note also that as indicated in (a), for the idealized stretching square honeycombs ($\theta = 0^\circ$), the compressibility in the $\beta_{22}$ direction becomes independent of the aspect ratio of the honeycomb and always has a value given by $2h/K_x$. 

$\beta_{22}^{\text{st}} = \frac{b \cos(\theta)}{I \sin(\theta)} \left[ \frac{(I \cos(2\theta) - h \sin(\theta))}{K_x} + \frac{(2I \sin^2(\theta) + h \sin(\theta) + 2h)}{K_x} \right]$  

(12)

Plots for the variation of the on-axis linear compressibilities $\beta_{11}$ and $\beta_{22}$ with the angle $\theta$ for various systems having different $h/l$ and $K_x/K_h$ ratios are shown in Figure 2. These plots confirm that in cases where $K_x$ is sufficiently large such that the honeycombs deform almost only through hinging, negative compressibilities may be achieved. The plots also confirm that for re-entrant configurations (i.e. negative $\theta$-values), the on-axis compressibilities are always positive. This is because the condition required for negative compressibility in the idealized hinging model, i.e. negative $\theta$-values, can never be satisfied since $E_{ij}/E_{ii}$ is always positive while $\nu_{ij}$ is always negative for on-axis loading. On the other hand, as noted above, non re-entrant hinging honeycombs and wine-rack models having $0^\circ < \theta < 90^\circ$ always exhibit negative compressibility in one of the two directions (but not both simultaneously), except for the particular $\theta$-value where the compressibility is zero ($45^\circ$ in the case of the wine-rack).

More importantly, the equations and plots also suggest that by controlling the geometric parameters $h$, $I$ and $\theta$ and the relative extents of stiffness constants, one can design a honeycomb to exhibit negative compressibility in either the $Ox_1$ or the $Ox_2$ direction. In particular, for the idealized hinging model, small $h/l$ ratios favour a larger range of negative $\beta_{11}$. However, there is a limit to the range of $\theta$-values over which such behaviour can be observed, and at most it can only cover a range of $0^\circ < \theta < 45^\circ$ when $h$ becomes zero, i.e. when the idealized hinging honeycomb resembles a wine-rack structure. This is in contrast to $\beta_{22}$, which for the idealized hinging model can assume negative values over a much larger range. In fact, all non re-entrant idealized hinging honeycombs always exhibit negative compressibility in the $Ox_2$ direction for $\theta$ above $45^\circ$. This $\theta$-range over which negative $\beta_{22}$ is observed can be further increased by increasing $h/l$, but at the expense of a lower range of negative $\beta_{11}$. In systems where there is concurrent stretching and hinging, the extent of negative compressibility is always less than that of the idealized hinging models, something which in real scenarios may even annul the negative compressibility effect. This is due to the fact that the honeycombs deforming through the stretching mechanism cannot exhibit negative on-axis compressibility (see Eq. (10) and Fig. 2).

All this is very significant due to the fact that this model suggests how materials having nanostructures which in particular planes may be described in terms of honeycombs or wine-rack geometries may exhibit negative compressibility under certain conditions only if they deform through the correct deformation mechanism. More importantly it specifies the conditions that are necessary for such property to be manifested. In particular, the model suggests that, for example, a wine-rack-type system will only exhibit negative compressibility in the direction where the model is already slightly extended (see Fig. 1b). In this respect, it is important to note that this hypothesis is supported by the recent work by Fortes et al. [2], whose analysis of the presented crystal structure data and mechanical properties clearly suggests that methanol monohydrate exhibits negative compressibility in the direction predicted by the model presented. Here it should be highlighted that not all real materials having honeycomb or wine-rack geometries will exhibit negative linear compressibility since for this property to be manifested it is required that the hinging mechanism is the predominant mechanism and that the geometry is suitable.

Before we conclude, it should be noted that for the mechanism resulting in negative compressibility to operate, it is required that the pressure is exerted on the system only from the outside, i.e. not on both sides of the same ligament. Thus, for example, if the pressure had to be exerted on the system through a fluid, then it would have been required that the system be non-porous, or that the pores of the system would be smaller than the dimensions of the fluid particles, as is likely to be the case in the methanol monohydrate system studied by Fortes et al. [2]. Also, it should be highlighted that the expressions derived here still fulfill the requirement that the overall compressibility is positive since, as noted above, a negative linear compressibility in one direction is accompanied by a positive linear compressibility in the orthogonal direction, where, as indicated by the equations and the graphs, the magnitudes are such that the area compressibility, given by $\beta_A = \beta_{11} + \beta_{22}$, is still positive. Furthermore, the property of negative linear compressibility is not limited to honeycomb or wine-rack models but may in fact be exhibited by any two-dimensional system having very
high positive Poisson’s ratios where $v_{ij} > E_i/E_j$ (e.g. some models based on rotating rigid units [19]). Similarly, in the case of three-dimensional systems, the requirement for negative linear compressibility in the $O_x$ direction is that $s_1 + s_2 + s_3 < 0$, something which must be the case for real materials (e.g. methanol monohydrate in the $a$ direction).

In summary, it has been shown through analytical modelling that non re-entrant hexagonal honeycombs and wine-rack-type systems may exhibit the anomalous property of negative compressibility in certain directions; the model correctly predicts the direction of negative compressibility in methanol monohydrate reported recently [2]. Given how rarely the property of negative linear compressibility is manifested, and the practical applications in which materials with negative compressibility may be used, we hope that this work will stimulate further studies aimed at identifying existing materials that exhibit this unusual property or designing new ones based on the model presented here.

The financial support of a Malta Government Scholarship Scheme (MGSS Grant Number ME 367/07/17) grant awarded by the Government of Malta to D.A. and of the Malta Council for Science and Technology (MCST) is gratefully acknowledged.